

# **Steel**

Class Notes and lecture material  
For  
MSE 651.01--

## **Physical Metallurgy of Steel**

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# STEEL

## Foreword

This document is intended to augment formal lectures on the general topic of the physical metallurgy of steels, presented within the MSE Department during the Fall Quarter, 1998. It is based on a variety of texts and published articles and also on personal experience. Specific references to sources are made within the document. However, the material is often in the form of knowledge that has been accumulated by the work of many people and is "well-known" by experts in the field. A detailed acknowledgment of the work of each contributor to the field is not attempted because that would be an awesome task. This document is not intended for publication and is restricted for use in MSE 651.01.

Texts: Steels; Microstructures and Properties by R.W.K. Honeycombe (Edward Arnold)  
Principles of the Heat Treatment of Steel by G. Krauss (ASM)  
The Physical Metallurgy of Steel by W.C. Leslie (McGraw Hill)  
The ASM Metal Handbooks.  
Handbook of Stainless Steels, Peckner and Bernstein (eds.) McGraw Hill 1977  
Tool Steels Roberts and Cary, Edition 4, ASM, 1980  
Ferrous Physical Metallurgy A. K. Sinha, Butterworths 1989.

## Introduction

Steel is a family of materials that is derived from ores that are rich in iron, abundant in the Earth's crust and which are easily reduced by hot carbon to yield iron. Steels are very versatile; they can be formed into desired shapes by plastic deformation produced by processes such as rolling and forging; they can be treated to give them a wide range of mechanical properties which enable them to be used for an enormous number of applications. Indeed, steel is ubiquitous in applications that directly affect the quality of our lives. Steel and cement constitute about 90% of the structural materials that are manufactured  
( Westwood, Met and Mat Trans, Vol. 27 A, June 1996, 1413).

What, then, is steel?

A precise and concise definition of steel is not an easy thing to present because of the very large variety of alloys that bear the name. All of them, however, contain iron. We might reasonably begin by describing a steel as an alloy which contains iron as the major component. This is only a beginning because there are alloys in which iron is the major constituent, that are not called steels; for example, cast irons and some superalloys. The major difference between a cast iron and a steel is that their carbon contents lie in two different ranges. These ranges are determined by the maximum amount of carbon that can be dissolved into solid iron. This is approximately 2% by weight (in FCC iron at 1146 °C). Steels are alloys that contain less than 2% carbon. Cast irons contain more than 2 % carbon. Many steels contain specified minimum amounts of carbon. This does not mean that all steels **must** contain substantial quantities of carbon; in some steels the carbon content is deliberately made very small and, also, the amount actually in solution is reduced further by the addition of alloying elements that have a strong tendency to combine with the carbon to form carbides.

Steels can be divided into two main groups; plain carbon steels and alloy steels. The latter can then be subdivided into many groups according to chemistry ( e.g. standard low alloy steels), applications (e.g. tool steels ) or particular properties (e.g. stainless steels) etc. Let us begin with

plain carbon steels; this group is the simplest to understand and it comprises steels that are used in the greatest tonnage.

### Plain carbon steels

A plain carbon steel is essentially an alloy of iron and carbon which also contains manganese and a variety of residual elements. These residual elements were either present within the raw materials used in the production process e.g. iron ore and scrap steel additions, or they were added in the production process for a specific purpose, e.g. deoxidization by means of silicon or aluminum. Hence they are called residual elements to distinguish them from alloying elements that are deliberately added according to specified minimum amounts. The American Iron and Steel Institute (AISI) has defined a plain carbon steel to be an alloy of iron and carbon which contains specified amounts of Mn below a maximum amount of 1.65 wt. %, less than 0.6 wt. % Si, less than 0.6 wt. % Cu and which does not have any specified **minimum** content of any other deliberately added alloying element. It is usual for **maximum** amounts (e.g. 0.05 wt. %) of S and P to be specified. ( see The Making, Shaping and Treating of Steel, USS 1970)

The manufacture of steel is a subject that is well beyond the ambit of these notes. But we should be aware that various manufacturing practices can affect the oxygen, nitrogen and sulfur content and hence the cleanliness of the product. The term “cleanliness” usually refers to the amounts of various phases such as oxides, sulfides and silicates that can be present in steel. The smaller the amount of these phases, the cleaner is the steel. These phases are in the form of particles called inclusions and they can have significant effects on the properties of steel and are normally undesirable. Thus, variations in the manufacturing process can have significant effects on the properties of the steel, so some brief comments are in order. For many years steels have been produced by casting the molten steel into molds and allowing it to solidify into ingots which were then processed by rolling etc. Steel produced by ingot metallurgy is subdivided into four categories according to the deoxidization process used. These categories are rimmed, capped, semi-killed and killed steel. When an undeoxidized steel is cast into an ingot, carbon monoxide is evolved during solidification because the solubility of oxygen decreases as the temperature decreases. By adding enough ferrosilicon and aluminum, much of the oxygen can be removed from solution and also iron oxide is reduced by the formation of silicon and aluminum oxides so that no gas bubbles form and the steel is quiescent as it solidifies. The result is a fully killed steel. Plain carbon steels containing more than 0.3% C, produced by ingot metallurgy, are usually fully killed. Semi-killed steels are those which are partially deoxidized. Ingots for which the evolution of bubbles of carbon oxide gas is permitted during solidification produce rimmed steel, while capping means the interruption of the rimming process by freezing the top of the ingot by putting a cast iron cap on it. The different practices produce ingots that differ with respect to segregation, inclusion content and as-cast microstructure.

There have been major advances in the production of steel during the last 20 years and continuous casting, in which great attention is being paid to the cleanliness of the steel, has become the dominant production method. According to R. D. Pehlke in Metallurgical Treatises, published by the Metallurgical Society of the AIME and reprinted in 1983, most steel produced by continuous casting is fully killed. Vacuum deoxidization is also being used to eliminate the oxygen, and the steel is protected by argon atmospheres in covered tundishes thereby yielding a cleaner steel with respect to its inclusion content. This is beneficial with respect to the mechanical properties and uniformity of the final product. Continuous casting also produces a product that is much closer to the final shape that is required for the application of the steel.

More and more steel sheet is now being produced in what are called mini-mills. These mills charge electric arc furnaces with scrap steel and iron, melt the charge, control the composition, and, via a tundish continuously cast it into slabs several inches thick and a few feet wide. This slab is immediately fed through a long furnace in which it is heat treated and from which it emerges at the temperature desired to begin hot-rolling and passes directly into a series of hot rolls. Problems can arise in controlling the residual element contribution to the composition of the product because of variations in the quality of the scrap steel charged into the electric furnaces. Copper is particularly undesirable because it is not easily removed from liquid steel, and as its concentration increases, it can produce cracks due to hot-shortness. This phenomenon arises because when the hot steel is exposed to air the iron is oxidized to form scale, much of which spalls off but the copper is not oxidized and accumulates beneath the scale at the surface of the steel. The copper penetrates the steel along grain boundaries and causes grain boundary cracking to occur during rolling.

### Alloy steels

It follows from the definition of a plain carbon steel, that if one or more additional elements are **deliberately** added to produce specified minimum contents then the product is an alloy steel. In general, this is so, but we should also note that small additions of rare earth elements such as cerium can be made to a plain carbon steel for inclusion control. ( One of the important roles of manganese is to combine with sulfur to prevent the formation of iron sulfides which can embrittle the steel. It has been discovered that additions of rare earth elements can produce high-melting point, complex sulfides and oxysulfides that are smaller and less harmful to the mechanical properties of steels than manganese sulfides can sometimes be.) The steel would not then be referred to as an alloy steel. The definition given is a very broad one and it indicates that a clear, concise, nice little subdivision scheme to describe all steels is not easily produced. As we shall see, there is a group of low-alloy steels for which the compositions are specified in this country according to schemes originally recommended by the AISI and the Society of Automotive Engineers(SAE), but alloy steels are also classified on the basis of some important property ( e.g. stainless steels) or on the basis of use (e.g. tool steels) or even as a consequence of a particular heat-treatment (e.g. maraging steel). To add to the confusion, there are steels that have particular names coined by the manufacturer and also steels that are characterized by an American Society for Testing Materials (ASTM) specification, e.g. A306 which specifies the mode of manufacture, permissible amounts of S and P but leaves the manufacturer to choose the carbon levels necessary to achieve specified tensile properties. The tensile properties determine the grade of steel, e.g. A306 grade 50 specifies a tensile strength of 50 to 60 KSI. The picture appears to be quite confusing. Our objective is to eliminate the confusion by understanding how the properties of steel are related to their microstructures, how particular microstructures are produced and what effects are produced by the alloying elements. There is, of course, a wide range of properties. Mostly we will concentrate on mechanical properties. The ASM. handbooks and the book "Making, Shaping and Refining of steel" put out by the old U. S.. Steel Co. and in a revised tenth edition in 1985 by W. T.Lankford, Jr. et al. published by the Association of Iron and Steel Engineers, present many details of properties and production processing. Our purpose is to develop a fundamental understanding. In order to do this, I propose to begin with pure iron, proceed to Fe-C, consider plain carbon steels, put in alloying elements and finally to select some particular classes of steel for examination.

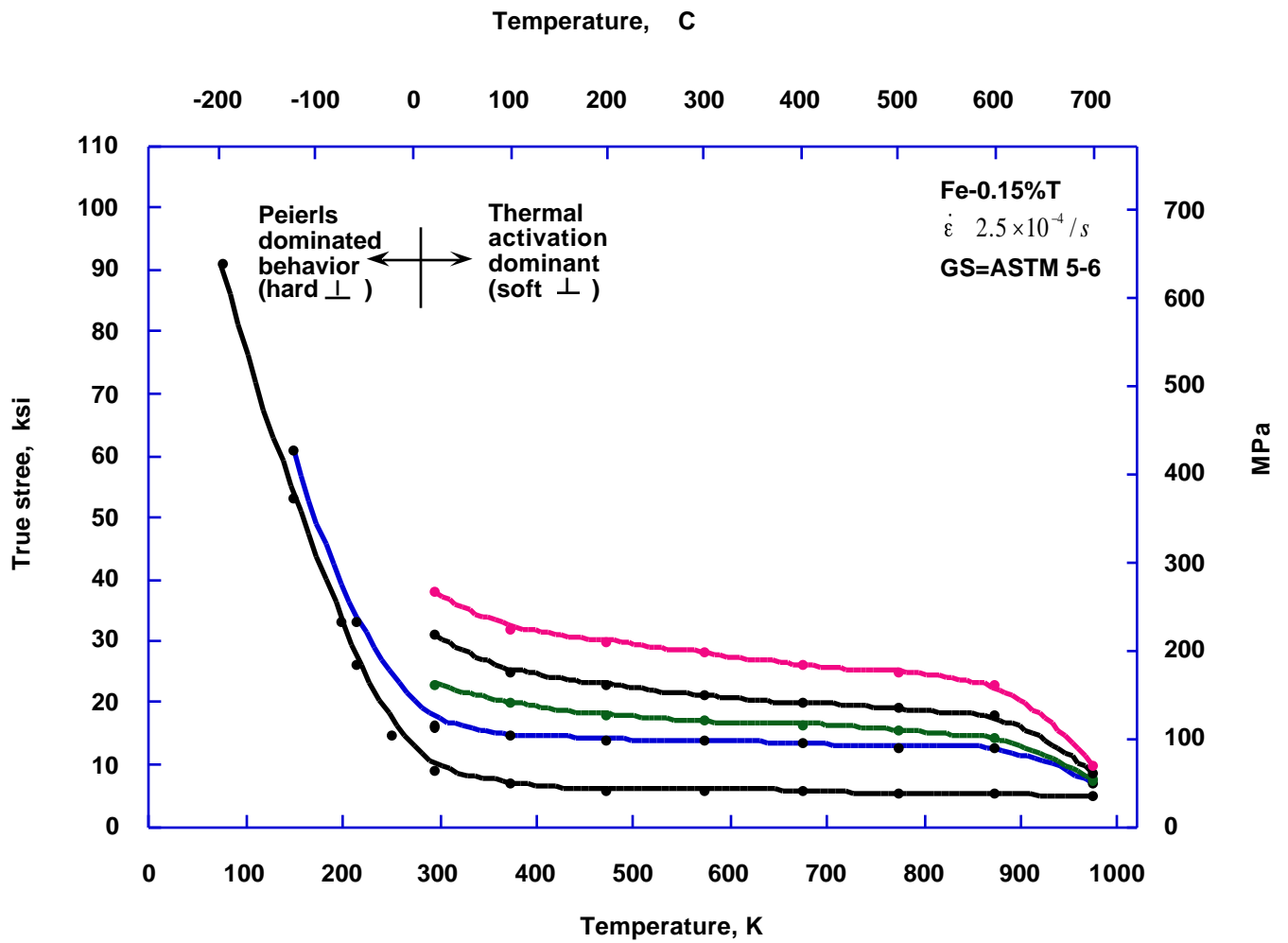
## Iron and its Solid Solutions

At normal atmospheric pressure, iron, in equilibrium, is BCC below 910°C, FCC between 910°C and 1390°C and then BCC up to its melting point of 1536°C. Hence, at normal ambient temperatures and below, iron is BCC. Its mechanical properties, as determined by testing in tension at room temperature and at typical strain rates of  $10^{-3}$  to  $10^{-4}$  sec<sup>-1</sup>, are functions of purity, grain size and dislocation content. The yield strength is also temperature dependent, increasing with a reduction in temperature as shown in figure 1 (W.C. Leslie, Met. Trans. 3, 9, 1972.) These results were obtained with iron to which Ti had been added to getter the interstitial elements. (For example, the carbon that combines with titanium is removed from solid solution. It has, therefore been “got” by the titanium which explains why the verb “to getter” was coined.) Above 300 K, dislocation glide can occur relatively easily so that the magnitude of the macroscopic yield stress is controlled by the effects of long range internal stress fields on dislocation motion. Therefore, the temperature dependence of the yield stress in this temperature realm is due to the temperature dependence of the shear modulus of iron which decreases gradually as the temperature is increased and vice versa. From 250 K downwards, the variation of the macroscopic yield stress with temperature increases linearly and much more rapidly than the variation above room temperature. The rapid increase in the flow stress at low temperatures appears to occur because the atomic displacements involved in the movement of individual dislocations by glide becomes difficult very rapidly. As the yield stress increases, the ductility decreases, and, if the strain rate is also increased, dislocation glide is replaced by twin formation and brittle fracture by cleavage can occur. The temperature where brittle behavior replaces ductile behavior depends upon the strain rate. Dislocation glide can still occur at temperatures as low as 4.2 K when the strain rate is small.

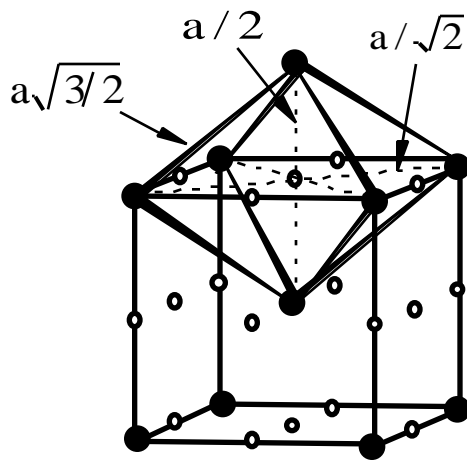
### Interstitial solutes in iron

See also Chapter 2 in Leslie's book and chapter 1 in "Principles of Heat Treatment of Steel by G. Krauss, ASM, 1980.

FCC crystals have octahedral interstitial sites at coordinates 0.5, 0.5, 0.5 and the equivalent 0.5,0,0 positions in the unit cell, see figure 2. These are symmetric sites; i.e. in the hard sphere-central force model for metallic crystals, the centers of these sites are equidistant from the centers of the nearest neighboring atoms. Using 2.52 angstroms for the diameter of FCC iron atoms (1 angstrom =  $10^{-10}$  meters) we find that 1.04 angstroms is the diameter of a sphere that will just fit in the octahedral site. We do this by noting that if the lattice parameter is “a” then the length of the diagonal of a face of the unit cell is  $a\sqrt{2}$ . This is also equal to  $2D_{Fe}$ , where  $D_{Fe}$  is the diameter of an iron atom that is assumed to behave as a hard sphere. Thus we can evaluate “a” and then the diameter of the octahedral hole which is equal to  $(a - D_{Fe})$ . The tetrahedral sites are at 0.25, 0.25, 0.25, for which we find the diameter of the hole to be 0.27 Angstroms. Because of this difference in size, the interstitial solutes C and N ( of which C has a radius of about 0.8 angstroms

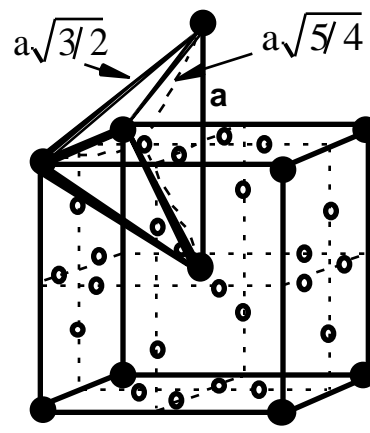


After W.C. Leslie, Met. Trans., 3:9 (1972).



OCTAHEDRAL

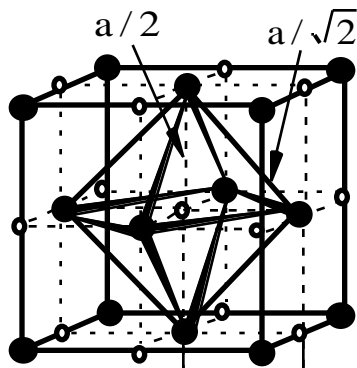
(a) ● Metal Atoms



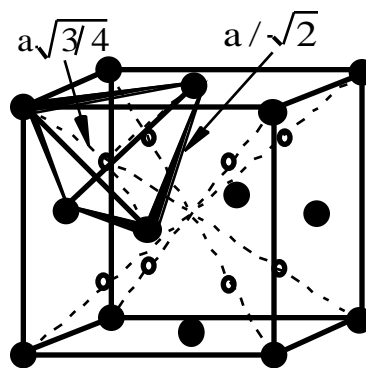
TETRAHEDRAL

(b) ● Metal Atoms

BCC



(a) ● Metal Atoms



(b) ● Metal Atoms

FCC

and N one near 0.7 angstroms) fit much more easily into the octahedral sites in the FCC structure than in the tetrahedral sites.

BCC sites are also octahedral and tetrahedral, but the octahedral site is not symmetric because two of the neighboring atoms are closer to the center of the site than the others. The sites are at the coordinates 0.5, 0.5, 0 (and the equivalent 0.5,0,0 ) and 0.5, 0.25, 0, respectively. Using the same diameter as before for an iron atom we find interstitial hole radii of about 0.19 and 0.36 Angstroms. Even though the octahedral holes are smaller than the tetrahedral holes the interstitial solutes reside in the octahedral holes because then they only have two nearest neighbors to displace markedly.

Consequences (see MSE 565)

The first consequence is that the solubility of C and N is greater in FCC iron than in BCC iron because the interstitial holes are larger in the FCC structure, even though the hard sphere model predicts the FCC structure to be the more close-packed. We will see that this is a very major consequence that has far reaching effects in ferrous metallurgy.

Dislocations create elastic strain fields in the crystal around them and generate major atomic displacements at and near their cores where the displacements cannot be described elastically. Consequently, because the interstitial solutes, C and N, are larger than the interstitial sites within the crystalline matrix they prefer to occupy sites along the dislocation cores and also those matrix sites that are located in places where the elastic strain field of the dislocation helps to overcome the size misfit. When BCC iron is annealed and slowly cooled, the interstitial solutes are able to diffuse to and occupy, preferentially, those sites that they prefer in the elastic strain fields. Thus the solute is not randomly dispersed throughout the iron but is segregated at preferred sites around the dislocations and along dislocation cores. Furthermore, this is true for dislocations of any character because the octahedral sites in the BCC structure are non symmetric so that the solutes cause tetragonal distortions by displacing two nearest neighbors more than the other four. This enables strong interactions with the shear strain fields of screw components as well as with the strain fields due to the edge components of dislocations.

The interactions between interstitial solute elements and dislocations in BCC iron at ambient temperatures are powerful. When the material is treated so that segregation takes place as, for example, by aging at temperatures that permit the solutes to diffuse, dislocations are pinned and many become immobile because moving the dislocation away from the segregated solute requires a very large stress. When a tensile test is conducted on a sample of such material at room temperature, most of the existing dislocations do not glide at yield. When plastic deformation begins it does so only at a few particular places within the steel where there are localized stress concentrations that are able to activate or create dislocation sources. ( Leslie used Ti gettered iron in an attempt to minimize the influence of interstitial solutes upon the yield stress) Consequentially, at yield there is a low density of mobile dislocations. However, the sample is forced to extend at the strain rate imposed by the testing machine so these dislocations must glide rapidly and this requires a high stress. When the dislocation sources (e.g. Frank-Read sources and double cross slip sources) are activated they generate new dislocation line and the density of mobile dislocations increases rapidly. This means that the rate of glide necessary to maintain the strain rate drops and the applied stress needed to produce that rate also drops. The result is a yield point phenomenon of an upper and lower yield stress and localized yield that causes Luders bands to form and spread along the sample. In tensile tests conducted at higher temperatures, serrated yielding occurs because the solute elements are able to diffuse fast enough to “catch up” dislocations and pin them again.



Consequently the stress required to maintain the strain rate fluctuates up and down like a series of mini yield point phenomena.

The material is subject to strain aging and blue brittleness. Strain aging refers to a process in which the dislocation density is first increased by plastic strain during a cold work operation and then the material is held (aged) at temperatures high enough for carbon and nitrogen to diffuse but not high enough for extensive recovery to take place. The resulting combination of pinned dislocations and the greater density of forest dislocations raises the flow stress significantly. Strain aging can be detrimental because of the loss of ductility that occurs as a consequence. ( Nitrogen diffuses more rapidly than does carbon at room temperature and it has a greater solubility in iron at this temperature. If the nitrogen content is high enough, strain aging and loss of ductility can arise after prolonged aging at room temperature. Effects due to carbon arise when the temperature is in the range of 100-200 Celsius.) Steel so treated can acquire a bluish oxide; hence the term “blue brittleness”.

The solubility of carbon in BCC iron is small ( about 0.02 wt. % maximum) and depends on what phase is formed when the solubility limit is exceeded. The equilibrium precipitate is graphite but the kinetics of the nucleation and growth processes of forming graphite is very sluggish. Metastable carbides are formed first when supersaturated solid solutions of Fe-C are aged. The precipitate that forms above 150 to 200°C is an orthorhombic, metastable carbide, Fe<sub>3</sub>C, that is called cementite. From room temperature to 200°C, another transition phase has been observed ( Honeycombe, page 8). This is an hexagonal carbide that contains less carbon than is in cementite and is called epsilon carbide.

Expressions for the solubility are: (from Leslie's book)  
for equilibrium with graphite... $\log(c) = 7.81 - 5550/T$   
for equilibrium with cementite.... $\log(c) = 6.38 - 4040/T$   
where T is in degrees Kelvin and c is in part parts million by weight.

The interstitial solutes diffuse very rapidly in BCC iron so that static and dynamic strain aging can occur at temperatures as low as 60° C. ( Dynamic strain aging refers to strain aging that occurs while the sample is being deformed). This is due to their small sizes and also because the diffusion process does not involve vacancies so that each solute atom usually has an empty site next to it into which it can jump. Honeycombe presents some diffusion coefficients for solutes in iron in his book, Steels-Microstructure and Properties, page 7. It is important to note that the diffusion coefficients vary exponentially with  $-1/T$  and that the activation energy for diffusion (of substitutional solutes also) is smaller in BCC iron than in FCC iron, so that diffusion can be more rapid in BCC iron than in FCC iron even though the latter is at a higher temperature.

#### Substitutional Solutes.

The majority of solutes in iron occupy substitutional sites. These are symmetric sites so that substitutional solute strengthening is not as effective, for similar concentrations, as interstitial strengthening. Nevertheless, because greater concentrations can be dissolved, substitutional strengthening at, and above, room temperature can be significant and of practical use. It is not clear what controls the degree of strengthening, but both size misfit and electronic differences appear to contribute. Co and Cr are not effective while P and Pt have strong effects. Ni, Si and Mn have significant effects. When the iron is free of interstitial solutes (either because of purification or because the solutes are scavenged by alloying additions such as Ti, which reduces the dissolved

solute concentration by combining with solute atoms to form second phases) the effects of substitutional elements are more clearly seen. Interestingly, experiments with these materials have shown that it is also possible for substitutional solutes to cause static and dynamic aging. Because these solutes diffuse much more slowly than do interstitial solutes, the aging temperatures are higher and recovery processes occur also. However, when interstitial solutes are present in solution, as is most commonly the case, then the aging effects due the interstitial solutes are dominant.

Slip in BCC iron and the Hall Petch relation. A brief review. See MSE 565.

When dislocations glide in BCC iron during and after general yield at ambient temperatures, they produce wavy slip bands. ( General yield refers to plastic deformation that occurs across the cross section of the sample not to localized micro yield processes that correspond to strains of the order of  $10^{-6}$  ) The dislocations are narrow and are not pairs of well separated partial dislocations because the stacking fault energies are high. Cross-slip is evidently easy. The wavy slip bands and prolific cross slip indicates that the plastic deformation of iron is dominated by screw dislocations because dislocations of other character cannot cross slip. Slip has been identified on the  $\{110\}$ ,  $\{112\}$  and  $\{123\}$  families of planes which, in combination with Burgers vectors parallel to  $\langle 111 \rangle$ , gives rise to 48 slip systems. Iron is therefore ductile and formable at room temperature and above. As the temperature is lowered, the stress required to make the dislocations glide becomes very large and the material shows a transition from ductile to brittle behavior when deformed at high strain rates. This transition is commonly identified by impact tests wherein notched bars are broken by impact and the energy expended in breaking the samples is measured. The transition from ductile to brittle fracture is associated with a marked reduction in the amount of energy expended. The fracture process is transgranular cleavage on  $\{100\}$  planes. A material that has a ductile to brittle transition temperature has obvious limitations for use below that temperature.

The Hall Petch relation relates the yield stress ( the lower yield stress for samples that show a yield point phenomenon) linearly to the inverse of the square root of the average grain diameter. Iron and low carbon steels have been shown to obey the Hall-Petch relationship with a proportionality constant near  $1.9 \text{ kg mm}^{-3/2}$  (  $0.31 \text{ mega Newtons M}^{-3/2}$  ), ( see J. D. Embury in Strengthening Methods in Crystals, Elsevier, 1971). Armco iron ( see below) behaves similarly. Hence grain size refinement is an important method of controlling strength in ferrous alloys. This is particularly so for High Strength Low Alloy steels.

Zone refined iron of 99.999% purity can be produced in small quantities but it has no commercial use. Slightly more impure iron can be produced in quantity, but it is only slightly harder and stronger than copper. The softness of iron of high purity is not useful. Iron is used for many applications because it is cheap and formable, e.g. enameled products like refrigerator doors; hence nearly all commercial iron is moderately impure. For example, Armco iron has typically: 0.012% C, 0.02% Mn, 0.05% P, and 0.025% S. These modest amounts of impurities provide significant strengthening without serious, adverse effects upon ductility. Annealed samples of zone refined iron have been found to have yield and ultimate tensile strengths of 7000 psi (48 MPa) and 24000 psi (165 MPa) with 40% elongation compared to Armco iron's 20000 psi, 45,000 psi and 28%. Note that these figures represent “ball-park” amounts because of the effects of grain size. Further increases in the yield stresses can be achieved by increasing the dislocation density by cold work but this usually reduces the ductility.

### Hall-Petch Relationship for Fe, 70/30 Brass, Al, and Cu

After: N. Hansen: Polycrystalline Strengthening, Metall. Trans. A, 1985, Vol. 16A, pp. 2167-2190

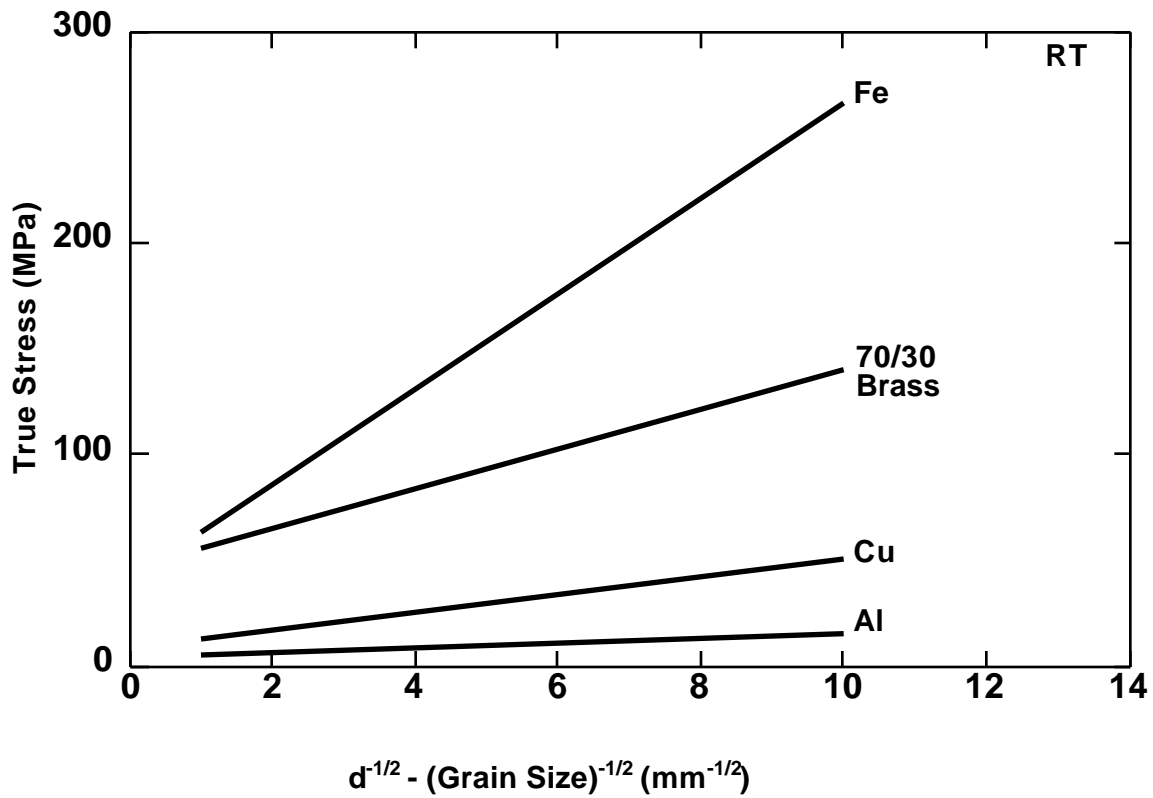


Fig. 9 – Yield stress – grain size relationship at room temperature for aluminum,<sup>69</sup> copper,<sup>70</sup> 70:30 brass,<sup>71</sup> and iron.<sup>72</sup>

## The Iron Carbon System.

(See MSE 542.01)

Review of nomenclature.

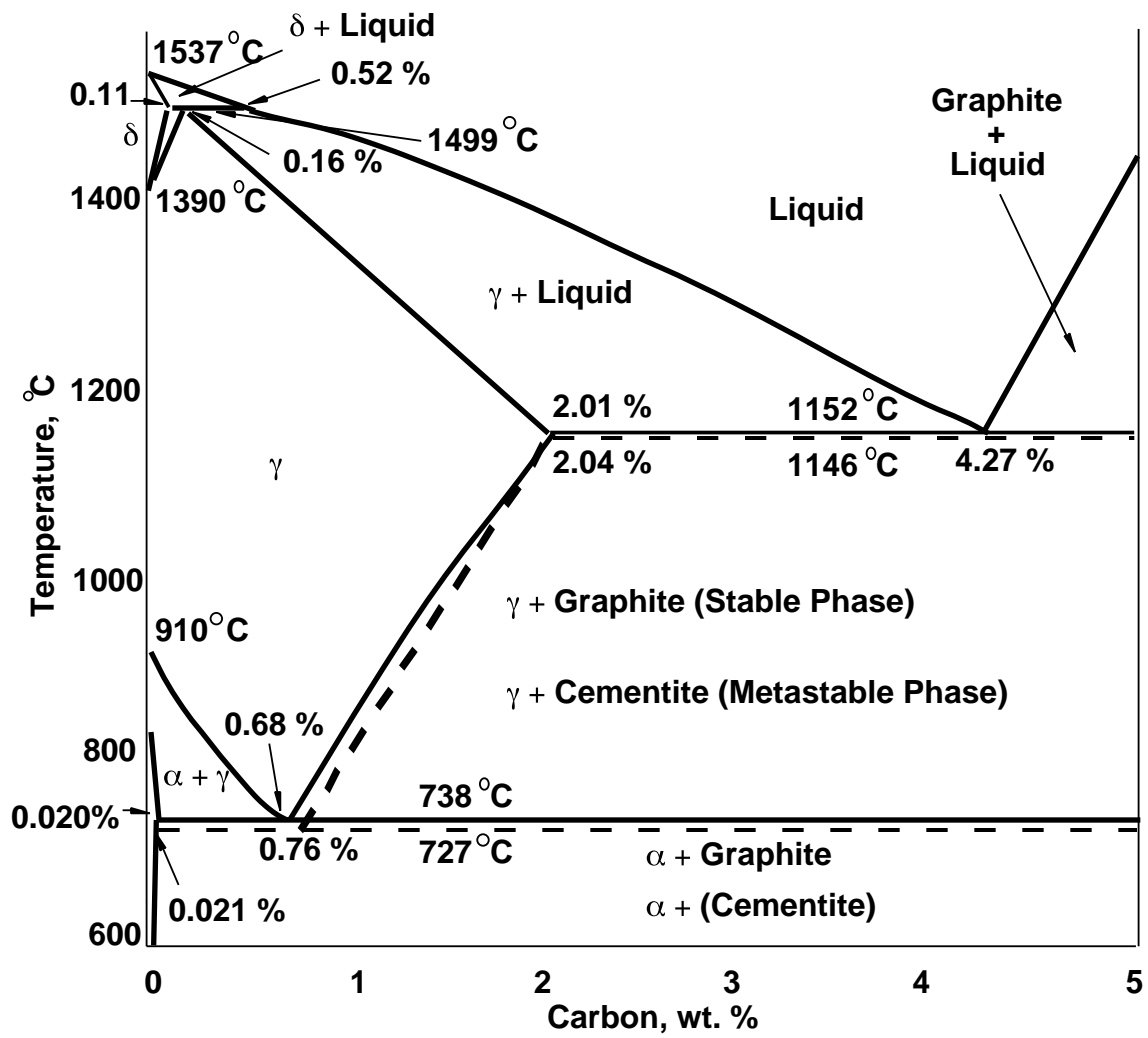
- 1) The equilibrium and metastable phase diagrams.

The equilibrium binary Fe-C phase diagram depicts the phase fields that involve graphite and the solid solutions of the allotropes of iron. However, graphite does not ordinarily form in commercial steels unless the steel is seriously overheated. This is because there exists metastable carbide phases that can nucleate and grow much more rapidly than can graphite when supersaturated Fe-C solid solutions are aged. The most important of these carbides is  $\text{Fe}_3\text{C}$ , which is called cementite. If the sulfur and phosphorus content are very low,  $\text{Fe}_3\text{C}$  can decompose into graphite and iron in about 8 hours at  $700^\circ\text{C}$ . Graphitization, as this type of formation of graphite is called, is undesirable because it has an adverse effect on the mechanical properties of the steel. Fortunately, graphite does not form during the treatments normally given to steels. Cementite is found in steel artifacts that are many hundreds of years old. Hence the relevant diagram for practical purposes is the metastable diagram on which cementite replaces graphite.

The iron-carbon, metastable phase diagram shown in figure 3, is a very valuable tool when one is considering the nature of steels. Provided it is borne in mind that the details e.g. the exact carbon composition at the eutectoid point and the exact temperature of the eutectoid isotherm can be changed by the presence of manganese and residual elements, it can be applied readily for considering plain carbon steels. Many of the phase transformations in alloy steels can also be considered using the binary diagram, but then it is important to evaluate the effects due to the alloying elements in more detail as their concentrations are increased because these effects can be pronounced and important. The iron carbon metastable phase diagram is particularly important with respect to ferrous metallurgy. It should be consulted so frequently that it becomes burned into one's memory.

- 2) **Phases:** **alpha ferrite** is the BCC solid solution of carbon in iron that exists in the low temperature range; **austenite** is the FCC solid solution, **cementite** is the carbide and **delta ferrite** is the BCC solid solution that can exist at high temperatures. When the term ferrite is used alone, it is usually understood that it is the low temperature phase otherwise the ferrite is qualified with the appellation delta. Earlier we observed that epsilon carbide can precipitate from supersaturated ferrite. However, this metastable phase is not shown in figure 3 which is really the iron cementite phase diagram.

- 3) It is customary in the USA to refer to the eutectoid isotherm as the  $A_1$  line, the boundary between the austenite and austenite/ferrite phase fields as the  $A_3$  line and the boundary between the austenite and austenite/cementite phase fields as the  $A_{cm}$  line. Then, for any particular alloy, the temperatures corresponding to the intersection points with these lines of a vertical line drawn through the composition of the alloy are called the  $A_1$  point etc. Because the temperatures at which the corresponding transformations begin during heating and cooling depend upon the rates of heating and cooling, the effects of heating and cooling are indicated by using c for chauffage and r for refroidissement i.e.  $A_{c1}$ ,  $A_{r1}$ . These are related to the kinetics of the phase transformations that occur during heating and cooling whereas the points on the diagram refer to equilibrium..



4) Note the extent of the gamma austenite field compared to that of the alpha ferrite field and reflect on the importance of this with respect to the existence of steel. Many of the microstructures that can be produced in steels, and therefore many of the properties that can be tailor-made, depend upon the fact that when austenite is cooled it can become supersaturated and therefore undergo phase transformations as it seeks equilibrium. Were this not so, the wealth of microstructures that can be produced by heat-treating steel would be severely curtailed. It follows that many functions now performed by steel would not be performed and world would be a rather different place.

5) When other alloying elements are added to Fe-C alloys the details of the phase diagram change. As we will see, these changes can be quite large; however, for plain carbon steels the changes due to the relatively low quantities of Mn, Si etc. are not great, so the binary diagram can be used as a reasonable guide to the constitution of these steels. This is still true for low alloy steels, but it is important to remember always that there will be differences from the binary diagram. Steels can be classified with respect to the eutectoid composition : a eutectoid steel has the eutectoid composition, a hypereutectoid steel has more carbon than a eutectoid steel and a hypoeutectoid has less.

6) The S.A.E. / A.I.S.I. and unified numbering system for plain carbon steels.

The first two systems are very similar and use a numerical code of 10xx and 10xxx. The more modern, unified numbering system uses G 10xxx etc. In these codes the 10 indicates that the steel is a plain carbon steel while the xxx's indicate a range for the carbon content . Typically compositions run from 1005 to 1095 but 10125 would have 1.25 wt.% C. Note the three steels 1044, 1045 and 1046 in the A.I.S.I. system. Here the first two digits inform us that the steels are all plain carbon steels. The xx's are now 44, 45 and 46. Because these digits are used to indicate the carbon content within a range of a few points, it would appear that the steels are indistinguishable. With respect to the carbon content this is true. Each has 0.43 to 0.5 wt.% C as the specified range. However, the ranges for Mn differ being 0.3 to 0.6, 0.6 to 0.9 and 0.7 to 1.00 wt.%. In fact , it is possible for one steel to satisfy the specifications for more than one standard steel. The point to note is that when the carbon ranges are the same, the higher Mn limit corresponds to the larger xx. Generally speaking, the numerical code gives you a fair idea of what the steel is. Then it is sensible to have access to tabulated compositions in Metal Handbooks, rather than to attempt to memorize many details.

For the sake of completeness we should note that carbon steels with more than 1.00 % Mn are identified by replacing the first 0 with 5 i.e. 15xx. There is a group of steels that possess more than 1 wt. % Mn and also have a minimum range of Si specified as between 0.15 and 0.35 wt. %. This is 13xx and its members, strictly speaking, are alloy steels. Also, whereas it is usual to keep the sulfur and phosphorus contents low to avoid embrittlement problems that they can cause, there are occasions when ductility is not a major concern and machinability is more important. In these cases, S and P are deliberately added because they endow the steel with good machinability properties . Hence we have the 11xx and 12xx series for which the first is resulfurized and the second is enhanced in both S and P, e.g. 1146 has 0.08 to 0.13 S and 1215 has 0.26 to 0.35 S and .04 to 0.09 P. Finally, some steels also have Pb (also for improving machinability) additions whereupon an L is included e.g. 12L14. Typically, the lead content lies between 0.15% and 0.35%.

SAE Number	Chemical Composition Limits (Ladle Analysis), Per Cent (3)				
	C	Mn	P, max.	S, max.	Corresponding AISI Number
1005	0.06 max.	0.35 max.	0.04	0.05	-
1006	0.08 max.	0.25-0.40	0.04	0.05	1006
1008	0.10 max.	0.30-0.50	0.04	0.05	1008
1010	0.08-0.13	0.30-0.60	0.04	0.05	1010
1011	0.08-0.13	0.60-0.90	0.04	0.05	-
1012	0.10-0.15	0.30-0.60	0.04	0.05	1012
1013	0.11-0.16	0.50-0.80	0.04	0.05	-
1015	0.13-0.18	0.30-0.60	0.04	0.05	1015
1016	0.13-0.18	0.60-0.90	0.04	0.05	1016
1017	0.15-0.20	0.30-0.60	0.04	0.05	1017
1018	0.15-0.20	0.60-0.90	0.04	0.05	1018
1019	0.15-0.20	0.70-1.00	0.04	0.05	1019
1020	0.18-0.23	0.30-0.60	0.04	0.05	1020
1021	0.18-0.23	0.60-0.90	0.04	0.05	1021
1022	0.18-0.23	0.70-1.00	0.04	0.05	1022
1023	0.20-0.25	0.30-0.60	0.04	0.05	1023
1025	0.22-0.28	0.30-0.60	0.04	0.05	1025
1026	0.22-0.28	0.60-0.90	0.04	0.05	1026
1029	0.25-0.31	0.60-0.90	0.04	0.05	-
1030	0.28-0.34	0.60-0.90	0.04	0.05	1030
1035	0.32-0.38	0.60-0.90	0.04	0.05	1035
1037	0.32-0.38	0.70-1.00	0.04	0.05	1037
1038	0.35-0.42	0.60-0.90	0.04	0.05	1038
1039	0.37-0.44	0.70-1.00	0.04	0.05	1039
1040	0.37-0.44	0.60-0.90	0.04	0.05	1040
1042	0.40-0.47	0.60-0.90	0.04	0.05	1042
1043	0.40-0.47	0.70-1.00	0.04	0.05	1043
1044	0.43-0.50	0.30-0.60	0.04	0.05	-
1045	0.43-0.50	0.60-0.90	0.04	0.05	1045
1046	0.43-0.50	0.70-0.90	0.04	0.05	1046
1049	0.46-0.53	0.60-0.90	0.04	0.05	1049
1050	0.48-0.55	0.60-0.90	0.04	0.05	1050
1053	0.48-0.55	0.70-1.00	0.04	0.05	-
1055	0.50-0.60	0.60-0.90	0.04	0.05	1055
1060	0.55-0.65	0.60-0.90	0.04	0.05	1060
1064	0.60-0.70	0.50-0.80	0.04	0.05	1064
1065	0.60-0.70	0.60-0.90	0.04	0.05	1065
1069	0.65-0.75	0.40-0.70	0.04	0.05	-
1070	0.65-0.75	0.60-0.90	0.04	0.05	1070
1074	0.70-0.80	0.50-0.80	0.04	0.05	1074
1075	0.70-0.80	0.40-0.70	0.04	0.05	-
1078	0.72-0.85	0.30-0.60	0.04	0.05	1078
1080	0.75-0.88	0.60-0.90	0.04	0.05	1080
1084	0.80-0.93	0.60-0.90	0.04	0.05	1084
1085	0.80-0.93	0.70-1.00	0.04	0.05	-
1086	0.80-0.93	0.30-0.50	0.04	0.05	1086
1090	0.85-0.98	0.60-0.90	0.04	0.05	1090
1095	0.90-1.03	0.30-0.50	0.04	0.05	1095

NOTE: LEAD. When lead is required as an added element to a standard steel, a range of 0.15 to

**After: Mechanical Behavior of Materials, N.E.Dowling, Prentice-Hall, 1999, pp.55, 56**

**TABLE 3.3 COMMONLY ENCOUNTERED CLASSES OF IRONS AND STEELS**

Class	Distinguishing Features	Typical Uses	Source of Strengthening
Cast Iron	More than 2% C and 1 to 3% Si	Pipes, valves, gears, engine blocks	Ferrite-pearlite structure as affected by free graphite
Plain-carbon steel	Principal alloying element is carbon up to 1%	Structural and machine parts	Ferrite-pearlite structure if low carbon; quenching and tempering if medium to high carbon
Low-alloy steel	Metallic elements totaling up to 5%	High strength structural and machine parts	Grain refinement, precipitation, and solid solution if low carbon; otherwise quenching and tempering
Stainless steel	At least 10% Cr; does not rust	Corrosion resistant piping and nuts and bolts; turbine blades	Quenching and tempering if <15% Cr and low Ni; otherwise cold work or precipitation
Tool steel	Heat treatable to high hardness and wear resistance	Cutters, drill bits, dies	Quenching and tempering, etc.

**TABLE 3.4 SOME TYPICAL IRONS AND STEELS**

Description	Identification	UNS No.	Principal Alloying Elements, Typical % by Weight							
			C	Cr	Mn	Mo	Ni	Si	V	Other
Ductile cast iron	ASTM A395	F32800	3.50	-	-	-	-	2	-	-
Low-carbon steel	AISI 1020	G10200	0.2	-	0.45	-	-	0.2	-	-
Medium-carbon steel	AISI 1045	G10450	0.45	-	0.75	-	-	0.2	-	-
High-carbon steel	AISI 1095	G10950	0.95	-	0.4	-	-	0.2	-	-
Low-alloy steel	AISI 4340	G43400	0.40	0.8	0.7	0.25	1.8	0.2	-	-
HSLA steel	ASTM A588-A	K11430	0.15	0.5	1.1	-	-	0.2	0.05	0.3 Cu
Martensitic stainless steel	AISI 403	S40300	0.15	12	1.0	-	0.6	0.5	-	-
Austenitic stainless steel	AISI 310	S31000	0.25	25	2.0	-	20	1.5	-	-
Precipitation hardening stainless steel	17-4 PH	S17400	0.07	17	1.0	-	4	1.0	-	4 Cu 0.3 (Nb+Ta)
Tungsten high-speed tool steel	AISI T1	T12001	0.75	3.8	0.25	-	0.2	0.3	1.1	18 W
18 Ni maraging steel	ASTM A538-C	K93120	0.01	-	-	5	18	-	-	9 Co, 0.7 Ti



## Phase Transformations in Iron

An important phase transformation in pure iron and its dilute solid solutions is the allotropic transformation between the BCC and FCC phases that occurs when the temperature is varied about 910 Celsius. Let us consider the transformation from FCC to BCC during cooling. A number of investigators have studied this transformation as a function of the rate of cooling from the high temperature at which the iron was initially FCC. Their work has been recently reviewed by Borgenstam and Hillert, *Met and Mat. Trans.*, 27A, 1501, 1996. When the cooling rates are small, of the order of a few degrees per second, the temperature of the iron falls below 910 degrees and the iron becomes super cooled. Then BCC crystals nucleate and grow when the degree of super cooling is sufficient to provide the necessary driving force. Nucleation is heterogeneous on grain boundaries and at grain boundary triple junctions. (See MSE 543) The beginning of the transformation can be detected experimentally by observing the rates of change in the temperature of the iron because of the effects due to the evolution of heat as the transformation occurs. For small cooling rates the degree of undercooling attained at the onset of the transformation is small and the total transformation is completed at high temperatures by diffusion controlled nucleation and growth processes that produce an equiaxed array of grains separated in general by high angle grain boundaries. The degree of undercooling at which the transformation begins, increases initially as the rate at which the FCC iron is cooled is increased but then remains constant at a plateau value. At the same time the intercrystalline boundaries of the BCC phase become blocky and faceted and the composition remains uniform. These are characteristics of the massive transformation and the BCC phase is called massive ferrite. This behavior has been observed to occur in iron with a few parts per million of dissolved carbon and also in iron containing 0.01 wt. % carbon. In the latter the massive ferrite plateau begins near 800 degrees at a cooling rate of several thousand degrees Celsius per second. The actual temperature of the plateau varies with the grain size of the FCC phase, being smaller the larger the grain size.

At still higher cooling rates above  $10^4$  K/sec, another plateau is observed at a lower temperature than the one described previously. At this plateau, the ferrite begins to form as acicular plates which emanate from original grain boundary positions and also form within grains. Such a morphology is usually called Widmanstätten, hence the phase is sometimes identified as Widmanstätten ferrite. It is generally agreed that the equiaxed and acicular ferrite forms by diffusion controlled processes. Cooling rates greater than  $10^5$  K/sec avoids these transformations and then another plateau occurs at a lower temperature still. The transformation that begins at this plateau is still from FCC to BCC but it now occurs so rapidly that it is not effected by diffusion. The ferrite produced comprises bundles of narrow, lath shaped crystals in which the dislocation density is high. These three plateaus have been observed in iron with a few parts per million of carbon and also in Fe-0.01 wt. % C. It has been reported that yet another plateau occurs in the latter material at even higher rates of cooling. At this fourth plateau that occurs at about 700 K the transformation is again FCC to BCC but the product consists of twinned plates. The diffusionless processes by which these transformations are produced are called martensitic which is the general name given to a transformation that produces a change in crystal structure in a displacive manner and does not require diffusion. The products of the transformations in these cases are called lath martensite and lenticular or plate martensite. In each case the transformation begins when the plateau is reached but the amount of the sample which transforms depends on the temperature to which the sample is cooled not on time at that temperature, unlike diffusion controlled nucleation and growth transformations. Lenticular martensite has not been observed to form in very pure iron and no one has succeeded in cooling FCC iron to below the lath martensitic start plateau without

forming martensite; i.e. a 100 % FCC phase cannot be retained by rapid cooling to room temperature.

### Phase Transformations in Plain Carbon Steels.

The mechanical properties of steel are controlled by controlling its microstructure and the nature of the phases within that microstructure. This is accomplished by choosing appropriate chemical compositions and thermo-mechanical treatments. The final microstructure of a steel depends upon its composition and its thermo-mechanical history. This history can involve heat-treatments alone, mechanical treatment alone or combinations of the two. Heat-treatments can change the microstructures of steels by processes such as recovery, recrystallization, grain growth and phase transformations. In order to appreciate these effects let us begin with the subject of phase transformations in steel.

#### Austenitization

Austenitization converts a steel into the FCC solid solution called austenite when the steel is heated into the austenitic phase field and held there long enough. It is the first step in the majority of heat treating processes and the nature of the austenite that is obtained is important because it has a direct effect upon the microstructures produced during subsequent treatments in which the austenite is transformed into other phases and the steel is returned eventually to ambient temperature. Austenitization also precedes many hot working processes used to form steel products because it occurs when the steel is heated to the hot-working temperatures. In our discussion of the allotropic transformation of FCC iron to BCC iron we paid very little attention to producing the FCC phase because in pure iron and dilute solid solutions a homogeneous polycrystalline aggregate is easily and rapidly formed when a sample is heated above 910 °C. This is not necessarily so in the case of steels because the starting material is usually a mixture of phases of different compositions which means that long range diffusion is necessary to attain homogeneity.

Inspection of the metastable Fe-C phase diagram, enables us to estimate the range of temperatures from which one could be selected for the austenitization process. These temperatures lie in the austenite phase field. When the temperature is chosen, the time has then to be selected. The optimum combination of temperature and time depends on the objectives of the total heat treatment process and upon the microstructure of the steel before austenitization. We recognize that the steel is initially at ambient temperature and has a microstructure that depends upon its past history. Commonly, it will comprise a mixture of cementite and ferrite. There could be free ferrite grains, discrete particles of the carbide embedded in ferrite grains and there could be regions of pearlite in which the two phases exist as a lamellar mixture. ( It is important to understand that cementite and ferrite are phases; **pearlite** is not a phase it is the name of a microstructure.) Furthermore, if the austenitization heat -up time is long, the microstructure could change somewhat before austenitization begins. The heating rate is an important part of the overall practical process, however, the most important changes that occur during austenitization do so above the A<sub>1</sub> line and in the austenite phase field.

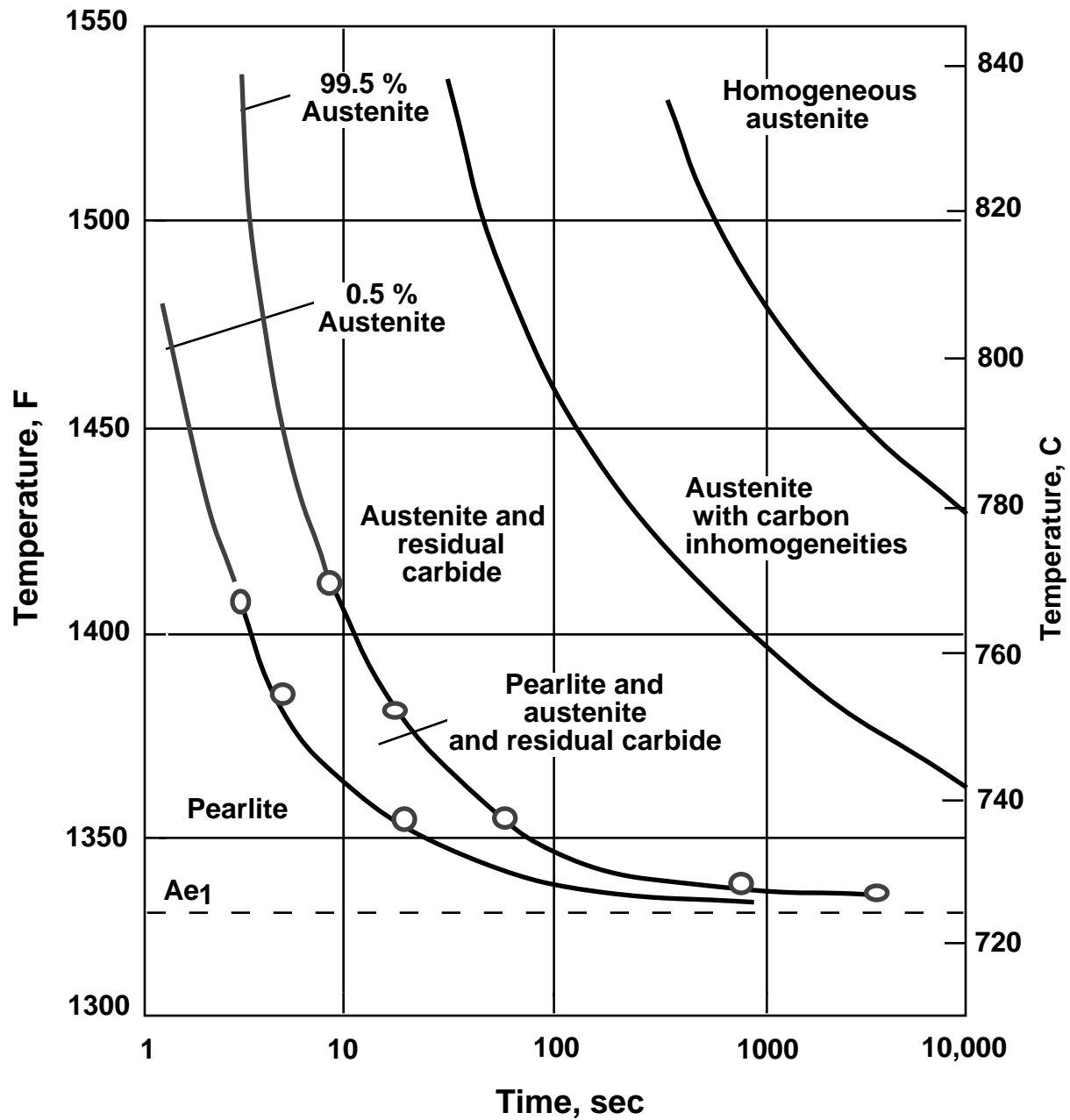
First, suppose we have a hypoeutectoid steel. When the temperature exceeds the eutectoid isotherm, the carbides wish to dissolve but the ferrite cannot accept the carbon residing in the carbides. Hence the first part of the transformation has to be the formation of some austenite. This occurs by a nucleation and growth process. The nucleation events are heterogeneous and take place on ferrite grain boundaries and on ferrite/cementite interfaces. When some austenite forms it

provides a sink for the carbon in the adjacent carbides and the simultaneous growth of austenite and dissolution of carbides takes place, and, when the temperature exceeds the  $A_3$  line, the austenite devours any remaining ferrite. Until these transformations are completed, the rate controlling parameters are the nucleation kinetics and the rates of diffusion of solutes in austenite. Because the nucleation process is heterogeneous, fine grained ferrite and finely spaced lamellae in pearlite cause the transformation to occur more rapidly than it would in a coarse microstructure. Furthermore, the finer the scale of the initial microstructure then the finer the austenitic grain size will be when the carbides have just all dissolved. At this point it is important to recognize that the purpose of an austenitization treatment is usually to produce austenite so that it can then be transformed into something else such as a mixture of ferrite and pearlite. For producing the most desirable mechanical properties in the final product it is usually necessary that the austenite be fine-grained. Its grain size will depend upon the nucleation rate which will in turn depend upon the availability of nucleation sites and also upon the temperature at which the nuclei form. When austenitization is complete, grain growth can take place and will do so at rates that are greater the higher the austenitization temperature. Thus it is generally desirable that the austenite be transformed as soon as possible unless, of course, hot rolling or hot forging is being done..

The end of a typical austenitization process does not usually correspond to the time at which the carbides have just dissolved because, although the steel is austenite, its composition is inhomogeneous because the carbon concentration at and near the positions originally occupied by the carbides exceeds the concentration elsewhere. Further time is required for the austenite to homogenize. The diffusion rate of carbon determines this time in a plain carbon steel. Manganese, however, diffuses substitutionally and therefore much more slowly than does the carbon. Compositional variations (segregation) of manganese in an ingot can persist within the steel and cause microstructural effects such as banding ( i.e. a cyclic variation in the local volume fractions of pearlite and ferrite with position) in subsequent heat treatments. We note that the range of diffusion is proportional to the square root of the product of time and the diffusion coefficient. This can be used as a guide for the selection of the time required for the composition to approach homogeneity when the scale of the initial compositional fluctuations is known.

It follows from the previous comments that the kinetics of producing homogeneous austenite can be retarded considerably in steels that contain alloy carbides (e.g. molybdenum carbides) because substitutional diffusion is much slower than interstitial diffusion.

We have noted that an important microstructural change to be considered during austenitization is grain growth. Some austenite grains continue to grow and, necessarily, others shrink and disappear causing a decrease in the number of grains per unit volume. Typically, the average grain size increases with temperature at a rate that is proportional to the square root of the



Austenitizing rate-temperature curves for commercial plain carbon eutectoid steel. Prior treatment was normalizing from 1610 F (875 C); initial structure, fine pearlite; second curve, final disappearance of pearlite; third curve, final disappearance of carbide; fourth curve, final disappearance of carbon concentration gradients.

time at the temperature. Usually a large austenitic grain size is undesirable because it leads to a coarse microstructure when the austenite is transformed back into the microstructure in which it will be used. Sometimes the austenitization heat treatment is performed only to create austenite and is immediately followed by the rest of the heat treatment. On other occasions mechanical work such as forging or rolling is carried out while the steel is austenitic. These processes can be accompanied by recovery, recrystallization and grain growth. A valuable effect derived from using aluminum to kill steels is relevant here. Aluminum forms fine particles of nitrides and oxides which impede grain boundary migration below 2000°F and thereby helps to keep the austenitic grain size small. Thus it is said to be a grain refiner (This is an example of metallurgical English. The aluminum-rich particles certainly do not free the steel of impurities. They impede grain growth and resist grain coarsening. Presumably, the lack of coarse grains makes the steel more refined in the same way that young ladies are presumed to be more refined than young men.)

After this description of the austenitization process in hypoeutectoid steels, the extension to eutectoid and hypereutectoid steels should be apparent; see figure 4.

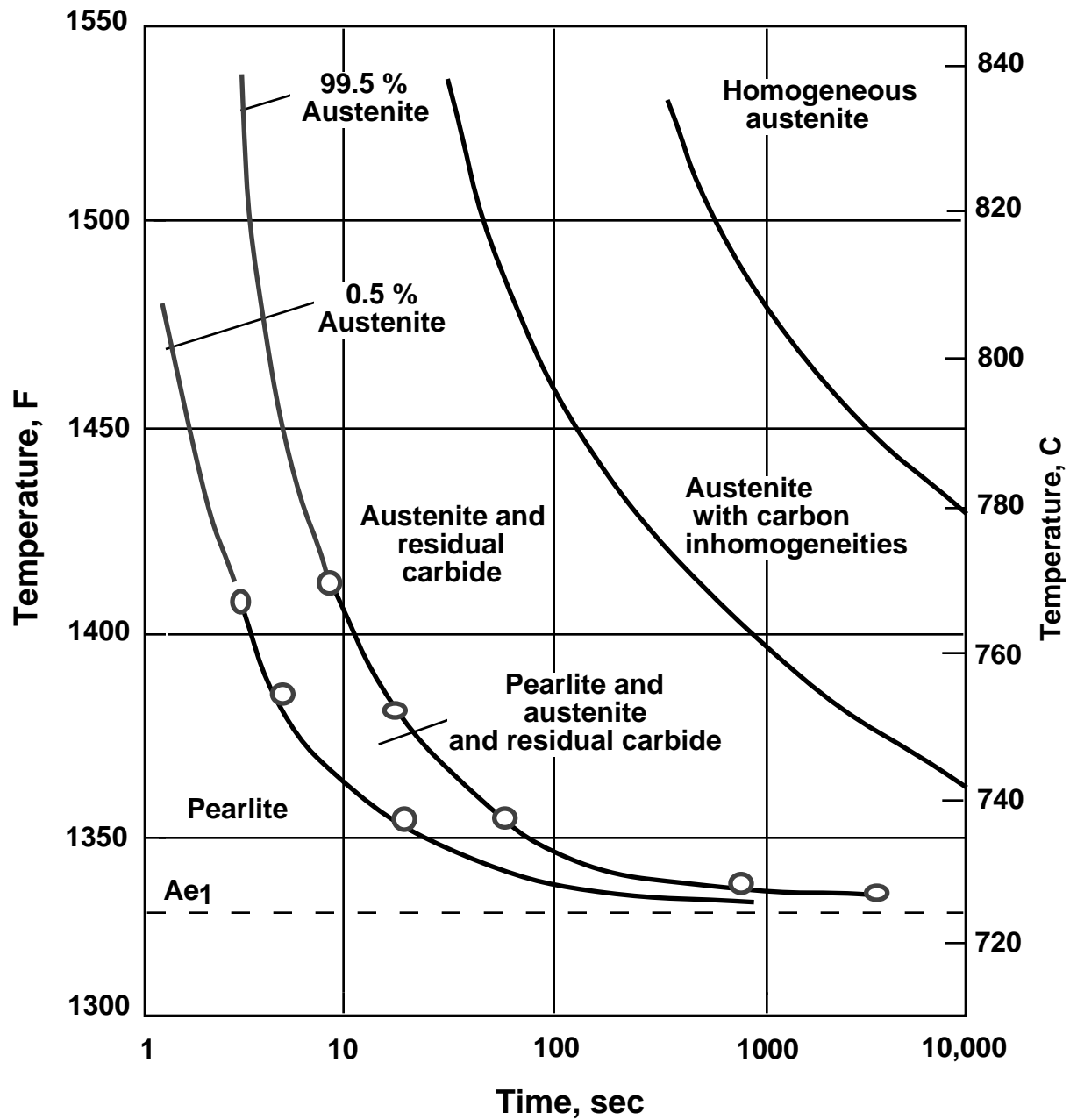
### The Decomposition of Austenite

The array of microstructures (and thus mechanical properties) that are obtainable in steels by various heat-treatments, depends on the manner in which austenite transforms when it is cooled to ambient temperatures. In order to appreciate how these microstructures are produced it is important to understand the various modes by which austenite can decompose. Indeed, this is imperative if one wishes to further develop and improve steels.

### Transformations in Steel of the Eutectoid Composition.

The mode of cooling from the austenitization temperature is a very important parameter to consider when discussing the transformation of austenite. A particularly important variable is the rate of cooling. It is customary, for obvious reasons of convenience, to describe cooling rates as "slow", "furnace cooling", "air-cooling", "water-quenching" etc. Such descriptions are not very precise because the actual cooling rate that a piece of steel undergoes will depend on particular conditions: it can depend upon its environment, the dimensions of the piece of steel, and will usually vary from place to place within the sample. Also, the cooling rate at any particular site within a sample will vary as the temperature at that site changes unless special precautions are taken to ensure that the rate is constant. Air cooling means simply that the steel is allowed to cool naturally in still air. Quite different microstructures can be produced in different forms of the same steel e.g. a half inch round bar versus a four foot diameter coil of rolled sheet.

If a piece of a plain carbon steel is austenitized and then cooled it will attempt to transform into a mixture of ferrite and cementite according to the phase fields indicated on the phase diagram. Inspection of the equilibrium compositions of these phases at the temperature of the eutectoid isotherm leads to the conclusion that a transformation to ferrite and cementite must require atomic diffusion and that the growth rates of the new phases will depend primarily on the rate of diffusion of carbon which has to undergo long range diffusion. The kinetics of such a transformation is



Austenitizing rate-temperature curves for commercial plain carbon eutectoid steel. Prior treatment was normalizing from 1610 F (875 C); initial structure, fine pearlite; second curve, final disappearance of pearlite; third curve, final disappearance of carbide; fourth curve, final disappearance of carbon concentration gradients.

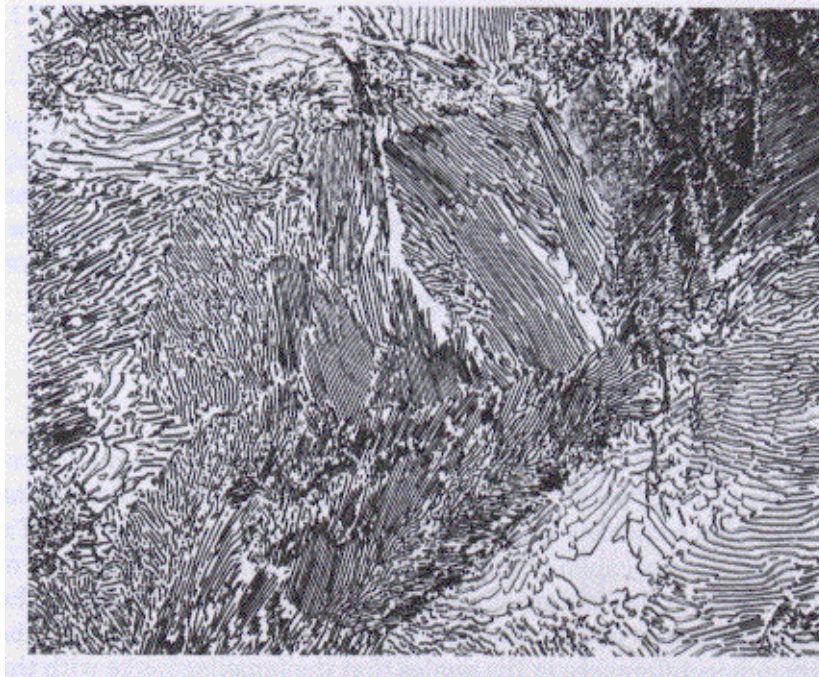
therefore a function of time and temperature. During continuous cooling, various parts of the sample transform at different times and hence at different temperatures. When the cooling rates are slow enough to allow diffusion to occur readily, the transformation is completed at high temperatures and occurs over a small range of temperature. This is the situation to which “furnace cooling” and “slow cooling” refer; the steel is close to its equilibrium state as its temperature drops. Under these conditions the lever rule and the phase diagram provide reasonable estimates of the volume fractions of various phases to be expected in the final microstructures. As the cooling rates are increased, the transformation to ferrite and cementite begins and ends at lower and lower temperatures and the steel is no longer close to equilibrium as it cools. Quantitative predictions from the phase diagram such as the volume fraction of free ferrite to be present in the final microstructure are no longer possible. Because of these complications, it is sensible to consider, first, what happens during isothermal transformations.

Strictly speaking, the term isothermal transformation of austenite implies that the transformation takes place at a constant temperature and, also, that none (or negligible amounts) of the transformation take place before the austenite arrives at this temperature. This is generally difficult to achieve in practice, especially when the transformation is rapid and the sample of steel is large. Initially, we will suppose that the samples that we are considering are so small that the temperature is always essentially uniform throughout them and that temperature changes can be made instantaneously. This supposition is made now to enable us to concentrate on the nature of the transformations and to defer until later considerations of changes that might occur while the samples are being cooled to the isothermal transformation temperature.

Let us suppose that an experiment has been conducted in which many samples of a plain carbon steel of the eutectoid composition (e.g. a 1080 steel ) were austenitized in the same manner, instantaneously cooled to, and held for various times at, selected temperatures below the eutectoid isotherm. Let us suppose also, that the microstructural changes that occurred within them were monitored. At this stage we shall not concern ourselves with **how** the changes are monitored, we simply suppose that they are. What are the results of such an experiment?

#### 1) Transformation temperatures within a hundred degrees Celsius of the eutectoid isotherm.

During the rapid quench to the transformation temperature, each sample remains a polycrystal of austenite. While the sample is at the transformation temperature, processes occur which eventually produce recognizable crystals of ferrite and cementite. The time taken for this to happen is called the incubation period. From a practical point of view, the magnitude of the incubation period that is determined experimentally, depends on the resolution of the technique used to monitor the process because the minimum size of a particle of a new phase that can be detected becomes smaller as the resolution increases. Because of this, let us arbitrarily define the end of the incubation period as corresponding to a volume fraction transformed of 0.5%. One might similarly define the end of the transformation as a transformed volume fraction of 99.5%. The incubation period is temperature dependent. It is large near the  $A_1$  line and decreases rapidly as the transformation temperature is reduced. This is because the magnitude of the thermodynamic driving force for the transformation increases as the degree of undercooling below the  $A_1$  line increases. The transformation begins at grain boundaries where particles of cementite and ferrite form adjacent to each other. These particles grow and the boundary advances into one of the grains,



**Pearlite in a furnace-cooled Fe-0.75C alloy. Magnification, 500x.**

**From: G. Krauss: Steels: Heat Treatment and Processing Principles, ASM International, 1990, p. 20.**



acting as a boundary between the untransformed austenite ahead of it and the region that has transformed behind it. As the interface moves, the particles of ferrite and cementite develop into plates so that the transformed volume comprises a lamellar array of alternating plates of these two phases. These events occur at various places on the grain boundaries and at triple junctions. The lamellar microstructure is called pearlite. It is important to note that pearlite is **not** a phase; the phases in it are ferrite and cementite. Pearlite is the name of the microstructural constituent that consists of alternating lamellae of the two phases. In each colony of pearlite, the lamellae are mostly parallel and are frequently curved. The spatial orientations of lamellae from colony to colony are not the same. Later, neighboring colonies of lamellae, differently oriented (in space), join together and continue to advance into the austenite. When the transformation occurs at low degrees of undercooling such groups of colonies become bounded from the austenite by an approximately spherically curved boundary and are called pearlite nodules. Eventually, as the nodules continue to grow, they impinge on one another and finally the samples are converted into an assembly of pearlite colonies. As the temperature at which the transformation is occurring is decreased, the nucleation process becomes so rapid that all of the grain boundaries are consumed very early in the transformation and the pearlite nodules are in contact along the areas where the boundaries existed.

The average inter-lamellar spacing in the colonies depends upon the temperature at which the pearlite was formed, decreasing with a decrease in the transformation temperature. It is customary to refer to this by using terms such as "fine" or "coarse" pearlite. The spacings can vary over the approximate range of 1 micrometer to 0.1 micrometers.

## 2) Transformations at lower temperatures

As the temperature at which the transformation occurs is decreased further, both the incubation time and the inter-lamellar spacing decrease. Then, near 550 °C, the sample does not transform entirely to pearlite, instead parts of the microstructure comprise non lamellar aggregates of small crystals of ferrite and cementite. At lower temperatures, the incubation period begins to increase again, and pearlite is no longer formed. Instead, the microstructure is made up entirely of fine aggregates of ferrite and cementite. These microstructures are called **bainite** and will be considered in more detail later.

## 3) Transformations during quenching.

The next important observation made in this experiment is that when samples are quenched to below a particular temperature (about 220°C in the present instance) it is no longer possible to retain all of the original austenite. This is entertaining considering that the incubation time for forming bainite had been increasing as the temperature fell and it was getting easier and easier to preserve the austenite phase. As the samples are quenched below this critical temperature, fine crystals of a BCT phase appear. The transformation that produces this new phase is called a martensitic transformation. It is an athermal transformation in plain carbon steels because it occurs during cooling and begins when the sample is cooled below a particular temperature; the amount of the new phase that is formed depends on the temperature to which the sample is cooled rather than the time it spends at that temperature. The temperature at which the martensitic transformation starts is called the  $M_s$  temperature. We recall that the martensitic transformation occurs in relatively pure iron which contains very little carbon. When rapid quenching suppresses the diffusion processes necessary for the formation of cementite in the steel and the temperature continues to fall, the free energy can be reduced by transforming the iron solvent from the FCC structure. The iron tries to

become BCC but is distorted to BCT by the supersaturation of carbon that remains in solid solution. This statement will be elaborated upon in the future.

In ferrous metallurgy it is customary to identify the phase that is produced in the steel as it is quenched below the  $M_s$  point by the name **martensite**. We will follow this custom, but it is important to note that the martensitic transformation is not limited to steel. It is a common mode by which materials can transform their crystal structures, e.g. brasses, titanium alloys, stabilized zirconia and cobalt. Hence, in materials in general, the term martensite may not necessarily refer to a phase that occurs in steels.

The amount of martensite that is formed during quenching, increases as the temperature to which the samples are quenched decreases. The transformation ceases when the temperature falls below the  $M_f$  temperature, where the samples of eutectoid steel are mostly martensite with a small amount of untransformed austenite dispersed within them. This untransformed austenite is called retained austenite. The amount that is present in a quenched sample depends upon the composition of the steel. In plain carbon steels, increasing the carbon content tends to increase the amount of retained austenite but only to a few percent. Retained austenite is more important in alloy steels because many of the alloy steels have  $M_f$  temperatures that are lower than the temperatures of the usual cooling baths, e.g. water or oil at room temperature.

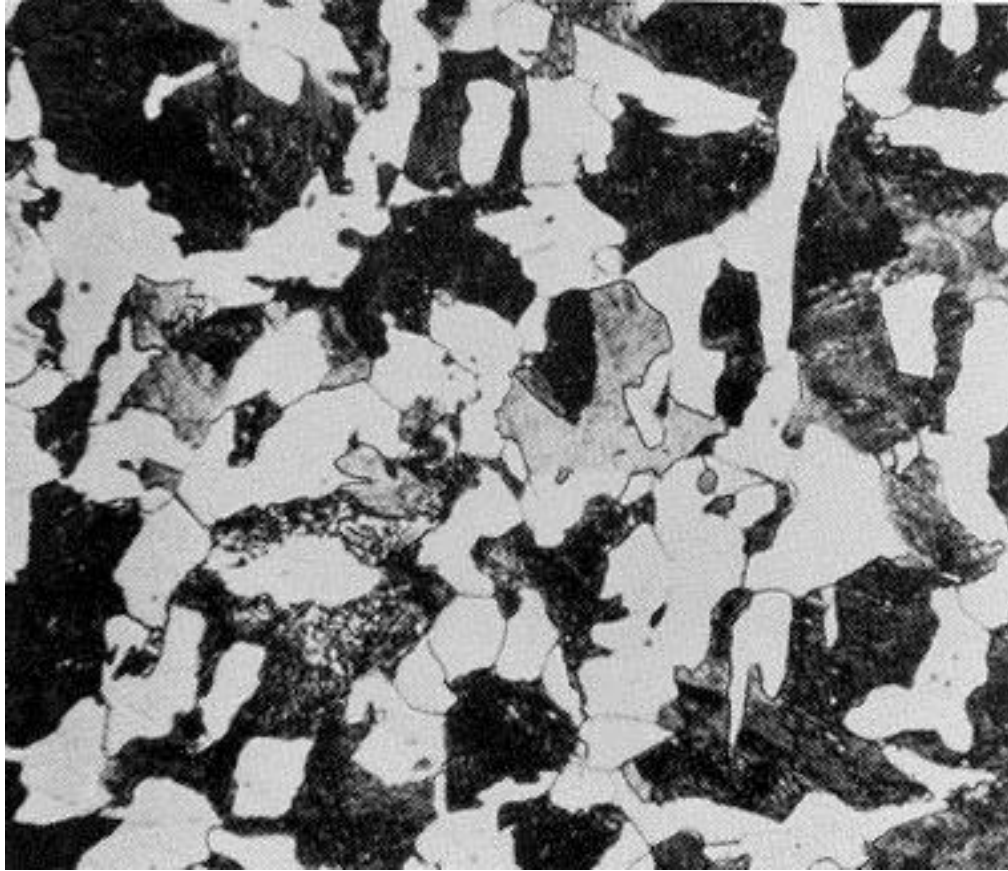
When the samples are held at the temperatures to which they have been quenched, further microstructural changes can occur. Austenite can transform to bainite and the martensite can decompose into ferrite and carbides. Details of the latter changes will be discussed later. However, it is appropriate to note, now, that the BCT martensite is a phase that does not appear on the phase diagram. This is because it is a metastable phase that readily transforms when held at temperatures above a couple of hundred degrees Celsius.

Transformations during cooling.

It should now be reasonably easy to recognize the main changes associated with the decomposition of the austenite in larger samples, continuously cooled at various rates. When the rate of cooling is slow enough for the transformation to begin and end just below the eutectoid isotherm the product will be coarse pearlite. As the cooling rate increases, finer and finer pearlite will appear and the spacings throughout the sample become more variable reflecting the fact that different colonies form at different temperatures. Mixed microstructures of fine pearlite and bainite then become possible. For large samples in which different parts cool at different rates the microstructures will vary correspondingly and one can expect to find pearlite, bainite and martensite in the same piece of steel.

Hypoeutectoid Compositions.

As these steels are cooled from the austenitizing temperature they pass through the  $\alpha + \gamma$  phase field before the  $A_1$  line is passed. Consequently, the first decomposition product that forms, provided the cooling rate is not too rapid, is the proeutectoid  $\alpha$  phase. During slow



**1045 steel bar. Structure is fine lamellar pearlite (dark) and ferrite (light).**

**From: Metals Handbook Ninth Edition, Volume 9, American Society for Metals, 1985, p.188.**

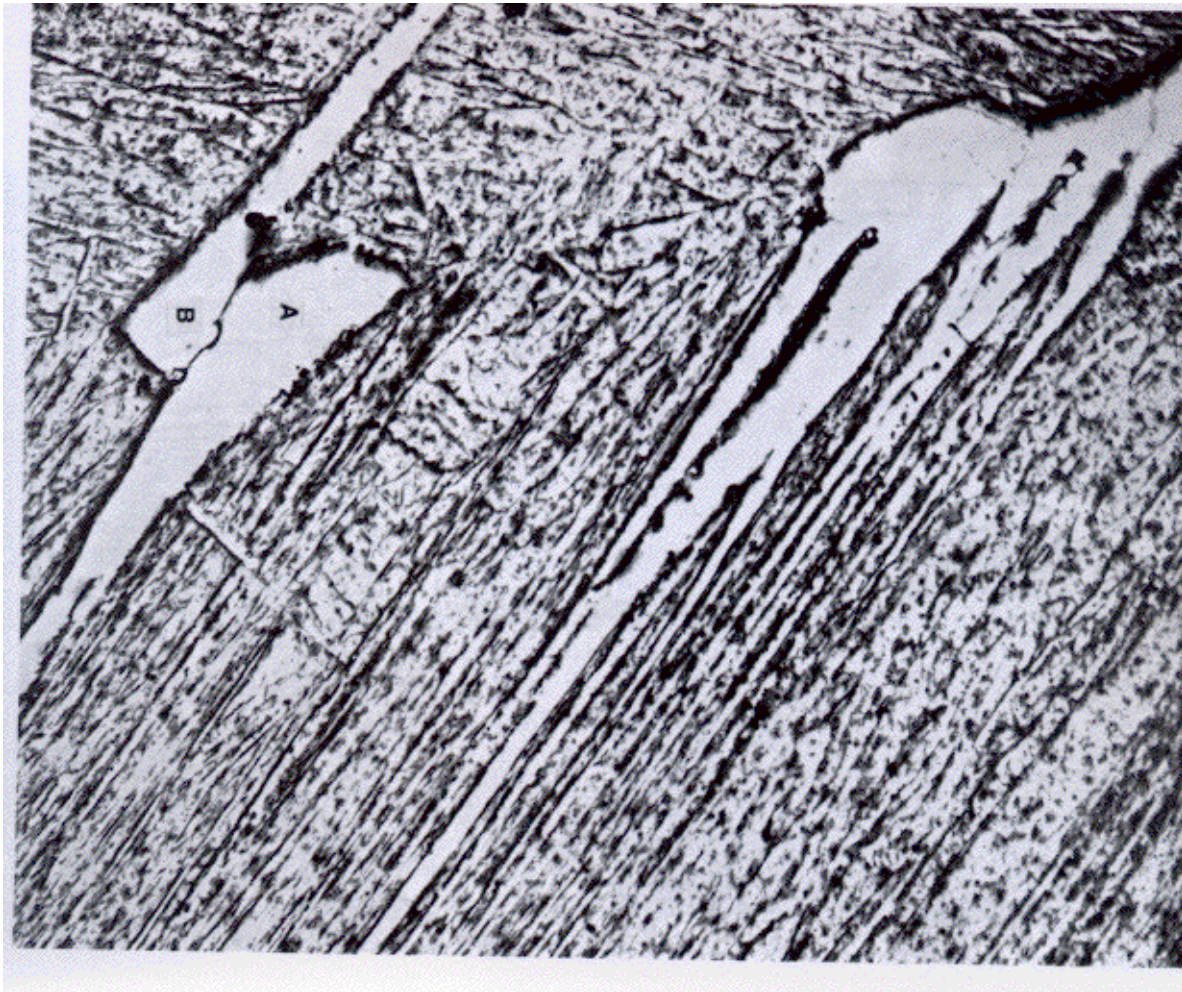
cooling, which allows adequate time for the diffusion processes to occur, the ferrite nucleates heterogeneously on the austenite grain boundaries and then grows along these boundaries and also into the austenite grain interiors forming equi-axed grains of ferrite embedded in the austenite. No preferred orientation relationships exist between the two phases. These microstructural changes involve the diffusion of the carbon ahead of the ferrite/austenite boundaries so that the growth is controlled by long range diffusion in the austenite. When the temperature reaches that of the  $A_1$  line, the microstructure will consist of a mixture of equiaxed ferrite and austenite grains. The composition of the austenite and its homogeneity will also depend on the cooling rate. Very slow cooling rates allow the composition with respect to carbon to be uniform and to approach the eutectoid composition at the  $A_1$  line. In such a case, the austenite is now a eutectoid steel and it transforms as described previously, as cooling continues.

As the cooling rates are increased, the austenite becomes inhomogeneous in composition and there is more of it present when the  $A_1$  temperature is reached than would be indicated by applying the lever rule to the phase diagram because the steel can no longer remain close to its equilibrium state as it cools. Proeutectoid ferrite continues to form as the temperature falls below the  $A_1$  line. Then pearlite appears and grows into the austenite. As the temperature at which the proeutectoid ferrite forms becomes lower and lower the morphology of the ferrite changes. Growth along the grain boundaries becomes markedly easier than growth normal to them. Therefore, films of ferrite form at the sites of the former austenite boundaries. Then, as the cooling rate increases further, ferrite side-plates emerge from these films and project into the austenite grains. These side-plates are wedge-like in shape and the broad faces comprise flat areas separated by ledges. The flat areas are interfaces across which special orientations exist. The growth process now involves the nucleation and side-ways migration of the ledges that separate the flats. These side-plates are called Widmanstätten plates. The microstructure on a polished and etched sample resembles feathers where the spine lies along the prior boundary and the quills project at oblique angles away from the boundary. Eventually, the under-cooling can create a thermodynamic driving force that is large enough to cause ferrite to nucleate within the austenite grains as well as on the boundaries. These nuclei also grow into plates. The microstructure of a hypoeutectoid steel that is cooled rapidly but at a rate that still permits the austenite to transform into ferrite plus pearlite will contain the Widmanstätten ferrite and fine pearlite. The volume fraction of pearlite present when the austenite has transformed will exceed that predicted by the appropriate tie-line on the phase diagram because the formation of pearlite begins before the equilibrium volume fraction of free ferrite has had time to form. This is an important point to bear in mind if one is trying to estimate the carbon concentration in a plain carbon steel by observing its microstructure after cooling.

Eventually, when the cooling rates become fast enough, bainite and martensite begin to form and, if the sample can be cooled fast enough, all of the diffusion-controlled transformations can be suppressed and only the martensitic transformation occurs.

Hypereutectoid steels.

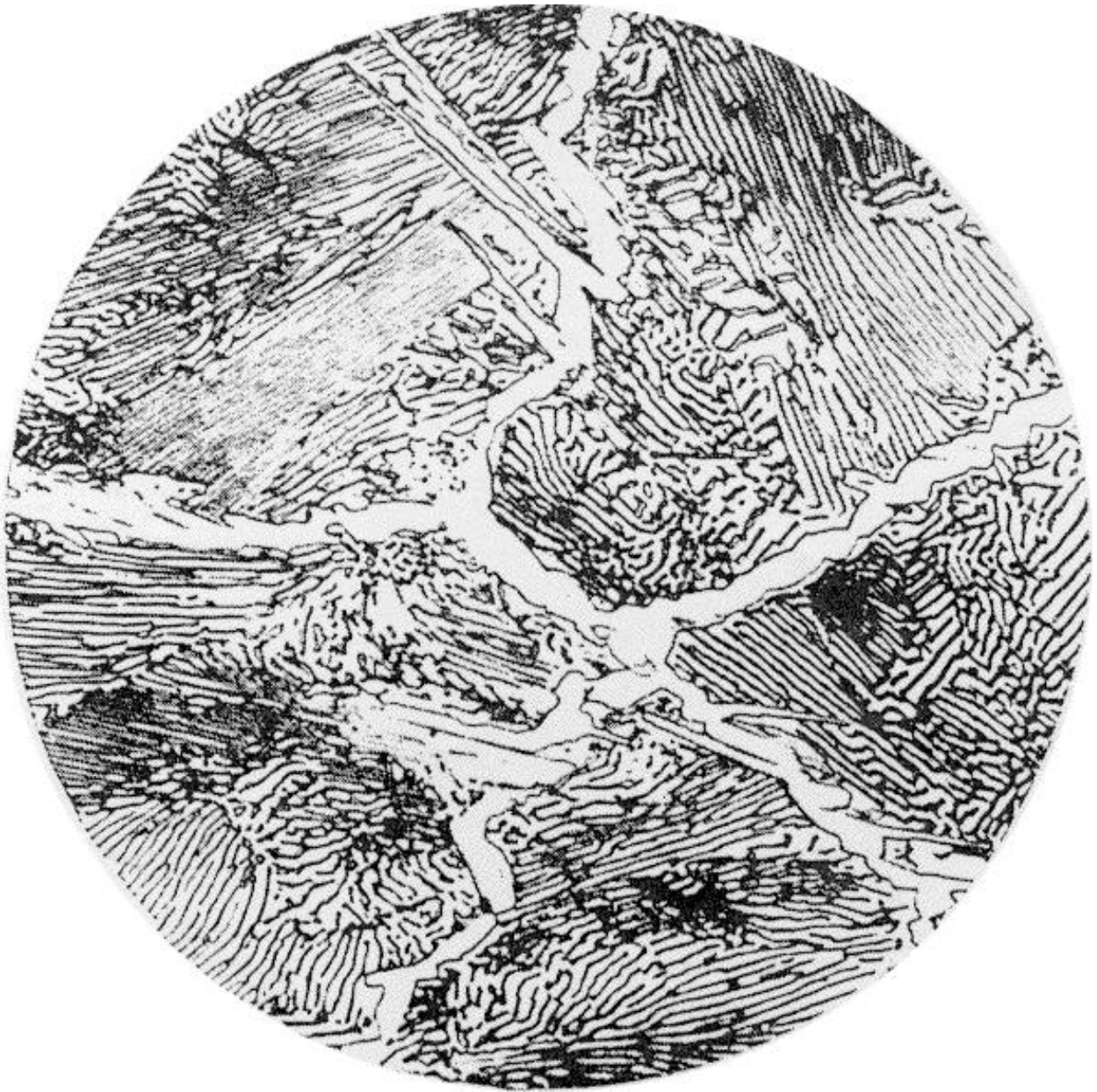
In this case the proeutectoid phase is cementite. The transformations and the resulting microstructures are very similar to those described above with the cementite replacing the ferrite. Widmanstätten plates of cementite occur but do not grow as easily as the ferrite.



**Wid manstatten side plate formation in a quenched Fe-0.2C alloy. Grains A and B, separated by a grain boundary, have orientations that favor growth into different austenite grains. Electron micrograph from an extraction replica.Magnification, 7500\*. Courtesy of R.N. Caron, Olin Corp., New Haven, CT**

**From G. Krauss, p40**





**Pearlite and G.B. Cementite in an hypereutectoid steel  
cementite appears white**

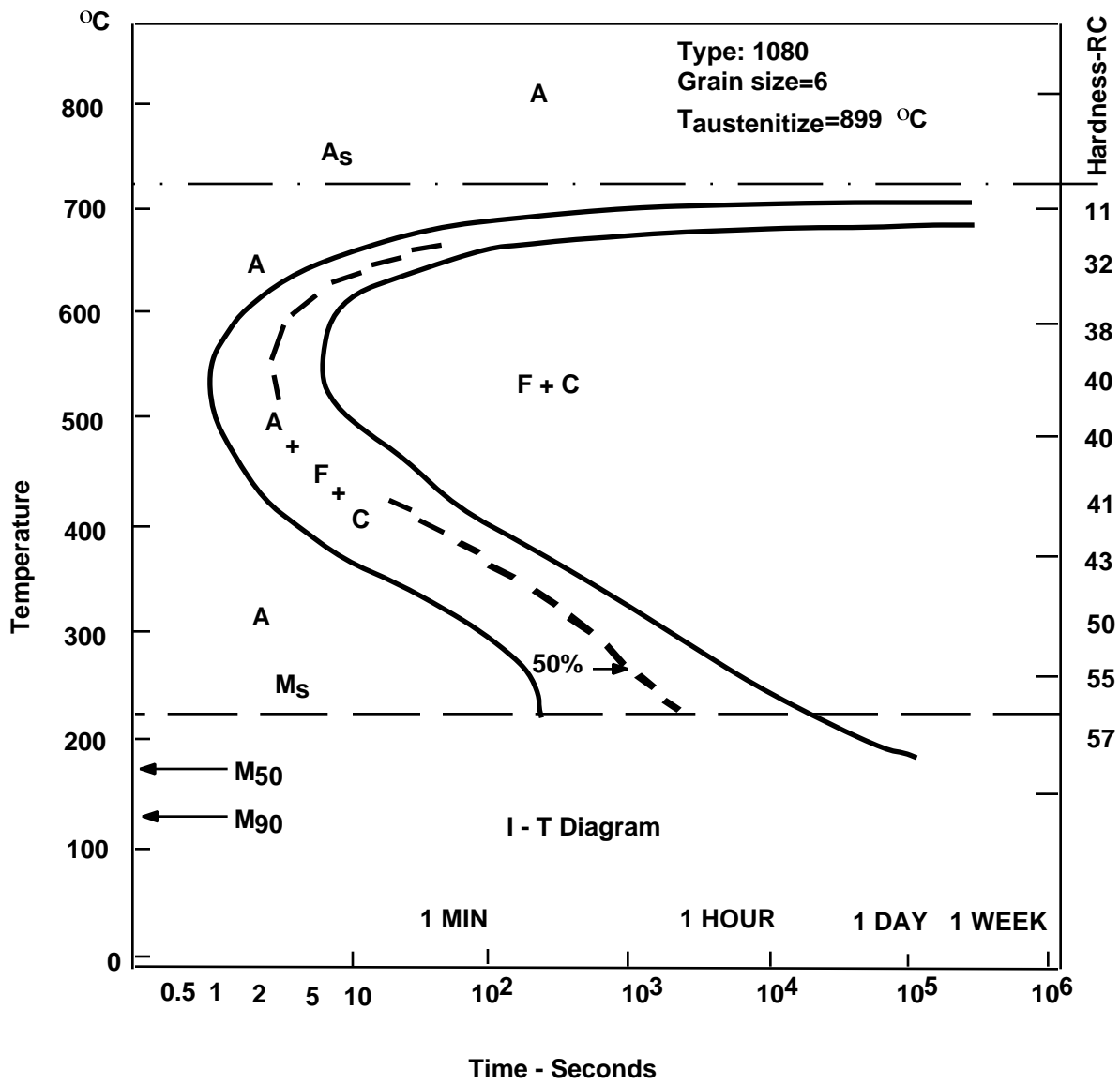
## Isothermal Transformation Diagrams in Carbon Steels.

We continue our description of the decomposition of austenite by considering reactions that occur at constant temperatures. Many experimental investigations of isothermal transformations in steel have been made. The results have been published in the form of TTT diagrams which depict the Transformations as a function of Time at Temperature. The diagrams have temperature as the ordinate and the logarithm of time in seconds as the abscissa. The times at which transformations begin and end at various temperatures are plotted on the diagram. A typical diagram is produced by the experiment described previously, in which small samples of the steel are austenitized so as to produce samples of austenite of the same grain size. The samples are small so that the temperature can be varied rapidly and temperature gradients minimized. However, cooling rates to the isothermal temperatures vary from experiment to experiment and from laboratory to laboratory so that particular diagrams, even if determined on identical steels, can show differences due to microstructural changes that occur during cooling. In one method of determining a TTT diagram, the samples are austenitized, quenched to a selected temperature, held at that temperature for various times and then rapidly quenched to room temperature or below. The progress of any transformation is then measured by means of quantitative metallography and the data assembled to produce the diagram.

A eutectoid steel TTT diagram.

A typical TTT diagram for a eutectoid plain carbon steel is shown in figure 4. Let us suppose that this diagram represents the true TTT diagram for an AISI 1080 steel, i.e. it depicts data from truly isothermal transformations. A horizontal line marks the  $M_s$  temperature which is the temperature at which martensite begins to form during cooling. The diffusion controlled transformations that occur above this line are described by a pair of "C" shaped lines that mark the beginning and end of the transformations. The products of the transformations are ferrite and cementite. Usually these curved lines present above the  $M_s$  line are not projected below it. However, it should be noted that unless the  $M_s$  temperature is so low that diffusion is suppressed, ferrite and cementite can still form below the  $M_s$  temperature from the untransformed austenite as aging is continued. Because the martensitic transformation in plain carbon steels is athermal, the martensite forms during the cooling process and the amount that forms depends upon the temperature to which the sample is cooled. Sometimes other horizontal lines are plotted to depict temperatures at which 50 % of the sample is martensite etc. Then the temperature below which no more martensite forms is sometimes shown as the  $M_f$  temperature.

Inspection of this diagram reveals that at small degrees of undercooling below the  $A_1$  line, the transformation takes a long time to begin. As the degree of undercooling is increased the incubation time decreases rapidly even though the transformation is occurring at lower temperatures where diffusion is less rapid. Eventually the incubation time reaches a minimum,  $t_m$  and then begins to increase again. The part of the "C" curves at this minimum incubation time is called the nose of the TTT diagram. The product of the transformation at temperatures above the nose is pearlite. Bainite is formed below the nose and mixtures of both microstructures are formed at the nose.





## Pearlite formation

The initiation process in the transformation that produces pearlite is the formation of neighboring nuclei of ferrite and cementite on a grain boundary in the austenite. Suppose that first of all a nucleus of cementite forms on the boundary. It will be rich in carbon which it has obtained from its immediate surroundings. This reduction in the carbon content encourages the nucleation of ferrite next to the nucleus of cementite. If this occurs and the cooperative process continues, adjacent nuclei of alternating ferrite and cementite are formed. These can then grow by a relatively short range diffusion process in which carbon diffuses parallel to the reaction front from in front of the growing ferrite to the growing cementite and the diffusion distance does not increase with time as would be the case for a continuous precipitation process. This is a plausible process that leads to the lamellar product. The colony can add more plates by additional nucleation or by branching events in which one plate, say a cementite plate, bifurcates into two.

Consider the steady state nucleation flux equation: (See MSE 543)

$$J = A \cdot \exp - \frac{G}{kT}$$

which relates the nucleation flux of particles of a new phase to the free energy of formation of a critically sized nucleus, the absolute temperature and Boltzmann's constant. There is no critically sized nucleus at the  $A_1$  line because all three phases can coexist in equilibrium at that temperature. The nucleation flux is zero because there is no chemical free energy available to provide the energy required to form an interface between a nucleus and the matrix. The chemical free energy of formation of ferrite and cementite from austenite becomes negative at temperatures below the  $A_1$  line, and, as the temperature drops, nucleation becomes possible. To illustrate the essence of the process, let us consider a simpler case; one in which a single phase, a, transforms to another single phase, c, and for which  $G_V$  is the chemical free energy change for forming a unit volume of the new phase. Let us relate this quantity to the temperature.

Let  $G_a$  and  $G_c$  be the molar free energies of the two phases and let  $H$  and  $S$  refer to the molar enthalpy and entropy respectively.

$$\text{Then } G_a = H_a - TS_a \text{ and } G_c = H_c - TS_c.$$

$$G = G_c - G_a \text{ for forming one mole of c from a.}$$

$G$  is zero when  $T = T_e$  which is the temperature at which a and c coexist in equilibrium. Using this fact and neglecting any changes in  $S$  and  $H$  caused by changes in the temperature, it is easily shown that  $G = H(1 - T/T_e)$  so that division by the molar volume of the new phase gives  $G_V$ . Note that when  $T > T_e$  then  $H$  is negative and vice versa.

Thus we see that as the temperature of the austenite is decreased below the  $A_1$  line, the absolute magnitude of the free energy change driving the nucleation processes in the transformation increases. This suggests that critically sized nuclei become smaller and smaller as the temperature falls and that the nucleation flux should increase because of the decrease in the magnitude of the free energy of formation of a critically sized nuclei. The free energy of formation of the critically sized nucleus is in the exponential term of the equation for the nucleation flux and its changes dominate the pre-exponential term (which contains the diffusion coefficient) in the temperature range above the nose. Of course, the nuclei to which we are referring, form at heterogeneous sites on the grain boundaries and the grain boundary energy that is thereby released augments  $G$ . The

fact that the driving force for the phase transformation to occur increases as the temperature falls, provides an explanation for the observation that the incubation period for the transformation to pearlite decreases as the temperature falls. This is a common observation for a solid state precipitation reaction that occurs by nucleation and growth.

Now we should recognize that the pre exponential factor contains the diffusion coefficient of the rate controlling diffusion process by which the transformation takes place. This gets smaller as the temperature falls and eventually the incubation period should increase again as cooling continues.

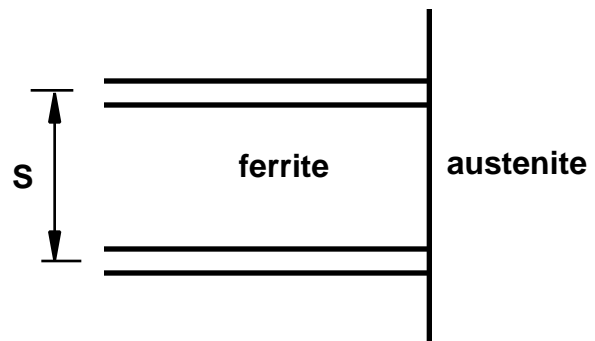
If the pearlite reaction continued to take place as the temperature is continually decreased, the decrease in the diffusion rates would become eventually become dominant and slow down the beginning of the transformation. Also, to determine, experimentally, that the transformation has begun, it is necessary that the products of the transformation be large enough to be observed. Usually this means that the new phases have grown considerably larger than the sizes of critical nuclei when they are visible. The growth rates are influenced by diffusion rates and the driving force derived from the free energy change. At temperatures near the eutectoid isotherm the driving force is small and the growth rates are correspondingly small. However, as the temperature is decreased the growth rate first increases and then decreases as the diffusion rates become dominant.. These effects lead us to predict that the kinetics of the transformation to pearlite would be described by "C" shaped TTT diagram. In the particular case that we are considering, a "C" curve is observed. However, the situation is more complicated than implied above because at the nose of the TTT diagram there is a change in the mode of transformation from that which produces pearlite to one which forms ferrite and cementite in the non-lamellar, bainite microstructure. This transformation also involves nucleation and growth controlled by diffusion. Hence it, too, should have kinetics described by "C" curves. Evidently the pearlite reaction is faster above the nose of the TTT diagram while the bainite reaction is faster below it. The "C" curves describing the two reactions merge at the nose.

The growth rate of a pearlite colony depends on the rate of diffusion of carbon. This diffusion process is required to move the carbon from the volume of austenite that is to become ferrite into the volume that is to become cementite. The diffusion distances are of the order of the inter-lamellar spacing. Metallography shows us that the inter-lamellar spacing is largest in pearlite that is formed at the highest temperatures and that it decreases as the temperature at which the transformation takes place is decreased. Why?

Consider the sketch to represent a portion of pearlite in which the spacing,  $S$ , extends from the centers of two neighboring cementite lamellae. For simplicity, curvature of interfaces is neglected.

Suppose the transformation interface advances a small distance  $x$ . The change in the free energy, per unit area of the interface, is given by:

$$G = G_v \cdot \delta x + \frac{2\gamma}{S} \cdot \delta x$$



where the first term on the right hand side contains the chemical free energy released per unit volume of pearlite formed and the other term contains the interfacial surface energy created.

At a particular temperature, the total free energy change varies with the spacing of the lamellae. As the spacing decreases, the interfacial area created increases. There is a critical spacing at which the free energy change becomes zero. Pearlite of smaller spacing will not form because it would raise the free energy of the system.

Let the critical spacing be given by  $S_{\min}$ . Then  $S_{\min} = -\frac{2\gamma}{G_v}$

$G_v$  is, of course, negative.

Hence  $G = \frac{2\gamma}{S} \delta x - \frac{2\gamma}{S_{\min}} \delta x$ . When  $\delta x = 1$ ,  $G$  refers to a unit volume of the pearlite and

then  $G = 2\gamma \left( \frac{1}{S} - \frac{1}{S_{\min}} \right)$ .

The growth of the pearlite in the direction shown, requires carbon to diffuse laterally at, or ahead of the interface. A number of treatments of this process have been published. We will consider one of the original treatments, (Zener, TAIMME Vol. 167, 550, 1946). It is not a detailed rigorous treatment but it serves well to illustrate the nature of the problem; many subsequent analyses have sought to elaborate on Zener's work.

Experimental studies show that the growth rates of pearlite colonies at fixed temperatures are constant and independent of time. This observation tells us that the diffusion process is a steady state process. For diffusion across an area,  $A$ , due to a concentration gradient  $\frac{C}{X}$  we can write the flux according to Fick's first law:

$$J = -D.A.\frac{C}{X}$$

Let us suppose that the rate of growth is such that the interface moves into the austenite at  $u$  cms. per sec. As the interface moves, the carbon composition in the volume that becomes ferrite, changes from  $C$  (the original composition of the austenite) to  $C_f$ . The compositions refer to volume. The width of the ferrite lamella is some fraction of the spacing  $S$ . Let us make it  $S.a$ , where  $a$  is a number less than one. Then, neglecting differences between the specific volumes of austenite and ferrite, the amount of solute that was transferred during one second of growth is

$$u.S.a.(C_f - C_a)$$

This is the flux of solute, Hence, omitting the negative sign which merely indicates that diffusion occurs down the concentration gradient, we have:

$$D.A.\frac{C}{X} = u.S.a.(C_f - C_a)$$

The true form of the concentration gradient is unclear. However, if we assume that the concentration is  $C_\gamma$  at the interface between the ferrite and cementite, and  $C_\alpha$  ahead of the center of the ferrite lamella, then an approximate expression is:

$$\frac{C}{X} = \frac{(C_\gamma - C_\alpha)}{b.S}$$

where  $b$  is another number less than unity.

The next problem we face is what to do with the area  $A$ . We have two extremes; the diffusion flux might be restricted to the boundary between the austenite and the pearlite, or it could be occurring over some distance ahead of this interface. Let's suppose the latter is the case, What can we choose for  $A$ ? Who knows? If diffusion does, indeed, take place in the austenite some distance ahead of the interface, then it seems reasonable that the distance will be smaller, the smaller the spacing becomes. Zener chose to make this distance approximately equal to  $S$ . Using all these approximations we have:

$$u = \frac{D.S.(C_\gamma - C_\alpha)}{S.a.(C_\gamma - C_\alpha).b.S} = \frac{D}{a.b.S}$$

If the thickness of a ferrite lamella is much greater than that of a cementite plate, then  $a.b$  is about a half.

This approximate treatment indicates that the growth rate at a given temperature is proportional to  $D$  and inversely proportional to  $S$ , a result that can be predicted intuitively. An important aspect of this relationship is that if it had been derived by means of a rigorously correct method it would still be a relation in which  $u$  is some function of the variables  $D$  and  $S$ . The point of this remark is that a theoretical description that enables one to evaluate  $u$  when  $S$  and  $D$  are known, is not particularly enlightening. It would be much more useful to be able to predict both  $u$  and  $S$  when only  $D$  is known. The meaning of this should become clearer as we continue with Zener.

In order to evaluate  $u$  and  $S$  explicitly, when  $D$  is known, we need another equation relating the three variables. In an attempt to obtain one, Zener noted that the rate of migration of an interface is often expressed as the product of a mobility and a driving force. Hence he wrote:  $u \propto |G|$ . Then because  $u$  is proportional to  $D$  and inversely to  $S$  we find

$$u \propto \frac{D}{S} |G|$$

Recalling that  $G = 2\gamma \left( \frac{1}{S} - \frac{1}{S_{\min}} \right)$  and substituting we obtain  $u = \frac{K.D}{S} . 2\gamma . \frac{S_{\min} - S}{S.S_{\min}}$  where  $K$  is a constant.

However,  $u$  and  $S$  cannot be separately evaluated. In this kind of a situation it is common to search for some extremum principle. Zener proposed that the spacing that would occur would be that which would maximize  $u$ . There is no obvious reason why this should be so, but it is a reasonable suggestion because the colonies that grew the fastest should make up most of the pearlite at the end of the transformation and experimentally determined spacings should belong to

them. Assuming this to be so, we can differentiate  $u$  with respect to  $S$  and equate the result to zero. Then, after a little algebra, we find that the spacing is twice as big as the minimum possible spacing.

Now the magnitude of the chemical free energy change for forming a unit volume of pearlite is proportional to the undercooling below the equilibrium temperature,  $\Delta T = (T_e - T)$ . Hence we may write:

$$G_v = q \cdot \Delta T$$

where  $q$  is a constant.

$$\text{Because } G_v = -\frac{2\gamma}{S_{\min}}$$

then

$$S = \frac{4\gamma}{q \cdot \Delta T}$$

Although this equation is not quantitatively correct, it is of the correct form because the average spacing in pearlite varies inversely with the undercooling.

A number of theoretical descriptions of the growth of pearlite have been published since this early treatment. References to these works can be found in Honeycombe's book. In general, they attempt to refine Zener's work by trying to take more parameters into account e.g. considering curved interfaces and the effects of alloying elements but the difficulty of separating  $S$  and  $u$  explicitly remains.

Pearlite has been the subject of many investigations in which the characteristics of its formation are compared to the predictions of early theories of nucleation and growth kinetics. It has also been the subject of crystallographic orientation studies. These studies are interesting and relevant to the topic of phase transformations, however, a knowledge of specific details is unnecessary for our purposes here.

### Bainite and Martensite.

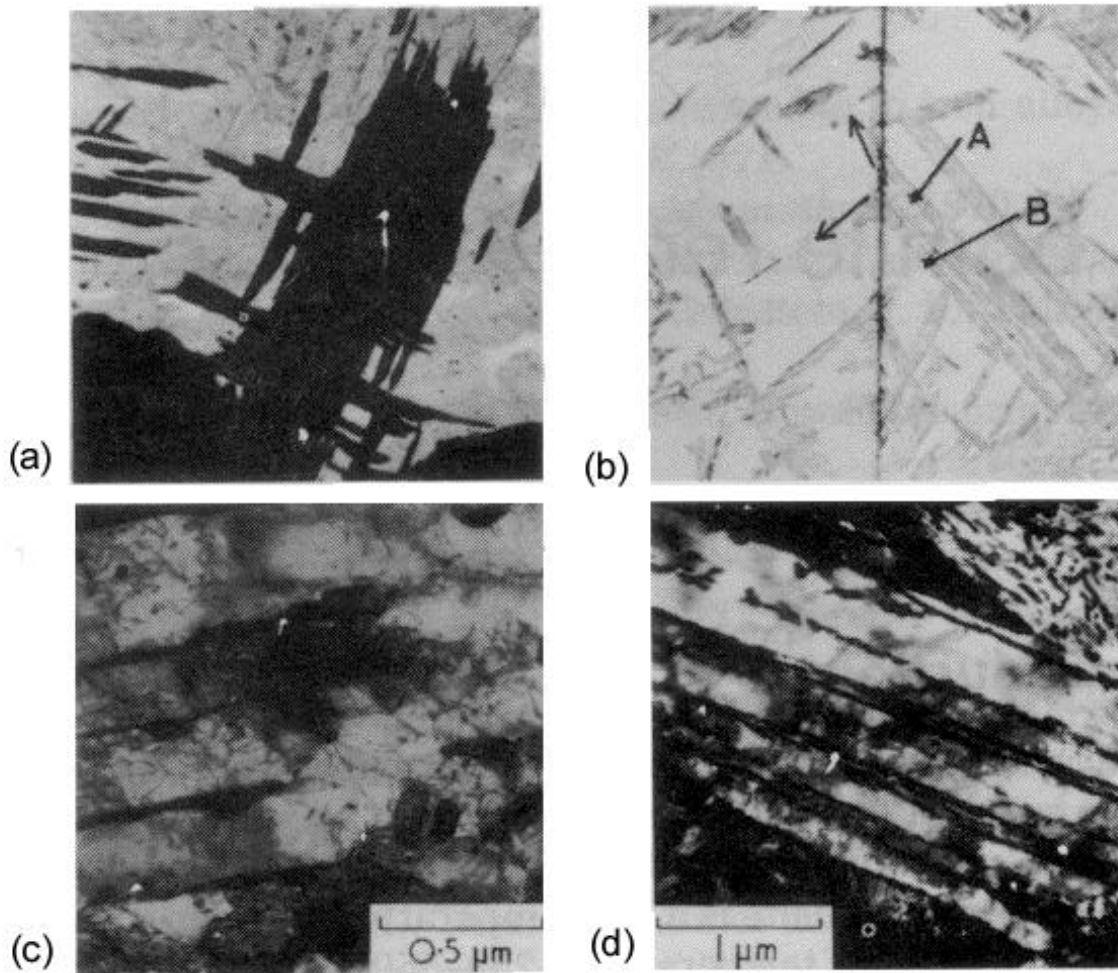
So far, we have been considering only the upper portion of the TTT diagram for a eutectoid steel. In this region that extends from the nose to the  $A_1$  line, the product of isothermal transformations is pearlite. Another type of microstructure is formed during isothermal transformations below the nose. In this temperature range, the lamellar product is replaced by mixtures of discrete particles of cementite in ferrite. Details of these microstructures vary with the temperature and also vary from steel to steel. In general, the product formed near the nose is called upper bainite and that near the martensitic start temperature is called lower bainite. It has often been stated that upper bainite looks like feathers in optical micrographs while lower bainite is more acicular. It is not easy to distinguish between them. In practice it is wise not to identify the microstructure unequivocally (particularly from a single photomicrograph) without additional supporting information. At this stage it is worthwhile for the reader to spend a few hours examining microstructures of plain carbon steel as shown in the optical photomicrographs that are presented in the ASM atlas of microstructures, eighth and ninth editions.

Numerous studies have been conducted by optical microscopy and by transmission electron microscopy. As a result, the following major characteristics have been identified. In upper bainite,

the ferrite comprises bundles or sheaves of fine, elongated grains that resemble laths. The cementite particles lie on the long boundaries between the individual laths. In contrast, at lower temperatures the ferrite crystals that form the sheaves appear more like needles and plates. Particles of cementite form both at the boundaries between the grains and within the crystals of ferrite. It is also observed that when the transformation to lower bainite is conducted in samples that have been previously metallographically polished, surface relief is generated because the flat surface becomes rumpled and tilted during the transformation. Surface relief is uncommon in transformations that only involve diffusion; it occurs generally during martensitic transformations.

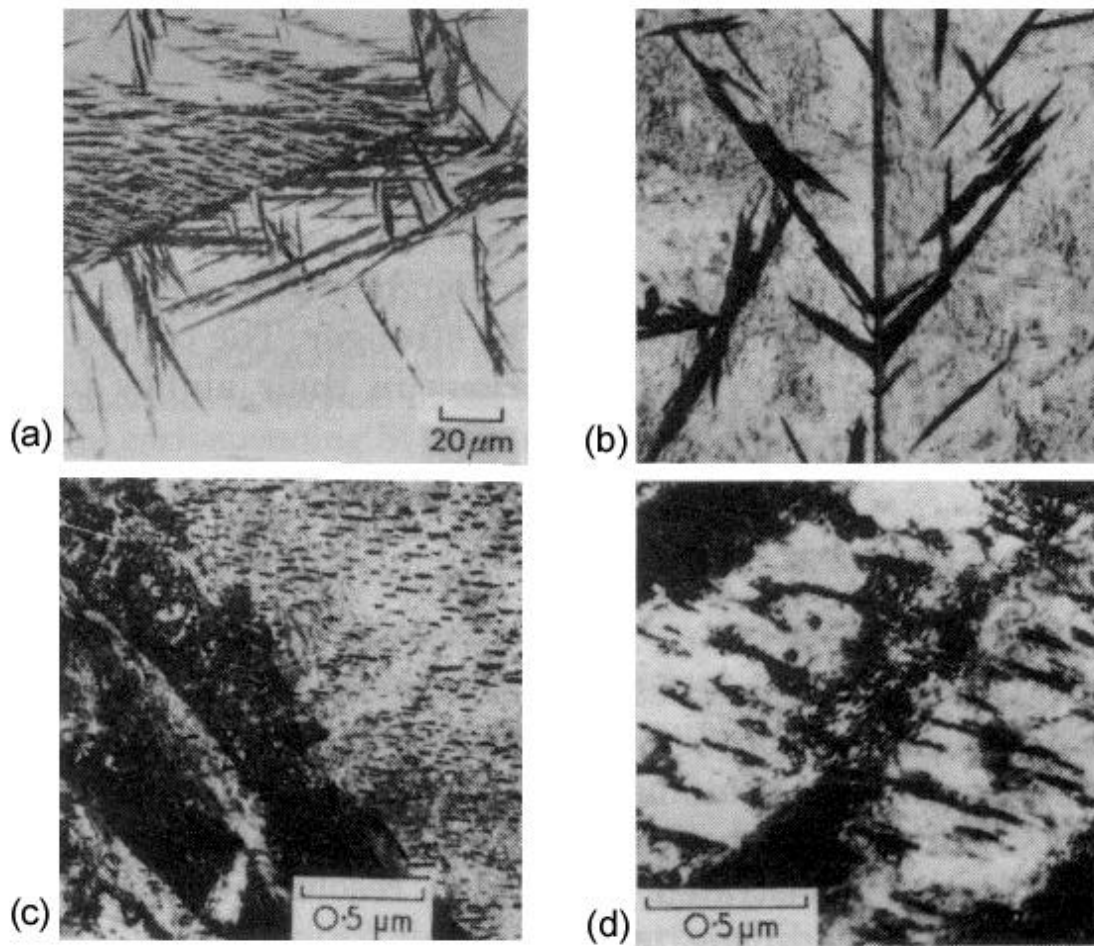
An understanding of the mechanism(s) by which the bainitic microstructures form has been actively sought for decades. Such details are really beyond the ambit of these notes, but it is interesting to consider some generalities of the subject. Opposing viewpoints have been presented and hotly debated by respected scientists. One issue concerns whether or not there is a contribution from a displacive or martensitic mechanism i.e. diffusion creates the carbides and the ferrite forms martensitically. Proponents of the viewpoint that there is such a contribution, have considered that the surface relief that forms when lower bainite is created is significant. The  $M_s$  point for the initiation of martensite is raised as the carbon content of the austenite is reduced. Thus, if the carbon content at various locations is reduced by the precipitation of cementite then the  $M_s$  temperatures for these locations would be raised and the allotropic change accomplished martensitically. Such a mode of transformation has been dubbed a diffusion paced martensitic mode. Others believe that the transformation is a diffusion controlled nucleation and growth process in which the crystals grow by the lateral propagation of ledges and the sheaves form because of sympathetic nucleation of new crystals at the boundaries of the prior crystals. Articles supporting both viewpoints have been published in the technical literature during the past five years so one can hardly say that the situation has been fully resolved to everyone's agreement but it seems fair to suggest that the nucleation and growth description is most favored. As more instrumental techniques for studying the bainitic microstructure are created and improved more complexities are revealed. Some examples of these microstructural details have been presented recently by Fang et al. in *Met and Mat Transactions*, 27A, 1535, (1996). They interpret their observations as showing that the needles or plates within the sheaves of lower bainite are built up of smaller units. They conclude that the bainite plates consist of subplates which consist of subunits which are made up of sub-subunits which consist of (you guessed it!) sub-sub-subunits. This conclusion, in part, concerns interpretations of topographical observations made using the relatively novel technique of scanning, tunneling microscopy and its validity awaits confirmation.

As the temperature of the austenite being quenched falls below the  $M_s$  temperature, a transformation of structure begins to take place while the temperature is falling. This marks the beginning of the martensitic transformation. A martensitic transformation can be defined as a



**Microstructure of upper bainite: a, 0.8C steel transformed 20s at 400°C, x670; b, 0.34C steel transformed at 400°C. Two surface composite micrograph, x330; c, 0.8C steel transformed at 450°C. Dislocations visible. Thin foil EM; d, 0.8C steel transformed 5s at 450°C. Thin foil EM.**

**From: Steels: Microstructure and Properties, 2<sup>nd</sup> ed., eds RWK Honeycombe and HKDH Bhadeshia, Edward Arnold, 1995, p.116.**



**Microstructure of lower bainite a, 0.8C steel transformed 30s at 300°C, x260; b, 0.8C steel transformed at 300°C. Two surface composite micrograph, x260; c, 0.8C steel transformed 6 min at 250°C. Thin-foil EM; d, 0.6C steel transformed at 300°C. Thin-foil EM.**

**From: Steels: Microstructure and Properties, 2<sup>nd</sup> edition, eds. RWK Honeycombe and HKDH Bhadeshia, Edward Arnold, 1995, p. 119.**

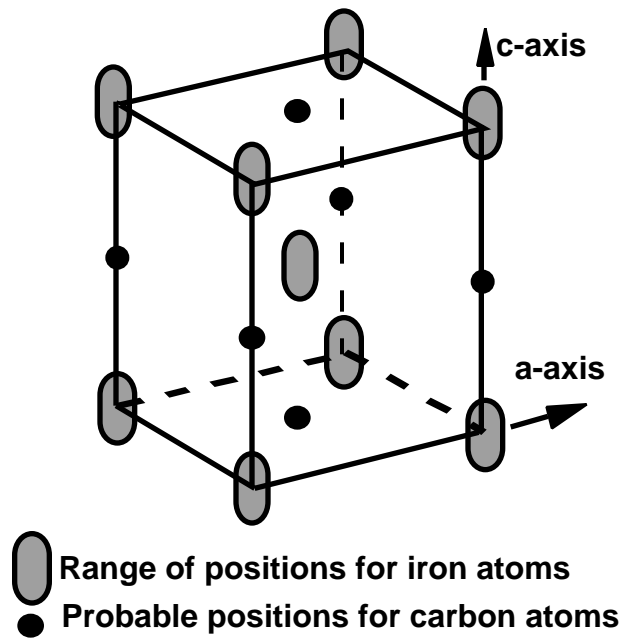


mechanism for changing crystallographic structure that does not require atomic diffusion. In most steels, this transformation occurs very rapidly during the quench and the fraction transformed depends on the temperature to which the sample is cooled, not on the length of time spent at that temperature. We note here that the quench rates that are of practical importance are those obtainable by plunging the steel into liquid baths such as iced brine; the effect of these treatments are under discussion here. Eventually, the transformation ceases at the  $M_f$  temperature. It is customary to call the phase produced by the martensitic transformation, martensite. It is important to recognize that the transformation rarely goes completely to 100%. A small amount of the microstructure in a eutectoid plain carbon steel can be retained austenite. The amount of retained austenite that is found in steels varies with composition tending to be more prevalent in steels containing high contents of carbon and other alloying elements. Obviously, if the  $M_f$  temperature is below that of the quenching bath and room temperature, austenite will be retained. For the sake of completeness we might as well note also that there are some steels in which it is possible for a martensitic transformation to occur as an isothermal transformation. Hence, the definition of a martensitic transformation does not include the word quenching. If a sample of a steel is partially transformed to martensite by being quenched to a temperature above the  $M_f$  temperature and then held at that temperature, the untransformed austenite can decompose to form bainite.

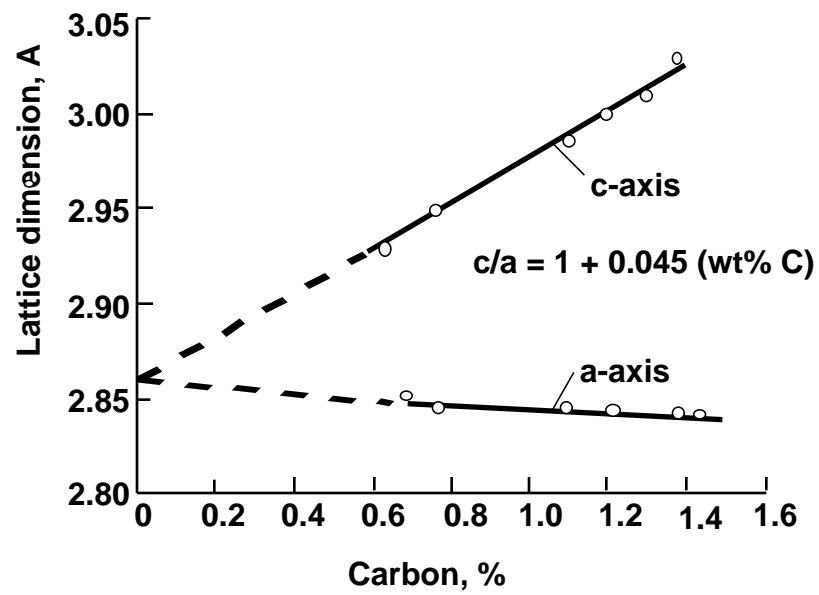
What is ferrous martensite?

Earlier we discussed experiments in which iron and dilute iron carbon binary alloys were quenched at rates above  $10^5$  K/sec. At these rates there is insufficient time for the structural change to be produced by diffusion. However, the samples became BCC. Evidently the iron knows another way to change its structure and, when prevented from doing it by means of diffusion, does it without using diffusion. Instead, it does so by means of a displacive transformation by which it is possible to displace the atoms from FCC positions to BCC positions without requiring them to hop from site to site by diffusion. The transformation is called martensitic. The displacements associated with the transformation in iron are illustrated in the sketches. These show what is called the Bain strain. This is a strain proposed by Edgar Bain to describe the distortion of a tetragonal cell in the FCC crystal into the BCC of the martensite.

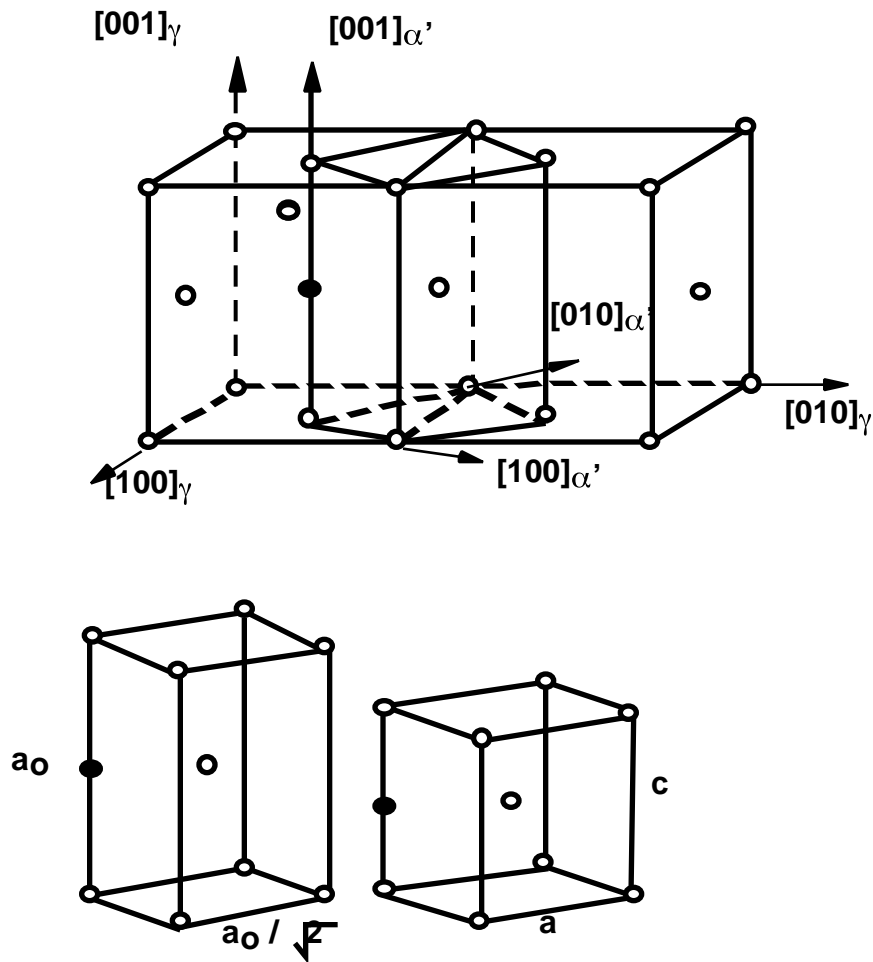
Now, when we turn to the case of a plain carbon steel and quench its austenite too rapidly for any change to be wrought by diffusion, the iron atoms still wish to adopt BCC positions. Cementite can only form when diffusion is possible because one out of four atoms in it is C, but the martensitic change is available for the iron. The possibility arises that the FCC solid solution can change to a BCC solid solution. This can happen if the free energy released is negative even though the transformation produces an intermediate metastable state. We find that it begins to happen when  $T_e - T$  becomes large enough, i.e. the temperature falls to below the  $M_s$  temperature. The martensite in pure iron is the stable phase, even though it contains numerous defects such as dislocations and boundaries. Because the carbon content is unchanged during the formation of martensite in a plain carbon steel, the phase is metastable and is a supersaturated solid solution if its carbon content exceeds the solubility in ferrite. Furthermore, inspection of the sketches illustrating the Bain strain shows that the carbon atoms that were previously randomly distributed in the octahedral sites of the austenite now occupy a particular selected set of sites within the martensite. When the carbon content exceeds about 0.2 wt.% the carbon atoms produce a significant tetragonal distortion so that the structure becomes BCT. The  $c/a$  ratio of the tetragonal unit cell increases as the carbon content



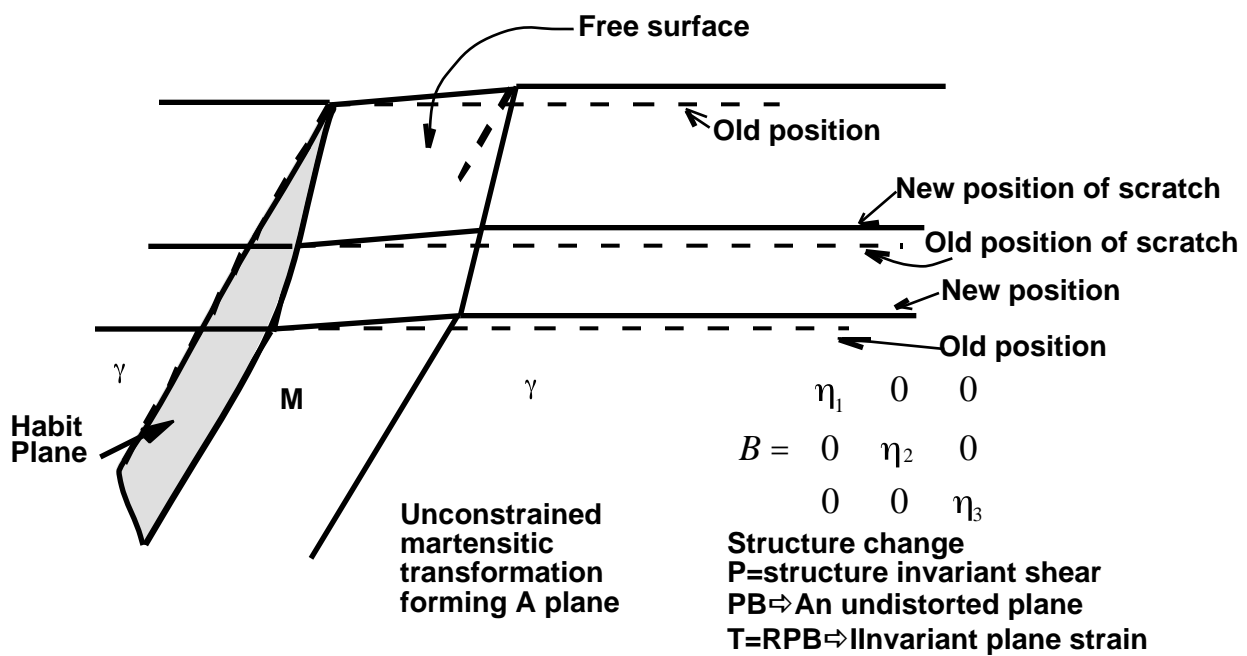
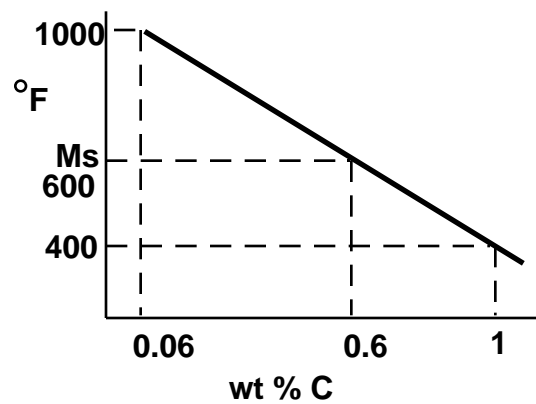
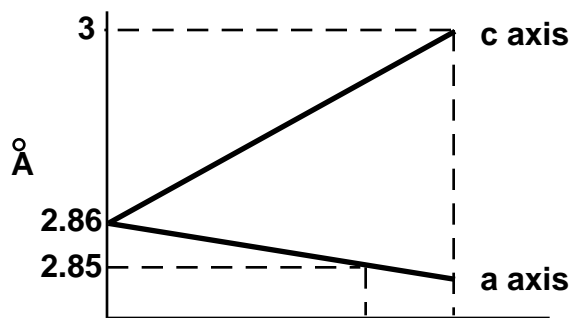
From: Bain & Paxton, p.35,36

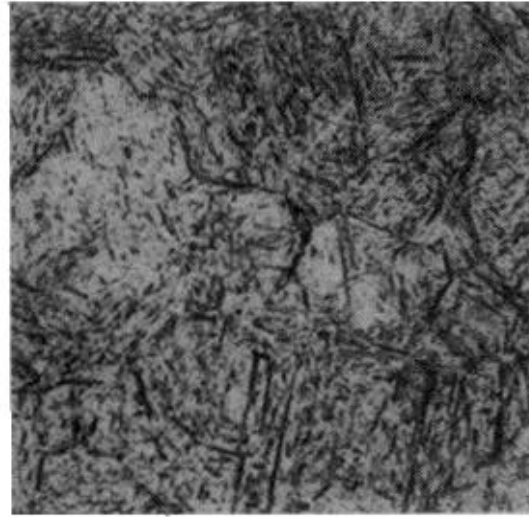
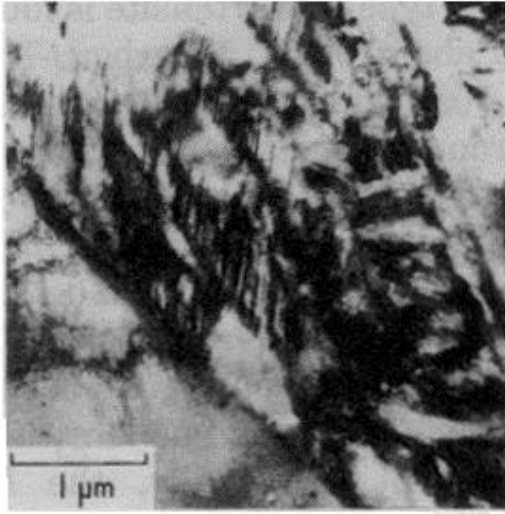


From: Leslie, p.71



In the above image, there are two FCC adjacent unit cells, with a lattice parameter  $a_\gamma$ . A BCT cell is obtained by connecting the 8 FCC sites. This cell has sides  $a_\gamma$  and  $a_\gamma/\sqrt{2}$ . Imagine that the BCT cell is removed and distorted so that its sides all become  $a_\alpha$ . In the below image, this is the case, with  $a=c$ .





**Fe-0.8C alloy quenched from 1100°C: a, optical micrograph x200; b, thin-foil EM showing twinning in martensite laths.**

**From: Steels: Microstructures and Properties, 2<sup>nd</sup> edition, eds. RWK Honeycombe and HKDH Bhadeshia, Edward Arnold, 1995, p.95**

increases. To a good approximation, the variations in  $c$  and in  $a$  are linear, with the  $c$  value increasing at a greater rate than the rate at which the  $a$  parameter decreases, as the carbon concentration increases.

The microstructure of martensitic steel is complex and varies in detail from steel to steel. Details depend upon the  $M_s$  temperature. In general lath martensite forms in the high temperature range and lenticular or plate-like martensite forms at lower temperatures. For plain carbon steels this translates into a dependence of the microstructure on carbon content because increasing the carbon content lowers the  $M_s$  temperature. Martensitic crystals in low carbon steels are fine laths which contain a high density ( $>10^{11}$  cms./cm.<sup>3</sup>) of dislocation line. As the carbon content is increased, crystals shaped like plates appear. Twins begin to replace the dislocations within the plates so that high-carbon martensite is composed mainly of twinned plates. The transformation is also associated with an appreciable volume increase because it replaces the close packed FCC structure with a BCT structure of smaller density. Because of this, the transformation creates residual stresses and strains related to the specific volume change in addition to the strains due to the misfit of the interstitial solute atoms. At high carbon levels these stresses can become so severe that the material cracks as the martensite forms. The cracks can range from small micro cracks that require microscopy to be detected, to large cracks easily visible to the unaided eye.

An important characteristic of the martensitic transformation is that it produces surface relief on a metallographically polished surface. This is due to the displacive nature of the transformation. When a portion of the austenite is converted to the other crystal structure, its physical shape is also changed. The total strain resulting from a martensitic transformation is the result of the shape change produced by the crystallographic change itself combined with post-transformation strains caused by creating the martensitic crystals within the austenite matrix. Experimental studies have shown that the transformation shape change transforms planes into planes and straight lines into straight lines but only special planes remain unrotated. Hence, portions of the free-surface of the sample become tilted from the previous orientation as the martensite forms.

The crystals of martensite vary from fine laths in low carbon steels, to plates in high carbon steels. The lath morphology is such that the laths form in packets of nearly parallel units; the individual units are often too small to be resolved in an optical microscope. The crystals have habit planes that tend to lie close to the  $\{111\}$  planes in the austenite. Orientations of  $\{557\}$  have been reported. Because these indices have two identical digits, there are 12 non parallel variants. However, they occur in groups of three with each group clustered about a  $(111)$  with only 16 degrees between members of a group. Because there are only 4 non parallel variants for  $\{111\}$ , lath martensite appears to be more orderly than does plate martensite. The habit plane of the plate martensite in carbon steel varies from  $\{225\}$  for steels with 0.92 wt.% C to  $\{259\}$  for 1.78 wt. % C. There are 12 variants for the former and 24 variants for the latter. Although each martensitic crystal could, in principle, choose any of these variants there is a tendency for certain variants to occur in groups. This is because the shape and volume change associated with the transformation are resisted by the austenitic matrix. This resistance encourages the choice of those variants which, in combination, provide the minimum macroscopic shape change. Lath martensitic crystals contain a dense population of dislocations that are associated both with the transformation itself and with the strains generated by the volume change. Plate martensite is much less dislocated; instead, the plates contain arrays of very fine twins. Excellent examples of martensitic microstructures can be found in chapter 3 of Krauss' book.

The total change in the shape caused by a martensitic transformation is the result of the shape change associated with the transformation alone and the strains arising from the interaction between the martensite and the matrix. It is usual to separate the two by calling any strains that do not refer to the transformation of the structure, post-transformation strains. An important result of the shape change is that previously flat surfaces become tilted and rumpled during the transformation. Studies of the formation of plate martensite have shown that the general shape change can be described as being produced by a homogeneous strain, i.e. a strain which does not change the degree of an equation. This conclusion has been reached because planes are tilted but remain planes, straight lines (such as a scratch on the surface of the sample) become kinked but remain made up of straight segments. There are distortions but these are attributed to the post-transformation strains, which are not relevant to the actual phase transformation mechanism. During the transformation, a crystal of plate martensite in contact with austenite at the habit plane clearly shares the same interface; hence, we conclude that if we were to describe the transformation by a homogeneous strain then the strain would have to leave at least one plane (the habit plane) of the austenite unchanged. Thus the strain that describes the transformation of austenite to martensite is a homogeneous invariant plane strain.

Theoretical attempts to determine the strain have led to the phenomenological theory of the martensitic transformation. The objective of this theory is to determine a strain that would produce both the crystallographic change and the shape change simultaneously when applied to austenite; it does not directly concern itself with the mechanism by which the transformation takes place. This is why it is a phenomenological theory. Let us consider some elements of this theory.

The first thing that the strain must produce is the conversion of the FCC unit cell into the BCT unit cell. This is usually referred to as the lattice strain. We have already met a strain that will accomplish this. It is the Bain strain introduced on page 20. It is obtained directly from the lattice parameters of the corresponding cells. The numerical values of the components of the Bain strain vary with carbon concentration because of the variation in the  $c/a$  ratio of the martensite. First we consider an origin of an orthogonal coordinate system located on a corner of the tetragonal cell drawn in the FCC lattice on page 20 such that the  $x$ ,  $y$  and  $z$  axes lie along the edges of the unit cell. The Bain strain causes strains of  $e_1$ ,  $e_2$  and  $e_3$  along these axes but leaves the angles between them unchanged. One can describe the coordinates of any other point by  $x$ ,  $y$  and  $z$ . Then if the lattice is deformed so that the coordinates become  $x'$ ,  $y'$  and  $z'$  then

$$x' = (1 + e_1)x = n_1x$$

$$y' = (1 + e_2)y = n_2y$$

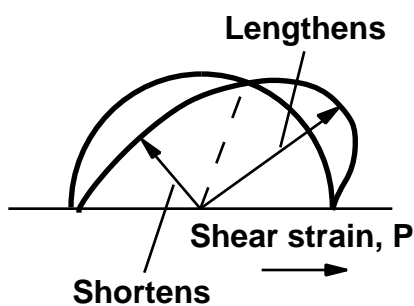
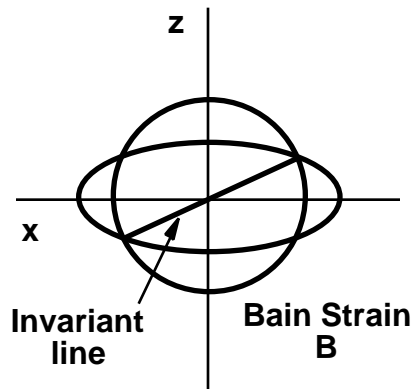
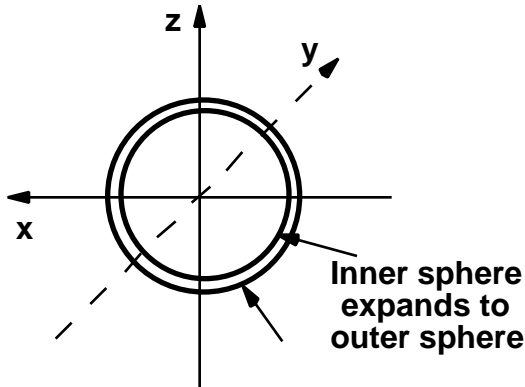
$$z' = (1 + e_3)z = n_3z$$

Where the  $n$ 's are called distortions.

For ferrous martensite  $n_1 = n_2$  are equal and greater than one;  $n_3$  is less than one. The actual values depend upon carbon content.

The change in shape produced by applying such a strain to a sphere is shown in the accompanying sketches appended to this text. It is clear that the “before” and “after” shapes now have surfaces that coincide along two circles. This shows that the Bain strain does not leave any

## THE INVARIANT PLANE IN A MARTENSITIC TRANSFORMATION



- 1) Let inner sphere be expanded isotropically by  $R = \sqrt{x^2(1+e)^2 + y^2(1+e)^2 + z^2(1+e)^2}$  where  $x, y, z$  are the coordinates of a point on the inner sphere.
- 2) All straight lines and planes in the inner sphere become straight lines and planes in the outer sphere. None are distorted.
- 3) Now apply the Bain strain to the sphere. Use a strain  $e_2$  and  $e_3$ . Typical values for Fe-C martensite (they vary with %C) are 0.12, 0.12 and -0.2 {note: In the martensite BCT cell  $c > a$  but  $a_y \rightarrow c$  and  $a_y/\sqrt{2} \rightarrow a$ }. The strain produces the ellipsoid shown. There are lines common to both. One is shown. No plane is invariant or distorted.
- 4) paper some lines are shortened and some are lengthened. It turns out that this can be reversed by a shear strain.
- 5) Note that shear shortens some vectors and lengthens others.
- 6) Hence there is a combination of strains, PB, such that at least one plane is undistorted. Often this plane is rotated. In this case  $R$  is a rigid body rotation that puts it back, and  $T = RPB$ .



plane in the sphere undistorted or invariant. Thus, whereas it can produce the lattice change it cannot describe the martensitic shape change. Therefore, it is necessary to seek additional strains which can change the shape but not the structure of the crystal. Such strains are shears produced by slip or by twinning. Particular shear strains,  $P$ , have been found which when combined with  $B$  produces a total strain,  $PB$ , that creates the martensitic crystal structure and leaves at least one plane undistorted. Usually it is found that when this  $P$  is determined the undistorted plane is not invariant but has been rotated. To take care of this, a rotation  $R$  is included to finally produce an invariant plane strain. The total transformation strain can then be written as

$$T = RPB$$

Although the theory is phenomenological, it is interesting to note that when it successfully describes a transformation, the martensitic crystals are found to be internally twinned by twins that correspond with the twinning shear used for  $P$ . The phenomenological theory has been successful in ferrous alloys e. g. binary Fe-Pt alloys, but it is only partially successful in carbon steels because it does not predict the variation of the habit planes observed. This may well be a consequence of the post transformation strains.

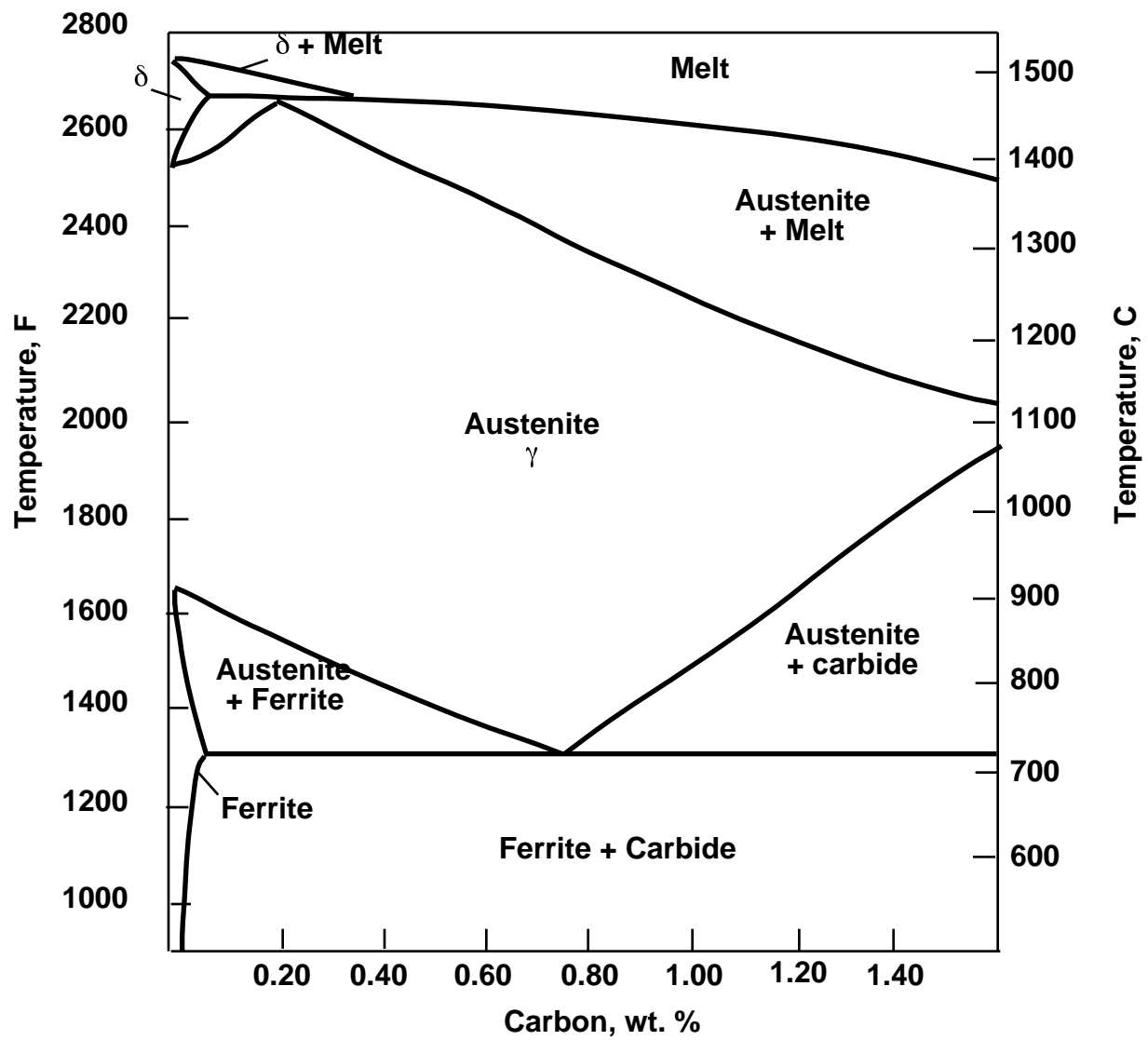
### Hypoeutectoid TTT Diagrams

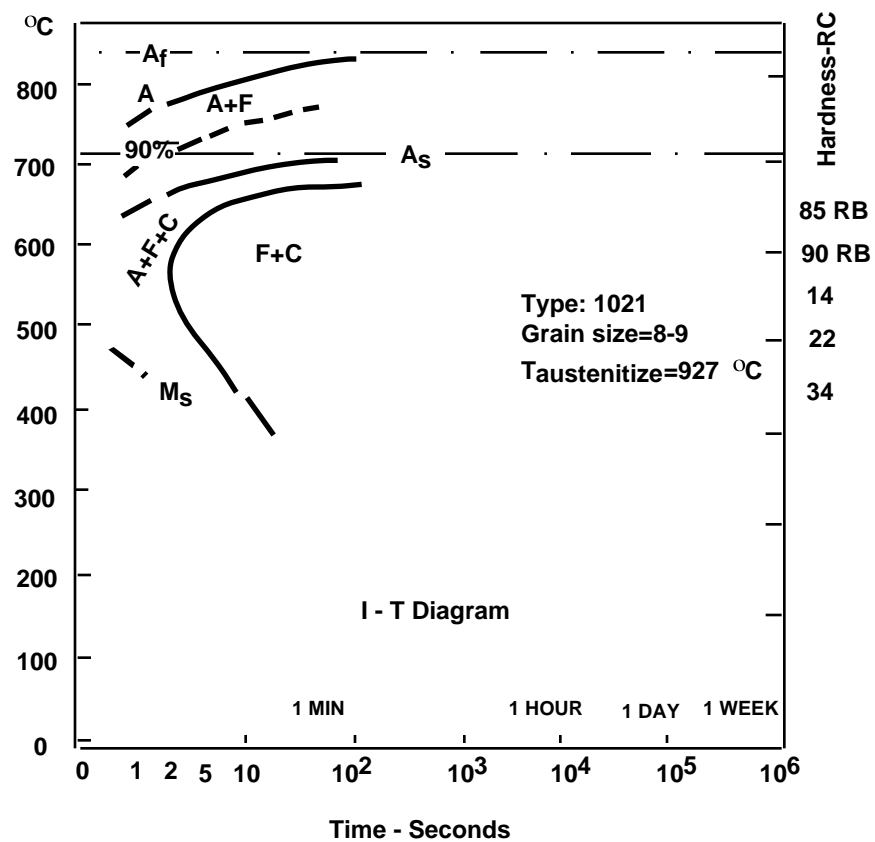
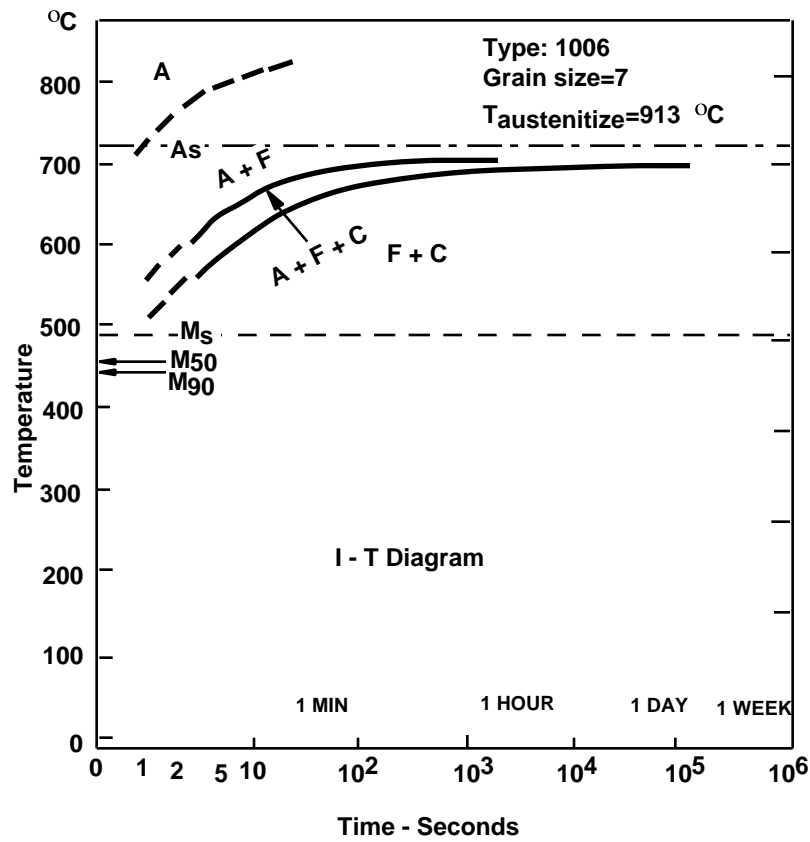
The first difference that arises in diagrams of hypoeutectoid steels compared to that of a eutectoid steel is the austenite can now transform at temperatures below the  $A_3$  point and a corresponding horizontal line appears on the diagram. When the austenite is held at temperatures between the  $A_3$  line and the  $A_1$  line it will eventually transform into a mixture of austenite and proeutectoid ferrite. Normally only the proeutectoid start-line is presented in published TTT diagrams; the finish line is omitted. The time-temperature behavior shown by the proeutectoid start line is controlled by the same nucleation considerations discussed before. The ferrite start line continues down below the  $A_1$  line. For transformations effected at temperatures not far below the  $A_1$ , the ferrite start line is followed by the start and finish lines of the ferrite + carbide transformation. Thus, during such isothermal transformations, ferrite crystals form first and then pearlite forms. At these temperatures the incubation times for the start of the transformations decrease as the carbon content of the steel is decreased. Eventually, the incubation times for the nucleation of the proeutectoid ferrite becomes so small that they cannot be measured with the resolution of typical experiments and the line ends at the ordinate axis. For compositions that allow the ferrite start lines to be distinguished, it is found that the ferrite start-line merges with the ferrite + carbide start-lines as the temperature is decreased, forming a nose on the diagram. As pointed out above, for low carbon contents, the transformation begins too rapidly near the nose for its initiation to be plotted on the diagram. In these cases, the lines simply merge with the ordinate axis which, typically, corresponds to 0.5 seconds. This is the second difference in the TTT diagrams: the nose of the "C" curve moves towards shorter times as the carbon content of the steel is decreased.

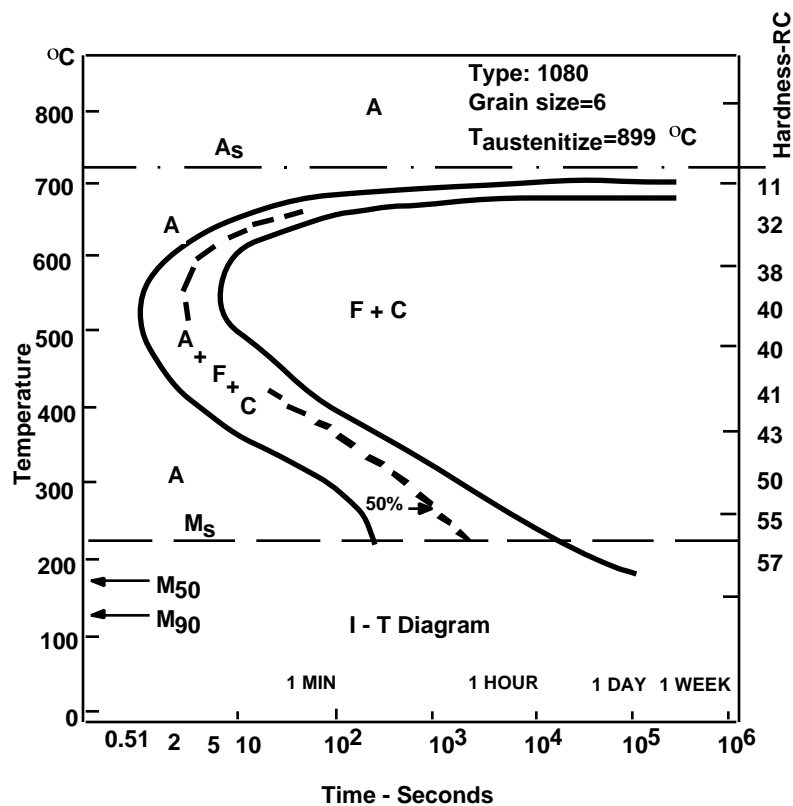
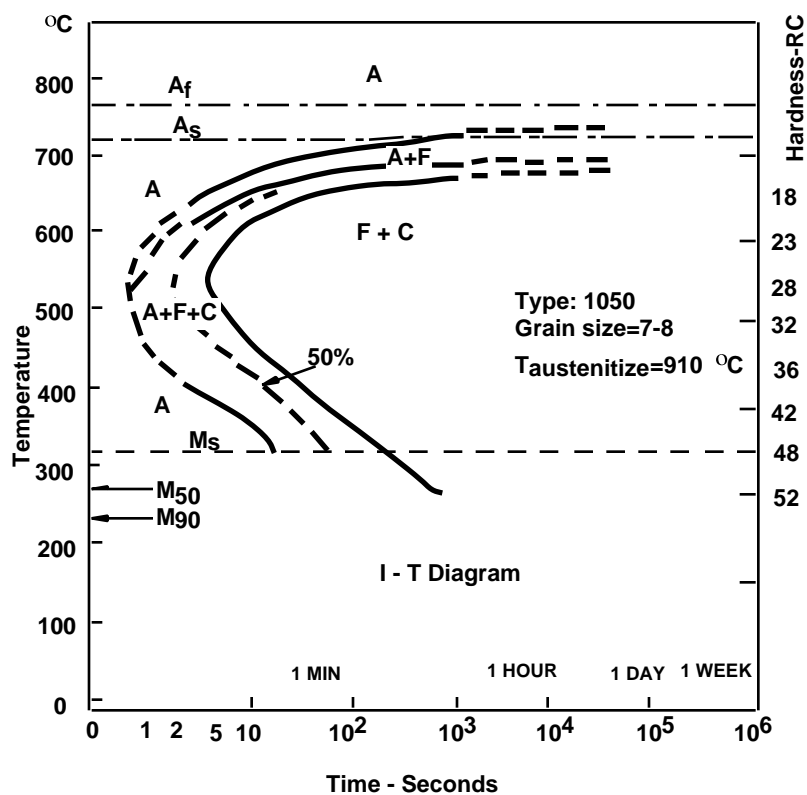
Another difference in the TTT diagrams is that the  $M_s$  temperature rises as the carbon content decreases.

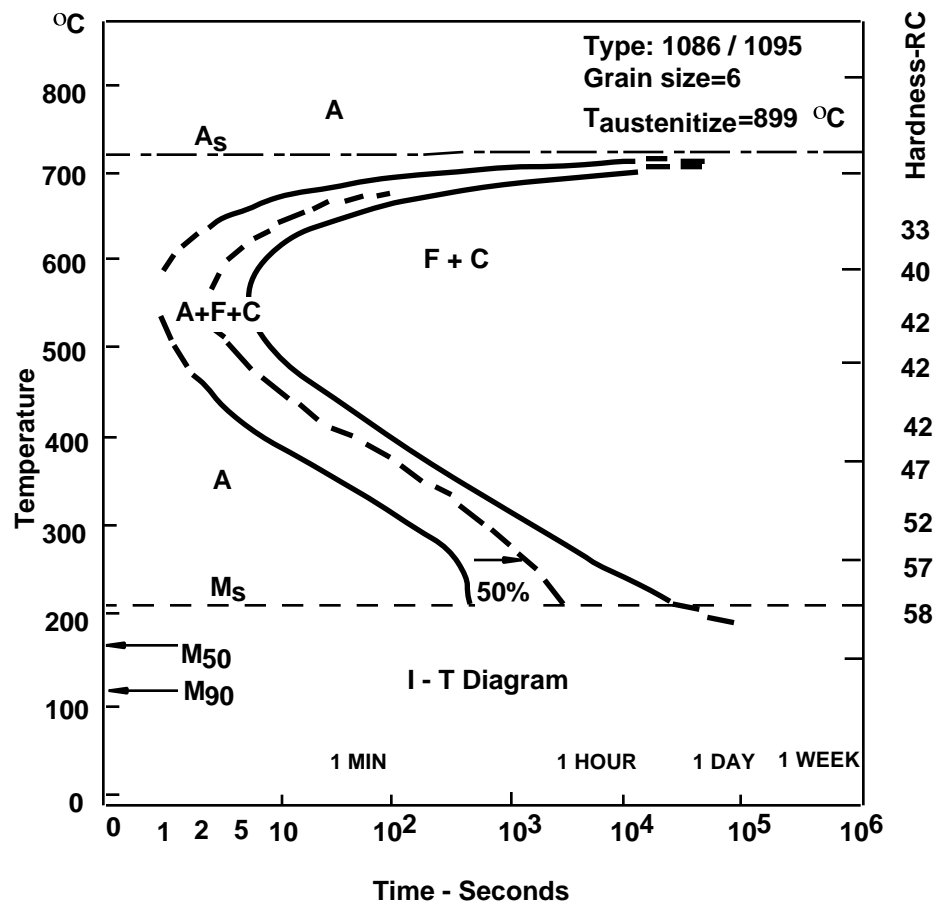
In hypereutectoid alloys, the proeutectoid phase is cementite so the diagrams are modified by the appearance of the cementite start-line. The martensitic transformation temperatures continue to be depressed as the carbon content is increased. Let us consider these changes in more detail.

After: Bain & Paxton, p13









After: Atlas of Time-Temperature Diagrams for Irons & Steels

### The nucleation of ferrite in hypoeutectoid steels.

Suppose that samples have been austenitized and rapidly quenched to and held at temperatures below the  $A_3$  point and above the  $A_1$  line. At these temperatures the steel will tend to transform to a mixture of austenite and ferrite because it is supersaturated with respect to the ferrite which means that the free energy change for forming a unit volume of ferrite from the austenite becomes negative (this refers to the bulk or chemical free energy). When the magnitude of this free energy change is large enough to compensate for other positive terms, such as the energy of creating new surfaces, the nucleation flux of ferrite crystals becomes significant. The start of the transformation is controlled by nucleation because the transformation is controlled by nucleation and growth. The nucleation flux depends on the free energy of formation of a critically sized nucleus. Experimental observations show that the ferrite nucleates heterogeneously on austenite grain boundaries. Let us suppose that lens shaped embryos form and each one eliminates an area of the grain boundary. Let the volume be  $V$ , the grain boundary area eliminated be  $A_b$ , the surface area of the particle be  $A_n$ , the surface energy of the ferrite/austenite interface be  $\gamma$  per unit area,  $\gamma_b$  be the specific grain boundary energy and suppose that there is no strain energy involved. Then, the free energy of formation of the embryo is:

$$G = V \cdot G_v + A_n \cdot \gamma - A_b \cdot \gamma_b$$

and the critical value is the maximum value for a given shape.

Note, now, that the critical value decreases as the magnitude of the (negative) free energy of formation of ferrite increases. This quantity is proportional to the under cooling below the  $A_3$  line. Inspection of the phase diagram shows that for a particular temperature of transformation, the under cooling increases as the carbon content decreases because of the slope of the  $A_3$  line. Hence, the nucleation flux is enhanced and the ferrite forms earlier as the carbon content is reduced in steels transformed at the same temperature.

The incubation time for the formation of proeutectoid ferrite continues to decrease for a given steel as the transformation temperature decreases below the  $A_1$  line. Also, at the lower temperatures, morphological changes such as the formation of Widmanstätten side plates of ferrite occur. Furthermore, nucleation of ferrite plates begins to take place within the austenite grains. Some time after the ferrite begins forming the pearlite transformation starts. The magnitude of the time interval between the ferrite start curve and the pearlite start line decreases as the temperature is lowered until either the two lines meet the ordinate axis or they merge at the nose of the diagram. The curves approach each other more and more closely as the temperature decreases because nucleation of pearlite becomes easier due to the increased driving force at the lower temperatures and also because of the carbon concentration immediately in front of the growing ferrite. Once a pearlite colony is nucleated it can grow more rapidly than the ferrite because the growth rate of the latter is controlled by long range diffusion. A consequence of this is that the final microstructure of the steel can often contain a smaller volume fraction of proeutectoid ferrite than that which would be predicted by applying the lever rule to the phase diagram.

The martensitic transformation attempts to convert the FCC iron to the BCC allotrope. The product is BCT because of the carbon incorporated in the crystals. The martensitic phase can then logically be regarded as an extension of the ferrite and therefore the driving force for its formation derives from the undercooling below the  $A_3$  line. Because the martensite is a metastable phase, the undercooling required for its formation is larger than that required for the formation of ferrite. The

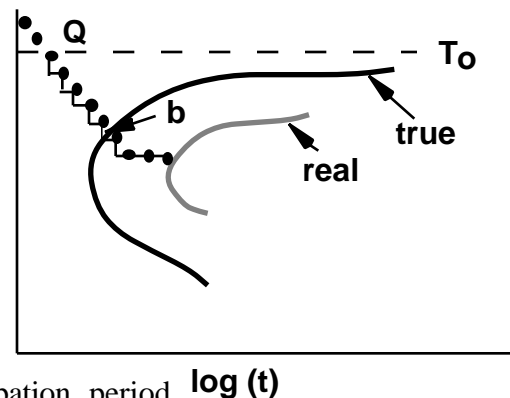
$M_s$  temperature is determined by the degree of super cooling necessary to provide an adequate driving force. In order to attain the high undercooling, the cooling rate must be fast enough so that a transformation that takes place by diffusion controlled mechanisms doesn't have time to occur. When this is so, the transformation begins when the  $M_s$  point is passed. Thus the first reason for an increase in the  $M_s$  temperature as the carbon content decreases, is because the  $A_3$  point moves to higher temperatures thereby increasing the amount of undercooling for a given transformation temperature. Also, the degree of supersaturation of the martensite with respect to carbon decreases as the total carbon content decreases. The reduction in the amount of carbon in the martensite reduces the strain energy associated with the misfit of the carbon atoms with the interstitial sites. This reduces the required driving force and hence the necessary undercooling. For these reasons the  $M_s$  temperature increases as the carbon content falls.

In the case of hypereutectoid steels, similar comments can be made with respect to the proeutectoid cementite phase. However, the martensite can still be regarded as an extension of the ferrite, and the austenite undercooling is determined by the extrapolation of the ferrite plus austenite/austenite phase boundary below the  $A_1$  line. Thus, the magnitude of the undercooling at a particular transformation temperature decreases as the carbon content rises. Simultaneously, there is an increase in strain energy within the martensite due to the increasing carbon content. These two effects combine to depress the  $M_s$  point further.

#### Continuous Transformation Diagrams.

Isothermal transformation diagrams provide valuable information about the kinetics of the transformation of austenite and are useful tools for considering heat-treatments. In practical heat-treatments, however, where the size of the part being treated is usually significant, the temperature and its rate of change vary with position within the part being heat treated. Also, there are heat treatments in which the austenite is cooled continuously. The real TTT diagram (i.e. the diagram that describes transformations in samples which cannot be quenched extremely rapidly) is not the same as the true isothermal diagram.

This is indicated in the sketch. A true isothermal start line or "C" curve is shown as well as a cooling path (dotted line) down to an isothermal transformation temperature. This cooling curve can be approximated by a series of isothermal steps linked by vertical, instantaneous temperature changes as is shown by the stepped line. Inspection of this sketch shows that as the temperature falls through the



transformation range below  $T_0$ , each of the horizontal steps represents a fraction of the incubation period corresponding to that temperature. In the 1930's, Scheil proposed that these "fractional incubation times" could reduce the time required for the transformation to begin during the final isothermal stage. This has been considered further by I.A. Wierszykowski in Met. Trans. 22A, 993, (1991). During a truly isothermal transformation that takes place at a temperature  $T_i$  the transformation begins when the time  $t = t_i$  i. e. when  $t/t_i = 1$ . All of the isothermal steps from a to b in the series drawn on the sketch, are too short for the transformation to have begun at any of the temperatures

concerned. Thus at point ,b, the austenite is still austenite. If the isothermal stage begins at b, then the transformation will begin after an additional time of  $t_x$ . We see that the real TTT curves will be displaced to the right on the diagram.  $t_x$  is smaller than the true isothermal transformation time for that temperature because some of the “pre-precipitation” microstructural changes will have already occurred. We are forced to conclude that even though a particular steel will possess a particular true TTT diagram, it has a variety of real diagrams in practice because of the influence of different rates of cooling which are themselves dependent on the size of the piece of steel and the nature of the quenchant used.

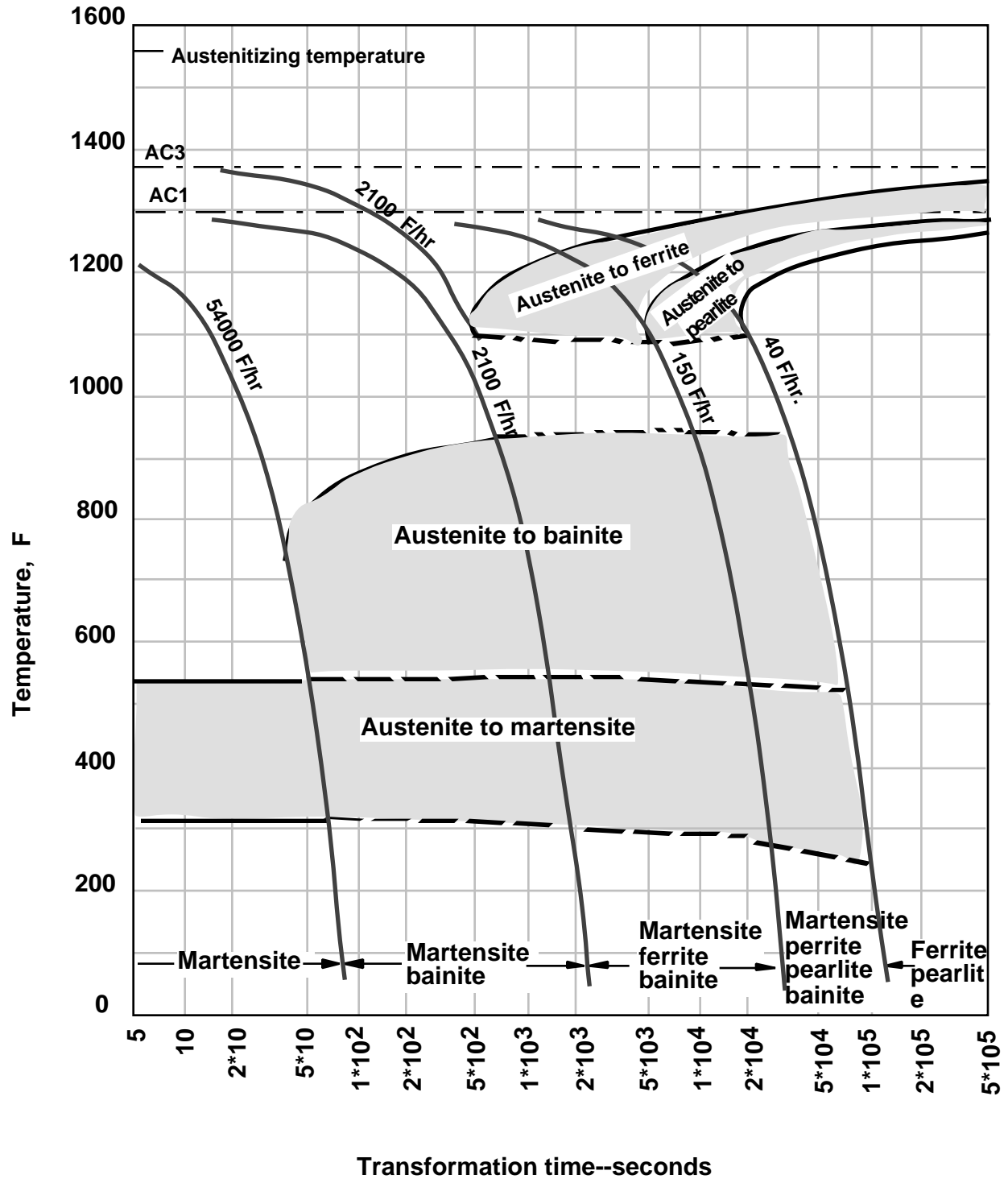
This has led to the creation of diagrams that predict the modes of transformation that take place during cooling. There are two main types of continuous cooling diagrams. The first type uses axes that show the temperature of the steel on the ordinate axis and the logarithm of time in seconds along the abscissa. Then lines are drawn on the diagram to show the cooling path in terms of the variation of temperature with time. If we consider one such cooling path and travel along it , downwards from the austenite, we encounter the start of a transformation. The location of this point is marked on the diagram and joined to similar points on other cooling paths to create curved lines that denote the initiation of the decomposition of the austenite. Similar lines which show the progress of the transformation in terms of the % completed are often appended between the start and finish curves. Then the diagram is divided into areas according to the nature of the product of the transformation. Diagrams of this type are determined experimentally by means of dilatometry.

When a steel part is austenitized and cooled, the heat is extracted from the free surface. In order for the center of the part to cool, heat has to be conducted to the free surface. The actual rates of cooling depend upon shape, size, thermal conductivity and the rate of extraction of the heat. For example, if a cylindrical bar is quenched in a bath of cold water, the surface cools the most rapidly and the center the most slowly. Thus, different parts of the steel will cool at different rates. To use a continuous diagram of the kind we are discussing requires a knowledge of the cooling rates at various positions.

The second type of diagram retains temperature as the ordinate axis but calibrates the abscissa in terms of diameters of steel bars cooled in air, oil and water respectively. These quenching media extract heat from the surface of a bar at different rates with the water quench being the most rapid. They are methods of cooling that are commonly used in practice. This statement is not intended to imply that all quenching oils extract heat at the same rates, so the diagrams provide guidelines but should not be regarded as quantitatively applicable. There are also variations in chemical composition among steels of the same designation which can change details of the transformation. With those caveats, the diagrams show the progress of the transformation at the center of bars of various diameters when they are cooled at those rates. It should be noted that this microstructure will not necessarily be found throughout the bar.



NOTE: THIS ALLOY STEEL HAS SEPARATE PEARLITE AND BAINITE CURVES.



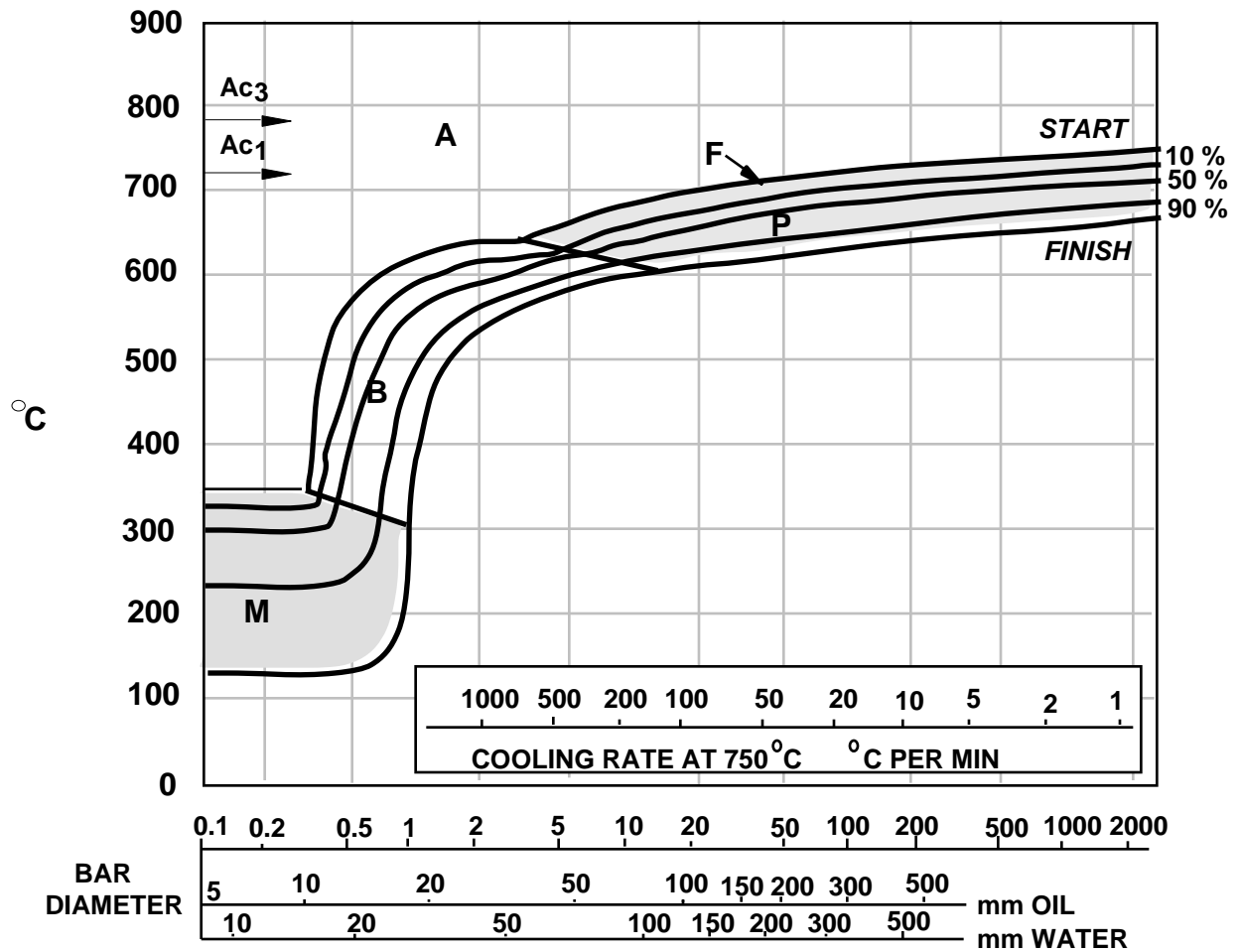
## CONTINUOUS COOLING TRANSFORMATION DIADRAM

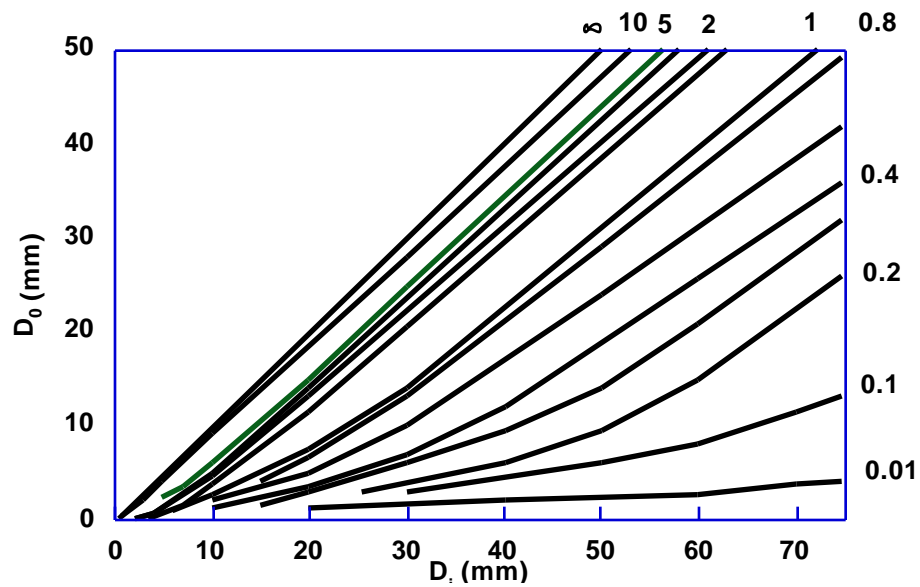
40 °C  
1038--1040

Austenitized at 850 °C  
Previous treatment rolled

Analysis Wt % (See note on page 8)

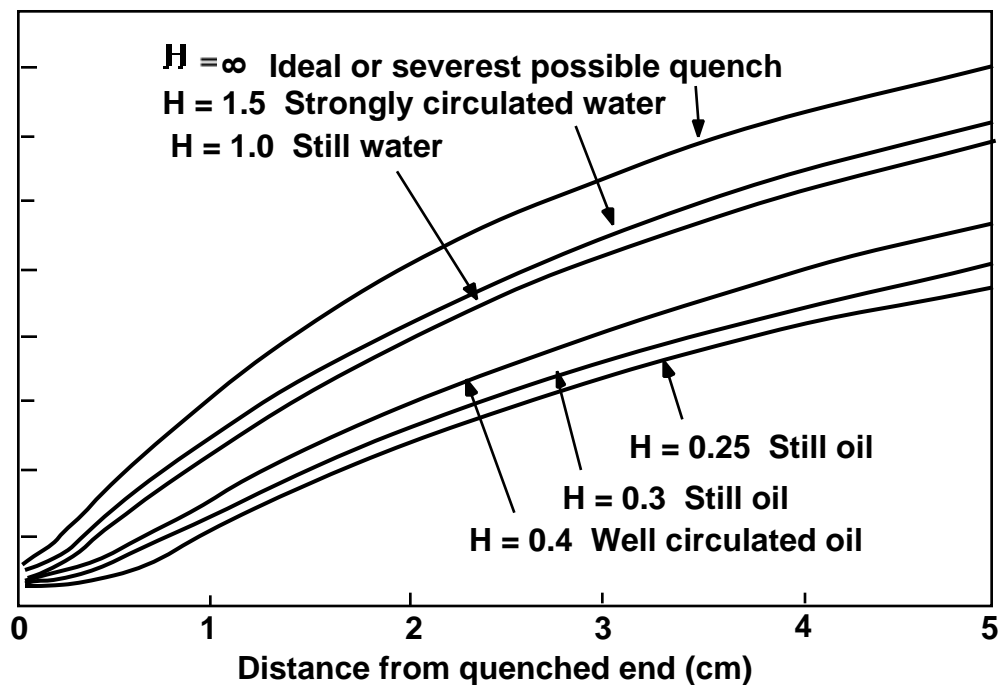
C	Si	Mn	P	S	Cr	Mo	Ni	Al	Nb	V
0.40	0.20	0.70	0.020	0.020	--	--	--	--	--	--



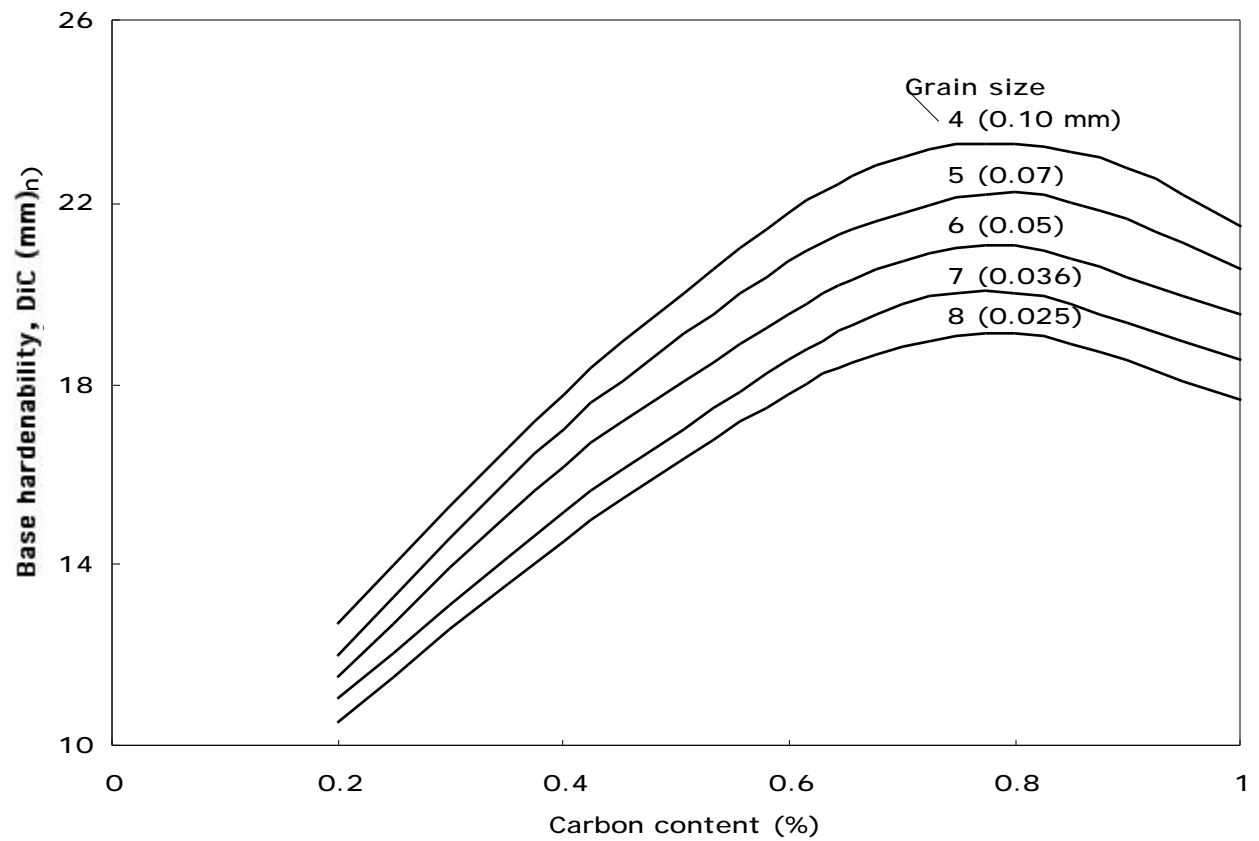


H-coefficients of quenching media

Agitation	Cooling medium		
	Oil	Water	Brine
None	0.25-0.30	1.0	2.0
Moderate	0.35-0.40	1.2-1.3	
Violent	0.8-1.1	4.0	5.0



After: Honeycombe, p.126,130



After: R.W.K. Honeycombe, Steels – Microstructures & Properties, p.131

### Comments on Mechanical Properties of Plain Carbon Steels.

#### Ferrite Pearlite steels.

Plain carbon steel is very often used when it consists of a mixture of ferrite and pearlite. The yield and ultimate strengths of these steels are controlled by the mechanical properties of the ferrite and cementite and microstructural details concerning how they are mixed together. We have already reviewed the behavior of iron when it is deformed in a tensile test. We have also noted the effects of solutes dissolved in iron. In particular, when the interstitial solutes, C and N, are allowed to diffuse they segregate at and around the dislocation lines. At room temperature this segregation can prevent most dislocations from moving under applied stresses so that yield requires the activation of sources at the sites of stress concentrations or the creation of new dislocation line. This gives rise to the yield point phenomenon in which the iron shows an upper and lower yield point and a Luders extension. At higher temperatures, serrated yield can occur. Another consequence of the interactions between the interstitial solutes and dislocations is the increase in strength and the corresponding reduction in ductility arising from strain aging. Ferrite is a BCC iron solid solution and it can behave as described above.

The flow stress in polycrystalline ferrite ( this is the lower yield strength if a yield point phenomenon occurs) is dependent on dislocation density and grain size. Taking these contributions to be additive, we can write the yield stress as:

$$\sigma_y = \alpha \mu \rho^{\frac{1}{2}} + m d^{\frac{-1}{2}}$$

where  $\alpha$  and  $m$  are material constants,  $d$  is the grain diameter,  $\rho$  is the dislocation density and  $\mu$  is the elastic shear modulus. The grain size dependence arises because the grain boundaries act as obstacles to the gliding dislocations.

Cementite is a hard and brittle phase. It tends not to deform plastically at ambient temperatures. It can crack. Hence, yield in a pearlitic microstructure is associated with the movement of dislocations in the ferrite. When dislocation sources are activated in the ferrite plates the glide paths of the dislocations are limited by the cementite plates because they cannot slip in the carbide. Instead they are forced to pile up at or near the ferrite/cementite interfaces. The first consequence of the lamellar microstructure of alternating ductile and hard, brittle plates is an increase in the yield stress of the material compared to that of the ferritic matrix because the inter-lamellar spacing is usually much smaller than the proeutectoid ferrite grain size. We expect that the increase in the yield stress due to the restriction of dislocation glide paths in the ferrite lamellae should be larger the finer the spacing in the pearlite. This expectation turns out to be true.

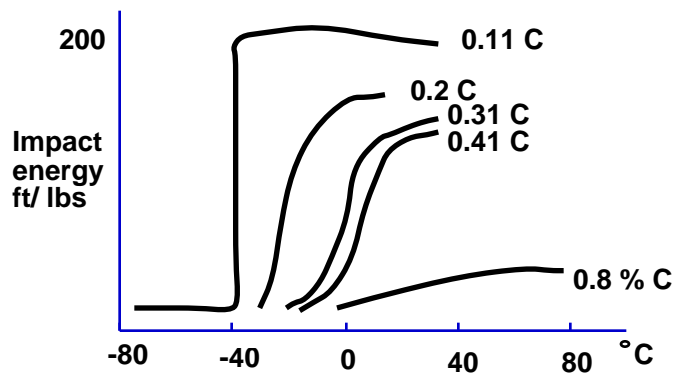
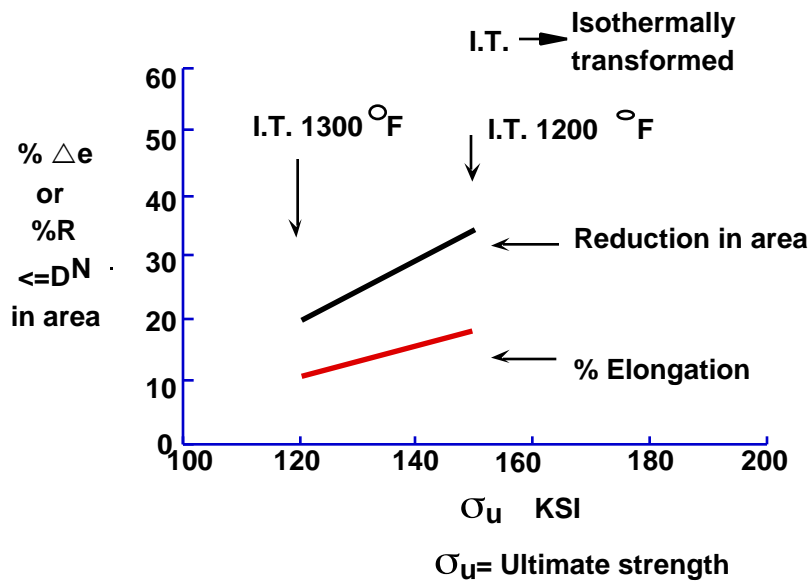
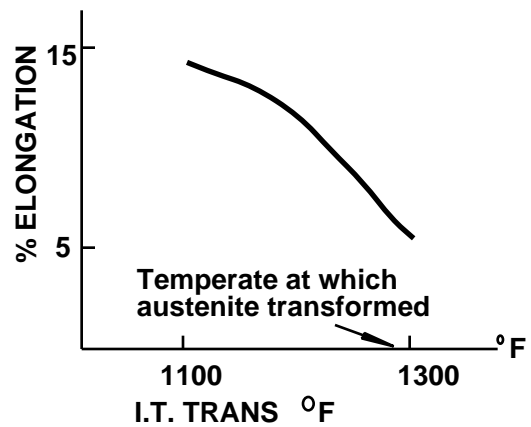
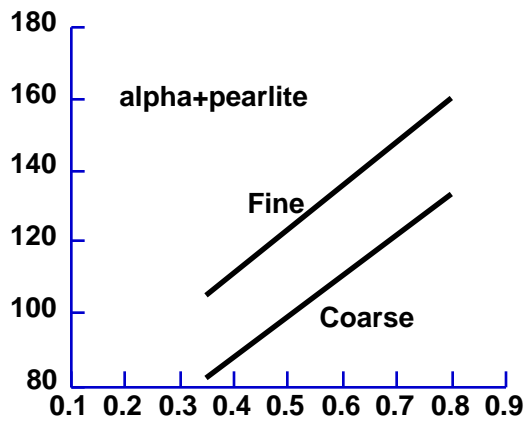
Stress concentrations are created at the ends of pile ups where the dislocations meet the ferrite carbide interfaces and eventually the carbides can be broken. This occurs more rapidly when the ferrite plates are thicker because more dislocations can participate in an individual pile-up for a given applied stress. The generation of cracks in the cementite plates can initiate general fracture which implies that coarse pearlite should fail before fine pearlite because the cementite plates are expected to crack sooner when the ferrite lamellae are thicker and, also, the cracks will be longer and therefore more able to propagate. This prediction is also true; fine pearlite is both stronger and more ductile than coarse pearlite.

A large tonnage of low carbon steel, containing 0.15 wt.% C and below is used in sheet form. Slow cooling from hot rolling processes or annealing heat treatments leaves these steels in the form of mixtures of ferrite and pearlite but the ferrite dominates the mechanical properties because it comprises most of the steel and is the most continuous phase. These hot rolled steels can have yield strengths of 25 to 45 K.S.I (172-310 MPa) and ultimate tensile strengths of 40 to 65 K.S.I (276-448 MPa). The yield strength can rise to 100 K.S.I. (690 MPa) as the carbon content of the steel is increased because the properties of pearlite eventually become dominant. When the carbon level becomes high enough for the pearlitic microstructure to influence the properties, the morphological details such as pearlite spacing also affects the yield and ultimate strength levels as shown in the sketches provided with this text.

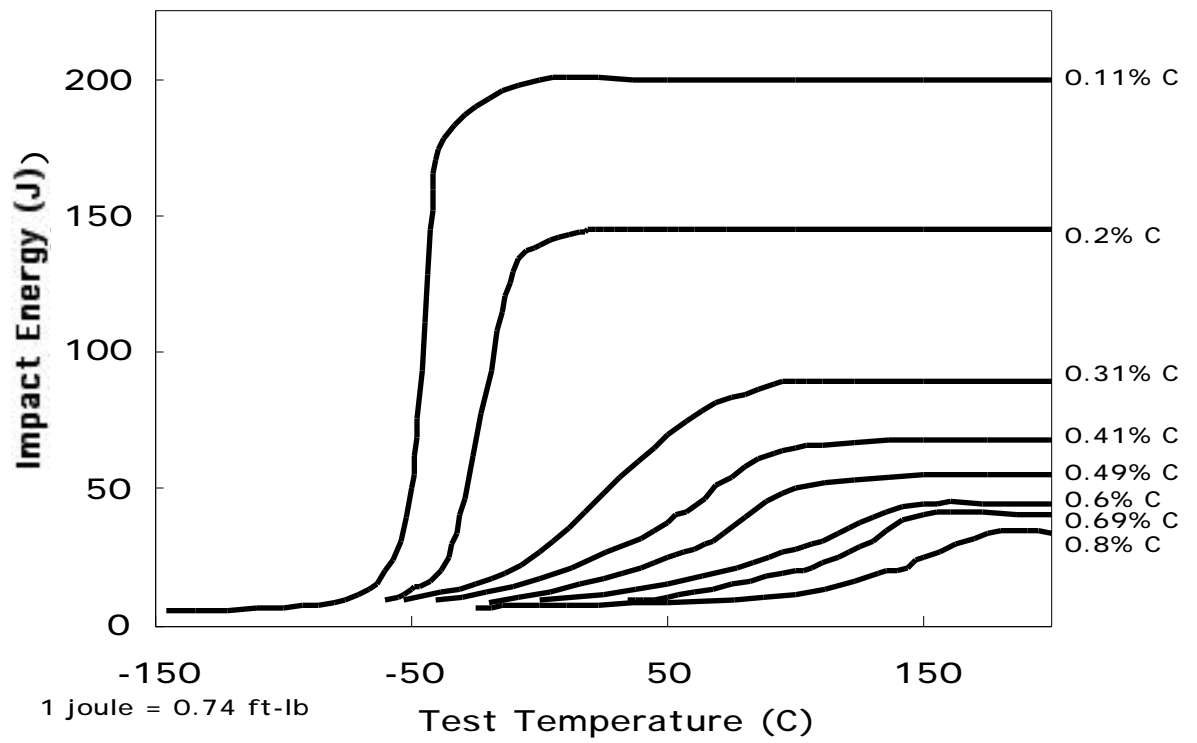
### Impact Properties of Ferrite Pearlite Mixtures.

The mechanical properties discussed above are those measured during standard low strain rate tensile or compression tests. The response of materials to high strain rates is also important. This is particularly true for BCC metals which, unlike FCC metals, can have a ductile to brittle transition temperature under impact loading. An indication of the response to impact loading is provided by the Charpy impact test in which a notched, square-section bar is broken by a swinging pendulum. Measuring the height of the pendulum at the beginning of the test and that to which it rises after breaking the sample, enables the energy consumed in breaking the bar to be calculated. When the bar breaks in a brittle mode the energy consumed is small. In this case the bar breaks into two pieces and the pendulum swings onwards and upwards. When the fracture occurs in a ductile fashion, a large amount of energy is consumed by the deformation processes that precede fracture as well as those that accompany fracture. Then the distance traveled by the pendulum after the fracture is smaller. Very ductile samples do not break and the pendulum is stopped. A crafty trick often done by certain professors I know, while teaching a lab course in which Charpy impact tests are being performed, is to sneak a sample of annealed, austenitic stainless steel into a group of brittle samples that break easily, then to watch them being tested and to chuckle like mad at the surprise of the person performing the tests, when the pendulum comes to a sudden halt with a loud clunk.

The nature of the fracture and the amount of energy consumed in an individual test depends upon the temperature of the specimen at the time it was tested. It is standard practice to perform Charpy tests over a range of temperatures. When considering the results of these kinds of tests, it is wise to bear in mind that microstructural features other than the those of the ferrite and pearlite can affect them. For example, a common ingredient in a carbon steel is MnS which is formed when the alloying element, Mn, combines with the residual impurity, S. The MnS is present in the form of inclusions in the steel and the morphology of these inclusions depends upon prior history. When the steel has been processed by hot rolling, the inclusions can be elongated and strung out in the rolling direction and are called, therefore, inclusion stringers. The important point is that the interface between the MnS and the steel is not strong. If the steel being tested happens to have stringers that lie parallel to and near to the notch, the fracture will not be representative of the steel itself, but of the interfaces between the inclusions and the steel. Burns and Pickering (JISI 202, 899, 1964) studied the effects of the volume fraction of pearlite on the impact properties of carbon steel

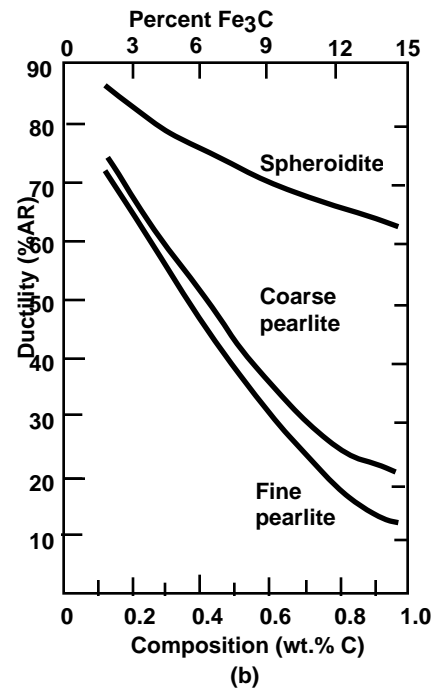
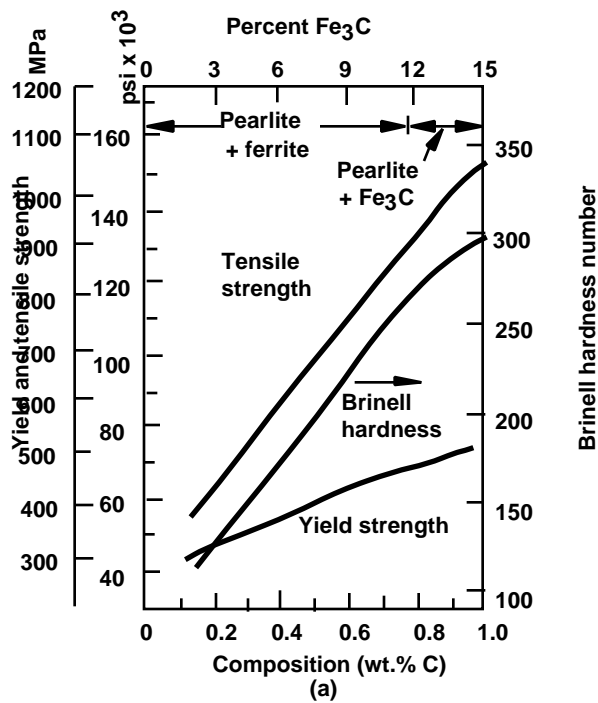
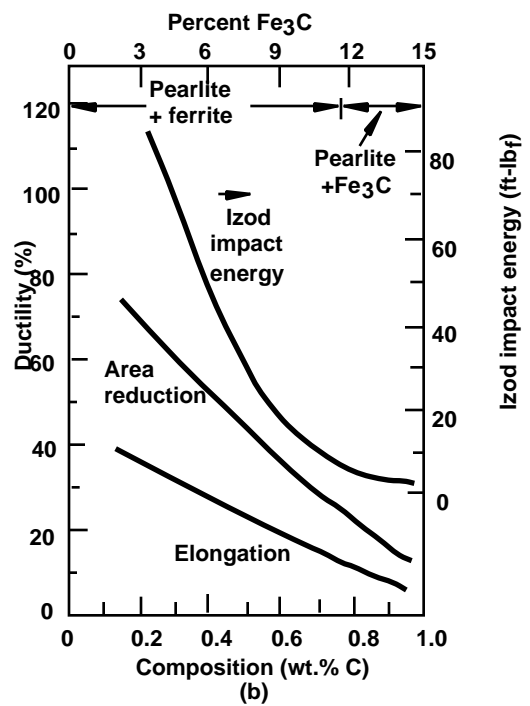
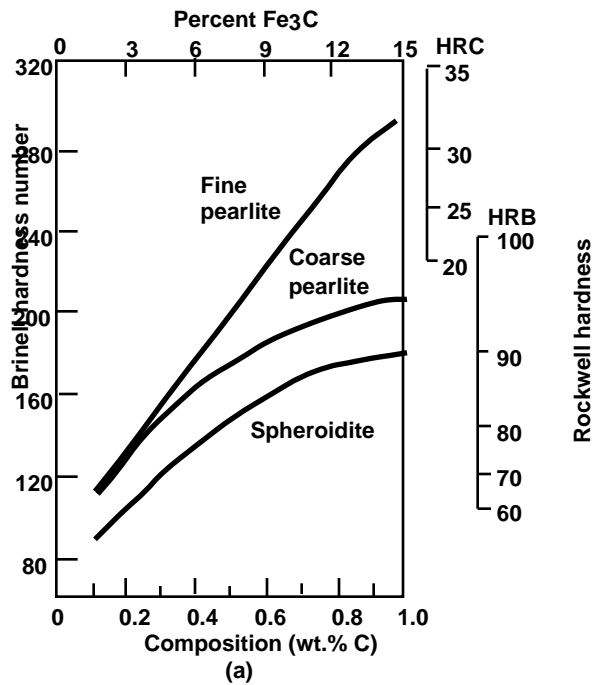


Charpy impact energy ft. lbs  
VS  
Temperature of impact as a  
function of % C in  
ferrite/pearlite steels with  
low inclusion content.



After: Honeycombe, p.167





After: Callister, p.323,324

in which the amount of the MnS present and its morphology was controlled in order to minimize its influence on the results. They found that 0.11 wt.% carbon steel had a flat upper shelf ( i.e. the energy vs. temperature plot was horizontal and at a high energy value) where the fracture was ductile and a large amount of energy was consumed. As the temperature of the test was decreased this steel showed a transition from a ductile to a brittle fracture that occurred rapidly near  $-40^{\circ}\text{C}$ . At lower temperatures the plot of energy consumed vs. the temperature of the test became horizontal again, forming the lower shelf. As the carbon content was increased, the energy associated with the upper shelf decreased and the transition from ductile to brittle fracture took place at higher temperatures. The temperature range occupied by the ductile to brittle transition increased. The eutectoid steel, which is entirely pearlitic, shows a gradual transition of the energy consumed as a function of temperature. Presumably, the gradual transition at the high pearlite levels occurs because even though the cementite plates crack, the total fracture path is tortuous in comparison to cleavage in the ferrite. Cleavage fracture in ferrite is a brittle fracture process in which the fracture path follows particular crystallographic planes in each grain, forming large, relatively flat facets.

Until approximately 20 years ago, pearlitic steels were commonly chosen as structural steels because of the useful strength levels that can be attained in them. Unfortunately, the use of medium to high carbon steels in structures such as bridges and grain elevators created the practical difficulties encountered in joining components made from these steels which were therefore commonly bolted and riveted together. Their use in such structures is not really desirable because the low toughness and high ductile to brittle transition temperatures can cause any failures that occur to be catastrophic. These days, alternative ways are used to get high strength while maintaining good toughness and a low ductile to brittle transition temperature, e.g. through the development of weldable, high strength low alloy steels.

In hypereutectoid steels the proeutectoid constituent is cementite. In steels cooled at rates which permit the formation of pearlitic microstructures, the proeutectoid phase has time to nucleate on and grow along the austenite grain boundaries. When this occurs the steel becomes less tough because the thin continuous film of cementite on the prior austenite grain boundaries becomes the most continuous phase and dominates the properties. The makers of Damascus swords in the middle ages, used steels with over 1 wt.% carbon but produced hard, tough blades by working the steel below the  $A_{cm}$  line. This destroyed the continuous films of cementite. Apparently European blacksmiths didn't know about that and couldn't use such high carbon steel. In modern times the undesirable effects of continuous cementite films along prior austenite grain boundaries can be important in case hardening treatments in which high carbon levels are created near the surfaces of parts that are then quenched and tempered. When such parts are broken it is common to find a region of the fracture which appears to be intergranular because the crack propagated along the proeutectoid cementite films.

#### Bainite and Martensite.

The lamellar microstructure of pearlite has a strong effect upon its toughness, with the toughness increasing as the spacing decreases. In bainite there is no lamellar structure. Instead, it is an array of sheaves of very fine laths, needles or platelets in hypoeutectoid steels and the fine carbides therein, are discrete particles. As a consequence, bainitic microstructures are generally tougher than pearlitic microstructures. Because of the fine scale of its microstructure bainite is also harder than pearlite in steels of the same carbon contents.

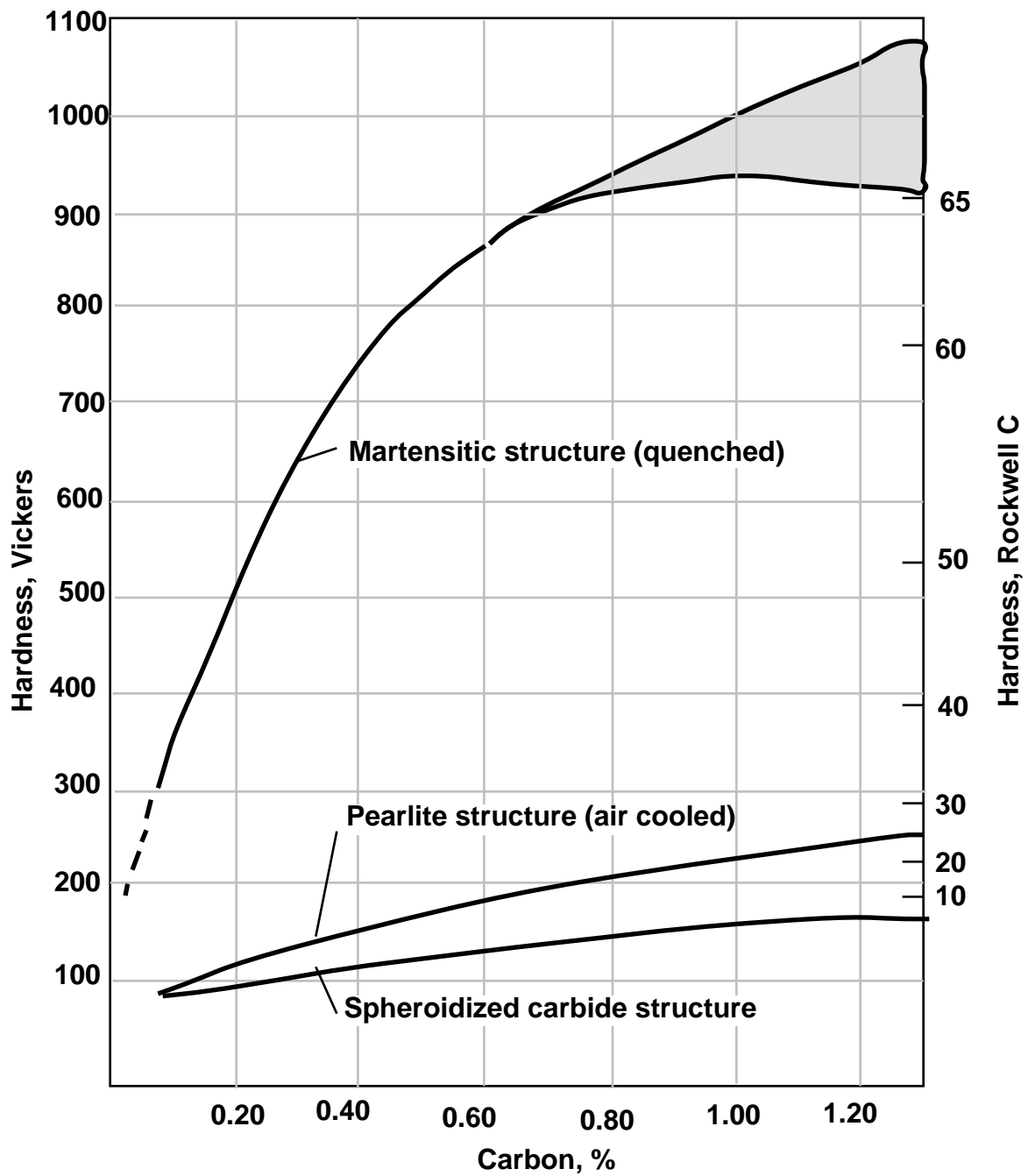
Martensite is a supersaturated solid solution in which the interstitial solutes interact strongly with dislocations. It is also composed of very fine crystals with many intercrystalline boundaries; it can be highly dislocated or twinned. For these reasons, it is the strongest form of a carbon steel. For example, the 0.2% proof stress is 120 K.S.I. (828 MPa) for martensite containing 0.1% C and 240 K.S.I. (1.65 GPa) for 0.4% carbon. Correspondingly, the Rockwell C hardness number increases from about 30 to 65 with a change in the carbon level from 0.1 to 0.6%. There is little change in the hardness for further increases in the carbon content. The hardness of freshly formed martensite is directly dependent upon its hardness content. This is shown in the appended figure. Also shown on this figure are the data for air cooled austenite (curiously labeled pearlitic) and spheroidized steels. Such steels consist of a polycrystalline array of ferrite crystals in which discrete globules of cementite particles are embedded. This microstructure represents the softest state of a carbon steel. A martensitic, plain carbon steel can be very hard and very strong. Unfortunately, freshly formed martensite (i.e. as-quenched) lacks toughness and is intolerant of small flaws which can initiate brittle fracture. For this reason, freshly quenched martensite is not knowingly used in practical applications. It is heat treated further in order to impart to it with some toughness. These heat treatments are generally compromising treatments because to gain toughness one has to sacrifice some strength. These additional heat treatments are called tempering treatments and are the subject of the next discussion.

### Tempering Reactions in Carbon Steel

The heat treating process that is applied to martensite in order to endow it with better toughness is called tempering. A tempering treatment consists of heating the steel to a selected temperature below the  $A_1$  line, holding it there for a certain time and then cooling it back down to ambient temperature. The transformations that occur and the property changes that are produced, depend upon the tempering time and temperature. The general aim is to raise the toughness of the steel. Because this is achieved at the cost of a reduction in hardness and strength, the process is always a compromise and is selected according to the intended application. A great deal of research has enabled us to understand much of what goes on, but there are still some uncertainties with respect to transition carbides.

On the basis of the research into the tempering process, it has become customary to divide the process into stages that occur in different temperature regimes. It should be recognized that this division is a convenient way of describing tempering reactions; the particular temperature ranges should be considered as guide lines and, obviously, neighboring stages overlap.

Stage 1 occurs at temperatures below 200 °C. Here, carbon atoms diffuse throughout the martensite and segregate at dislocations and intercrystalline boundaries. Because the  $M_s$  temperature for carbon steels is higher than room temperature, it is possible for these segregation processes to begin when the martensite is first formed, especially if the cooling rate below the  $M_s$  point is slow. In this case, one refers to the changes as being produced by auto tempering. For steels of less than about 0.2 wt.% C no carbides form in this stage. When the carbon content is greater than 0.2 wt. %, very fine particles of a transition carbide nucleate and grow within the martensite. This carbide is richer in carbon than cementite and is described by the formula  $Fe_{2.6}C$ . It is metastable. It has a hexagonal structure and is referred to as epsilon carbide. Several



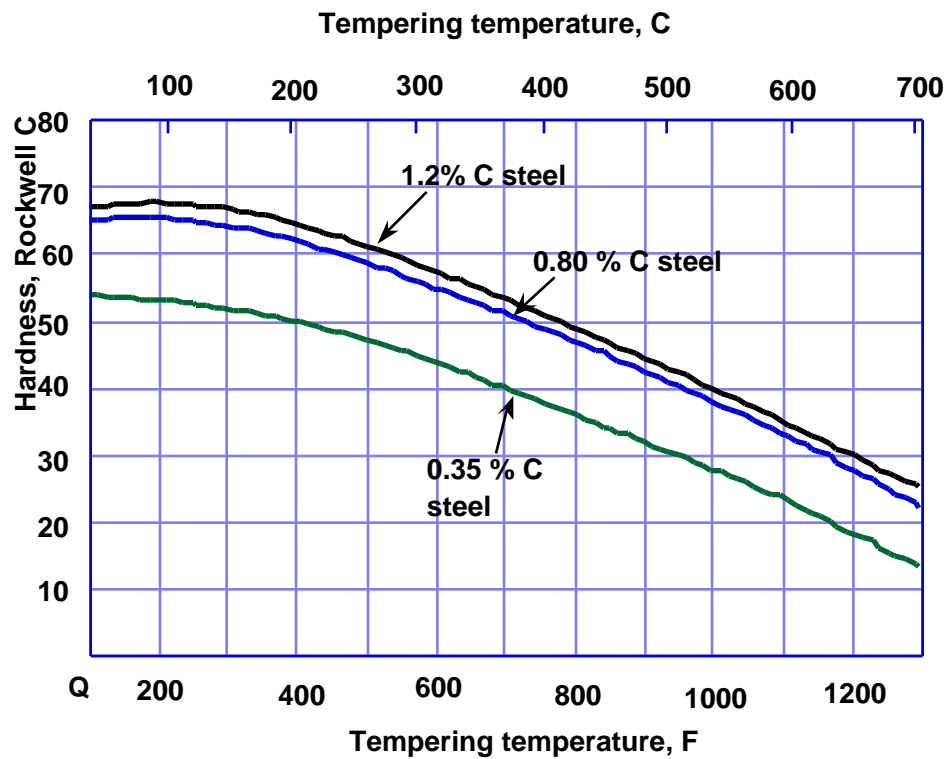
After: Bain & Paxton, Alloying Elements in Steels, 2<sup>nd</sup> edition, p.37

researchers have claimed to have observed the presence of another metastable carbide in high carbon steel. This one has been christened eta carbide. It is orthorhombic  $\text{Fe}_2\text{C}$ . There is, however, still uncertainty because the experimental confirmation of these claims is not easy. It is generally accepted that epsilon carbide definitely forms. When it does, the martensite retains some degree of tetragonality because it still contains more carbon in solid solution than would ferrite; there are no changes in the morphology of the martensite crystals. Thus the first stage of tempering involves the segregation of carbon to various defects in the microstructure and the conversion of the martensite to low carbon martensite plus epsilon carbide when the total carbon content is high enough.

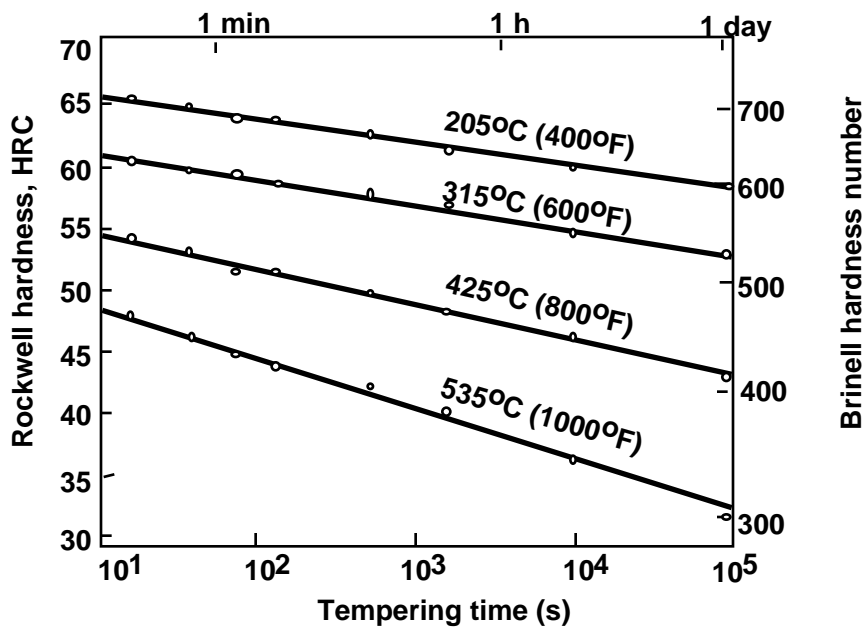
During stage 1 tempering, there are changes in the physical properties such as electrical resistivity which can be used to monitor the progress of the changes. However, there is not much of a reduction in the hardness; indeed, it can increase slightly for steels of medium to high carbon levels. Obviously, these changes involve diffusion and are therefore time dependent. A common practice is to use tempering times of one hour so much of what follows will refer to the changes produced by tempering treatments one hour long .

The second stage of tempering occurs between 200 and 300°C. It is not very important in plain carbon steels because it refers directly to the conversion of retained austenite to bainite. The quantities of retained austenite in carbon steels are not large. However, they can be large in alloy steels especially those for which the  $M_f$  temperature is below 0°C; stage 2 is important when there are significant quantities of retained austenite included within the martensite.

Cementite begins to precipitate out from solid solution at about 300°C. This is the beginning of stage three. The precipitates nucleate on heterogeneous sites such as intercrystalline boundaries. Because the martensitic crystals form with specific orientation relationships with the austenite crystal in which they grow, they do not grow across austenite grain boundaries. In effect, the prior austenite grain boundaries are retained as surface defects. At the beginning of stage three, the heterogeneous nucleation process at the sites of the prior austenite grain boundaries tends to produce sheets of cementite particles. The matrix loses tetragonality and becomes BCC ferrite as its carbon content drops because of the diffusion of carbon to these growing carbides . If the steel is sufficiently rapidly heated to the tempering temperature then no transition carbides form. If transition carbides were present due to a previous tempering treatment or because they formed during a slow heat-up, then they dissolve during stage three. The phases present become ferrite and cementite. When tempering is carried out at temperatures near 300 °C, the ferrite crystals remain acicular during the times usually used. Because the diffusion coefficient of carbon increases with an increase in the temperature, the cementite particles are able to grow more rapidly and to decrease in number per unit volume, as higher tempering temperatures are used. The hardness after tempering becomes increasingly smaller; an effect which becomes more and more significant as the tempering temperature becomes higher. Eventually the temperature becomes high enough to cause the dislocation content to decrease in a similar manner to the changes in the dislocation content of cold-worked metals during recovery processes. At about 600°C, the ferrite grains are able to grow and become equiaxed. These morphological changes in the ferrite grains are similar to those that occur during recrystallization in cold worked ferrite. Because of this, these later processes have been said to comprise a fourth stage of tempering, but that name has also been assigned to secondary

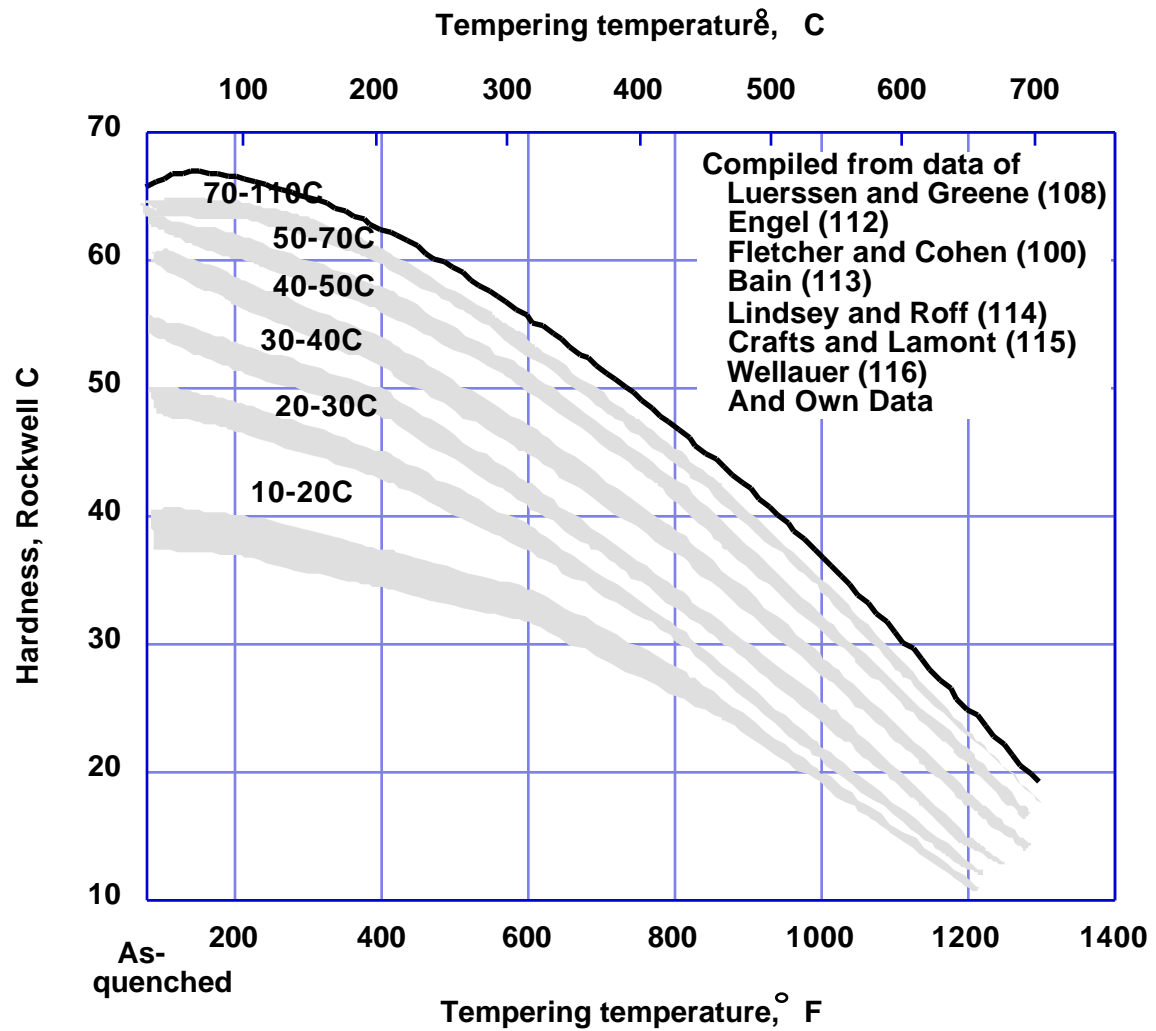


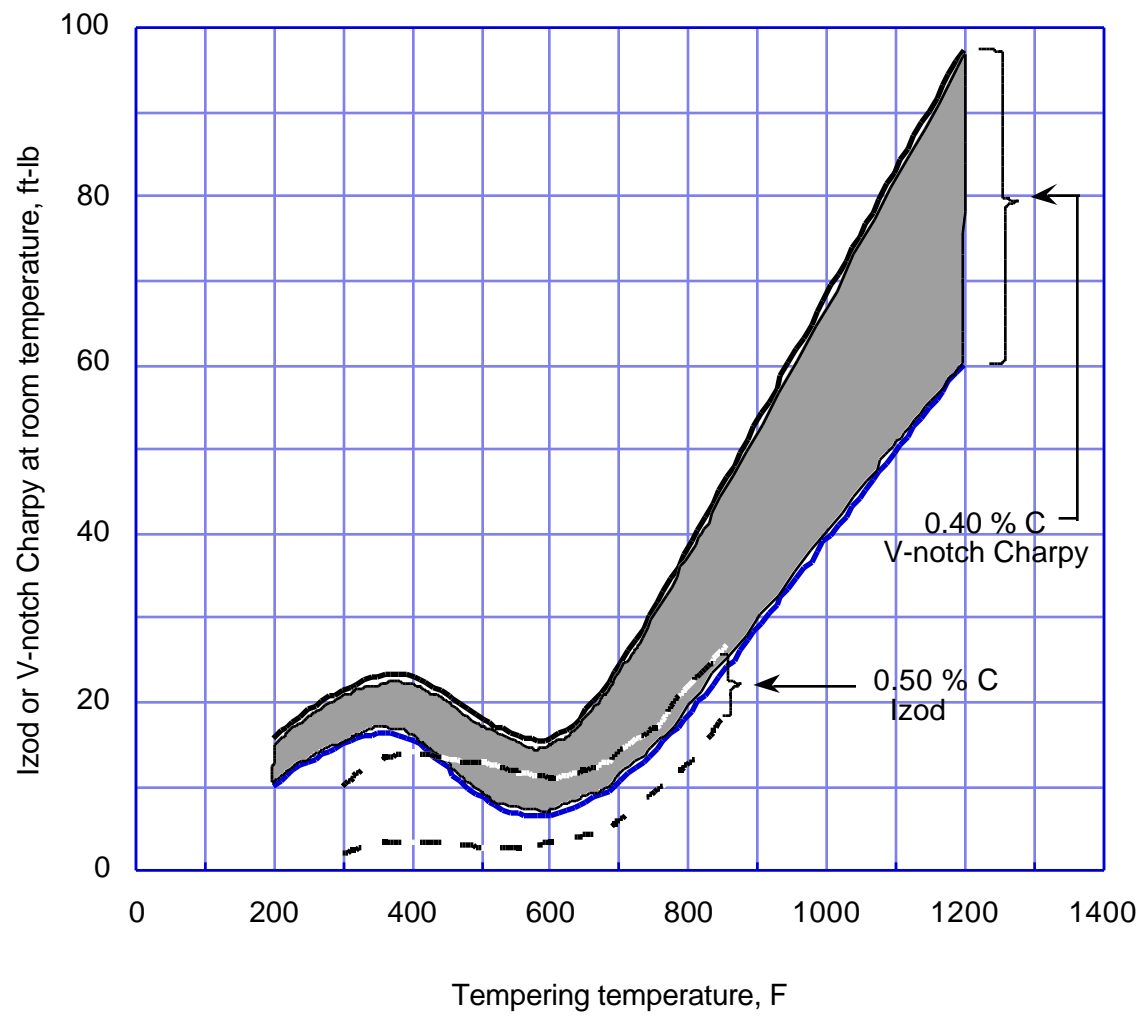
After: Bain & Paxton, p.38



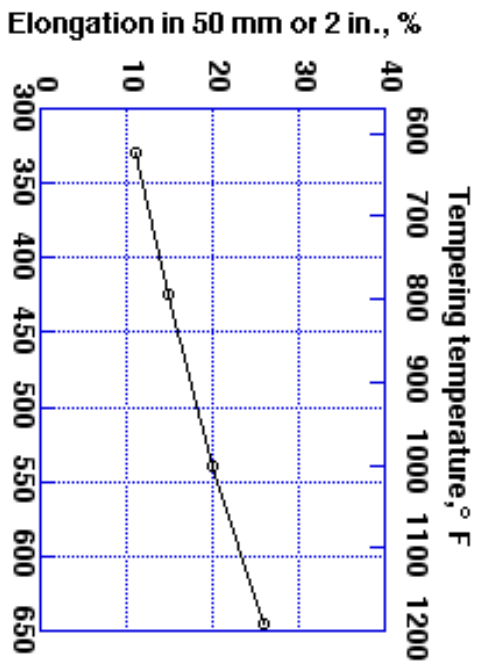
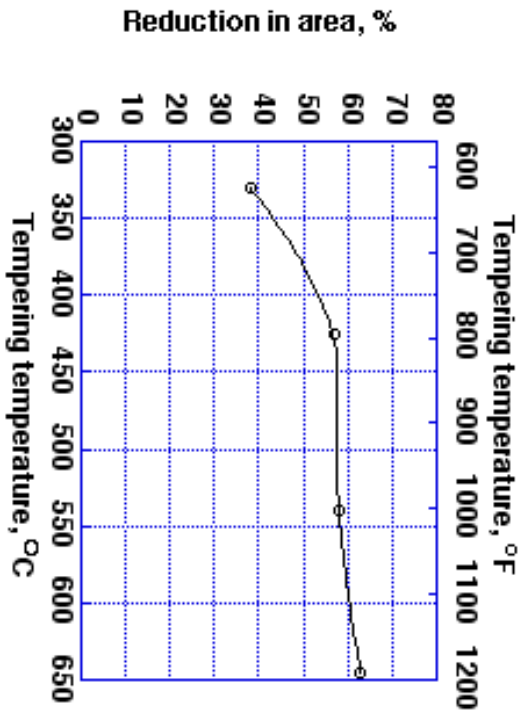
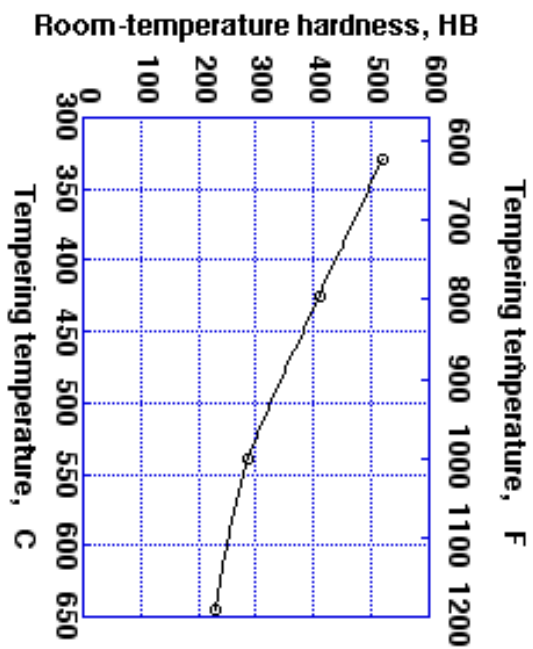
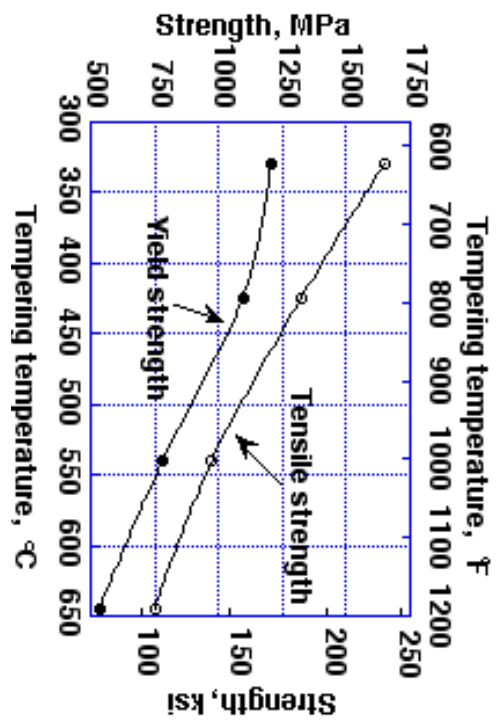
After: Callister--page329

After: Krauss: Steel: Heat Treatment and processing principles, p205,206









hardening processes that can occur during the tempering of alloy steels so to avoid confusion we won't use it for carbon steels. Instead, we will consider all of processes that occur above three hundred degrees Celsius as belonging to stage three.

These various stages offer a convenient way of regarding the tempering reactions. However, it is important to recognize that the temperatures that have been quoted to delineate the stages are merely guidelines. Obviously the stages overlap because the dominant type of change and the rate thereof depends upon temperature and time and does not change discontinuously. It is also worthwhile pointing out a common error made by students new to this subject when they describe tempering reactions in small samples that have been rapidly up-quenched to high tempering temperatures such as 600 °C. The error is to describe the transformations that take place as those of stages 1,2 and 3 occurring sequentially. Unless the heat-up time is slow enough, epsilon carbide will not form at this temperature and pearlite not bainite can form from retained austenite because the tempering temperature is above the position of the nose of the TTT diagram.

#### Effects of Tempering on the Mechanical Properties of Martensite in Carbon Steels.

During stage one, the hardness change after an hour of tempering is not great. But as the temperature is increased the hardness begins to fall rapidly and continues to do so as the temperature increases. Examples of this behavior are presented. It is tempting to believe that as the hardness falls the toughness rises. In general this is true, but in detail it is not. When carbon steels are tempered at temperatures near the beginning of the onset of stage 3, say 350°C or 500°F, there is often a reduction in the Charpy impact energy. This is traditionally known as 500 degree embrittlement. The drop in toughness seems to be associated with the formation of sheets of plate-like cementite particles along boundaries and can be aggravated by the segregation of elements such as As, Sb, and P. Tempering at this temperature is normally avoided. Similar phenomena also occur in low alloy steels, as we will see later. The tensile strength of a carbon steel is related to hardness and falls as the hardness is reduced. Clearly, the choice of tempering conditions depends on the importance of the relevant properties.

The advantages gained by heat treatments that use austenitization, quenching to martensite and then tempering the martensite are that the desired microstructure can be obtained either throughout the part or at selected locations. Obtaining the desired microstructure means that the proper mechanical properties can be obtained where required. All of this is true provided that the part being heat treated can indeed be converted to martensite when the austenite is cooled. If it can not be so transformed then the required microstructure cannot be produced. This brings us to the concept of hardenability which concerns the question of how much of a steel bar can be converted into martensite by a specific quench. **This question is of central importance in quench hardening heat treating processes.** The TTT diagrams of plain carbon steels show us clearly that the production of martensite requires very rapid cooling rates. These cooling rates are so fast that it is not possible to transform large parts into martensite. Thus, the excellent properties provided by tempered martensite cannot be obtained in thick components made of carbon steel simply because they cannot be cooled fast enough. The reason is that plain carbon steels have low hardenability. We define the **hardenability** of a steel as that property that enables it to avoid transformations that occur by diffusion and, instead, to transform to martensite when cooled from the austenite phase field. A steel with a low hardenability must be cooled very rapidly. As the hardenability increases, the necessary cooling rate decreases. Note that the hardenability refers to the ability of the steel to transform to martensite; it does **not** refer to the magnitude of the hardness of the martensite.

Because of the very useful and desirable properties that can be achieved with tempered martensitic microstructures, research into methods of increasing the hardenability of carbon steels became an important endeavor many years ago. It was found that profound effects can be obtained by adding alloying elements to steel. This is the first reason for the existence of low alloy steels. Often the alloying elements that are added to control the hardenability of the steel do not markedly improve the mechanical properties obtainable in the tempered martensite in comparison with those of similarly tempered martensite in plain carbon steel; they do, however, increase the hardenability so that the martensite can be produced in the first place. Before we consider the roles of alloying elements in steel, we will complete this description of heat treating processes by summarizing some heat treating practices.

### Heat Treating Practices.

The microstructure of a steel depends upon its prior thermo-mechanical history. For example, a hot rolled plain carbon steel can consist of equiaxed ferrite grains and pearlite nodules. If the steel does not have the microstructure desired for its application or for the next process that is to be performed on it, then the microstructure is changed by heat treating. A number of standard processes exist. These will be briefly described before we return to the story of martensite.

### Normalization

This heat treatment is performed to refine grain size and to obtain a carbide size and distribution that provides a favorable starting point for subsequent heat treatments; it is usually done to hypoeutectoid steels. It comprises austenitization at 100 to 150 °F above the  $A_{C3}$  line followed by an air cool. A standard rule of thumb is to austenitize the steel for 1 hour per inch of thickness. This rule of thumb has been used for many years. However, because computing has become easier, empirical and semi-empirical studies are being made to determine soak times more accurately. It is important to recognize that the microstructural details produced by normalization will depend on the size of the part; a thin part cools more rapidly in still air than does a thick part.

### Full Anneal

This process is used to make the steel relatively soft and to endow it with good machinability. The microstructure is large-grained ferrite and coarse pearlite. Austenitization is conducted at a high temperature to produce a large grained austenite and to dissolve all the carbides. The steel is then cooled slowly enough to allow the desired microstructure to form by the transformation of the austenite at temperatures near to the  $A_1$  line.

### Isothermal Annealing.

This has essentially the same aim as the full anneal. It is more efficient for small parts because furnace cooling can be replaced by transferring the parts between constant temperature baths containing molten salts. The steel is then usually protected from scaling and oxidation by the molten material into which it is placed. These salts are various mixtures of compounds such as alkali metal hydroxides and nitrates that are chosen for particular temperature ranges. Baths of molten lead were used effectively for this purpose before concerns about the dangers of lead to human health became influential.

### Spheroidization

In the spheroidized microstructure the carbides are discrete globules embedded within the ferritic matrix and also resident on grain boundaries. Steels with this microstructure are in their softest state and are most easily mechanically formed. It is often part of overall treatments given to high carbon tool steels that are formed into particular shapes before being hardened. It can be produced by cooling very slowly from 100°F above the eutectoid isotherm or by a long isothermal treatment just below it. Spheroidization can also be obtained by cyclic processing in which the temperature of the steel is cycled above and below the A<sub>1</sub> line.

#### Process Annealing and Stress Relieving

This terms normally mean some form of treatment in which the steel is heated to and held at a temperature below the A<sub>1</sub> line. Recovery processes occur which removes or diminishes residual stresses that might be present from previous treatments. Recrystallization can also be produced in cold worked parts.

#### Quench and Temper.

The purpose of these heat treatments is to produce parts in which a desired hardness is obtained, either throughout the part or in the vicinity of its surface. It involves austenitization, quenching to room temperature or below and reheating to and holding at a tempering temperature below the A<sub>1</sub> line. The first part of the process is intended to form martensite. The tempering temperature and time are selected to produce the required hardness.

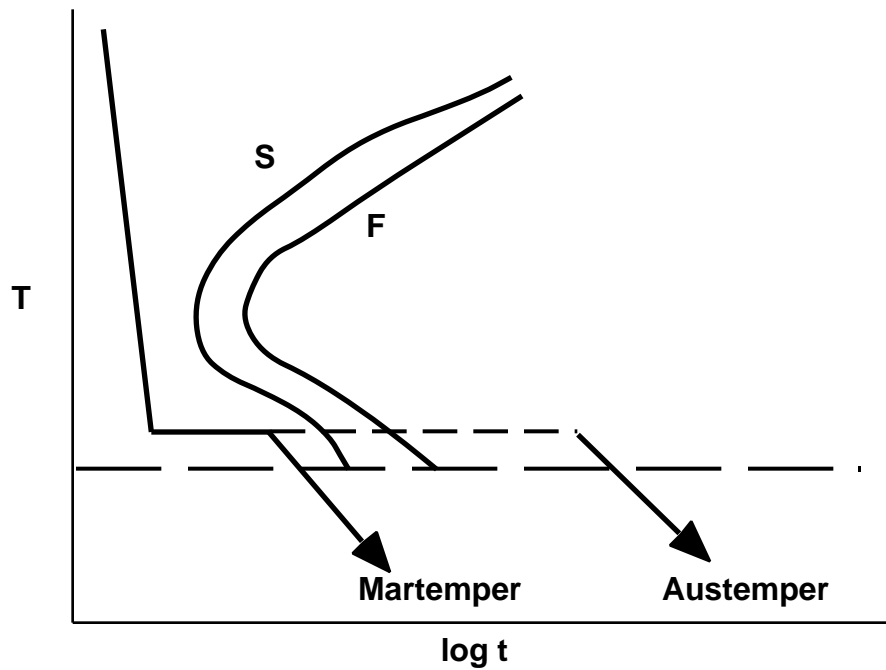
Excellent properties can be obtained by this procedure. However, there are serious limitations for plain carbon steels. This is because the transformations that occur by diffusional processes are not easily avoided during cooling. Consequentially, very severe quenching rates are necessary and even then only small samples can be converted to martensite throughout. The rapid quench rates are undesirable because there is no opportunity for stress relief during cooling; warping and distortion are more likely to occur during rapid quenching. These stresses superimposed on the transformation stresses due to the volume expansion that occurs when martensite forms, can help to cause quench-cracking. The situation is that carbon steels of the correct microstructure could perform adequately in many applications, but it is often not possible to produce the microstructure because the part cannot be cooled fast enough. This is the first reason for the development of low alloy steels in which one of the roles of the alloying elements is to slow down diffusional transformations to enable martensite to be produced during slower cooling rates.

#### Martempering.

A modification of the quench process that relieves the thermally induced stresses initially generated by thermal contraction is called martempering. In this process, the part is first quenched rapidly until its temperature has fallen below that of the nose of the TTT diagram but is still above the M<sub>s</sub> point. It is held at that temperature to relieve stresses by becoming of a uniform temperature and then finally cooled through the M<sub>s</sub> point. This process is possible when the bainitic transformation takes much longer to begin than the changes associated with the nose of the diagram. Note, also, that the steel can be relatively slowly cooled from the isothermal hold and still form martensite which serves to minimize distortion further.

## Austempering.

As we discussed earlier, bainite can have useful hardness and toughness values. When they are adequate for the application, the formation of bainite can be chosen instead of martensite. To allow this, the steel is quenched to a temperature below the nose and held there until the bainitic transformation is completed. This avoids the problems associated with the rapid volume changes during the martensitic transformation. The process is termed austempering.



## **The Effects of Alloying Elements in Steel.**

Alloy steels are those steels that contain minimum specified amounts of alloying elements in addition to those found in plain carbon steels. The list of elements that are important in alloy steels, in addition to those that we have already considered in plain carbon steels, includes Cr, Ni, Mo, Nb, Ti, W, Co, Cu, V, Si, Al and B. These elements produce a variety of changes in the behavior and properties of steel. Because the equilibrium condition of the steel is now described by phase diagrams applicable to the Fe-C-x (etc.) systems, the alloying elements have important effects on the details of phase transformations in steel. These effects concern both the kinetics of the transformations and, because additional phases not present in plain carbon steels can be created, the type of transformation. Alloying elements also have pronounced effects on phenomena such as recovery, recrystallization and grain growth.

### **Classification of Alloying Elements**

The purpose of this section is to attempt to divide the long list of alloying elements into groups that have similar effects. The properties of carbon steels depend upon the properties of the individual phases that comprise the steel, the volume fractions of these phases and the manner in which they are arranged within the total microstructure. Two very important phases that can exist in steel are the FCC and BCC solid solutions that are called austenite and ferrite. The first method of classifying alloying elements is based on the effect of the alloying element on the austenite and ferrite phase fields on binary phase diagrams of iron and the alloying element. This classification divides the alloying elements into two main groups called austenite stabilizers and ferrite stabilizers.

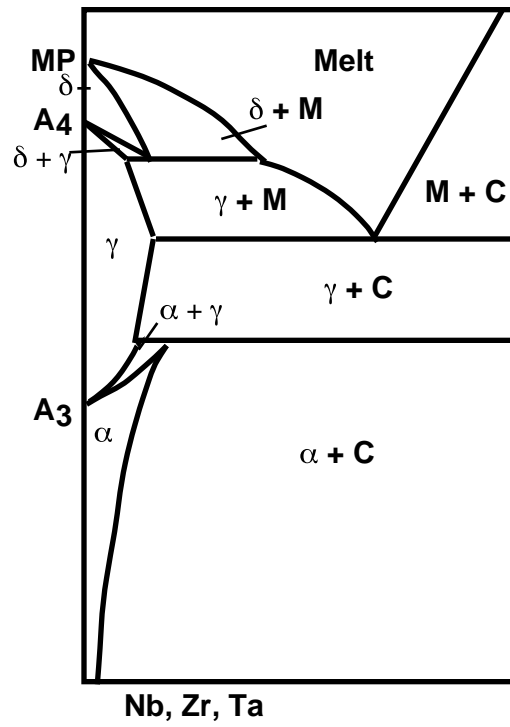
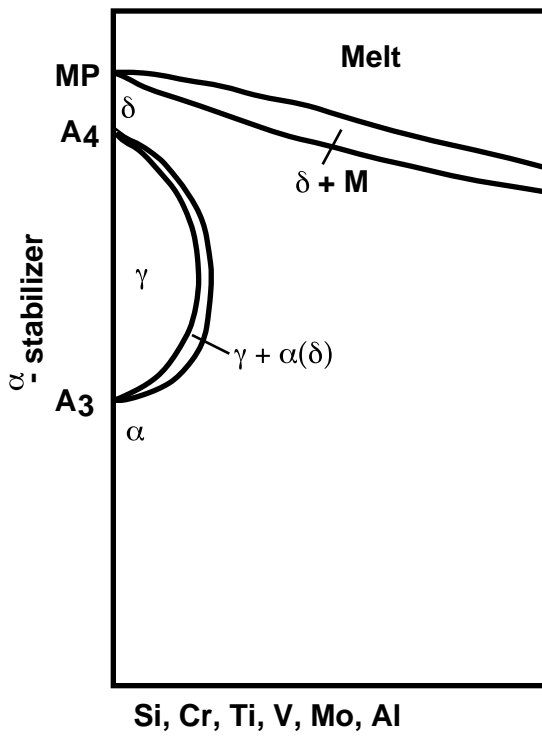
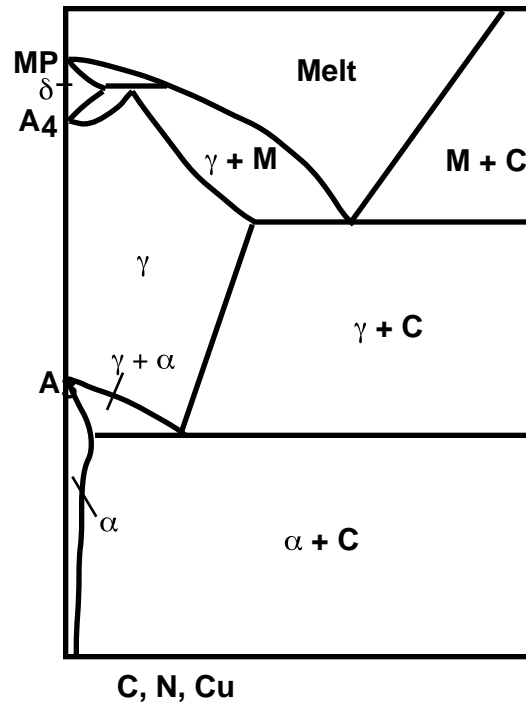
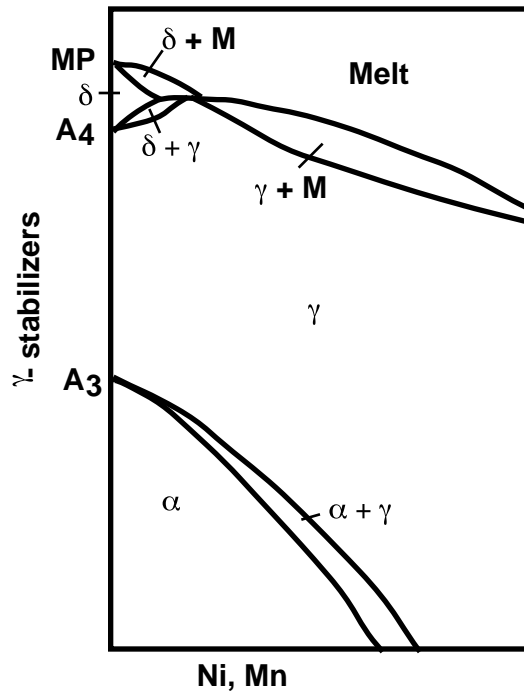
#### **a) Austenite Stabilizers.**

If we examine the metastable iron carbon binary phase diagram we see that adding carbon to iron favors the existence of austenite over ferrite. This is so because it decreases the temperature of the austenite to alpha ferrite transition ( the  $A_3$  point ) and also increases the temperature of the austenite to delta ferrite transition. Thus carbon expands the gamma field and is therefore called an austenite stabilizer. Those elements that behave similarly are also called austenite stabilizers. When the binary phase diagrams with iron of these elements are examined (examples are included in the appended figures) it is found that they can be sub divided into two groups. In one group the addition of the alloying element depresses the FCC to BCC transition temperature towards room temperature before other phases appear. Examples of such elements are nickel and manganese. In contrast, in the iron carbon system the austenite phase field is limited by the appearance of cementite. Nitrogen and copper act similarly in that they expand the gamma field. Nitrogen forms a nitride phase that limits the austenite phase field whereas the phases in the iron copper system are solid solutions.

Other austenite stabilizing elements are Pt, Ir, Os, and Ru.

#### **b) Ferrite Stabilizers.**

The second main group consists of those elements that favor ferrite over austenite. Again, these can be divided into two sub-groups. In one, the FCC field is restricted and separated from the BCC field, in which alpha and delta ferrite fields merge together, by a two phase area. The FCC area is called a gamma loop . Examples are Cr, Ti, V, Mo, Si and Al.



The second sub-group restricts the gamma field by lowering the delta ferrite transition temperature and raising that of alpha ferrite while also producing other phases. Examples are B, Nb, Zr and Ta.

When the quantities of alloying elements present in a steel are small of the order of a few weight percent or less, it is usually possible to consider the equilibrium states of the alloy steel by means of the Fe-C binary phase diagram while, of course, recognizing the diagram is an approximation. This becomes unreliable as the alloy content increases. Then ternary diagrams or pseudo-binary diagrams are employed for Fe-C-X systems. These difficulties increase as the number of different alloying elements added to the steel increases. Therefore, parameters that are important in heat treating processes such as austenitization temperatures and the eutectoid composition etc. are determined directly by experiments.

Alloying elements can also cause additional phases to appear within the steels. These phases include alloy carbides and intermetallic compounds. Because cementite is a very important phase in carbon steels it follows that effects of alloying elements on cementite are also important. With this in mind, it is customary, also, to divide the alloying elements into groups according to their propensity to form carbides.

#### Carbide Formers.

These elements either do not object to the presence of cementite, e.g. Mn dissolves in cementite, or they form carbides themselves, e.g. Ti. They are ranked according to the stability of their carbides in the iron matrix.

Moderate carbide formers....Cr, Mo

Strong carbide formers...W, Ta, Nb

Very strong carbide formers... V, Ti, Zr

When significant amounts of these elements are present, the situation with respect to microstructural constituents can become complicated. Steels can possess cementite, mixed carbides i. e. cementite containing dissolved alloying elements, and a variety of alloy carbides in which there is little iron. Nitrogen tends to prefer to reside in the carbides giving rise to carbonitride compounds. It can also combine with some alloying elements such as aluminum to form nitride precipitates.

#### Graphite Stabilizers.

Some alloying elements dissolve in ferrite and thermodynamically oppose the formation of cementite. This encourages the formation of graphite and so these elements are called graphite stabilizers. Examples are Ni, and Si. In fact, silicon is so effective that it enables the formation of graphite from the melt in cast irons and is, therefore, a particularly important alloying element in those materials.

#### Effects of Alloying Elements on Hardenability.

There are many applications for which the properties of tempered martensite are particularly suitable and, indeed, often necessary for the application to be successful. Unfortunately, these desirable properties can only be obtained in components that can first be converted to martensite.



This imposes severe restrictions on the use of plain carbon steels because of the generally low hardenability of these steels. When it is desired that martensite forms throughout the part (this is usually called through hardening), rapid quenching throughout is necessary which restricts the sizes of parts that can be successfully treated. Very high quench rates bring about the risk of distortion and cracking and this can pose serious practical problems. Carbon steels are generally of low hardenability because the diffusion controlled reactions by which austenite can transform can occur rapidly in them. Hardenability can be increased if the rates at which these transformations take place can be reduced. Research has shown that this can be achieved by adding appropriate alloying elements. With the exception of cobalt, which has a negative effect, all alloying elements that are added to steel, raise the hardenability **provided** that they are dissolved in the austenite. **This is an important condition.** The effects alloying elements have on the hardenability of steels are the primary reason for the development of the AISI/SAE standard low alloy steels

The AISI/SAE standard low alloy steels are listed in ASM handbooks and in numerous texts and journals. These steels are identified according to a numerical code in which the final pair (trio if there are five digits) of digits describes the carbon content as is so for plain carbon steels and the first two numbers indicate the principal alloying elements. The standard steels are manganese steels with code numbers 13xx; molybdenum steels described by 40xx numbers; molybdenum and chromium steels which use 41xx numbers; molybdenum, chromium and nickel steels assigned 43xx numbers and chromium steels which use 51xx numbers. Other variations of compositions have 6xxx and 7xxx etc. The series 2xxx and 3xxx refer to steels which contain nickel as the principal alloying element. Some of the other combinations of alloying elements, however, are more effective at raising the hardenability than is nickel alone and provide a given increase at a lower cost. Hence, nickel steels are not used as much as they used to be. Indeed, these days they are often omitted from some tables of standard low alloy steels. When the hardenability is of prime importance for the application of an alloy steel, it is possible to obtain steels which are manufactured with closely controlled compositions so as to ensure that a specified hardenability is obtained. Such steels are identified by adding the letter H to the numerical code.

Other elements that are added to standard alloy steels are V, B and Pb. Vanadium is a very strong carbide former and forms fine carbides that along with the aluminum compounds in killed steels, inhibit grain growth during austenitization. This is effective because its carbides can persist at temperatures close to 2000°F which is much higher than typical austenitization temperatures used for standard low alloy steels. When present, lead resides in steel in the form of small globules of lead; its solubility in ferrite is very small. It is added because it improves the machinability of the steel. Boron is added to increase the hardenability. This is the only reason that it is added. When boron is present in a standard alloy steel, the code designation is amended by inserting the letter B between the second and third digit e. g. 50B44.

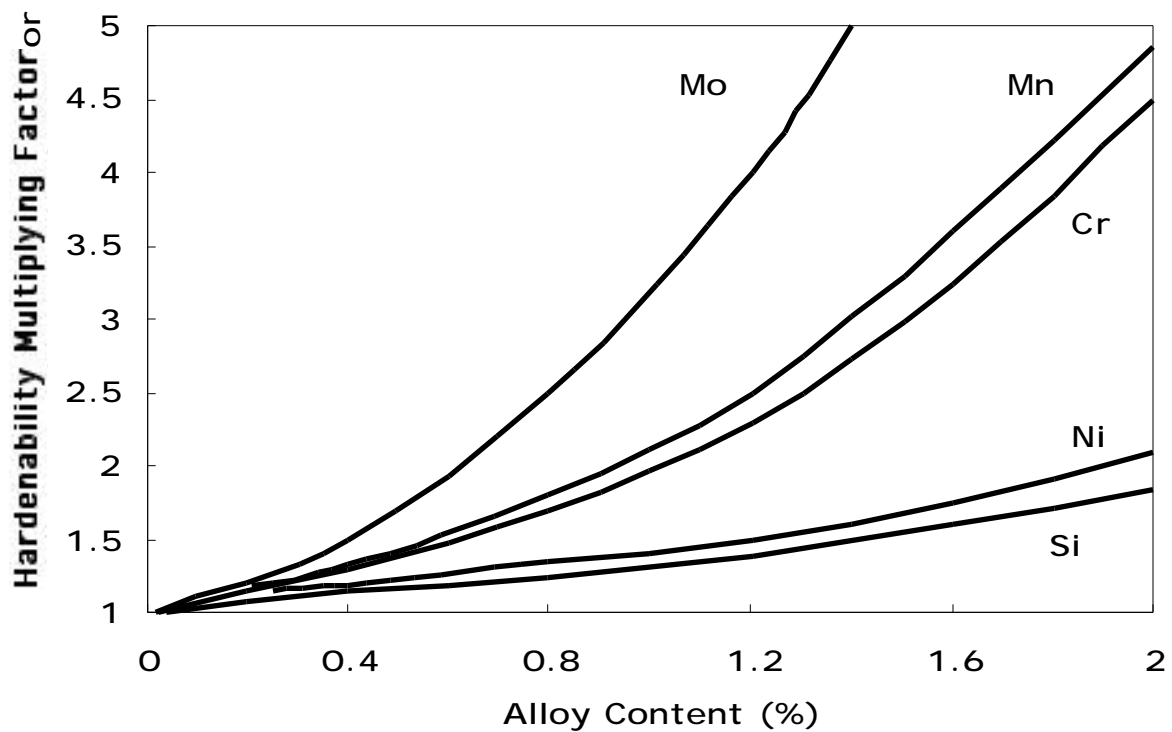
In order to consider the effects of alloying elements on the hardenability of steels it is necessary to consider the effects that they have on phase transformations in steel. The first of these concerns the effects on austenitization; then there are the effects upon the formation of proeutectoid ferrite, pearlite and bainite; then lastly, of course, are the effects on the martensitic transformation itself.

# SUMMARY OF THE AISI-SAE DESIGNATIONS FOR COMMON CARBON AND LOW ALLOY STEELS.

Designation <sup>1</sup>	Approx. Alloy Content, %	Designation	Approx. Alloy Content, %
<i>Carbon Steels</i>			
10XX	Plain carbon	<b><u>Nickel-molybdenum steels</u></b> 46XX	Ni 0.85 or 1.82; Mo 0.25
11XX	Resulfurized	48XX	Ni 3.50; Mo 0.25
12XX	Resulfurized and rephosphorized		
15XX	Mn 1.00 to 1.65	<i>Chromium steels</i> 50XX(X)	Cr 0.27 to 0.65
<i>Manganese steels</i> 13XX	Mn 1.75	51XX(X)	Cr 0.80 to 1.05
		52XXX	Cr 1.45
<i>Molybdenum steels</i> 40XX	Mo 0.25	<i>Chromium-vanadium steels</i> 61XX	Cr 0.6 to 0.95; V 0.15
44XX	Mo 0.40 or 0.52		
<i>Chromium-molybdenum steels</i> 41XX	Cr 0.50 to 0.95; Mo 0.12 to 0.30	<i>Silicon-manganese steels</i> 92XX	Si 1.40 or 2.00; Mn 0.70 to 0.87; Cr 0 or 0.70
<i>Nickel-chromium-molybdenum steels</i> 43XX	Ni 1.82; Cr 0.50 or 0.80; Mo 0.25		
47XX	Ni 1.45; Cr 0.45; Mo 0.20 or 0.35	<i>Boron steels</i> <sup>2</sup> YYBXX	B 0.0005 to 0.003
81XX	Ni 0.30; Cr 0.40; Mo 0.12		
86XX	Ni 0.55; Cr 0.50; Mo 0.20		
87XX	Ni 0.55; Cr 0.50; Mo 0.25		
94XX	Ni 0.45; Cr 0.40; Mo 0.12		

Notes: <sup>1</sup>Replace "XX" or "XXX" with carbon content in hundredths of a percent, such as AISI 1045 having 0.45% C, or 52100 having 1.00% C. <sup>2</sup>Replace "YY" with any two digits from earlier in table to indicate the additional alloy content.

From: N.E. Dowling, "Mechanical Behavior of Materials," 2<sup>nd</sup> edition, Prentice Hall, 1999.



$$D_i = D_{ic} \times 2.21(\%Mn) \times 1.40(\%Si) \times 2.13(\%Cr) \times 3.275(\%Mo) \times 1.47(\%Ni)$$

(weight percentages)

where  $D_{ic}$  = ideal critical diameter for given grain size and carbon content.

After: Honeycombe, p.131,132

## Austenitization.

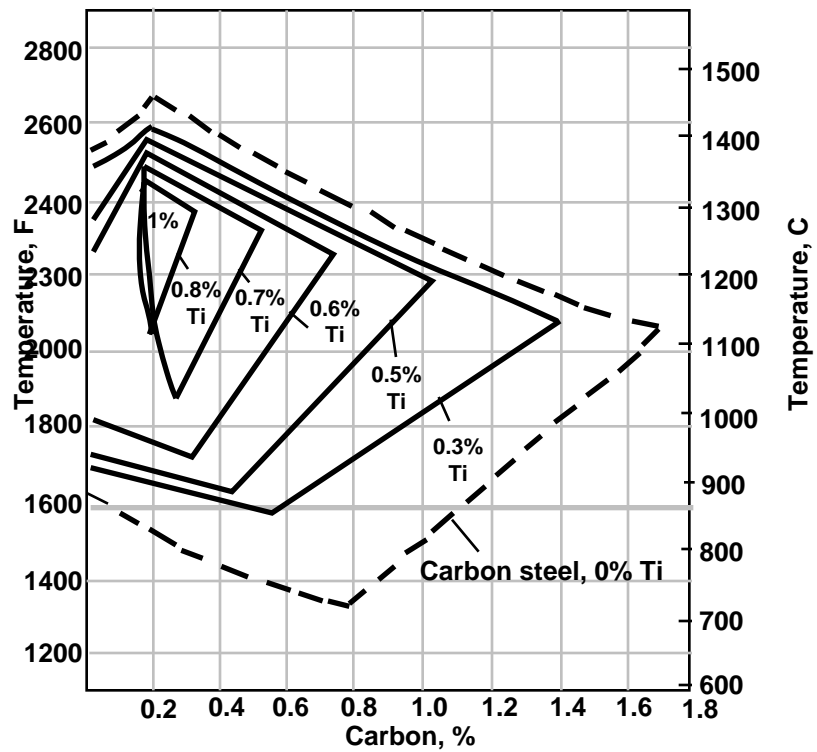
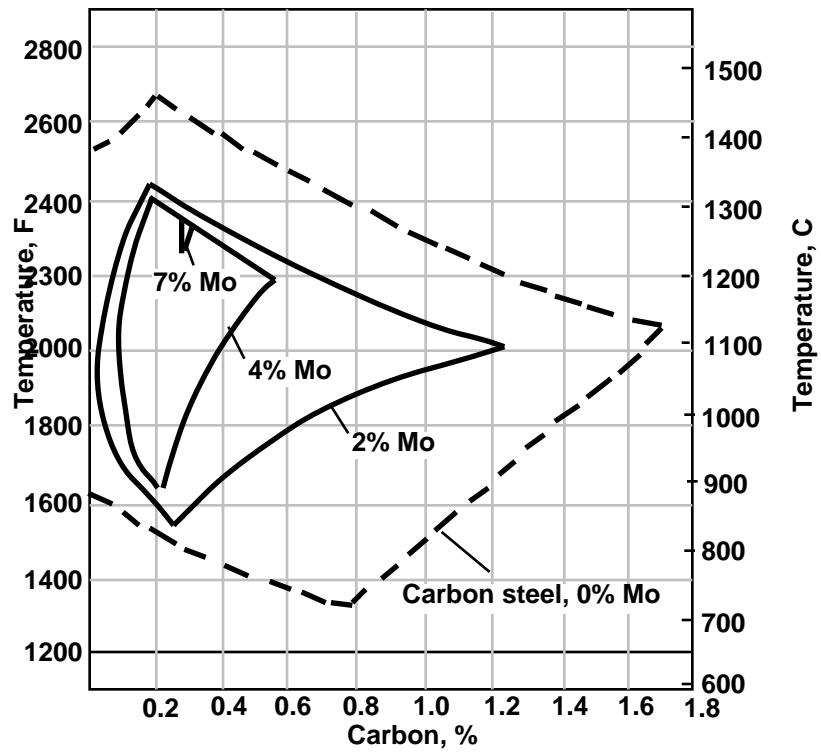
Let us now define the "eutectoid temperature" as the lowest temperature at which austenite can be formed. For ternary Fe-C-X alloys, in which the alloying element is X, both the eutectoid temperature and the eutectoid composition can vary from the values that apply to the binary Fe-C system. For small quantities of the element referred to as X, the changes are usually small, except for elements (like vanadium) that are very strong carbide formers and very strong ferrite stabilizers. Some examples, shown in the appended sketches, demonstrate the modifications to the austenite phase field caused by selected alloy additions.

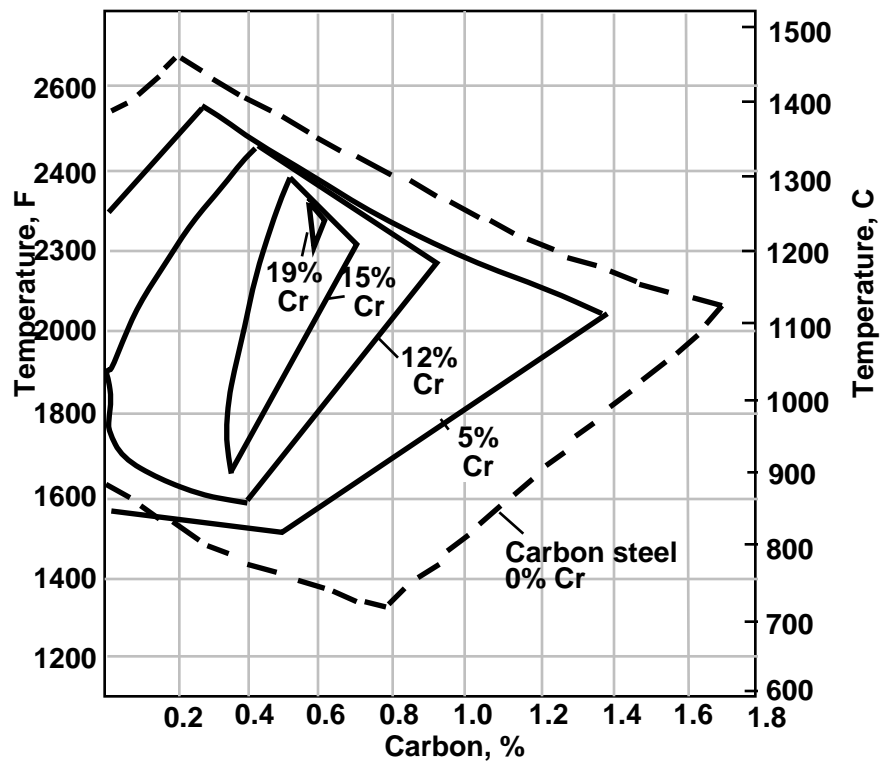
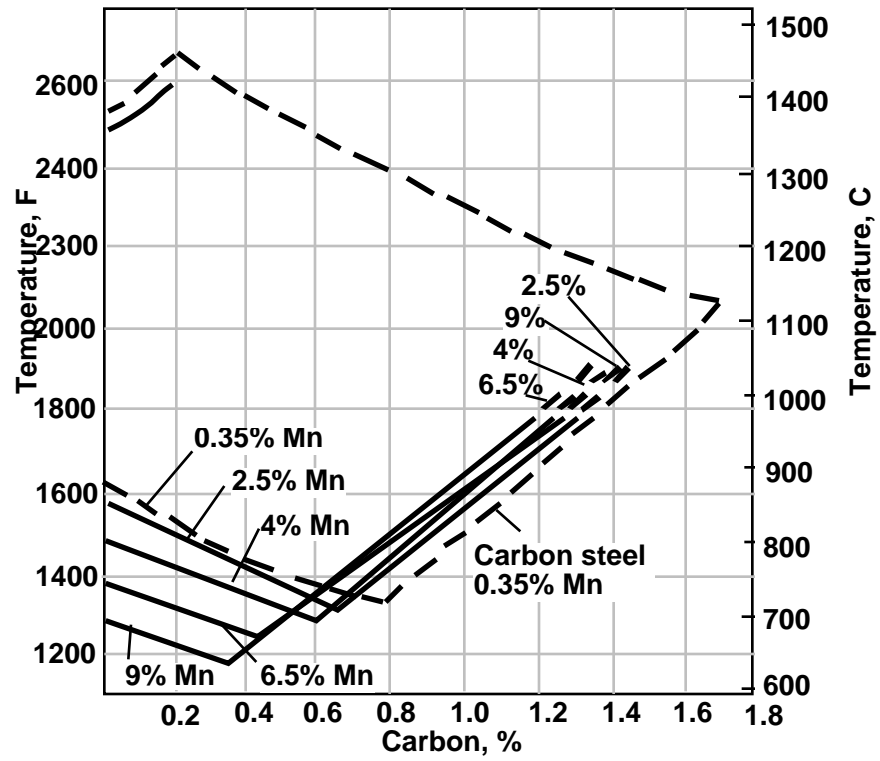
There are three main consequences of these effects upon austenitization.

1) When the steel contains alloying elements that are both ferrite stabilizers and moderate to strong carbide formers, the austenitizing temperatures may have to be higher than those used for treating plain carbon steels of similar carbon contents.

2) If the starting microstructure contains alloy or mixed carbides, longer austenitizing times can be required to produce homogeneous austenite. Consider the dissolution of cementite. When the FCC phase forms in contact with the cementite, carbon can diffuse into it and the carbide begins to dissolve. Continued dissolution is paced by the rate at which carbon can diffuse away from the carbide/austenite interface. Then, when the carbide has just dissolved, there will be a local, carbon-rich volume of austenite where the carbide had existed. Continued diffusion of the carbon in the austenite is necessary to obtain homogeneity. The rate of diffusion of the interstitial solute, carbon, is much greater than those of substitutional elements. Carbon diffuses rapidly even at temperatures just above the Fe-C eutectoid temperature of  $727^{\circ}\text{C}$  ( $1333^{\circ}\text{F}$ ) so homogeneity is obtained in short times. In contrast to the case of the dissolution of cementite, the dissolution of an alloy carbide, e.g. a molybdenum or tungsten carbide, both the dissolution process and attaining solute inhomogeneity will take much longer because tungsten and molybdenum diffuse much more slowly than does carbon. Indeed, this can directly affect the quantity of austenite in the steel. As an example of this effect, let us suppose that the steel contains a few wt. % of tungsten in the form of tungsten carbides. As the carbides dissolve, the adjacent austenite becomes enriched with tungsten while much of the carbon diffuses away. Because tungsten is a ferrite stabilizer and restricts the range of austenite stability it is possible for ferrite to form again in the tungsten rich volume. Thus complete austenitization is paced by the diffusion of the tungsten. This can be important in steels with high tungsten and molybdenum contents because such steels must be austenitized at high temperatures. Examples occur in tool steels.

3) When very strong carbide formers are present, a similar story would be told if homogeneous austenite were required. However, the alloying elements (Nb, V, Ti) which form carbides that are stable at temperatures well above the normal  $A_1$  line of a carbon steel, are not added to low alloy steels with the intent of increasing the hardenability. They are added because of the effects due to their carbides. Indeed, if a steel that contains fine vanadium carbides is austenitized at temperatures at which the carbides do not dissolve, the effect of the vanadium is to reduce the hardenability. This is due to two reasons. First of all, carbon increases the hardenability when it is dissolved in austenite. Thus, if some of the carbon is not in solution because it is combined with the vanadium, then a decrease in the hardenability is produced by the addition of the vanadium. Second, during the





austenitizing process the migration of the austenite grain boundaries is resisted by the carbides. This produces a finer grain size than for the case of a homogeneous austenite formed in similar austenitizing treatments. Thus, when the steel is cooled again, the rate of heterogeneous nucleation on grain boundaries is enhanced which shortens the time required to initiate the decomposition of austenite and the hardenability is reduced accordingly. This example demonstrates that if one is considering the effects of alloying elements on the hardenability of a steel, it is imperative to consider how the element is incorporated in the steel. If it is not dissolved within the austenite then it cannot directly raise the hardenability, but it might, indirectly, lower it.

The elements that are present in standard low alloy steels primarily for increasing the hardenability are:- Cr, Mo, Ni, Mn and B. Mo and Cr are also carbide formers. Thus they can retard the rates of tempering reactions and cause alloy carbides to form during tempering of martensite. Another important role of Mn in general is to scavenge sulfur by forming MnS so as to reduce the likelihood of iron sulfide forming at grain boundaries. This is particularly important when the steel does not have a very low sulfur content as was generally so before the advent of modern steel-making technology. Although the presence of manganese sulfides in steel can adversely effect the toughness of the steel, its effects are not usually as serious as those due to the presence of iron sulfides on grain boundaries. Boron is added **only** for hardenability control. The standard low alloy steels are usually completely austenitized during hardening heat treatments except when a very strong carbide former, such as V, has been added so that its carbides can inhibit grain growth and thereby refine the austenitic grain size.

The formation of proeutectoid ferrite.

The SAE/AISI standard low alloy steels are hypoeutectoid steels. Even though many are intended for use at high strength levels in the tempered martensitic condition, high carbon contents are usually unnecessary because the increase in the martensitic hardness produced by carbon occurs most rapidly in the hypoeutectoid range. Therefore, proeutectoid ferrite is the first phase to form when austenite is transformed at temperatures above the "nose" on the TTT diagram. The kinetics of the transformation of austenite to proeutectoid ferrite is retarded, in general, by the presence of both austenite stabilizers and ferrite stabilizers. This is probably due to effects such as solute drag on migrating interphase boundaries and the rate of diffusion of carbon.

An example of the effect of Mo on the growth of proeutectoid ferrite is provided by results that have been obtained by thermo-ionic microscopy. In this technique, the growth of ferrite is observable in-situ within the microscope while the sample is undergoing the transformation. It is possible to photograph the process. Observations on the rates of thickening of lens shaped grain boundary allotriomorphs of ferrite growing in Fe-0.11 wt. % C and Fe-0.11 wt. % C-1 wt.% Mo have shown that the half-thickness of the ferrite lens increases linearly as a function of the square root of time (Kinsman and Aaronson, transformation and hardenability in steels, Climax Molybdenum, p. 39, 1967). This is consistent with a process that is controlled by long range diffusion of carbon and, indeed is quantitatively so for the iron carbon alloy. The slopes of the lines decrease when Mo is added, showing that the growth rate is slower. Clearly Mo retards the transformation and the fact that there is still a linear dependence on the square root of time suggest that the Mo interacts with carbon and reduces the rate at which it can diffuse away into the austenite. Another possible contribution could be segregation of the molybdenum to the ferrite/austenite interfaces which could reduce the migration rates of those interfaces.

The beneficial effects due to boron occur when the boron is in solid solution in the austenite. The solubility is very low. Consequently, numerical values describing it have been difficult to determine with good precision. It has been estimated to lie between 0.001 and 0.005 wt. %. Boron is chemically reactive with other alloying elements in steel, particularly carbon and nitrogen. When compounds are formed with other alloying elements the amount dissolved can be reduced. The usual practice is to add boron within the range of 0.0005 to 0.003 wt. %. Also, the steels are fully killed with aluminum. In addition, small quantities of titanium and zirconium, which react strongly with nitrogen, are added to help to scavenge the nitrogen and to keep more of the boron in solution. One might question this practice and ask why one shouldn't just add more boron. Unfortunately, this is not a solution. If more than 0.003 wt. % boron is added, the hardenability begins to decrease again and, at about 0.004 wt. %, iron boride precipitates on the austenite grain boundaries and causes a reduction in the final toughness.

Boron increases the hardenability primarily by delaying the start of the transformations to ferrite and pearlite. It does not seem to affect the time to complete these transformations. This has led to explanations of the boron effect in terms of the interaction of boron with austenite grain boundaries. It has been suggested that boron segregates at the grain boundaries because it is able to reduce the grain boundary energy and that this reduction in energy makes the boundaries less effective as heterogeneous nucleation sites. An alternative explanation suggests that borocarbides,  $\{Fe_{23}(C,B)_6\}$ , precipitate at the grain boundaries and inhibit the nucleation of ferrite and cementite thereon. Perhaps both phenomena participate. It is generally accepted that the austenite grain boundaries are affected in some manner because the transformations begin at the boundaries and the effect of boron is greater in fine grained austenite than it is in coarse grained austenite.

The increase in the hardenability due to additions of boron is greatest for steels of low carbon contents. There is no effect at the eutectoid composition; the hardenability of hypereutectoid steels is decreased by boron additions. A valuable characteristic of boron is that it increases the hardenability without lowering the  $M_s$  temperature. This is valuable because lowering the  $M_s$  temperature causes martensite to form at lower temperatures which increases the likelihood of quench cracking occurring and can increase the amount of retained austenite.

#### Pearlite formation

When pearlite forms during the transformation of austenite in standard low alloy steels, the carbide in the pearlite is essentially cementite. The cementite can contain some dissolved carbide forming alloying elements which replace iron but it forms preferentially to the alloy element carbides, e. g. chromium carbide, even though the formation of the latter would provide a greater reduction in the free energy of the system. This is because it can grow much more rapidly due to the much greater rate of diffusion of carbon compared to the rates of diffusion of substitutionally dissolved elements. Nevertheless, the rates of nucleation and growth of pearlite in the alloy steels are smaller than those in plain carbon steels. When graphite stabilizers, e. g. Ni and Si are dissolved within the austenite it is energetically favorable for them to remain in solution. This means that they have to diffuse away from the carbide as it grows and they do so slowly because they are substitutionally dissolved. One expects both the start and finish lines of the pearlite transformation to be affected. Mn partitions to the cementite but it also slows down the reaction. Cr and Mo, when present alone, interact more strongly with pearlite formation than the elements mentioned previously. They cause significant shape changes to the start and finish lines on isothermal transformation diagrams. These changes are probably mainly due to the reduction in the rate of diffusion of carbon caused by interactions with the dissolved Cr and Mo, but solute drag may also



effect interphase mobility. When Mn, Ni, Mo, and Cr are all present together in the same steel, their combined effects are dramatic. In some steels, the effects on proeutectoid ferrite and pearlite formation are so strong that the start and finish curves for these transformations are separated from those of the bainite transformation by a region in which the austenite remains in metastable equilibrium for long times. In these cases the TTT diagrams show the two types of transformation separated by a "bay". This confirms earlier statements herein that the nose in plain carbon steel TTT diagrams happens to be where transformations taking place by different mechanisms merge.

An interesting example of thermo-mechanical processing can be carried out with steels that possess bays in their TTT diagrams. They can be austenitized and cooled to a temperature within the bay and then deformed by rolling or forging while still austenitic. This increases the dislocation density present in the austenite prior to the formation of martensite or bainite when the steel is finally cooled. The combination of the effects due to the additional dislocation line introduced during the plastic deformation with those due to the formation of martensite can produce significant improvements in mechanical properties. This type thermo-mechanical treatment is referred to as ausforming. Steels that have useful properties when ausformed are often called ausforming steels.

### Bainite formation

In general, the kinetics of the reactions that form bainite are retarded by alloying elements. Presumably, the effects arise for reasons similar to those mentioned for the transformations that occur at higher temperatures. The bainitic transformation in steels that have a bay in the TTT diagram, however, takes place more rapidly than the transformations that occur at higher temperatures. This suggests that the larger driving force associated with the greater degree of undercooling at which the bainite forms negates the retarding effects somewhat, because, in these steels, bainite can form more rapidly than pearlite.

Examples of the effects of alloying elements on TTT diagrams are shown in the accompanying sketches. Appropriate changes are also found in continuous cooling diagrams.

### Martensite formation.

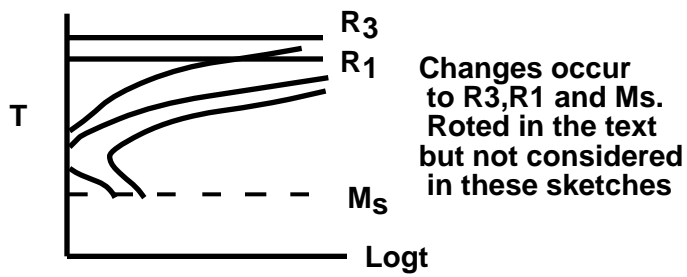
In a few instances, it is possible for alloying elements to cause the martensitic transformation to take place isothermally. In such a transformation, no martensite forms while the austenite is cooled to the temperature chosen, but it begins to form after an incubation time while held at that temperature. In this case, the kinetics of the transformation can be described by "C" shaped curves on a temperature-time plot. An example of an isothermal martensitic transformation has been observed in an Fe-0.6 wt. % C -6 wt. % Mn alloy, in which austenite can be retained after quenching and then, while the temperature is held constant, martensite begins to form. Each of the martensitic crystals grows rapidly; it is the initiation process that is time dependent. Isothermal martensitic transformations are rare and do not occur in standard low alloy steels, where the transformation is athermal. Therefore the  $M_s$  temperature remains an important parameter. Because austenite stabilizing alloying elements expand the realm of austenite and, in particular, reduce the minimum temperature at which the austenite is stable, they are expected to lower the start and finish temperatures for the martensitic transformation in order to attain the necessary degree of undercooling. This is so in practice and C, Ni and Mn have strong effects. The carbide formers, Mo and Cr, also lower the  $M_s$  temperatures even though they are ferrite stabilizers and would be expected to enhance the driving force for the transformation. Presumably, these alloying elements cause changes that make the transformation more difficult. It is not obvious what these changes are. It is

possible that the initiation sites are affected. Solid solution strengthening of the austenite and changes to its shear modulus which might resist the necessary shape change may contribute. Nevertheless, all five elements lower the martensitic start temperature.

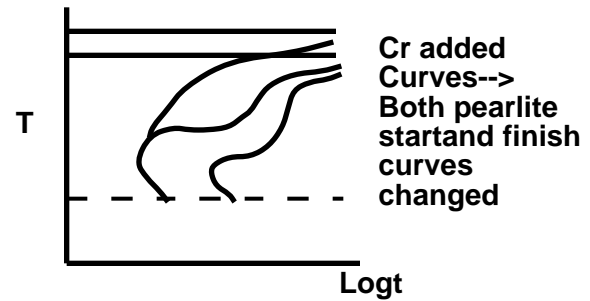
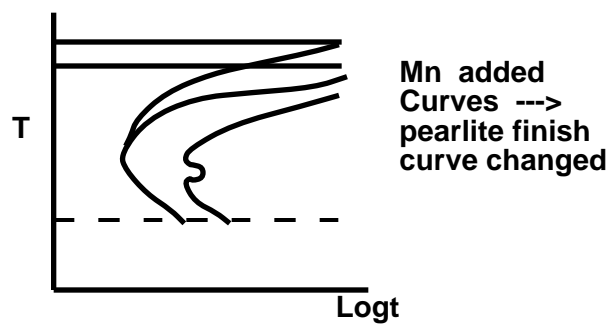
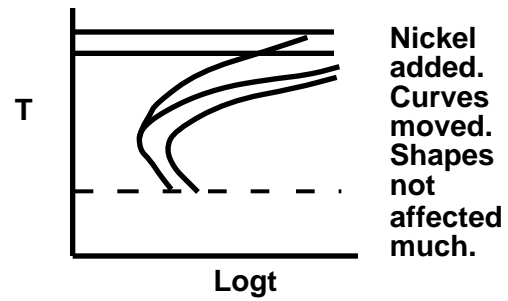
Numerous amounts of experimental data have been accumulated for particular families of alloy steels in order to assess the effects of composition on the start of the transformation. Using such data, a number of empirical equations have been published which relate the  $M_s$  temperature to the percentages of C, Mo, Cr, Mn, and Ni in the steel by means of multiplication factors. Several different ones have been published. Such empirical equations can be of practical use in material selection but they provide little help towards elucidating the fundamental reasons for the particular effects.

While we are on the subject of the martensitic start temperature, we should now recognize that steels with significant concentrations of alloying elements that depress the temperatures at which martensite forms, can retain large amounts of austenite when quenched to room temperature. If more martensite is desired, the steel must be cooled below room temperature. If this is not done before the tempering treatment then the decomposition of the retained austenite which will occur during tempering, can have significant effects on the final microstructure and properties.

This is a suitable time to introduce the  $M_d$  temperature. It has been observed that the  $M_s$  temperature can be raised by the application of stress to the steel sample. This is because a crystal that forms during a martensitic transformation has a different shape than the volume of steel from which it formed. Therefore, if there is help available to achieve this shape change, the transformation will be accomplished more easily. If it can occur more easily, then it will require less thermodynamic driving force for it to occur which means that the necessary degree of undercooling below the  $A_3$  line will be smaller. Hence, we deduce that if an applied stress is locally oriented so that it helps the transformation to produce the shape change it will allow martensite to form at a higher temperature than that which pertains to the unstressed condition. In general, tensile stresses are found to be more effective than compressive stresses, but rolling can have appreciable effects. The highest temperature to which the  $M_s$  temperature can be raised by applied stresses is defined as the  $M_d$  temperature. When this temperature lies above room temperature and the  $M_s$  is below room temperature, it is possible to retain the austenite at room temperature and then to form some martensite by working the metastable austenite at room temperature. This can be important in highly alloyed steels such as stainless steels.

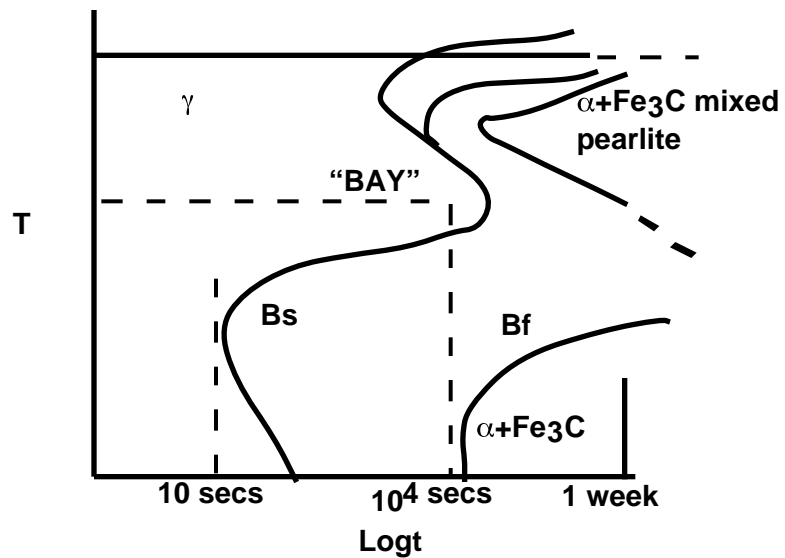


plain C Steel Hypoeutectoid.  
e.g. 1040



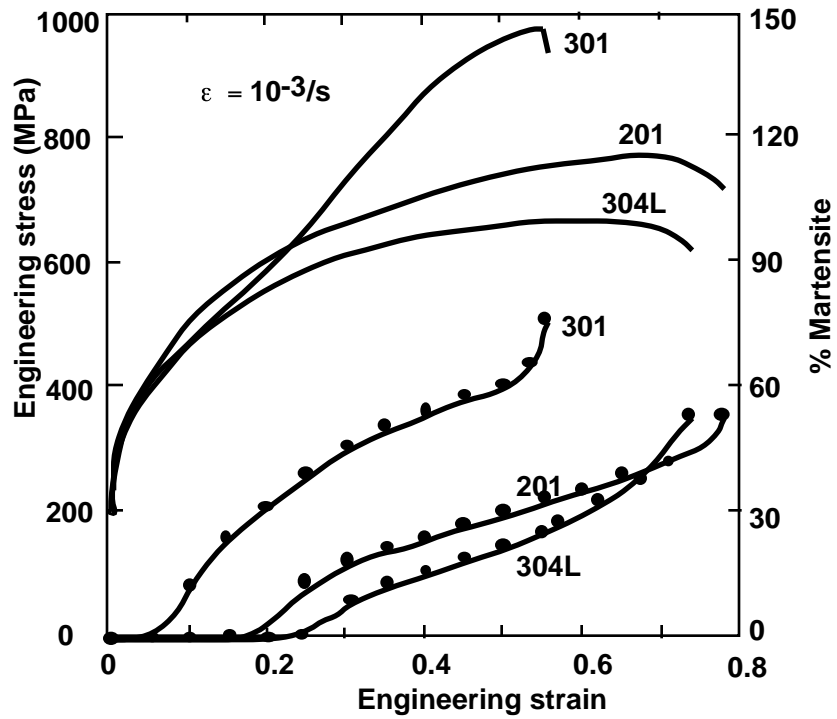
$$M_s \text{ } ^\circ\text{C} = 539 - 423 (\%C) - 30.4 (\%Mn) - 17.7 (\%Ni) - 12.1 (\%Cr) - 7.5 (\%Mo)$$

Example of empirical relation

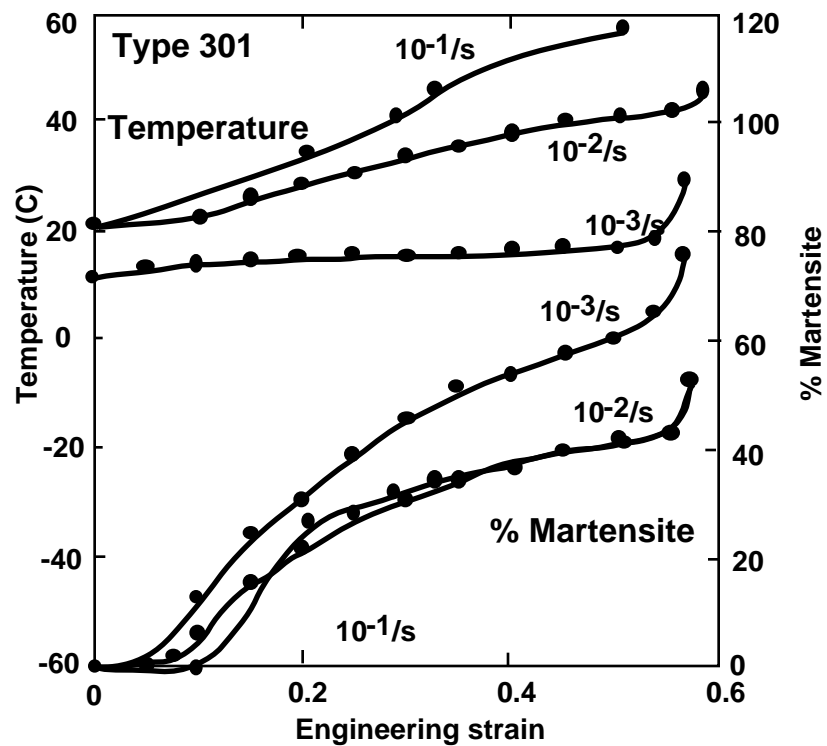


A.I.S.I 4340  $m_o = 0.33 \%$ ,  
 $Ni = 1.79 \%$

$Cr = 0.80 \%$   
 $Mn = 0.78 \%$



After: V. Talyan, R.H. Wagoner, and J.K. Lee: *Formability of Stainless Steel*, Mater. Trans. A, 1998, Vol.29A, pp.2161-2171.



## **The Hardenability of Steels.**

### Basic concepts for selecting steels for hardenability

Earlier in this article, we introduced that property of steel which determines how rapidly the steel must be cooled in order for transformations that occur by mechanisms that require diffusion to be suppressed and which is called hardenability. This property is very important in engineering design with respect to selecting particular steels and heat treatments for manufacturing a very wide range of components. In this section we will explore this property in more detail.

When hardenability is important in the material selection process, it is self evident that it would be useful to have a method of quantitatively comparing the hardenability of steels. How can this be done?

Possible method #1; The depth of hardening.

Consider a cylindrical bar of steel that has a radius  $R$  and a length that is several times larger than  $R$  so that end-effects can be eliminated from consideration when examining the microstructure and properties of the material inside the bar. Now suppose that this bar is austenitized at  $T_a$  and quenched in a particular quenching medium, say water at  $20^\circ\text{C}$ . After the quench, the bar is sectioned perpendicularly to its length and hardness measurements are made on the cross section at locations that span the diameter of the bar. The hardness value at a particular location reflects the nature of the microstructure at that location: for the steels that we are considering, the hardest microstructure produced by continuously cooling austenite is that corresponding to 100% martensite, the softest microstructure is equiaxed ferrite grains and colonies of coarse pearlite, (the spheroidized microstructure doesn't form in these treatments). The hardness varies from the softest to the hardest condition as the microstructure varies between these two extremes. It is important to recognize that the value of a single, particular hardness measurement in this experiment has no direct significance with respect to hardenability. It is the variation of the hardness with position that is significant because this provides information about the variations of microstructure. Similar microstructures in different steels (e.g. 100% martensite) can have quite different hardness. The data obtained are used to create a graph of hardness versus position in the bar. Now, provided the radius  $R$  and the hardenability of the steel are both appropriate, the microstructure near the surface can contain the maximum amount of martensite that can form in the steel when it is quenched to  $20^\circ\text{C}$ . The microstructure at the center of the bar can contain ferrite plus pearlite. Therefore, the variation of the hardness with position shown on the graph reveals the variation of microstructure. When this experiment is carried out for a variety of steels using bars of the same size, the same heat treatments and the same quenching medium, a collection of graphs are obtained. Then we define a "depth of hardening" as the magnitude of the distance from the outside surface to the position where the hardness is less than that very near the surface by a specified percentage. When the specified percentage is chosen, the graphs can be used to rank the steels in an order corresponding to their depths of hardening. A depth of hardening to the depth at which a particular microstructure was formed. The smaller the specified decrease in hardness, the larger will be the % of martensite in the microstructure. In any case, greater the depth of hardening the greater the hardenability.

If one is to use the depth of hardening approach one must choose the "specified hardness percentage decrease". Should it be 15%, 40%, or what? Let us consider the microstructures. When a bar of steel is austenitized and quenched so that it is cooled below the  $M_f$  temperature, it is possible for it to be almost entirely transformed to martensite or to have a rim of martensite at its

surface and various mixtures of martensite, cementite and ferrite within. Typically, the microstructure varies from almost fully martensitic through various mixtures that include bainite and pearlite. The thickness of the martensitic rim can be measured by quantitative metallography. But in order for that to be done it is necessary to define what is meant by the thickness, because the variation of the % martensite in the microstructure is gradual. This is the same dilemma that we met when considering how to specify the depth of hardening. Many experiments have shown that for the standard etchants, such as nital that attacks intercrystalline and interphase boundaries, the 50 % martensite is the most easily recognized microstructural mixture. Furthermore, it so happens that the rate of variation of the hardness as the microstructure changes, is most rapid where the 50 % martensite mixture is located. For these reasons, this microstructural mixture is most readily located experimentally and, therefore, the thickness of the martensitic rim usually refers to the location at which the microstructure contains 50 % martensite. Similarly the depth of hardening is the depth at which the hardness corresponding to 50 % martensite is located on a cross section; this is the place where the rate of decrease in hardness with position is the greatest. Hence, if two steels are quenched in the same medium and so examined, the steel with the larger depth of hardening is the steel with the greater hardenability.

N.B. The term “depth of hardening” under discussion here should not be confused with the term “case depth” in carburized parts such as axles and gear teeth. The case depth is usually specified in terms of a specific hardness value such as that depth at which the hardness is RC 50.

#### Method #2. The critical diameter

When bars of the same steel but with different diameters are quenched in the same quenchant, it is found that there is one particular diameter for which a microstructure of 50 % martensite is found at the center of the bar. This diameter is called the critical diameter. It is the diameter of a bar that has a depth of hardness equal to its radius. Thus, if several steels are compared, the steel with the greatest hardenability will possess the largest critical diameter.

#### Method #3; The critical cooling rate

The nature of the microstructure of a given steel at any location within a quenched bar is mainly dependent upon the rate at which that location cooled. If we make the approximation that any effects due to stresses generated by thermal contraction are negligible, then we can expect all locations that had the same rates of cooling to have the same microstructures. On this basis, we can refer to a critical cooling rate as that cooling rate that will produce the 50 % martensitic microstructure. The critical cooling rate decreases as the hardenability of the steel increases.

Whereas these kinds of observations clearly allow different steels to be ranked in order of their hardenability, they do not provide a quantitative measure of the property. A knowledge of the critical diameters in different quenchants is of practical use but, because the performance characteristics of nominally similar quenching media can vary with time and place, they do not provide an absolute value for the hardenability. This problem was investigated by Grossman and his colleagues 50 years ago with the objective of describing the hardenability by a parameter that is independent of the quench bath (“Elements of Hardenability, M.A. Grossman, ASM, 1952). There

has been a great deal of work done since, but the early work established the basic concepts and the terminology.

### The quenching process

Let us consider the quenching process more closely. When a hot bar of steel is immersed within the quenching fluid, heat is extracted from the surface of the bar and the temperature of the surface is decreased. This creates a temperature gradient in the bar. The rate of flow of heat from the interior of the bar, down the temperature gradient, depends upon the conductivity of the steel. The combined effects of the rate at which heat is extracted and the rate at which it is conducted to the surface from within, determines the rates of cooling at various locations within the bar. The cooling rates at the surface of the sample being quenched vary with time during the quench and thus with the actual temperature of the surface. For example, in experiments ( see "The Hardenability of Steels, by C.A. Siebert, D.V. Doane and D.H. Breen, ASM 1977) in which half inch diameter bars of nickel-5%Si, containing embedded thermocouples, were heated to 850°C and immersed in water, the surfaces of the bars almost immediately became separated from the water by a blanket of steam. While this separation existed, the temperature at the centers dropped to about 650°C at a relatively slow cooling rate. Experimentally determined values ranged up to 50 degrees per second. In the next phase, liquid water made contact with the sample and steam bubbles formed rapidly. These bubbles rose from the surface due to gravity and convection turbulence. During this stage the cooling rate rose to over 300 degrees per second as the temperature dropped to about 450°C at the center of the bar. At this stage the nucleation and growth of steam bubbles ended and the rate of cooling became dominated by convection in the coolant. This caused a rapid decrease in the cooling rate which decreased to less than 50 degrees per second during the time taken for the temperature to drop another 100 degrees. Evidently, the heat transfer process during quenching in water is not a simple one. It is interesting to note that it is fortuitous that the greatest cooling rates for water happen to occur at temperatures corresponding to the nose of TTT diagrams for low to medium carbon steels. This is fortuitous because these temperature ranges are those through which the steel must usually be cooled fastest in order to avoid diffusion controlled phase transformations. Should it have happened in practice that the cooling rate was small in these temperature ranges, quench hardening of steels and the martensitic transformation in steels might never have been discovered!

The greatest possible rate at which heat could be removed from the surface of a quenched bar, for a given thermal conductivity, would occur if the quenchant was able to immediately lower the temperature at the surface of the bar to that of the bath and hold it there during the cooling process. The quenching power of a quenching medium is described by a coefficient  $H$ . Its value for the case above is . Of course, such a quenching process is unobtainable practically and is defined as an ideal quench. Although this quench is unobtainable it is quite closely approached by quenching into vigorously agitated, iced brine.

Newton's law of cooling relates the rate of loss of heat through a unit area of a solid surface in contact with a coolant fluid to the temperature difference between the surface and the adjacent fluid by a heat transfer coefficient,  $f$ . The value of the coefficient depends on the materials concerned and the state of the system as well as on the units used. An example of units is calories/cm<sup>2</sup>.sec. degree Celsius. Obviously,  $f$  can vary widely being much smaller for an object cooling in still air than for one cooling in rapidly flowing cold water. In order for the heat to be transferred to the quenching medium it has to get to the surface of the bar. The rate at which it can do this depends upon the thermal conductivity,  $k$ , which has units of similar kind i.e. calories/cm.

sec. degree Celsius. The early workers took the ratio of  $H = \frac{f}{2k}$  to describe the severity of a quench.

(the factor of two arises because the experimental results were related to the diameters of the quenched bars not the radii). It has units of length<sup>-1</sup>. For the ideal quench, H is infinity because f would be infinite.

The ideal diameter

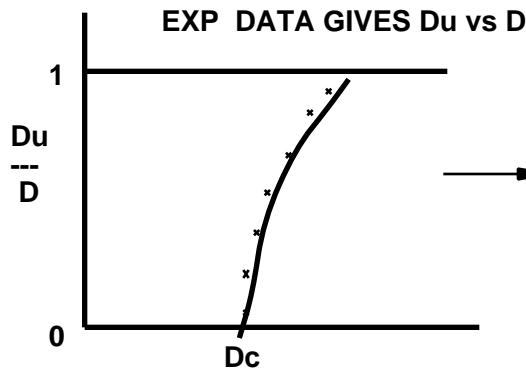
Grossman introduced a term called the ideal diameter which he defined as that diameter of a bar that would just harden through when quenched in an ideal quench. It is written as  $D_i$ . Hence  $D_i$  is equal to  $D_c$  for an ideal quench.

If it were possible to list the ideal diameters of various steels, the list would provide an absolute indication of the hardenability of each steel. Consider the results of experiments in which the effects of bar diameter and different quench baths are investigated. When a quenched bar is sectioned and examined either microstructurally or by a hardness survey, and it is found that its diameter exceeds the critical value, then one can define the diameter of the material that contains less than 50 % martensite as  $D_u$ . This is illustrated in the appended sketches.

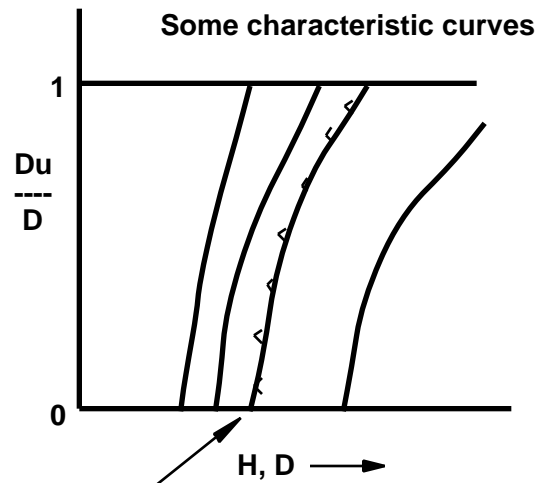
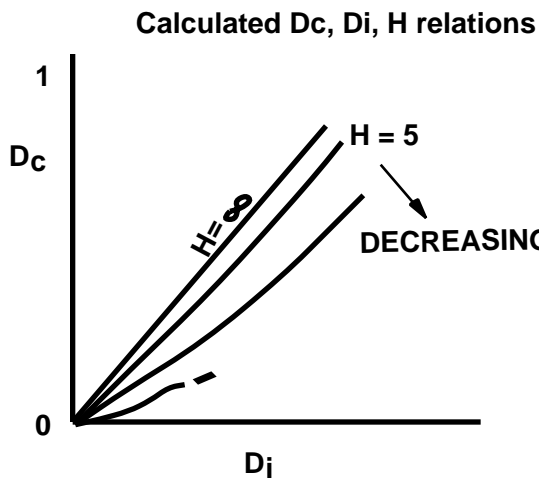
When a series of different diameter bars are quenched into the same bath, the form of the variation of the untransformed diameter caused by variations of the bar diameter, D, is as shown in the graph of  $D_u/D$  versus D. The intercept of that curve on the abscissa, reveals the critical diameter for that steel and quenching medium. Now, if two steels of different hardenability are quenched in two different baths, then it is possible to find a combination such that the two critical diameters are equal, but the two curves differ at other diameters. This is shown in the sketch, where H1 and H2 are the quenching powers of the two baths, and h1 and h2 denote the hardenability of the two steels.

On the basis of experimental observations and computations assuming a constant thermal conductivity, constant H, no effects due to stress and that the microstructure was a function only of the local cooling rate, Grossman predicted that the curve of  $H.D_u$  versus  $H.D$  would have the same form for all those steels for which  $H.D_c$  is the same. This means that two such curves would superimpose on one another when an appropriate scale is chosen. Such a scale is obtained when  $D_u/D$  is plotted against  $H.D$ . These curves are called characteristic curves. Sets of them have been produced, which allow the quenching power of any bath to be estimated. The procedure is as follows.





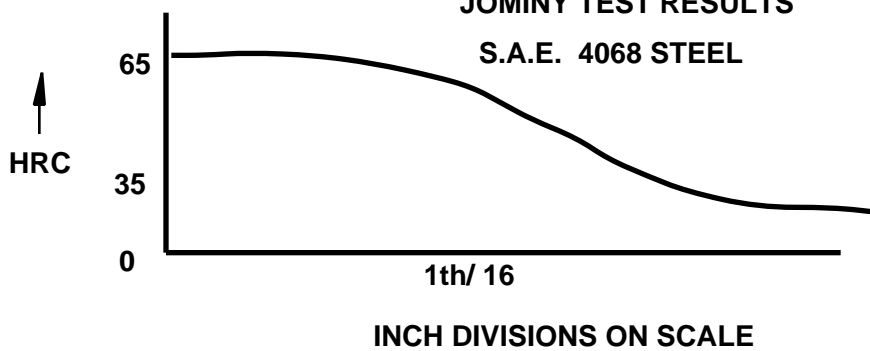
Plot of  $D_u/D$  vs  $D$  yields  $D_c$  and the data to fit to the characteristic curves



Thus,  $H$  &  $D_c$  gives  $D_i$

### JOMINY TEST RESULTS

S.A.E. 4068 STEEL



By experiment, the values of  $D_u$  and  $D$  are determined for a given steel in a given bath. The results provide  $D_c$ . Then, the results are compared to the set of characteristic curves to find the particular curve with the best fit. Knowing  $D_c$  the value of  $H$  is determined. The final step is then to consult calculated graphical relations among  $D_c$ ,  $D_i$  and  $H$  to obtain  $D_j$ .

It turns out that when steels are quenched in violently agitated iced brine, an  $H$  value of 5 can be attained. This value produces results that are close to those predicted for an infinite value of  $H$ . Other examples of  $H$  are: 2 for still brine, 0.9 to 1 for still water and 0.25-0.3 for still oil.

These graphs have practical use. However, results obtained from bars that have diameters that are much bigger than the depths of hardening cannot be made to match the characteristic curves. Presumably, this is due to the approximations used. For example, the assumption that  $H$  is constant is invalid. Experiments have shown that the value of  $H$  assigned to a quenching bath is not constant throughout the quench and can vary with the size of the bar. This is to be expected from the temperature versus time behavior described earlier for quenched cylinders. Nevertheless, the  $D_j$  values provide a useful guide to hardenability, provided that the effect of the size of the bar on  $H$  is taken into account.

#### The Jominy End-Quench Test.

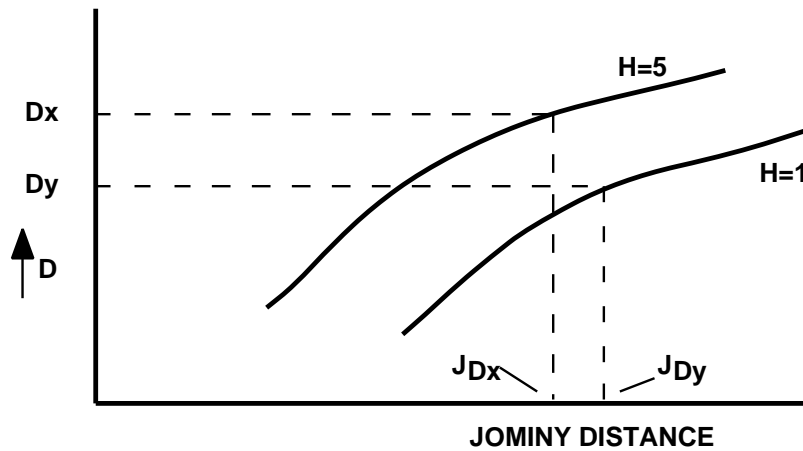
The most widely-used test for measuring hardenability is the Jominy end-quench test. This test involves quenching the end of a bar of particular dimensions in a specified manner. Typically, the test bar is one inch in diameter and four inches long. It is austenitized and placed in a jig that suspends it vertically above a half-inch diameter water pipe which points upwards. The water pressure in the pipe is set (prior to the test) such that when a fast-opening valve is activated, the jet of water emitted from the pipe rises to a height of 2.5 inches above the end of the pipe. When the test bar is put in place, its lower end is 0.5 inches above the end of the pipe. The valve is opened immediately and the water sprays onto the end of the bar. When everything is correct, the water only contacts the end of the bar and then sprays outward and downward resembling an umbrella. Meanwhile, the end of the bar becomes dark and the boundary between the dark and red-hot steel can be observed to move upwards. It is kind of entertaining to watch.

When the end-quench is complete, a flat surface, 0.15 inches deep is ground along the length of the bar. This has to be done with care lest any microstructural changes are induced by the heat generated in the grinding process. Then Rockwell C hardness measurements are made at intervals of one sixteenth of an inch along the bar. The results are plotted as hardness versus distance from the quenched end.

Numerous investigations have been carried out to correlate the results of a Jominy test with other measures of the hardenability. An example is shown later, from Siebert et al (page 11). In this diagram, the diameters of bars that have the same cooling rates at their centers as those at particular distances along a Jominy bar are plotted against the Jominy distance. Curves for two different quench severity's are presented. The graph enables the determination of the distance along a Jominy bar of the location at which the cooling rate would be the same as at the center of the bar. The hardness at the center of the bar can now be obtained from the results of the Jominy test.

The Jominy distances involved are called Jominy equivalent cooling rates or Jominy equivalent conditions,  $J_{ec}$ . Lets consider another example of their use. Suppose a particular part is

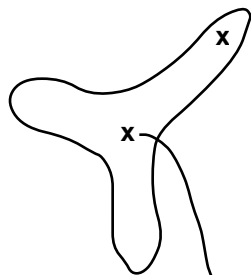
to be manufactured and heat treated in a currently available process that uses a particular quenching medium and the hardness value for particular locations within the part are specified. An appropriate steel is to be chosen. One procedure is to manufacture a number of the parts using a relatively shallow hardening steel such as 8620 or 1040 and also make Jominy test bars of the same heat of steel. These parts along with the Jominy bars are heat treated in the production facilities. Following the heat treatment, selected parts are sectioned and the hardness at the critical locations is measured. Meanwhile the Jominy bars are tested to determine the end-quench data. Then by comparing the hardness values measured on the parts with the end quench data, the Jominy distances corresponding to these hardnesses can be found. These are the  $J_{ec}$ 's for the particular locations; i.e. these locations cooled similarly to the corresponding positions on the Jominy bars. It is important that the test bars and parts are exposed to the same thermal history. Finally, end quench data available for various steels produced for selection on the basis of hardenability can be examined to choose one which will produce the specified hardnesses at the measured  $J_{ec}$ 's. This procedure requires the test steel and those of the members of the group from which the selection is to be made to have similar thermal conductivity so that the cooling rates are similar at similar Jominy distances. When steels of suitable hardenability are identified the final choice is made taking into account other factors. For example, it is usual to choose a steel with the lowest satisfactory carbon content and of the minimum hardenability necessary for the job. This reduces the risk of problems that might arise with respect to quench cracking and distortion if the quenching process is vigorous.



The jominy distance is that distance along a jominy bar at which the hardness is that obtained at the center of a bar quenched in a medium of H

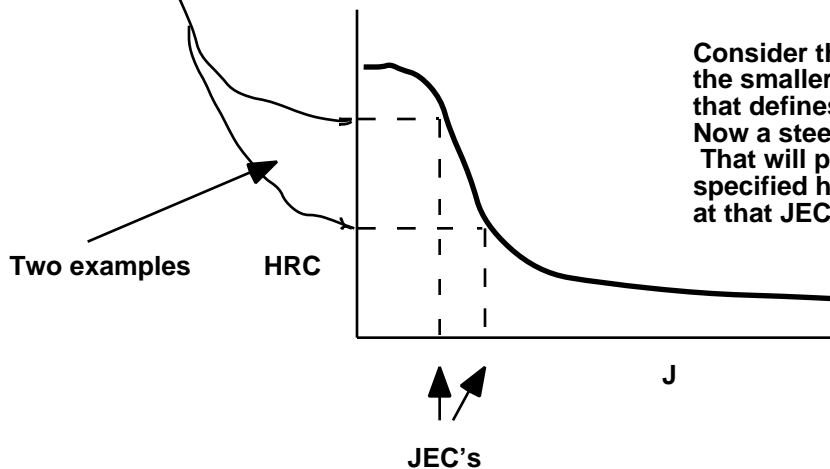
X locations have required specified minimum hardnesses

Fabricate from, say 1040 or 8620. Heat treat in currently available process. Also heat treat with the componets, jominy test bars of the same steel.

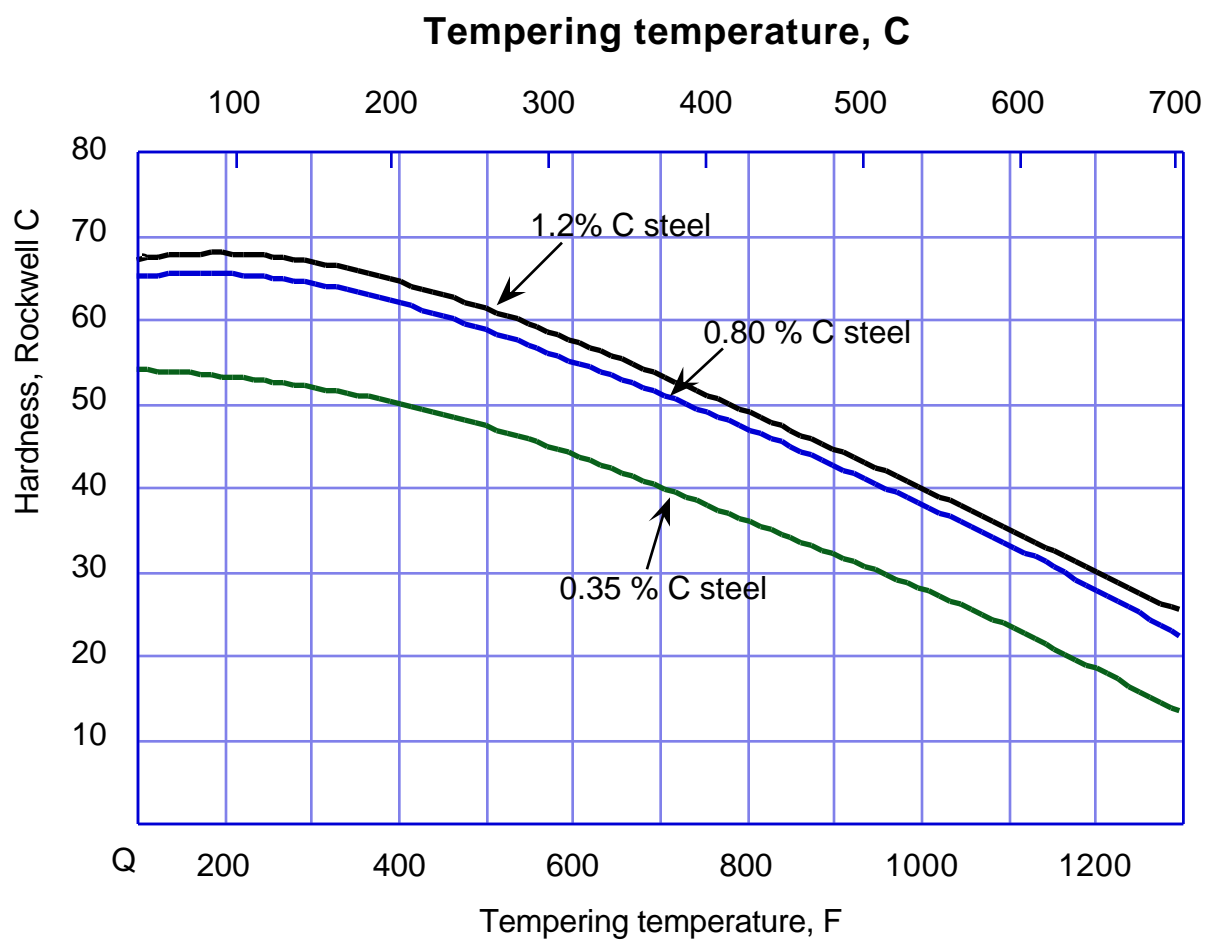


Measure hardness at X. Perform jominy tests.

Compare to obtain JEC.



The Effects of Alloying Elements on Tempering Reactions



## The Effects of Alloying Elements on Tempering Reactions

The reactions that take place when martensite is tempered involve solute segregation and clustering at crystal defects, precipitation from solid solution, particle coarsening and grain growth. In general, alloying elements dissolved in the martensite reduce the rates at which these processes occur. Also, alloying can decrease the  $M_s$  temperature and give rise to significant quantities of retained austenite when the quenchant is at or near room temperature. Accordingly, the decomposition of this austenite during tempering can have important effects and therefore stage two tempering processes can become important unlike the case for hypoeutectoid plain carbon steels. As quenched, the steel will have a smaller hardness than would be predicted from the carbon concentration of the steel because of the crystals of retained austenite distributed within the martensite. Then, when the austenite transforms to bainite during tempering in the appropriate temperature range, the net hardness can increase. The austenite stabilizers, Mn and Ni, are effective elements for lowering the martensitic start temperature. In the following discussion of the effects of alloying elements upon tempering reactions in martensite we will neglect effects due to retained austenite. Obviously, this is being done so that we can focus on martensitic reactions.

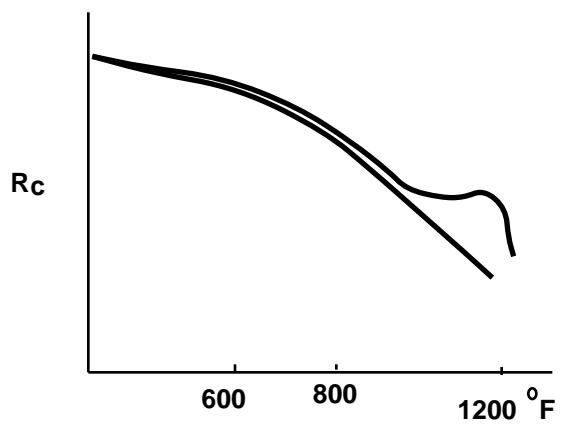
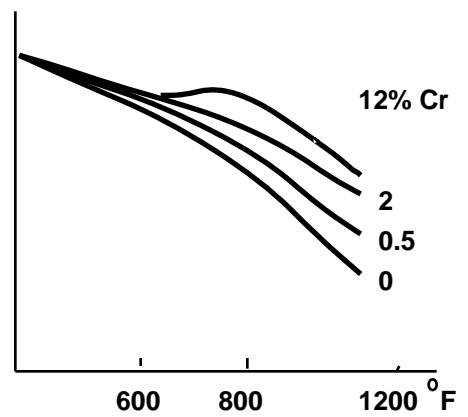
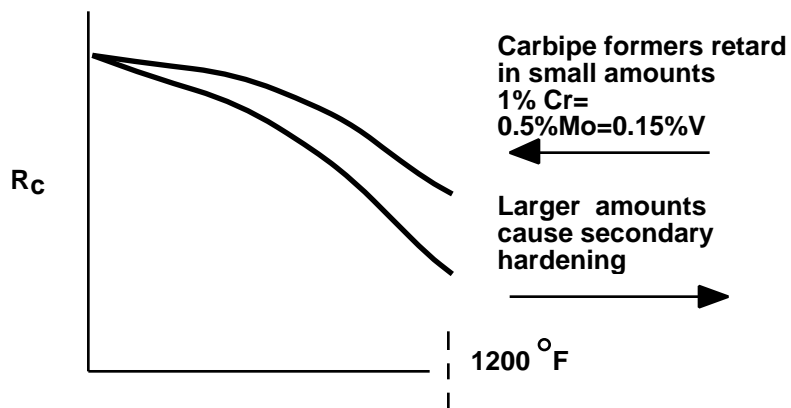
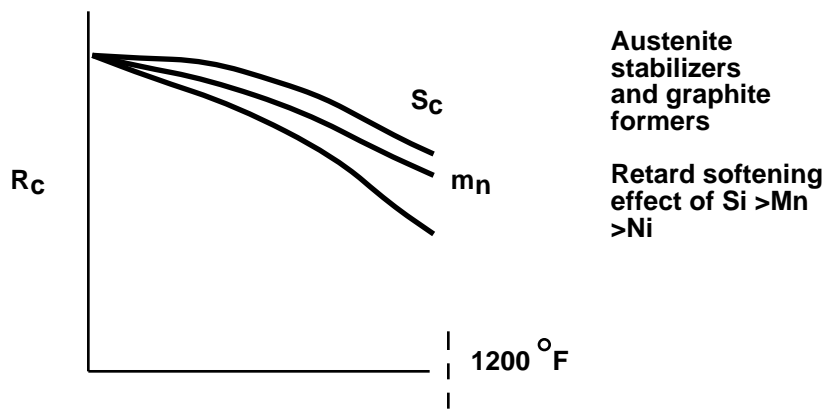
### a) Graphite formers and Mn.

Si and Ni partition to ferrite and avoid being incorporated in cementite. This means that the rate of growth of the carbide particles depends on the rate at which these elements can diffuse out of the way. They do so by substitutional diffusion with the result that the growth rates of the cementite particles are retarded in comparison to the case of rate control by the diffusion of carbon.

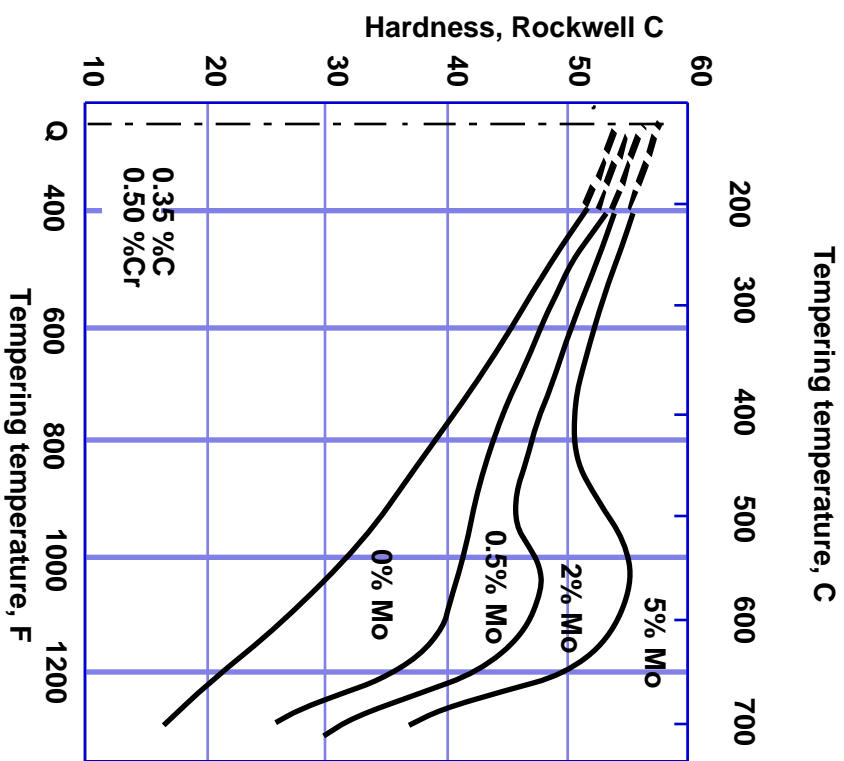
Mn can be incorporated into the carbides and does not need to diffuse away. However, it still retards the growth rate, possibly by reducing the diffusion rate of carbon. At high tempering temperatures where the growth of ferrite crystals becomes important, the solutes can impede the migration rate of the ferrite/ferrite interface by solute drag. Solute drag refers to an effect that can arise due to the tendency of solutes to segregate at or away from intercrystalline boundaries. Segregation lowers the effective surface energy and hence the driving force for boundary migration.

### b) Carbide Formers.

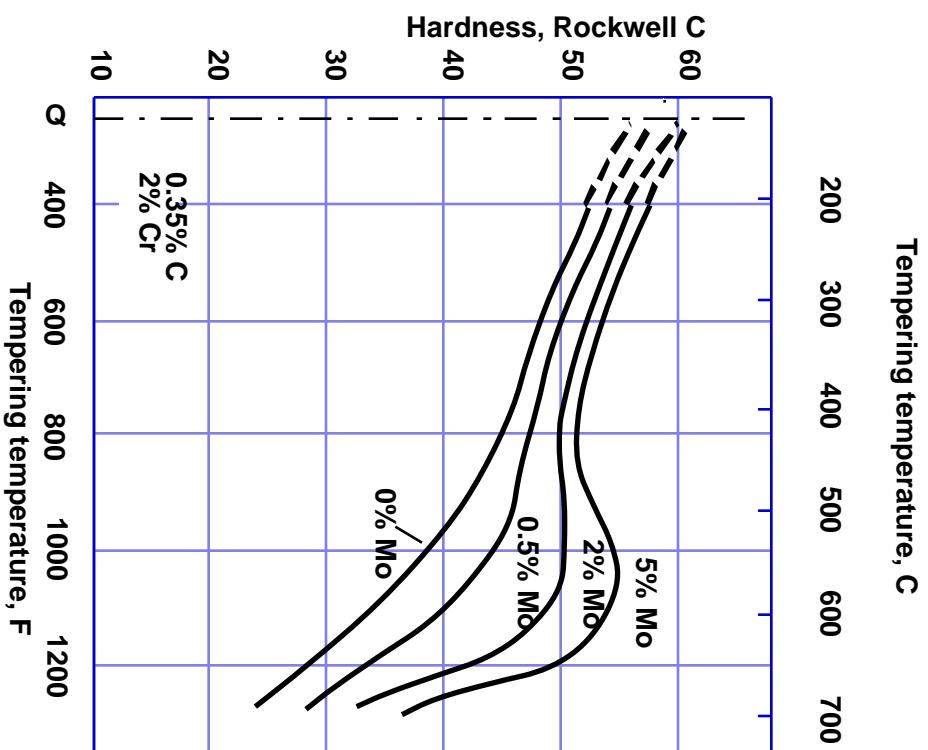
These elements retard the rates of the transformations that occur during tempering. Equivalent effects require smaller amounts of solute the greater the affinity of the solute for carbon. For example, 1 wt. % Cr, 0.5 wt. % Mo and 0.15 wt. % V have similar effects. At these alloying levels, tempering times of 0.5 to 1 hour produce carbides that consist primarily of cementite due to the comparatively high carbon content and also because the rate of diffusion of the carbon is so much faster than those of the alloy elements. The retardation in the carbide growth rate suggests that the solutes diminish the rate at which carbon can diffuse in the steel. Alloy carbides that are rich in alloying elements can form instead of cementite in more concentrated alloy steels at high tempering temperatures. When this happens their growth rates are controlled directly by the diffusion rates of the (substitutional) solutes.



Strong C.F.'s move peak to high T



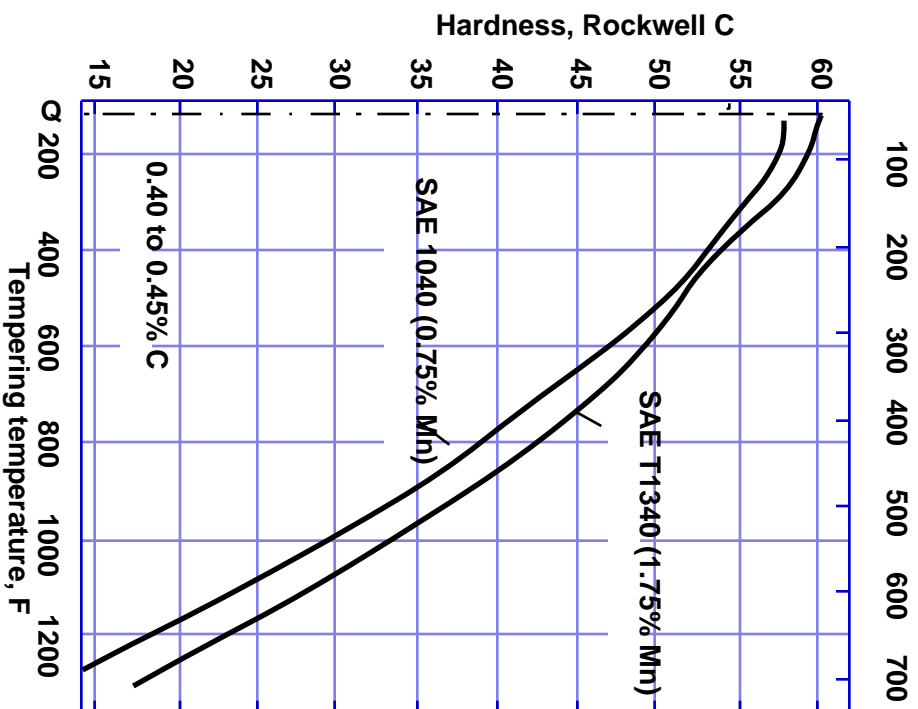
Softening with increasing tempering temperature, of quenched 0.35% C, 0.5% Cr steels as influenced by molybdenum



Softening with increasing tempering temperature, of quenched 0.35% C, 2.0% Cr steels as influenced by molybdenum content

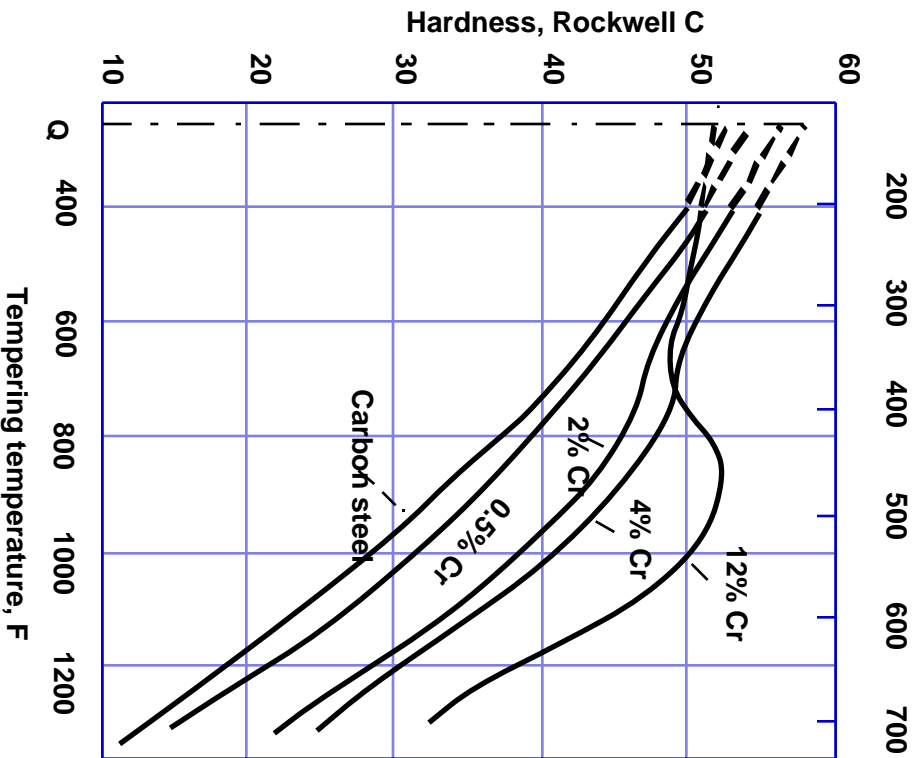


Tempering temperature, C

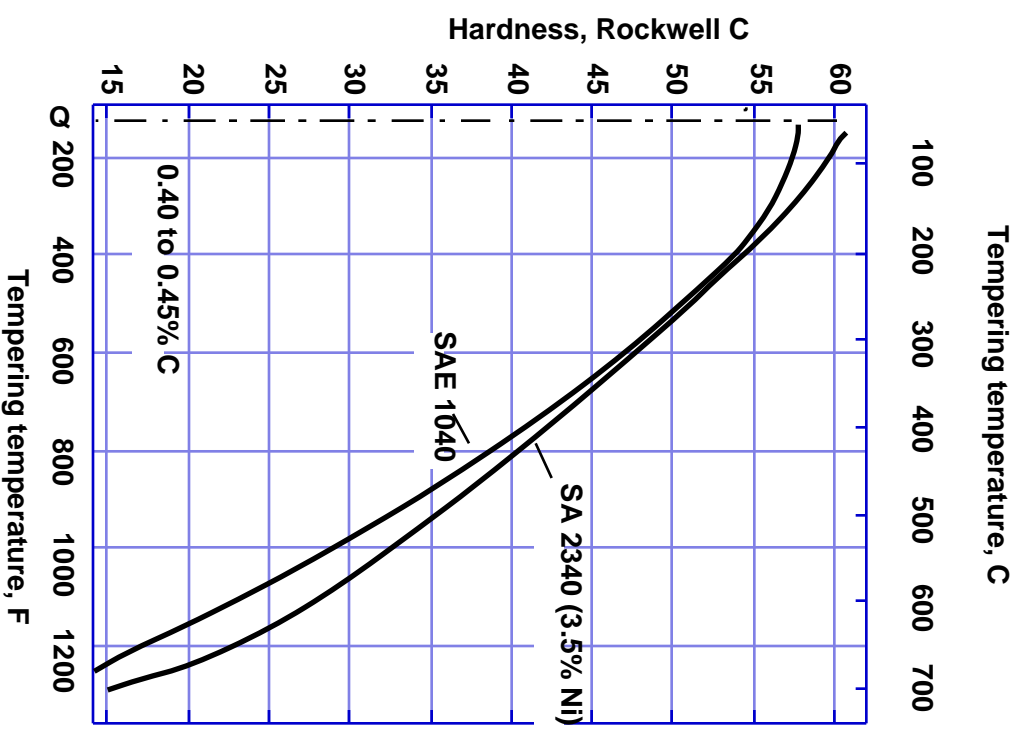
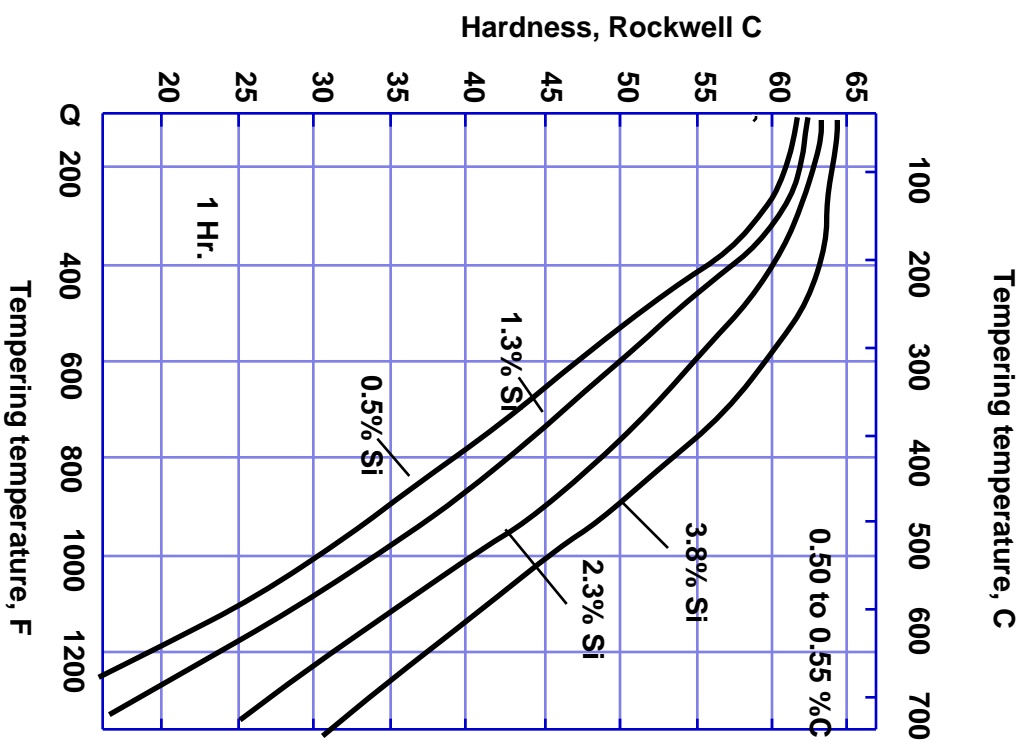


Softening with increasing tempering temperature, of quenched 0.40% C, 0.45% C steels as influenced by an increase of manganese from about 0.75 to 1.75%.

Tempering temperature, C



Softening with increasing tempering temperature, of quenched 0.35% C steels as influenced by chromium content



Softening with increasing tempering temperature, of quenched 0.40% C, 0.45% C steels as influenced by about 3.5% Ni

Hardness measurements provide a convenient method of following the progress of tempering reactions because these reactions change the hardness of the steel. The hardness in hypoeutectoid steels is usually gradually reduced by tempering because the carbon initially dissolved in the martensite forms precipitates of carbides causing the martensite to become softer and to lose its tetragonality. Eventually, when the precipitation of cementite is complete, continued tempering causes the average size of the carbides to increase in order to reduce the total area of the ferrite/carbide interphase boundary. This process reduces the number of carbides per unit volume which causes the spacing between them to increase. It is the spacing between these carbides that determines how effective they are at hindering the glide of dislocations. Therefore, the steel softens continuously. At the high tempering temperatures of 800°F and above, plain carbon, and many low alloy steels continue to soften because of the coarsening of the carbide population and, also, because of ferrite grain growth. However, in alloy steels in which significant amounts of alloy carbides can form, the new carbides replace the coarsening cementite-rich carbides with a new, fine array of alloy carbides. Note that the rapidly diffusing carbon enables relatively pure cementite to form first because the nucleation and growth of the alloy carbides is paced by substitutional diffusion. When the dense array of fine alloy carbides forms, the gliding dislocations meet a higher density of obstacles to slip and the hardness of the steel is increased. This phenomenon is called secondary hardening and is clearly of practical importance because it provides another method of obtaining a microstructure of high hardness and toughness. The particular temperatures at which secondary hardening occurs depends on the species of carbide that forms and increase as the stability of the carbide increases.

It is important to recognize that this discussion of the effects of alloying elements applies to situations in which the alloying elements were initially in solution in the austenite. When this is not so, important changes can arise. Let us consider an example to predict the kind of changes that can occur. We select an AISI 1050 steel to which 1 wt.% V has been added and which has a microstructure that contains vanadium carbides. First, let us austenitize the steel at a temperature that is high enough to transform the steel into homogeneous austenite. Then suppose that the steel is successfully transformed to martensite during quenching. Because the vanadium and the carbon are dissolved in the martensite, the events described earlier take place during tempering. Now suppose we repeat the experiment but this time the steel is held at a temperature that is not far above the A<sub>3</sub> point during the austenitization treatment. At this temperature the ferrite is converted to austenite but the vanadium carbides are not dissolved so the austenite contains them when it is quenched. The first effect that we predict is a change in the hardenability of the steel. The hardenability will be decreased in comparison to that of the previous case because the vanadium is not dissolved in the austenite and, also, there is less carbon in the austenite because some resides in the undissolved carbides. The hardenability will also be reduced because the grain size of the austenite will be smaller than in the previous case due to the lower temperature of austenitization and because the vanadium carbides inhibit grain growth. In fact, the hardenability could now be so low that we may fail to produce a uniformly martensitic sample. That could certainly cause problems if a fully martensitic component was a required result of the heat treatment. However, let us suppose that we are fortunate and that the sample is successfully transformed into martensite. What then? The hardness of the as-quenched martensite will be lower than that of the martensite produced in the first experiment because it has less carbon dissolved in it. Also, it is possible for a reduction in the hardness to arise due to auto-tempering that could occur because of the increase in the M<sub>s</sub> temperature due to the absence of Vanadium and the reduction of carbon in the austenite. When such samples are tempered, the transformations that occur will be very similar to those that would occur in a plain carbon steel that contains less carbon than a 1050 steel. Secondary hardening would not take place.

## Embrittlement During Tempering

The aim of a quench and temper treatment is to produce a microstructure that has a particular set of mechanical properties. The microstructural changes that take place in low alloy steels during tempering usually cause a reduction in the hardness of the steel unless, of course, secondary hardening occurs. The decrease in hardness is usually accompanied by an increase in the toughness as shown by the results obtained during impact tests. However, there are occasions when this is not so and, instead, the toughness falls. This reduction in the toughness raises the ductile to brittle transition temperature and can reduce the energy absorbed during fracture at and above room temperature. There are two types of embrittlement. One is called tempered martensite embrittlement. It is also referred to as 500°F embrittlement and one step embrittlement. The other is simply called temper embrittlement or, perhaps preferably, two step embrittlement. The one step and two step terminology is less confusing.

Let us review some pertinent aspects of fracture in metals. First, from the macroscopic point of view, a very ductile fracture is obviously associated with extensive plastic deformation. Most of this plastic deformation precedes the fracture itself, and creates distortion such as elongation, bending and reduction in thickness. The work done during the gross deformation accounts for the high values of the energy absorption in the total failure. In contrast, a very brittle fracture takes place without the production of any obvious distortion and smaller amounts of energy are absorbed during the failure.

In the preceding paragraph, ductile and brittle failures were described from the macroscopic point of view. On the microscopic scale the ductile failure mode produces characteristic fractographic features visible at magnifications above a few hundred times. These features are called dimples. They are small craters or holes bounded by raised ligaments and their presence demonstrates that the crack propagated by a process that involved a ductile failure mechanism. Studies of the ductile fracture process under a tensile stress, has shown that micro voids nucleate and grow in the metal ahead of the crack. The crack advances through this array of micro voids by tearing the metal ligaments that separate neighboring voids, leaving behind the tell-tale dimples on the fracture surfaces. The nucleation of the micro voids is frequently easier at small included particles in steels; then it is common to observe the particle sitting in the dimple when the fracture is examined with a large enough resolution. The process of micro void coalescence is a ductile process and the fracture is therefore a ductile fracture. However, it is not necessarily true that a fracture that proceeds by micro void coalescence, will be associated with extensive, macroscopic plastic deformation. It could be initiated at a reduction in section or some other stress concentrator. In these cases, there can be little indication from the macroscopic view, that the failure took place mechanistically by a ductile mode.

Fractures which occur by cracks that do not propagate by micro void coalescence can occur in metals. BCC and CPH metals can break by cleavage. The initiation of a crack in a cleavage fracture may involve some localized plastic flow but the crack is sharp and advances by material separation at its end. If plastic deformation does occur ahead of the crack then the crack can become blunt and stop. Here we have an inherently brittle process on the microscopic and macroscopic scales. Cleavage cracks tend to follow particular crystallographic planes, typically {100} in BCC crystals. Adjacent parts of the crack can advance along different, but parallel planes. These adjacent parts then become connected on the final fracture surface by steps that are called cleavage steps.

Fractures that occur by cleavage and by micro void coalescence usually produce distinctive characteristic topographic features on the fracture surfaces that enable them to be distinguished and readily identified. A cleavage failure usually takes place rapidly and consumes less energy than does a ductile failure.

Because cleavage cracks follow particular crystallographic planes, the fracture paths pass through grains and the fracture is called transgranular. Intergranular fractures during which the cracks follow the grain boundaries within the material can also take place. These fracture surfaces are characteristically smooth and comprise curved and flat facets that clearly reveal the intercrystalline boundary path followed by the cracks. Again, there is usually little or no micro void coalescence involved. The energy consumed during the fracture is small because the crack follows a path across which there is weak cohesion. This mode of failure is brittle on both microscopic and macroscopic scales and can occur in FCC metals as well as BCC and CPH metals.

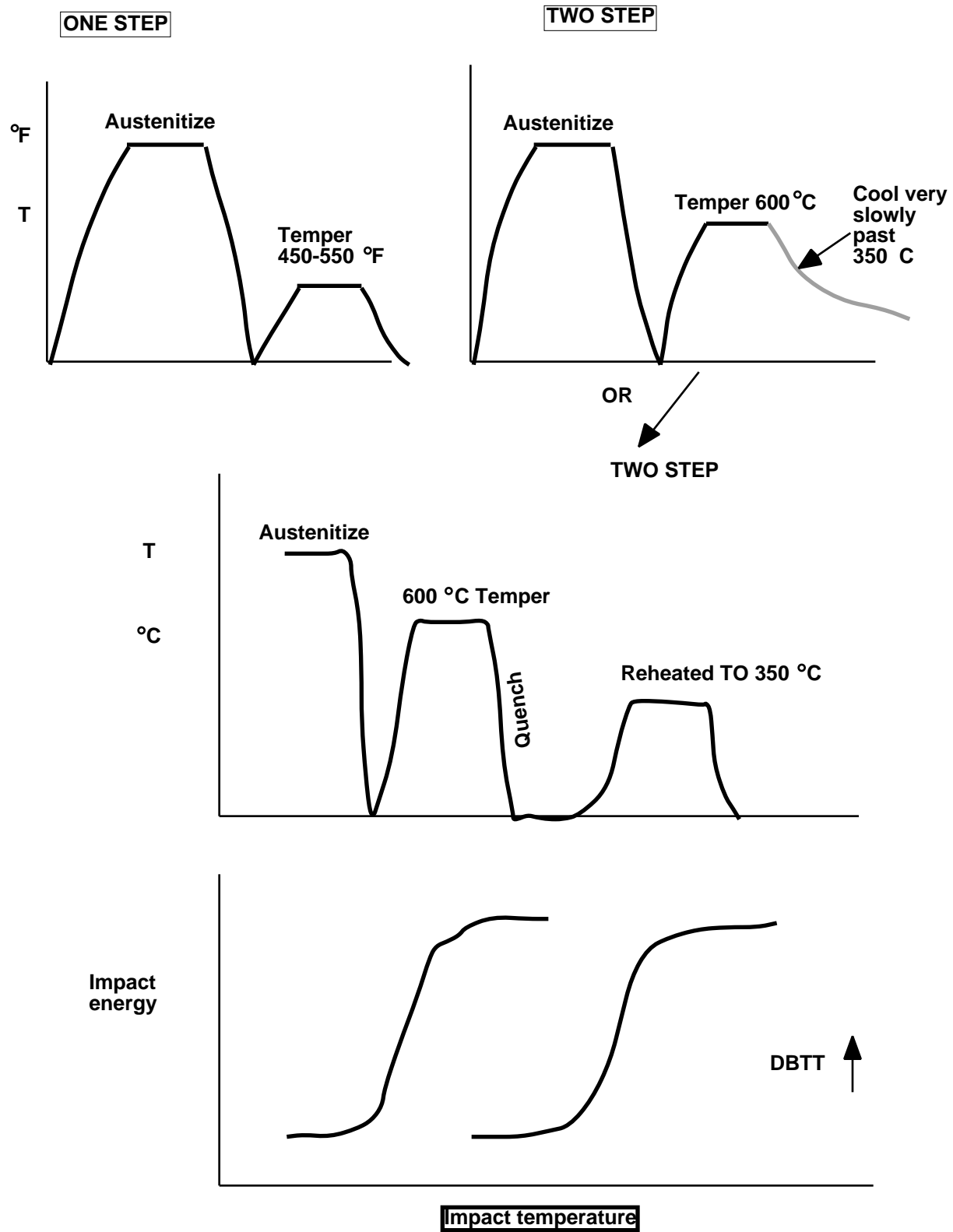
We have described three modes of fracture that can occur when metals are broken. It is important to realize that a metallic component can fracture by more than a single mode. Fracture surfaces can show regions of micro void coalescence and regions of cleavage. As the percentage of the former decreases so does the energy consumed during the failure and the metal becomes less tough.

The toughness of steels is of great practical importance. It is to be expected that some components that are made of steel will contain small cracks or similar flaws. The tolerance of the material to defects decreases as the toughness goes down and catastrophic failure can occur under “normal loading conditions”. If a material that would normally be expected to have adequate toughness under certain conditions develops a microstructure that permits crack propagation in a brittle mode, it is said to have become embrittled. As we said earlier, this can happen during tempering.

#### One Step Embrittlement.

This form of embrittlement can occur in standard low alloy steels that are heat treated for high strength levels, e.g. quench and tempered 4140. It can also occur in plain carbon steels that contain phosphorus. A typical treatment that produces it is austenitization, quenching to martensite and tempering in the region of 450°F to 550°F. (Hence the old name of 500 degree embrittlement.) The embrittlement manifests itself by raising the ductile to brittle transition temperature and by reducing the amount of energy absorbed during the impact in comparison to those pertaining to samples tempered immediately above and below this range.

This range of tempering temperatures corresponds to the beginning of stage three tempering in which sheets of cementite needles and platelets precipitate heterogeneously on interlath boundaries. Sheets of cementite particles can also be deposited from retained austenite when this austenite transforms during the tempering treatment. In general terms, invoking the principle that the properties of the whole sample are dominated by those of the most continuous phase, one might



expect a deterioration of toughness with these microstructural changes. This seems to be true when the steels are relatively free of P and N because the fracture paths follow the sheets of cementite. Furthermore, the embrittlement is effected during the tempering time required to produce these microstructures. These times are typically about an hour. The fracture paths are transgranular and the failure mode is often a mixture of cleavage and microvoid coalescence. However, when the steel contains high amounts (say 0.03 wt. %) of P, the embrittlement is associated with intergranular failure along prior austenite grain boundaries. This suggests that the embrittlement is also associated with a diminution of cohesive strength across prior austenite grain boundaries due to the segregation thereon of impurities within the steel as well as with precipitates of cementite.

### Two Step Embrittlement.

This is a loss of toughness because of the occurrence of intergranular failure along prior austenite grain boundaries. At first sight, it is very similar to the intergranular mode of failure in one step embrittlement, but it does not afflict plain carbon steels. It arises in alloy steels containing Ni, Cr and Mo that are converted to martensite, tempered at 600°C (note the switch to Celsius) and then **slowly** cooled past 350°C. The cooling rate must be very slow, as is unfortunately the case in practice when heat treating very large turbines made from steels containing Ni, Cr, Mo and V. If the steel can be cooled rapidly from the tempering temperature then it is not embrittled. Indeed, this form of embrittlement is reversible by reheating to 600°C and then cooling rapidly. Unfortunately, that cannot be done with very large components. Even when it is possible to cool fast enough to avoid the problem, the embrittlement demon lies in wait. If the susceptible steel is heated into the 375 to 500°C range subsequently and held there, it will become brittle. Hence the term two step embrittlement. The kinetics of the embrittlement process exhibits “C” curve behavior during isothermal aging at various temperatures. The nose of the curve, where the rate of embrittlement is most rapid, occurs typically at about 550°C. At this temperature significant embrittlement can occur in times of the order of an hour. At 375°C several hundred hours are required. This is particularly unfortunate because this temperature range is often encountered in practical applications and, eventually, flaws in the steel can become super critical as the toughness gradually falls with time.

A great deal of research has been devoted to understanding two step embrittlement. Much of this work has employed Auger spectroscopy to analyze the composition of fracture surfaces immediately after breaking the sample, in situ, within the apparatus. As a result of this work, there is general agreement that the loss of toughness is due to the segregation of tramp elements in the alloy steels. Elements that are known to cause embrittlement are P, Sb, Sn and As. In addition, the alloying elements Ni, Mn, Si and Cr seem to exacerbate the problem. It appears that these elements, particularly Ni, encourage the segregation. Molybdenum is beneficial. It retards the embrittlement.

### Surface Hardening Treatments in Steel Components

Most of our discussion about quench hardening and tempering heat treatments has so far been concerned with through hardening components. There are many applications of steel for which through hardening is unnecessary, but for which a high hardness at and near the exterior surface is important. Obvious examples are those in which wear resistance and dent resistance is important, e.g. gears and bearing shafts. Other examples include power transmission shafts subject to bending and torsion actions that create much higher mechanical stresses at the surface regions than in the interior. In such instances it is desirable to produce the hard strong microstructures at and near the exterior surfaces. Such microstructures can be unnecessary in the interiors. Indeed, they are often undesirable. For example, although hard, wear resistant surfaces can be required for

a shaft it can be also important that the less severely loaded interior be tough and resistant to crack propagation. These requirements have led to the development of a variety of commercial practices aimed at surface hardening components.

#### Flame and Induction Hardening.

One way to produce a microstructure at the surface of a component that is different from the microstructure in the interior, is first to produce the interior microstructure by a uniform heat treatment applied to the whole part and then to selectively heat treat the surface only. In these treatments the composition of the steel is uniform; the heating and cooling is not uniform. The removal of heat from a quenched bar is partially controlled by the rate at which it is conducted through the steel to the cooled surface. The relatively low thermal conductivity of steel is an enemy when one is trying to through harden bulk pieces. It becomes an ally, however, when one only wishes to austenitize a region near the surface because it enables surface regions to be austenitized using high rates of energy input without the interiors being significantly affected.

Probably the oldest technique for surface hardening is flame hardening in which heat is applied directly to the surface concerned using torches that burn gases such as oxygen-acetylene mixtures. In passing, it should be noted that steel plate is often cut by means of flame torches which can alter the microstructure and properties of the steel near the cut surface. The objective of the flame hardening process is to austenitize the steel at and near the surface and then to remove the flame and rapidly quench the work to produce martensite and, finally, to use the flame to temper the martensite. Many variations on the theme can be envisioned ranging from hand held torches wielded by workers of various skill levels and experience to automated ignition, burn and quench assemblies, e.g. a rotating shaft within a surrounding, stationary array of burners.

The use of high frequency, oscillating, magnetic fields induced in the surface layers of steel parts is an important method of surface hardening. This is achieved by using appropriately shaped induction coils made from hollow, water-cooled copper tubing that are placed near the surface ( or even selectively near parts of a surface). The oscillating field produced by the induction coils induces electrical eddy currents in the steel. These eddy currents are produced within a certain depth of the outer surface called the skin depth. This depth decreases as the oscillating frequency is increased. The eddy currents cause Joule resistance heating in the skin depth which rapidly raises the temperature of the steel at the surface. Then, after the appropriate time, the power is interrupted and the part is quenched. The process is readily automated. It is more adaptable than flame heating because a wide variety of coil configurations are possible; for example, the interior wall surface of cylindrical tubes can be induction hardened. Usually, surface hardening by localized heat treatment techniques is applied to steel components that have uniform compositions. The selection of the steel must be made with this in mind so that the appropriate carbon content for the required hardness is chosen; often medium to high carbon steels are used.

The use of induction heating is not restricted to producing changes close to the surface. For example, the mechanical engineering analysis of an axle might specify a particular minimum tensile yield strength at the  $3/4$  radius position from the center of the shaft. This translates into a certain hardness that is to be produced there in the tempered condition and thereby specifies the minimum carbon content for the steel. The  $3/4$  radius position mentioned in this example can be relatively distant from the outer surface e.g. in a 3 inch diameter axle. In this case, the choice of the steel will also include hardenability considerations. Induction heating for longer times and in the lower frequency ranges enables the appropriate austenitization to be achieved. However, in many cases



when the needed depth of hardening is quite shallow, the induction heating time is completed within a few seconds (lengthy heating cycles allow time for heat conduction into the workpiece). This means that the austenitization time is very short which can have significant effects on the microstructural changes. We note first that coarse microstructures such as massive carbides widely dispersed in large grained ferrite are not suitable as a starting microstructure because the time required to produce relatively homogeneous austenite is too long. A high temperature excursion can compensate by raising the diffusion rates but this increases the risk of obtaining a large austenitic grain size. Refinement of the initial microstructure such as by normalization is helpful. An interesting observation that has been made is that the hardness of martensite manufactured in treatments using rapid heating and short austenitization times exceeds that obtained in the same steel by conventional through hardening heat treatments. The increases can be about 5 points on the Rockwell scale. This has not been completely explained, but is probably related to refinements in the comparative scales of the microstructures.

In short time induction heating processes, the depth to which the steel is austenitized is small. Shape changes due to thermal expansion and transformation of structure are accommodated by plastic flow in the hot metal. Then, when the rim transforms to martensite during cooling it tries to expand but the core on which it sits is relatively cool and resists plastic flow. The result, often, is that the surface is in compression. This can endow the part with an increased resistance to fatigue because fatigue usually requires tensile stresses. During treatments in which the heating depth is greater, the situation can be reversed and the surface can be put into tension which is not good when fatigue resistance is important.

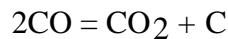
### Case Hardening

In the methods described above, locally different heating and cooling rates are used to produce different microstructures in particular locations in the steel components of uniform compositions. It is possible to produce similar kinds of effects by means of through heating treatments given to steels in which the composition varies locally, i.e. from the surface to the interior. Surface hardening refers to all treatments that are intended to make the surface of articles harder than the material in their interiors. If this is done then the article is encased (completely or partially in selected places) in a hardened layer. Case hardening would appear then, to be another term for surface hardening. This is true, but I have separated it here because it has been my experience that when the term case hardened is used, much more often than not it refers to a surface hardening process that depends on modifying the composition near the surface. In these processes the case depths are relatively shallow, unlike the case of an induction hardened automobile axle. The method employs solid state diffusion to enrich the surface with carbon, nitrogen or both.

## Carburizing.

Because the factor that has the greatest effect on the hardness of martensite is its carbon content, increasing the concentration of carbon at the surface of a component provides a means of endowing the surface with a greater hardness than the interior. The process by which this is done is called carburizing. It is possible because austenite can accept up to 2 wt. % carbon in solution. It is done by exposing austenite to an appropriate environment that maintains the concentration of carbon at the surface of the steel at a chosen high value while carbon diffuses into the steel. The eventual case depth will then be a function of the surface concentration, temperature and time. When the carburization is completed, the steel is quenched to render the case martensitic and is then tempered. The quenching process can be done at the end of the carburization time or the part can be cooled down and then re-heat treated for case hardening. We will consider a gas carburizing process to illustrate some of the principles.

An important reaction is



If we consider a particular mixture of the gases and a piece of austenite at equilibrium at a given temperature and a total pressure of one atmosphere, then the carbon would be dissolved in the austenite so that the C in the equation would correspond to the carbon concentration in the austenite that is in equilibrium with the particular mixture of gases. If the CO content is increased, the reaction will move to the right increasing the components on the right hand side, and, in particular the carbon concentration in the austenite. Similarly, if the austenite was put in oxygen it would be decarburized as CO and CO<sub>2</sub> are created. The variation of carbon concentration in austenite as a function of the partial pressures of CO and CO<sub>2</sub> is shown on page 404 of Darken and Gurry's Physical Chemistry of Metals.

When a piece of low carbon austenite is placed in a gas mixture for which a greater carbon content in the austenite corresponds to equilibrium, the reaction will proceed to the right until the required carbon concentration is established at the surface of the steel. This happens rapidly provided there are adequate quantities of the gas mixture available and it is continually being mixed. The result is that a chosen carbon concentration can be established and maintained at the surface. Meanwhile carbon diffuses down the concentration gradient into the steel. The diffusional flux into the steel is slow enough under the usual conditions for the chemical reaction at the surface to maintain the composition there.

Practically, carburization is not carried out using pure CO and CO<sub>2</sub> mixtures. Typical commercial atmospheres use mixtures of natural gas, which provides methane, and nitrogen which acts as a diluent. Active gases in the mixtures are CO, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O, O<sub>2</sub> and CH<sub>4</sub>. The appropriate mixtures generate and maintain chosen carbon levels. Carburization temperatures are usually in the range of 850 to 950 Celsius. Carburization times depend upon the desired case depth. A common definition of the case depth is that depth below the surface at which the hardness is RC 50 in the final quenched and tempered part. Thus, hardnesses a few points higher are required in the as-quenched part which enables the carbon level at that location to be predicted. Typical case depths are less than a tenth of an inch and are often fractions of that. I have seen specifications calling for case depths of 0.002-0.006 inches: this is simply a statement that implies neither approval or disapproval.

The time required for the carburization treatment can be estimated from the appropriate solution of Fick's second law.

$$\frac{C_x - C_s}{C_0 - C_s} = \operatorname{erf} \frac{x}{2 \sqrt{Dt}}$$

Where the subscript s refers to the surface of the austenite, x refers to distance into the austenite and the suffix 0 refers to the initial base steel being carburized. Other symbols have their usual meanings.

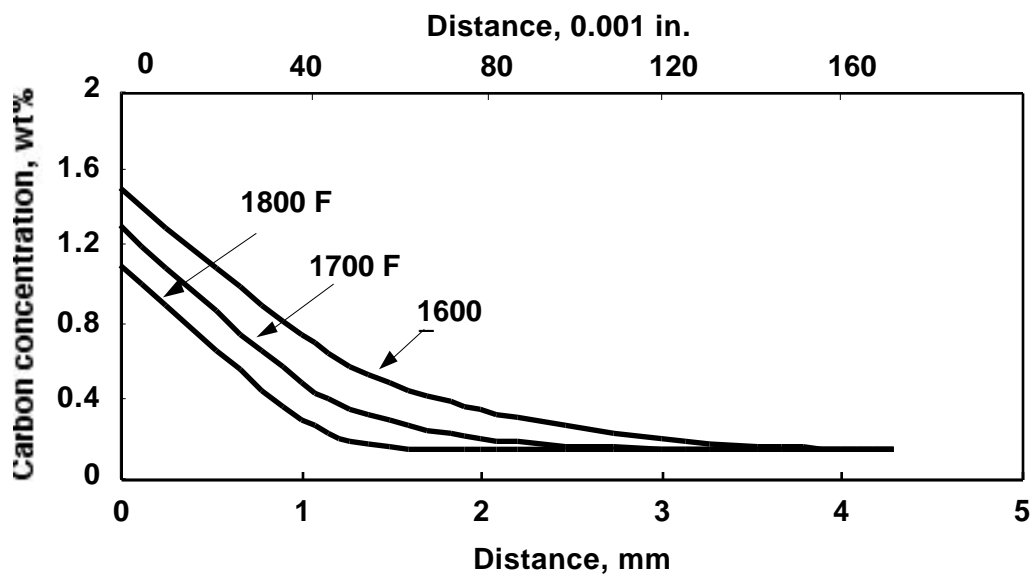
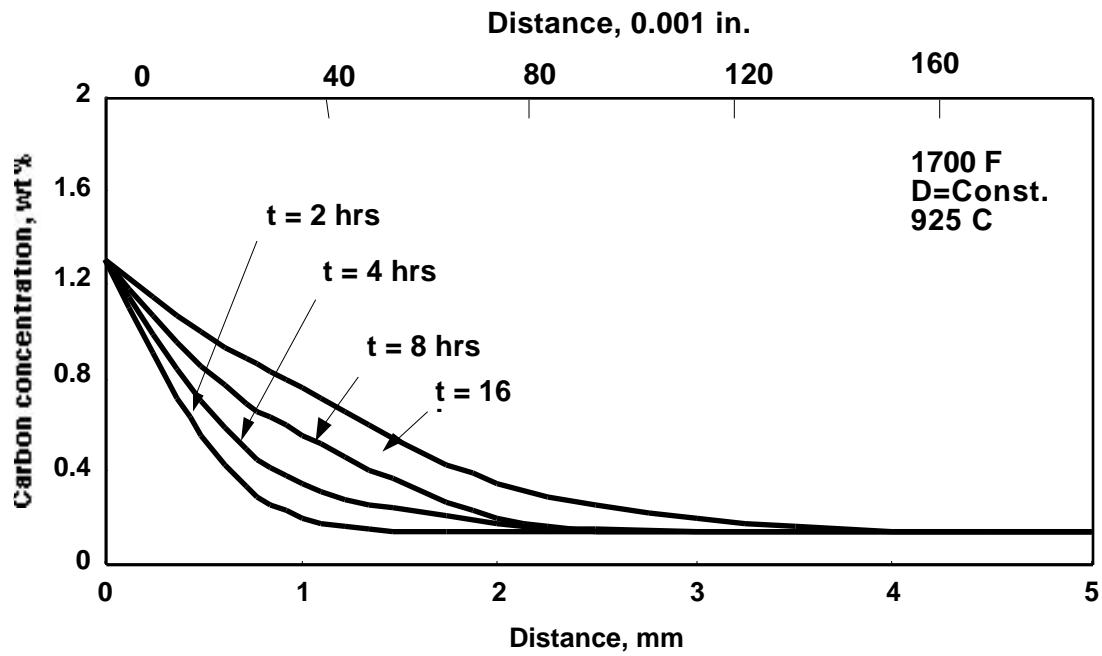
Such solutions have been cast in the form of: case depth =  $K(t)^{1/2}$  and tabulated results published.

The microstructures in the carburized case depend upon the details of the temperature -time history. Examples can be found in the metal handbooks and in Krauss' book. A major difference exists in samples that were quenched directly from the carburizing furnace compared to samples that were first cooled and then re-austenitized and quenched. In the latter case, the re-austenitization of the ferrite produced on cooling from the carburization furnace produces a fine grained austenite in contrast to that which exists after prolonged carburization because the re-austenitization temperature is lower, usually below the  $A_{cm}$  line. In this case, the steel matrix is austenitized and the proeutectoid cementite forms into globular particles that are retained as such, dispersed in the martensite, when the samples are quenched. The microstructure so formed comprises fine crystals of martensite that is about as hard as it can be and a dispersion of proeutectoid particles that is beneficial for wear resistance. In contrast, the austenitic grain size at the end of the carburization time is large. Often the part is cooled below the  $A_{cm}$  before it is quenched. This reduces the thermal shock by decreasing the temperature difference between the sample and the quenching medium. However, proeutectoid films can grow along the austenite grain boundaries during this stage and these films are retained along the prior austenite grain boundaries during quenching. Many of the martensitic plates are bigger because the grains in which they form are large and, also, the retained austenite is less finely dispersed.

In some applications the steel that is carburized has a relatively low bulk carbon content. Many have about 0.2 wt.%. This usually means that the microstructure within the core is a mixture of ferrite and pearlite with ferrite being the dominant phase. As an extreme example, the metal parts which have raised letters on their end faces and used to be used in typewriters to print letters by striking a dyed ribbon were often made of carburized (shallow case depth) AISI/SAE 1010. On the other hand, there are many applications for which strong cores are necessary as well as hard cases. Thus, the steel chosen will have a hardenability large enough for the core to become martensitic or bainitic during the quench. Krauss gives the examples of carburizing steels shown in the accompanying figure. Others appear in the handbooks.

#### Nitriding Steels.

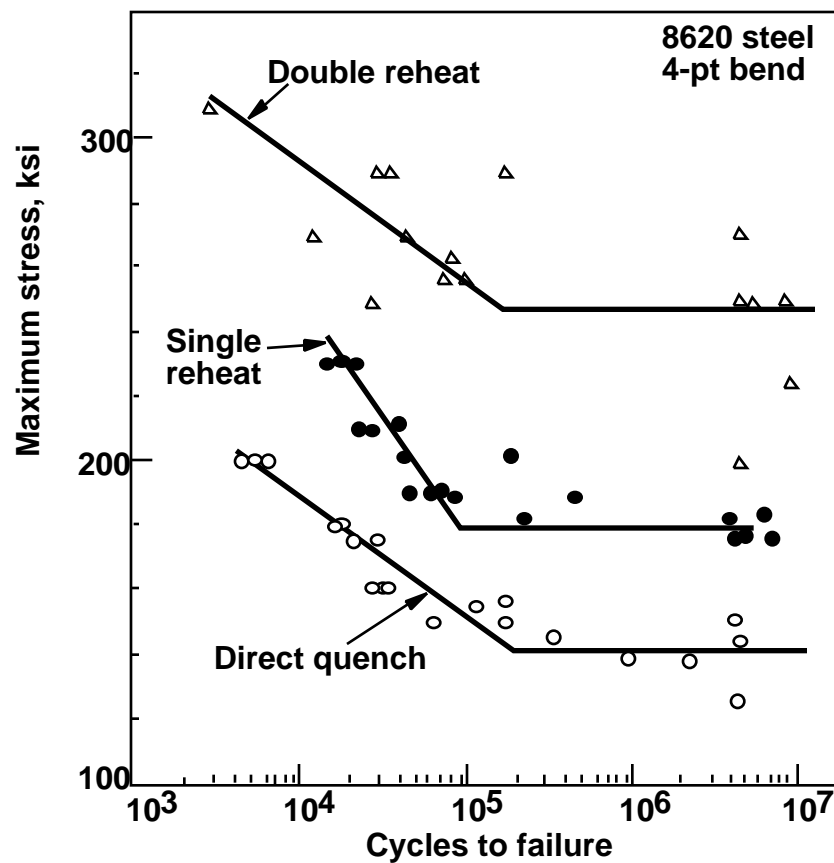
The carburizing process requires that the parts be quenched. The quenching action and martensitic transformations always create the risk of distortion, warping and cracking. Case hardening can also be done via the formation of numerous precipitates of nitrides near the surface



From: Krauss PP290,291

Case Depth Calculated by the Harris Equation			
	Case depth (in.)		
Time, t	after carburizing at(a):		
(h)	1600 F	1650 F	1700 F
2.....	0.025	0.030	0.035
4.....	0.035	0.042	0.050
8.....	0.050	0.060	0.071
12.....	0.061	0.073	0.087
16.....	0.071	0.084	0.100
20.....	0.079	0.094	0.112
24.....	0.086	0.103	0.122
30.....	0.097	0.116	0.137
36.....	0.108	0.126	0.150

1. Case depth =  $0.025 \sqrt{t}$  for 927 °C (1700 °F);  $0.021 \sqrt{t}$  for 899 °C (1650 °F);  $0.018 \sqrt{t}$  for 871 °C(1600 °F). For normal carburizing (saturated austenite at the steel surface while at temperature).



From: Krauss, pp292,299

of the steel. This process is called nitriding and, in contrast to carburizing, is performed while the steel is largely ferritic not austenitic. Thus, the process does not involve rapid temperature changes and allows excellent dimensional control.

Typically, the steel to be nitrided is a medium carbon steel that is initially quenched and tempered at temperatures from 540°C to 700°C. The high tempering temperature is intended to minimize microstructural changes that might occur during the subsequent nitriding processes that are carried out at lower temperatures. These temperatures are typically 500 to 525°C. Nitriding is conducted in controlled atmospheres that use the decomposition of ammonia to generate nascent nitrogen on the surface of the steel. This nitrogen diffuses into the steel and also combines with the iron at the surface to form iron nitride. The reaction is  $\text{NH}_3 = \text{N} + 3\text{H}$

Nitriding steels contain alloying elements that form nitrides so that the nitrogen that diffuses in forms numerous very fine precipitates. Aluminum is used for this purpose; e.g. 1.3 wt.% Al. The case depth, in this case the depth of the precipitate band, is shallow, usually less than half a millimeter, even though nitriding times can exceed a 100 hours. During single stage, nitriding treatments in which a single nitriding atmospheric composition is maintained, a “white layer” is formed. (So-called because in standard etchants for steels it is unattacked.) This layer is iron nitride and is hard but it can crack and spall. When this is unacceptable the layer is removed by surface grinding. Alternatively a two stage nitriding process is used in which, after the first stage, the atmospheric conditions are changed so that iron nitride no longer forms at the surface and the existing layer is removed because its nitrogen content dissolves into the steel. Because the two processes described are successful, combined processes have been developed in which both carbon and nitrogen are simultaneously diffused into the surface. These are carbonitriding and nitrocarburizing and are done to both austenite and to ferrite.

## Ultrahigh Strength Steel

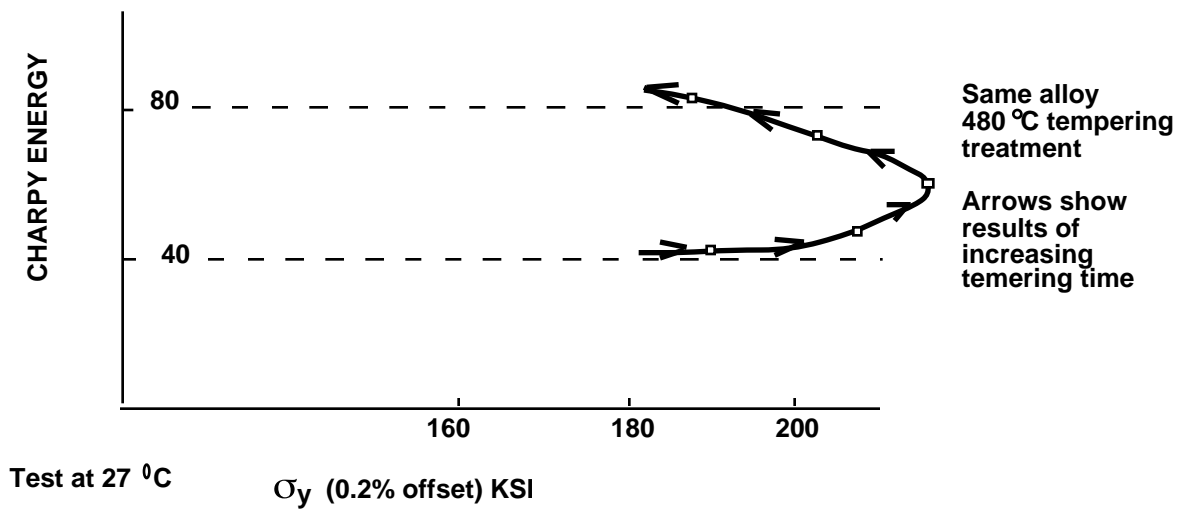
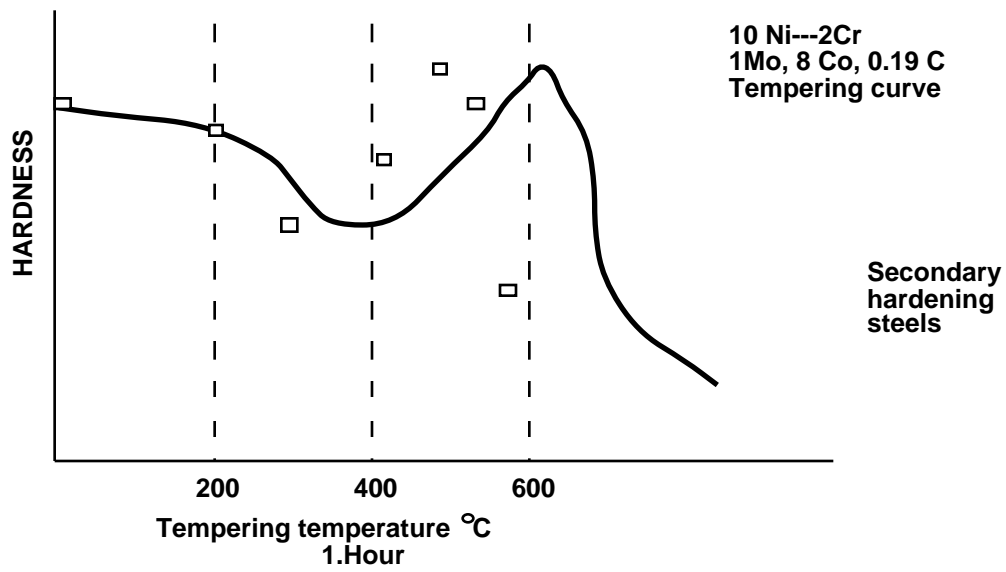
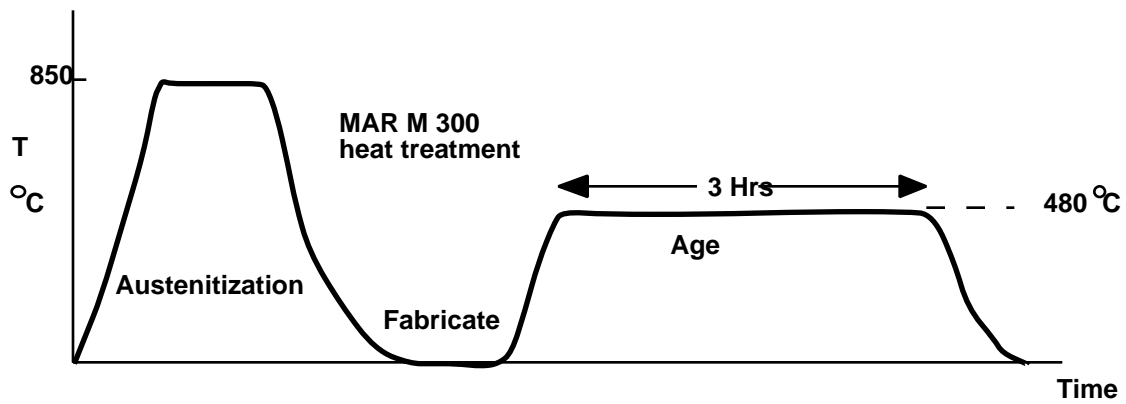
As a general guide, yield strengths of 690 -1380 MPa (100 -200 KSI) are considered to be high, and those above 200 KSI and up to 300 KSI are very high. Steels with strengths near and above the upper end of the latter range are called ultrahigh strength steels. 100 KSI = 689.5 MPa. To obtain high strengths it is usually necessary to heat treat the steel to convert it to tempered martensite. Some standard low alloy steels such as 4130, 4140, 4330 and 4340 in the tempered martensitic condition can have yield strengths above 200 KSI. Greater strengths are obtainable by modifying the compositions of the standard steels. High strengths can also be produced by combining plastic deformation processes with heat treatment in what are called thermo-mechanical treatments. Examples of applications which ask for very high yield strengths are aircraft landing gear, submarine hulls and high pressure chambers.

Because high and ultrahigh strength steels have very poor toughness when converted to martensite it is necessary to temper them. Temperatures as high as 300°C can be required. This is necessary in spite of the fact that the tempering reduces the yield strength: the objective is a compromise that gives acceptable strength and toughness and, hopefully, high enough values of both for successful application. While it is true that harmful residual stresses can be reduced during such tempering treatments and the toughness can be improved, practical problems arise because one step tempered martensite embrittlement lurks dangerously nearby. The search for ways by which these standard alloy steels might be modified in order to reduce the risk of one step tempered martensite embrittlement has been the subject of much research in the past few decades.

### Modified standard alloy steels.

It is generally accepted that one step tempered martensite embrittlement is associated with the formation of sheets of carbides at the beginning of stage 3 tempering and, also, the segregation of some solute elements such as phosphorus at prior austenite boundary sites. The carbides form by nucleation and growth processes and thus the time required for their appearance within the microstructure can be increased if the kinetics of the transformation can be retarded. When appropriate alloying elements that might accomplish this are considered, graphite stabilizers come immediately to mind because they retard the rates of nucleation and growth of cementite. Additions of Si have been found to be effective for this purpose. It is able to delay these reactions sufficiently for useful residual stress relief and concomitant toughness improvement to be obtained during tempering at 300°C before harmful quantities of carbides form. In general, the toughness of the decomposition products of austenite is always improved by refining the austenitic grain size. Also, in the present case there is an added advantage to having a small austenite grain size. When the grain size of the austenite is reduced, the area of the prior austenite grain boundaries is increased. Thus contributions to embrittlement from solute segregation at these interfaces should be reduced. Following this reasoning, vanadium is often added in order for it to form carbides and nitrides which restrict grain growth during austenitizing.

Many of the modified alloy steels have trade names e.g. INCO 300M, which is 0.35-0.45 % C, 0.65-0.9 Mn, 1.45-1.8 % Si, 0.7-0.95 % Cr, 1.65-2 % Ni, 0.3-0.45 % Mo, 0.05 % V with P and S less than 0.025 %.





Here we have V to lower the austenite grain size and thereby improve toughness in the final product; Mn, Mo, Si, Ni and Cr to increase hardenability; Si to strongly retard cementite formation which enables tempering to be done while minimizing the risk of embrittlement; Mo helps to defend against the segregation, of tramp elements at grain boundaries. Ni is not a desirable element with respect to intergranular failure by temper embrittlement because it tends to promote segregation. If, however, this form of tempered martensite embrittlement is indeed avoided, then the Ni that is dissolved in the matrix has a strong, favorable effect on toughness during transgranular fracture. Minimizing P and S reduces segregation. Modern steel making techniques produce cleaner steels than those made earlier and this also improves the fracture toughness.

Even when very high strength steels are successfully treated to take advantage of the strength of tempered martensite while remaining free from one step tempered martensite embrittlement, they are still not very tough and they do not tolerate flaws. Generally, it is to be expected that large structures will contain flaws such as pre-existing cracks or sites at which cracks can form more easily than elsewhere. The fracture toughness of a material that contains such a flaw determines the critical applied stress at which the flaw will propagate. The lower the toughness the lower the stress for a given flaw to propagate. Typically, cracks propagate by cleavage below the DBTT and by micro void coalescence above it. For the ductile failure mechanism, scanning electron microscopic studies have demonstrated that inclusions in steels are often involved in the formation of the voids. When the fracture surfaces are studied, small inclusions are found inside many of the dimples. This indicates that the interface between the inclusion and the matrix is one across which there is weak bonding so that it is a site at which a void can more easily nucleate. When a steel contains inclusions they can often dominate the impact toughness even when other favorable microstructural changes are made. Thus as the yield strengths of the steels are increased to higher and higher levels it becomes increasingly important to control the inclusion content and shape. S and O must be reduced. Additions of rare earth elements such as Ce are beneficial for making very small spherical oxide inclusions.

### Precipitation Hardened Steels

The strengthening mechanisms used in the modified standard alloy steels described above are those provided by the martensitic transformation. It is unfortunate that the tempering process is necessary because it tends to reduce the strengths initially achieved. This led people to consider whether or not secondary hardening processes during tempering could be effective enough to produce ultrahigh strength steels. One example is a group of steels called maraging steels which were so named because the martensitic transformation was used to obtain a saturated solid solution in which precipitation hardening was subsequently obtained by aging the steel at a suitable temperature.

These steels were first developed in the 1960's and have been used in aircraft landing gear. They contain a rather high content of Ni which makes them expensive. This partially explains why they have not been as widely used as their properties would imply that they should be.

A typical example is Mar M 300 for which the yield stress can reach 350 KSI (2.4 GPa).  
.03 % C max., 0.1 % Mn max., 0.1 % Si max., 18 % Ni, 5 % Mo, 9 % Co, 0.6 % Ti, 0.1% Al.

A typical heat treatment is as follows:- austenitization at 850°C, cool to room temperature and age for 3 hours at 480°C. Yield strengths can be as high as 350 KSI with 6 % elongation in tension. During austenitization essentially all the alloying elements are dissolved. Hence the steel has a high hardenability, and is air-hardenable in thick sections. Note that because the steel contains less than 0.03 % C, the diffusion controlled transformations that have to be avoided in order to form martensite those that form ferrite and those that involve precipitation of intermetallic

compounds among the iron and the alloying elements. These compounds grow by means of substitutional diffusion which is a sluggish process compared to interstitial diffusion. Because the martensite has a low carbon content it is relatively soft, typically in the range of about RC 25-30. This means that it is machinable so that parts can be easily manufactured after the martensitic transformation has occurred. The martensite has the low-carbon, lath type of microstructure and contains many dislocations and interfaces. These become important during aging process because they are catalytic sites for heterogeneous nucleation of the intermetallic compounds. During aging, many small precipitates of  $\text{Ni}_3\text{Mo}$  and  $\text{FeTi}$  form. These precipitates provide the barriers to dislocation glide that are necessary for the high strength. Also, because they nucleate heterogeneously on dislocations, they pin much of the dislocation density present initially which prevents recovery from taking place during the aging process. Recovery, of course, would reduce the yield stress. The cobalt provides some solution strengthening and it has been suggested that the cobalt-rich matrix undergoes short range ordering which would also contribute to strengthening.

Vacuum melting techniques are used to minimize P, O, S and N; this is necessary to ensure that the toughness is acceptable. Finally, it is interesting to note that these steels have been found to have good resistance to stress corrosion cracking.

The maraging steels contain very little carbon and the precipitation reactions described above involve substitutional elements that form intermetallic compounds; carbides are unimportant. In contrast, the phenomenon of secondary hardening that can occur during tempering of martensite in appropriate steels is associated with the precipitation of fine carbides that are rich in alloying elements such as Mo and Cr. Because the tempering treatments that cause secondary hardening are carried out at higher temperatures than those used in the heat treatments of low alloy and modified low alloy steels, improved toughness can be expected. This can be advantageous provided the secondary hardening precipitation processes are able to produce ultrahigh strengths. Much research has been devoted towards this objective and a class of steels containing Ni, Co, Cr, and Mo has been developed during the last 25 years, in which secondary hardening yields very high strengths and good toughness. At this stage, in this document, we are familiar with the general roles and effects due the Ni, Cr, Mo and carbon but what about the cobalt? The principal effects discovered during this research are: cobalt additions cause an increase in the  $M_s$  temperature in contrast to the reductions caused by the other elements; it dissolves mainly in the matrix and provides some solution strengthening and, importantly, it accelerates the kinetics of the nucleation and growth of the alloy carbides responsible for secondary hardening. Let us consider some examples.

Speich et al. in *Met Trans.*, 4, 303 (1973), describes an investigation in which they studied 19 steels that had compositions that were variations around a basic mixture of 10 wt. % Ni, 2 wt. % Cr, 1 wt. % Mo, 8 wt. % Co and 0.12 wt. % C and which contained small amounts of Si and Mn and trace amounts of Al, N, S and P. The highest carbon content was 0.19 %. This is rather smaller than the carbon levels in some of the modified xx40 standard steels because low carbon content promotes weldability. Typical heat treatments were austenitization at  $845^\circ\text{C}$  and quenching into water after which samples were tempered at temperatures that spanned the range from  $100\text{--}700^\circ\text{C}$  for various times. Based on the results obtained in these experiments, detailed experiments were conducted by tempering in the range of  $480\text{--}510^\circ\text{C}$  which spanned the secondary hardening peak.

It is important to remember that the microstructural changes produced during tempering are functions of time and temperature. First, we consider the effects of temperature at fixed tempering times of one hour. The investigation showed that initially, as the tempering temperature was

increased, either there was little variation in the hardness or some softening occurred due to the precipitation of cementite during tempering below the secondary hardening range. Then when the temperature became high enough, typically in the 420-480°C range, the cementite dissolved and the precipitation of numerous very fine particles of (Mo,Cr)<sub>2</sub>C alloy carbides began. These microstructural changes caused secondary hardening to begin and, as the tempering temperature was increased further, the hardness rose to a peak and then declined again. A notable aspect of these results is that the rate at which the hardness decreased as the temperature increased, when the temperature was above the value that gave peak hardness, was rapid, more rapid than its rate of increase with temperature for temperatures that were below. We will refer to this again when we consider the reasons for overaging later. The height of the peak in the hardness versus tempering temperature, increased with increasing carbon content because the volume fraction of the carbide phase increased accordingly. It also increased with an increase in the molybdenum content, reaching a maximum at 1%. Chromium additions shifted the tempering curve to slightly lower temperatures but this effect saturated out at about 2%. Cobalt did not partition to the alloy carbides yet its presence in the alloy raised considerably the peak hardness and also the yield strength that could be obtained in a given tempering time. Presumably, this is due primarily to the fact that Co enhances the kinetics of the transformation. Yield strengths of over 180 KSI (1240 MPa) were obtained.

The observations described above, showed that a hardness peak is obtained when tempering is carried out for fixed times of one hour at different temperatures. This is, in general, similar to the usual behavior of precipitation hardenable alloys, for which aging at a constant temperature causes a gradual increase in hardness with time until a peak is reached. Then the hardness decreases from the peak value as time elapses while aging is continued. Ordinarily during this process in precipitation hardenable alloys the toughness decreases as the hardness rises and then increases again as the hardness decreases. An interesting observation made in the work being described here for secondary hardening was that when the Charpy impact energy and yield strength of the samples were both determined as a function of tempering time, the curve obtained by plotting impact energy values against the yield strength values was an inverse “C” shaped, as shown in the appended figures. This curve shows that as tempering in the secondary hardening range begins, **both** the strength and toughness initially increase. This is in contrast with the usual behavior of materials in which the toughness generally decreases as the material becomes stronger. Eventually, as the tempering time grows longer, overaging begins and the strength begins to fall while the toughness continues to increase, as in the usual behavior. Consequently, a tempering treatment can be chosen to obtain an optimal combination of strength and toughness. The authors concluded that nickel was beneficial with respect to the toughness. This work led to many subsequent investigations of similar steels which has resulted in the commercial development of steels such as:

AF1410...0.16 % C, 10 % Ni, 13.8 % Co, 2 % Cr, 1 % Mo, 0.16 % Mn and trace amounts of Ti, Al, S, P with O and N in parts per million,

and AerMet 100 which was developed in the early 1990's and has compositions near 0.16 % C, 11 % Ni, 3 % Cr, 1.2 % Mo, 14% Co, and small amounts of Mn and Si.

These steels are vacuum melted and manufactured with careful attention to cleanliness so that they contain low amounts of impurities. Recent publications describing the microstructural phenomena in these steels are by Raghavan and Machmeier in Met Trans. 24A, Sept. 1993, page 1943 and in Met Trans. 27A, Sept. 1996, page 2511.

The strength of these steels is controlled by the inherent flow stress of the matrix, the dislocation density and sub cell size, the grain size and the effects due to the precipitate population. The initial microstructures of the martensites are controlled by the particular heat treatments and the  $M_s$  temperature of the steel. It is generally true that the tendency for martensite to adopt a twinned plate morphology, increases as the  $M_s$  temperature decreases. Conversely, the tendency for the formation of dislocated lath martensite increases as the  $M_s$  temperature increases. Autotempering reactions occur more readily the higher the  $M_s$  temperature is. Lath martensite predominates in AF 1410 while partially twinned plate martensite predominates in the Aermet 100. Secondary hardening is produced in the martensite of both types of steel by the precipitation of a high density of  $M_2C$  carbides during tempering. Here the M stands for metallic elements. The ratio of metal atoms to carbon atoms is 2: 1 but the metal atoms in the carbides include Mo, Cr and Fe; the precise composition of the carbides depends on the total composition. For example, if the molybdenum composition in the alloy is raised, then the molybdenum content of the carbides is increased.

The austenitizing treatments used in the investigations referred to above did not produce completely homogeneous austenite. Instead, the austenite contained some MC and  $M_{23}C$  carbides that were retained in the martensite after quenching but they did not participate in the tempering reactions. When these steels are quenched to room temperature it is usual for them to contain a small amount (1-2 %) of retained austenite. Refrigeration eliminates the retained austenite. Combinations of tempering times and temperatures that allowed cementite to form but which did not produce secondary hardening e.g. for temperatures below about 427°C, produced plates of cementite on plate, lath and twin boundaries in the martensite. Then in the temperature range of 450-485°C secondary hardening occurred. Samples tempered at 510°C rapidly overaged. There seems to be general agreement that the secondary hardening peak occurs when the optimum population of  $M_2C$  is generated. Here optimum refers to the particle size and spacing. Furthermore, the more recent investigations show that at peak hardness, the carbides are needle-shaped and coherent with the matrix and that the sudden, rapid softening at the higher temperatures is caused by a transition from coherency to incoherency, rather than carbide coarsening due to Ostwald ripening. This description is based on details of the TEM observations in which characteristic contrast effects indicated that for the peak hardness the particles were surrounded by coherency strain fields. This contrast was absent around carbides that formed at 510°C.

It appears to be agreed that the passage of dislocations through the precipitate array is by Orowan looping of dislocations around the particles. When looping occurs in the absence of strain fields around precipitate particles, the dominant microstructural parameter that effects the stress required to force a dislocation to glide through the array is the inter-particle spacing. The observation that overaging sets in rapidly when coherency is lost and before there is any significant change in this spacing suggests that the interactions between the strain fields of the carbides with those of the dislocations are an important contribution to the strengthening effects of the carbides. This allows us to begin to understand the effects due to the variations in the composition of the steel on the secondary hardening curves. For example, increasing the molybdenum content to 1 % increases the molybdenum content of the carbides. This changes the lattice parameters of the carbides because of the different atomic sizes of its constituents. Because the magnitude of the coherency strain depends upon the differences in the lattice parameters of the two phases it will change and therefore so will the magnitude of the resistance to the glide of dislocations due to the coherency strain fields.

## High Strength Low Alloy Steels (HSLA).

There are many applications of steel for which the steel is not heat treated to produce hardening via the martensitic transformation. Instead, it is used directly as supplied. Naturally, the successful use of the “as manufactured” steel depends on how well the manufacturing process produces material in the appropriate form and with the desired properties. Examples of the form of the steel are plates, sheets and bars. Plain carbon steel sheet and plate is easily produced by hot rolling wherein the steel is rolled while austenitic and then cooled. After natural cooling these steels have microstructures that consist of mixtures of proeutectoid ferrite and pearlite. The mechanical properties depend upon details of the microstructure as has already been described. For many applications e.g. ships, gas and oil pipe lines and oil-drilling platforms, it is essential that the steel has good formability and good weldability as well as reasonably high strength and toughness. Increasing the carbon content of the steel increases the strength but decreases the weldability because it raises the hardenability, changes the properties of the transformation products in the heat affected zones and enhances residual stresses in the vicinity of the weld. For good weldability it is desirable to keep the carbon contents low. This is also desirable for good toughness. Unfortunately, reducing the carbon content in the interests of improving weldability and toughness decreases the volume fraction of pearlite in the steel; this reduces the yield strength.

What can be done to solve this dilemma?

Contemplation of the relevant factors reveals that both the yield stress and the toughness of low carbon steels can be increased by refining the ferrite grain size. The final grain size of the proeutectoid ferrite in hot rolled products depends upon the grain size of the austenite when it transforms during cooling and, also, on the rate of cooling after the final rolling pass. Recrystallization takes place in the austenite during hot rolling. Recrystallization can occur in semi-killed, low carbon, unalloyed steel at temperatures as low as 760°C. It is not possible to hot roll the standard low carbon steels in the range of 900-1000°C and also produce fine grained austenite because dynamic recrystallization takes place during rolling. This means that unless the cooling process is accelerated by, say, water cooling, the final product of such treatments has coarse ferrite grains which lowers the strength and toughness.

Because of these limitations on plain carbon steel, a new class of low carbon steels has been developed in the last few decades. The objective has been to produce a material with good strength, toughness, formability and weldability. The carbon content is kept at or below 0.25 wt. %. These steel are called high strength low alloy (HSLA) steels. Sometimes they are referred to as microalloyed steels because they do not contain large amounts of alloying elements.

Before we see what kind of steels these are, let us ask how we would go about designing a steel which will have these properties when manufactured in the physical form (e.g. rolled sheet or plate) in which it is intended to be used? The first thing that must be recognized is that the properties of the ferrite are the important properties because the ferrite dominates the contributions from the small volume fraction of pearlite that might be present. Thus we must consider the factors that control the properties of ferrite. These are:

- grain size; fine grain size raises toughness and yield stress,
- dislocation content; a high density of dislocations raises the flow stress,
- precipitates; a distribution of finely spaced precipitates provides precipitation hardening,
- solutes, elements dissolved in the ferrite provide solution strengthening.

1) How do we produce a fine grain size in the ferrite and still use high rolling temperatures to form the austenite?

First we must find a way of inhibiting dynamic recrystallization and grain growth in the austenite because fine-grained austenite provides many more heterogeneous nucleation sites for the proeutectoid ferrite than does coarse grained austenite. Then, provided grain growth can be controlled, the transformation during cooling should yield a fine-grained ferrite. It is well known that refinement of the austenitic grain size can be done by putting particles of second phases into the austenite, so we need to arrange that suitable particles are in the steel during the hot working process. If these particles are also inherited by the ferrite then they will also impede ferrite grain growth. O.K. Has this been done? Yes.

It was recognized that the logical candidates for these second phase particles are carbides and nitrides. Ti, Nb, and V form carbides and nitrides in steel; Al forms nitrides. Also, any excess amounts of these elements that are left in solution in the ferrite, will contribute to solution strengthening. In practice, the highest temperatures experienced by steel during the rolling process are those existing at the beginning of the process. At these temperatures, above 1000°C, the austenite containing small quantities of the alloying elements mentioned is mostly a solid solution in which the alloying elements are dissolved. Then, as the temperature drops, precipitation of carbides and nitrides occurs and the progress of recrystallization and grain growth is impeded. These elements are very effective for this purpose and only small additions are required. As an example of the effect, we note that a 30 % reduction in thickness at 815°C in a semi-killed, low carbon steel is accompanied by 10 % recrystallization, while for the same amount of recrystallization to occur when 0.03 wt. % Nb has been added, a 50 % reduction is required at 925°C.

These HSLA steels are produced to mechanical property specifications, e.g. 950A sheet and strip has specifications of a yield strength of 50 KSI(345 MPa) and a tensile strength of 70 KSI (483 MPa). The actual contents of Nb etc. are not specified. The yield and ultimate strengths of the high strength low alloy steels range from 40 to 80 KSI and 60 to 95 KSI respectively. Typically the steels contain 0.25 wt. % or less of carbon and 1 to 1.65 wt. % Mn. The Mn helps to control any sulfur and provides solid solution strengthening.

Leslie points out an interesting fact in his book. The use of small additions of Nb to carbon steel in order to strengthen the ferrite was patented in 1936. But it was just a scientific curiosity then because of the cost of Nb and, more importantly, because there was no real commercial demand for such steels. 20 or so years later the price of Nb dropped and also the need for pipe line steel appeared. Economics drove the renewal of interest. The buck demands respect!

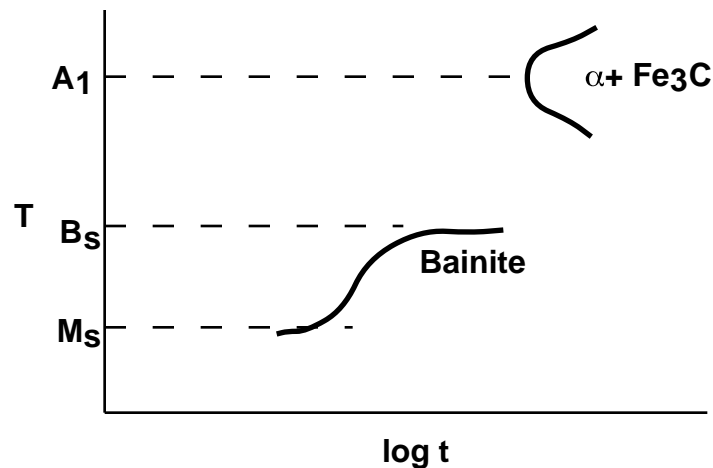
2) In method 1) described above we concentrated on producing grain refinement in the final rolled product.

What other microstructural characteristics could contribute? An additional way of strengthening ferrite is to increase its dislocation density. How might we accomplish that without cold work? Previously, when we considered the microstructural characteristics of ferrite we noted that equiaxed ferrite forms in slowly cooled austenite. This morphology indicates that the ferrite forms at relatively high temperatures while the steel is being cooled. When this occurs, the dislocation density within the grains is of the order of  $10^8$  cms/cm<sup>-3</sup>, which is not particularly high from the point of view of strengthening. However, if we contrive to make the ferrite form at low

temperatures, then the ferrite morphology changes from equiaxed grains to acicular grains and, because the ferrite is not exposed to the higher temperatures during cooling, recovery processes are suppressed. Such acicular ferrite can contain a dislocation density as high as  $10^{10}$  cms per  $\text{cm}^3$ . Acicular ferrite can be made to form by cooling the steel rapidly. However, it is more desirable to avoid this necessity and to arrange for the acicular ferrite to form during air cooling.

For this to happen, the ferrite formation has to be retarded. This can be done economically by adding Mn and Mo. An example is : C 0.08 %, Mn 2.18 %, Si .1 %, Mo 0.38 %, Nb 0.07 %, Al 0.02 % and N 0.007 % (this composition is in wt. %). These alloy additions refine the austenitic grain size and also cause the beginning of the transformation to be retarded because the ferrite start curve on the TTT diagram is displaced to longer times. Therefore, the austenite decomposes at lower temperatures as it cools, yielding fine grained, acicular ferrite and a greater dislocation density. It turns out that the ferrite is often then supersaturated with respect to Nb so that precipitation can occur if the steel is reheated. An interesting discovery that was made when these dislocated acicular ferrites were produced, was that the yield point phenomenon disappeared. Instead, the steel began to yield gradually with a rounded stress strain curve and then work hardened rapidly. This suggests that the microstructure produced in this manner, contains a significant population of mobile dislocations. For steels of the composition above, yield can occur at 70 KSI in samples in the hot rolled, air cooled, condition. For comparison, the lower flow stress in a 0.08 % C plain carbon steel is about 25 to 30 KSI.

A logical extension of the acicular ferrite case is to arrange to produce low carbon bainite. To do so, Mo and B are introduced to form a bay in the TTT diagram; the carbon level is raised to increase the strength and Nb is added to control the austenitic grain size. The result is to separate the ferrite and pearlite curves from the bainite curves so that the transformation to bainite is easily achieved, as is clear from the TTT diagram sketched below. Such steels can yield in the range 65-120 KSI.



In summary, HSLA steels are low carbon steels with various combinations of small (micro-alloying) additions of Nb, V, Ti, Mo, and B. They have increased in popularity during the last quarter of a century. However, versions of such steels existed before, where the strength was provided by solution strengthening and solute clustering. USS Corten steel has the composition:

2. % C, 0.35 % Mn, 0.5 % Si, 0.4 % Cu, 0.1 % P and 0.8 % Cr. One of the principal reasons that it has been used is that it is an example of a weathering steel in which the combination of the Cu and P affects the rusting process so as to produce a tightly adherent, reddish patina that protects the steel and, so some people claim, looks pretty.

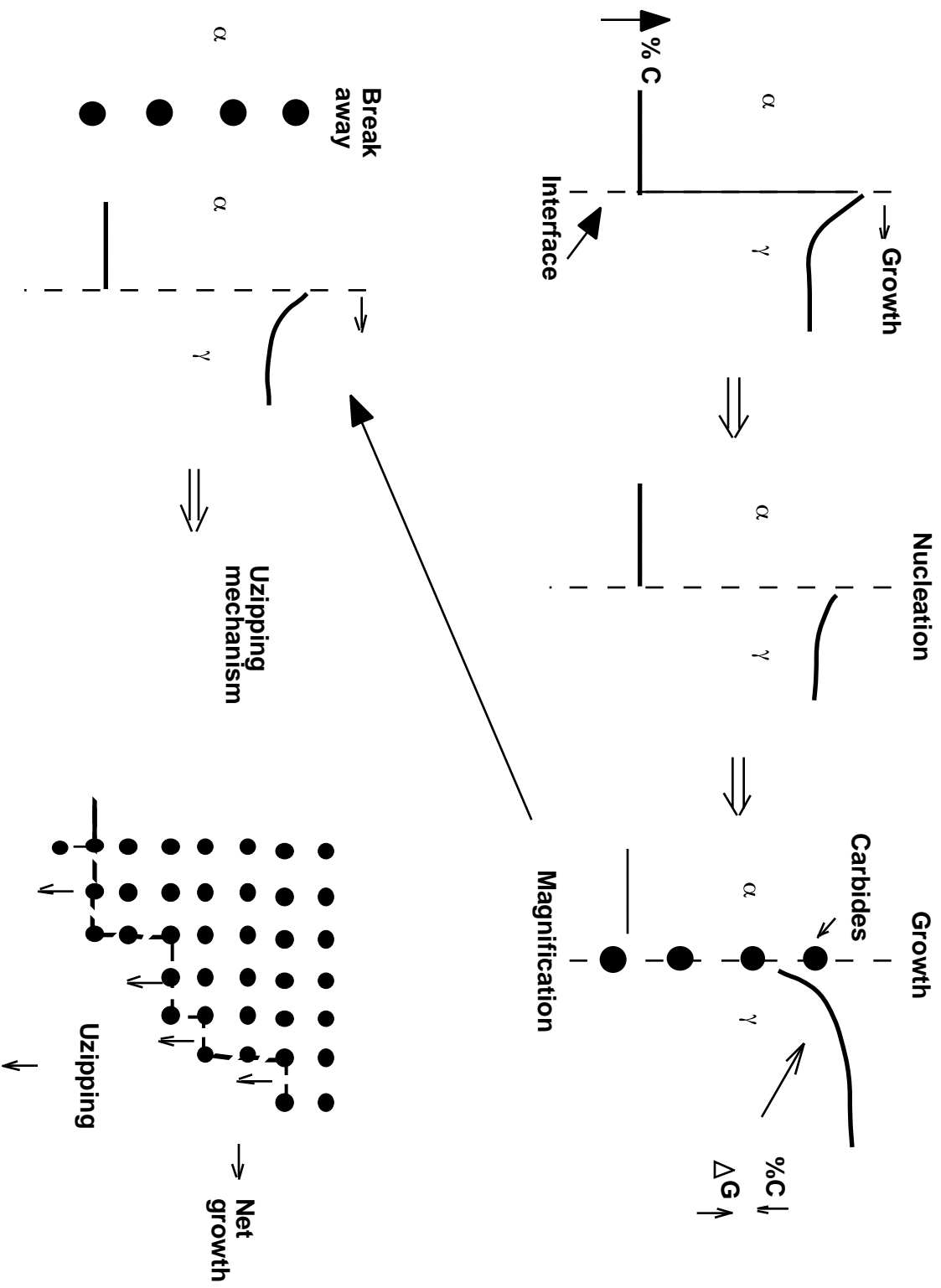
### 3) Precipitation Hardening.

Grain refinement is a very desirable way of strengthening these types of steel because this also improves toughness. Often precipitation hardening is used in addition. In order for precipitates to be effective obstacles to dislocation motion, they must be closely spaced. This means that the precipitates used for refining the ferrite grain size are of little use for precipitation strengthening, because they are large and their spacing scales with the grain size. This is fine for anti-recrystallization purposes because the scale of the microstructure is larger but finer spacings are necessary for additional strengthening due to precipitation hardening. How can we bring this about? One obvious approach is to seek additional alloying elements that will be retained initially in solid solution in the ferrite and then enable a distribution of fine precipitates to be produced by aging. Copper additions such as those in Corten steel can do this. We will consider another type of reaction first, however, because it turns out that the solubility of the niobium and vanadium carbides are greater in austenite than in ferrite. Thus if the matrix composition of the austenite in which the grain refining precipitates have formed is inherited by the ferrite, then the ferrite is supersaturated and another population of fine precipitates can occur as ferrite forms or as it is aged. This occurs more readily for vanadium additions than for niobium.

An interesting mode of precipitation occurs in these alloys. It has been observed in other alloy systems since its was discovered in HSLA steels. It is called interphase precipitation. Its major characteristics are that the precipitation occurs on the interface between the ferrite and the austenite and the final morphology is regularly spaced sheets of small particles within the ferrite. Very small particles, of the order of 5 NM, can form in closely, spaced arrays that are effective strengtheners.

The precipitation mechanism begins after a ferrite grain has nucleated in the steel as it is cooling from the rolling process. Heterogeneous nucleation of the carbide phase then occurs along the austenite/ferrite interphase boundary. The particles of carbide e.g. VC, pin the boundary which stops migrating, and then the carbides grow. As they grow they deplete the carbon concentration in the austenite at the interface. When the concentration drops as indicated in the sketches, the driving force for forming ferrite is increased. Eventually it becomes large enough to overcome the restraint of the precipitates on austenite/ferrite interface and allow the ferrite to grow.. Then, as the interface advances, the carbon gradient ahead of it builds up again until nucleation of the carbides can occur again and the process repeats itself. The observations of the phenomenon suggest that the boundary "un-zips" from the sheets of precipitates so that its forward migration is actually accomplished by the sideways movement of boundary ledges.





The fact that copper rich precipitates can form in copper bearing steels was mentioned at the beginning of this section. In the early Seventies there was a great deal of interest in the nature of the precipitation of copper from iron and low carbon steel primarily because of fundamental aspects of phase transformations. There has been continued interest, however, as copper bearing HSLA steels have been further refined. Alloys have been developed which have very low carbon content, over 1 wt. % Cu for precipitation hardening, additions of substitutional elements such as Mn, Ni, Mo and Cr for hardenability along with Nb, Al and N for grain size control. An example is A710 which is described in the 1995 ASTM book of standards. A particular example of this group is HSLA-80 which is so designated by the US navy for ship building. It is appropriate to end the section by returning to this topic to consult recent work.

An example of HSLA-80 is: 0.05 wt. % C, 0.5 wt. % Mn, 0.009 wt. % P, 0.002 wt.% S, 0.28 wt. % Si, 1.12 wt. % Cu, 0.88 wt. % Ni, 0.71 wt. % Cr, 0.2 wt. % Mo, 0.035 wt. % Nb, 0.02 wt.% Al, 0.009 wt. % N. A typical A710 is very similar. Detailed studies of the phase transformations in these alloys both during continuous cooling and during isothermal aging have been described recently by S. W. Thompson, D. J. Colvin and G. Krauss, *Met. & Mat. Trans.* 27 A, 1557 (1996) and S. W. Thompson and G. Krauss *ibid.* page 1573.

Inspection of the compositions of the steels shows that austenitic grain size control is effected by the niobium, aluminum, nitrogen and carbon. The S and P contents are low to minimize undesirable effects due to inclusions and segregation. Leaving aside consideration of the copper for the moment, inspection of the remainder of the composition leads one to conclude that these alloying elements will be in solid solution. It would be reasonable to predict that if the austenite is cooled sufficiently slowly, the austenite to ferrite transformation should produce predominantly relatively equiaxed grains with normal dislocation content. This is so in practice. These authors refer to this microstructure as polygonal ferrite. However, they also observe that even with this low a carbon content, small pockets of austenite become enriched in carbon and transform to upper and lower bainite and martensite. More rapid cooling reduces the amount of polygonal ferrite and increases the amounts of Widmanstätten ferrite side-plates and acicular ferrite. These authors also observe small equiaxed ferrite crystals which they call granular ferrite. Some martensite associated with a little retained austenite can form although the bainitic transformation is suppressed. Their results enabled them to present a continuous cooling diagram. The complexities of the microstructural characteristics are impressive, but the ingredients for good properties are there; fine ferrite grain size, acicular, dislocated ferrite etc. Let us now turn to the precipitation reactions.

It was discovered many years ago that supersaturated binary alloys of Cu in BCC Fe could be obtained by solution treating and quenching. Isothermal aging of the metastable solid solutions caused precipitation of copper. Initially, metastable BCC copper precipitates appear within the ferrite, presumably because they match the ferrite structurally and can form coherently which is favorable for nucleation. These precipitates grow to about 4 NM and transform in-situ to the FCC structure. In the HSLA alloys under discussion, the copper is in solution when the steel is austenitic. If the austenite is rapidly quenched so as to form martensite, the degree of tetragonality is small because of the small amount of carbon in solution and the copper is essentially in solution in a BCC host. Thompson and Krauss show that when the quenched steel is aged at 455, 565 and 675°C FCC copper precipitates form. They also show, as previous work had indicated, that copper precipitation can also take place during slower cooling treatments. Previous work had indicated that

## HEAT TREATMENTS TO PRODUCE PERRITE AND PEARLITE

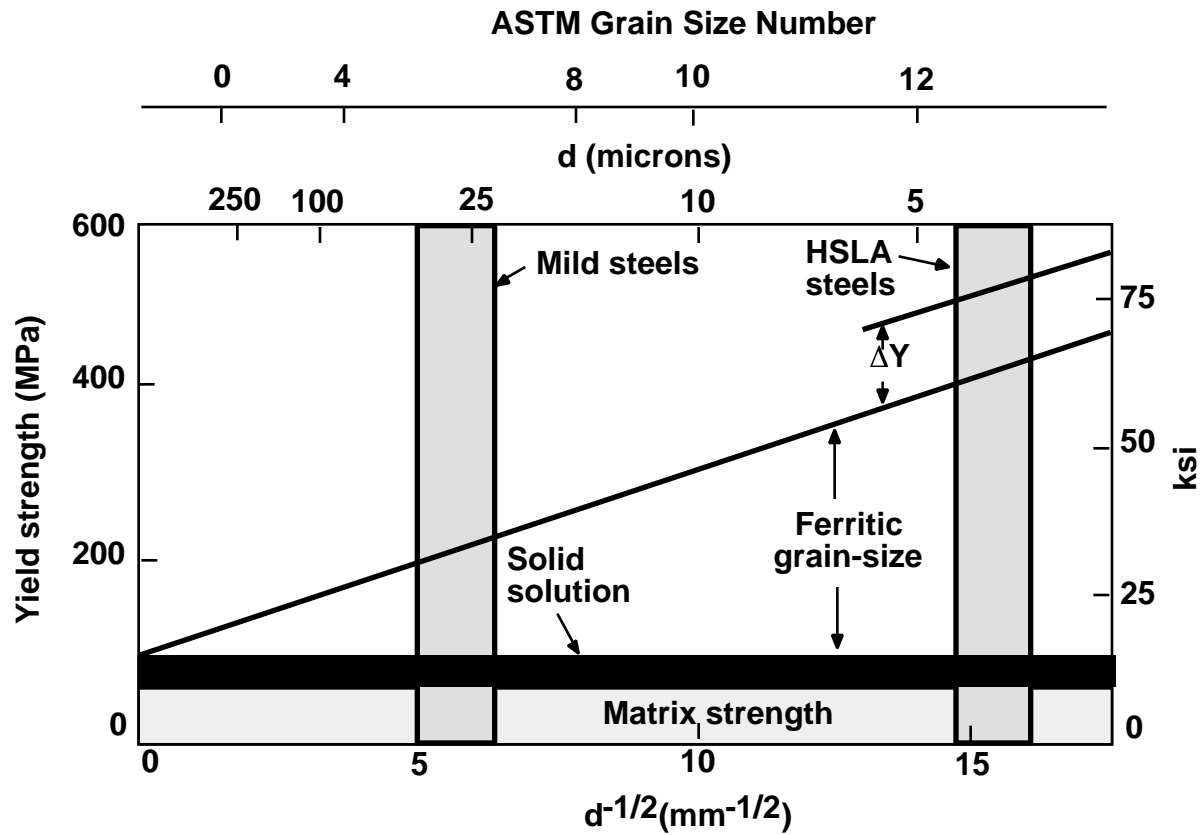


Fig. 5.24. Yield strength as a function of grain size in low-carbon steels. Contributions of various other strengthening mechanisms are indicated. (Ref 5.30)

From: Krauss, p.137

the copper precipitation in appropriately cooled austenite began near 675°C. Accordingly Thompson and Krauss compared the morphology of the copper precipitates produced during isothermal aging at 675°C with their morphologies when formed during continuous cooling experiments. The results showed that the precipitates produced in the isothermal aging experiments were predominantly located at dislocations, indicating that in these materials, precipitation from a supersaturated single phase at this temperature was nucleated heterogeneously. In contrast, detailed transmission microscopic studies established that when the copper precipitated during continuous cooling of the austenite, the dominant mode of precipitation was interphase precipitation at interphase boundaries between ferrite and austenite. There is a useful consequence of this. The precipitates are not restricted to be located at dislocations in the ferrite and may form in successive finely spaced lines of precipitates that are effective at precipitation strengthening.

### Interstitial Free Steel

Now that we have discussed HSLA steels which have low carbon contents, it is an appropriate time to mention interstitial free steel. These are steels in which the concentrations of interstitially dissolved solute elements are very small. This is accomplished by the dual processes of taking care to reduce the carbon and nitrogen levels during the manufacture of the steel and by scavenging these elements from solid solution by adding small quantities of niobium, aluminum and titanium. One of the original reasons for producing such steel was that it was discovered that reducing the carbon concentration improved the quality of enamel coatings. The formability is also improved. Today, interstitial free (IF) steels represent the state of the art for sheet steels which have exceptionally good deep drawing properties. The properties of the final product are determined by the chemistry of the steel and the particular thermo mechanical history. These two determine the nature of the ferrite and the nature of the second phase particles present. An example of such a steel is discussed by Rauf and Boyd in “Microstructural Evolution During Thermo Mechanical Processing of a Ti-Nb Interstitial-Free Steel Just Below the  $A_{T3}$  Temperature” Met. Trans. 28A,1437, 1997.

The steel that they describe had the following composition in wt. %: C 0.0038, N 0.003, S 0.006, P 0.006, Mn 0.17, Si 0.008, Ti 0.018, Ni 0.019, Al 0.043. Note that it is very rich in iron but is still called a steel. Perhaps now is a good time to re-read the section from the first page that followed the question “What, then, is a steel?” The final microstructures comprised ferrite grains in which there was a dispersion of a variety of fine particles of nitrides, sulfides and carbides. The nature of the ferrite matrix depends upon the characteristics of the austenite at the end of the hot rolling process and the manner in which it is cooled. As we should expect, the basic behavior is essentially that which was described for iron on pages 8 and 9. Equiaxed ferrite forms when the cooling rates permit the ferrite to form at high temperatures. In the language of IF steel such ferrite is called polygonal ferrite. Increasing the cooling rate eventually suppresses the polygonal ferrite because the austenite then transforms by the massive transformation that creates the characteristic blocky, massive grains.

This is another example of a class of steels that has been developed with the object of tailoring certain desirable properties for particular applications. Steel sheet is commonly formed into complicated shapes for use in a variety of applications, as in the automobile industry for example. Good formability and high strength are desirable for production reasons and for weight reduction so as to economize on fuel use by the final product. A summary of desirable properties is:

- high ultimate tensile strength for a good strength to weight ratio;
- no yield point phenomenon because that can cause non-uniform strains during the forming process;
- a low initial yield strength, a rapid work hardening rate and a high ratio of the ultimate tensile strength to the initial yield strength.

These properties give rise to uniform straining, eliminate or minimize the occurrence of plastic instabilities and produce high yield strength in the deformed regions of the final part because of strain hardening.

If we consider these properties with respect to the behavior of plain carbon ferrite /pearlite sheet we note that this material has some shortcomings. Slowly cooled, hot rolled, low carbon, plain carbon steel sheet usually deforms via upper and lower yield points followed by Luders band propagation. This causes non uniform straining and localized thinning during forming. Because the Luders extension is localized, the plastic strain rate within the band is high which causes the flow stress to be relatively high. This reduces the magnitude of the ratio of the ultimate tensile strength to the lower yield stress. When the necessary strength levels of the steel sheet require the presence of significant volume fractions of pearlite colonies, difficulties arise because of local failure mechanisms associated with the formation of cracks and pores in and adjacent to carbide lamellae.

What can be done then?

Question 1. How do we eliminate the yield point phenomenon?

a) Temper rolling. This is a process wherein the steel sheet is passed through rolls that bend it and re-flatten it in order to introduce fresh, unpinned dislocations which can then glide during forming and thus eliminate the upper yield point. This process has been used for years. The problem with it is that it uses up some of the available ductility before the forming process can properly begin and it tends to reduce the practical UTS/YS ratio.

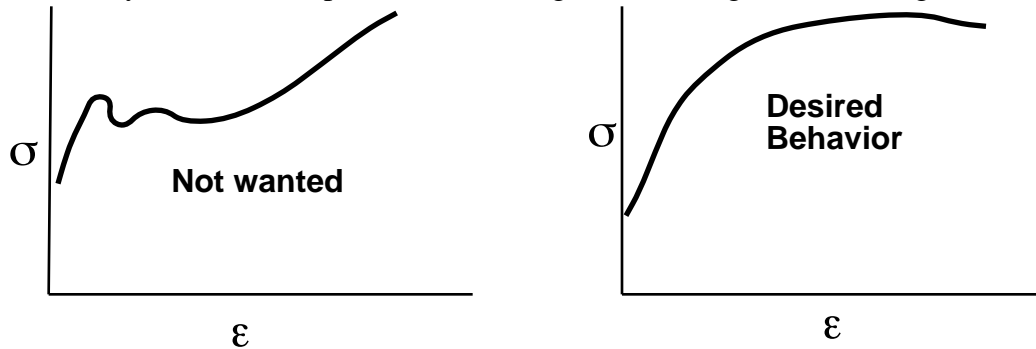
b) Because the yield point phenomenon is caused by carbon and nitrogen interstitial solutes, removing these elements from the steel would eliminate the problem. However, this would lower the strength and would not be a useful solution unless other modifications can be found to raise the flow stress and we've already considered high strength low alloy steels.

c) When the dislocations in ferrite are pinned by the interstitial solutes, the pinning forces are so strong that the dislocations cannot break away unless the local stress is very high. Thus we need some way to produce local stress concentrations within the steel. In essence, we need to be able to modify its microstructure so that either some clean dislocations exist in the as-produced material or to generate residual stress concentrations that can be superimposed upon the applied stresses so that slip is activated. These stress concentrations will have to be distributed throughout

the steel in order for them to cause macroscopically uniform plastic flow. This would be a fine solution if we can find a way to do it.

#### Question 2

Assuming that we will be able to solve question one we now have to ask question 2. How do we create a low yield stress, a rapid work hardening rate and a high tensile strength?



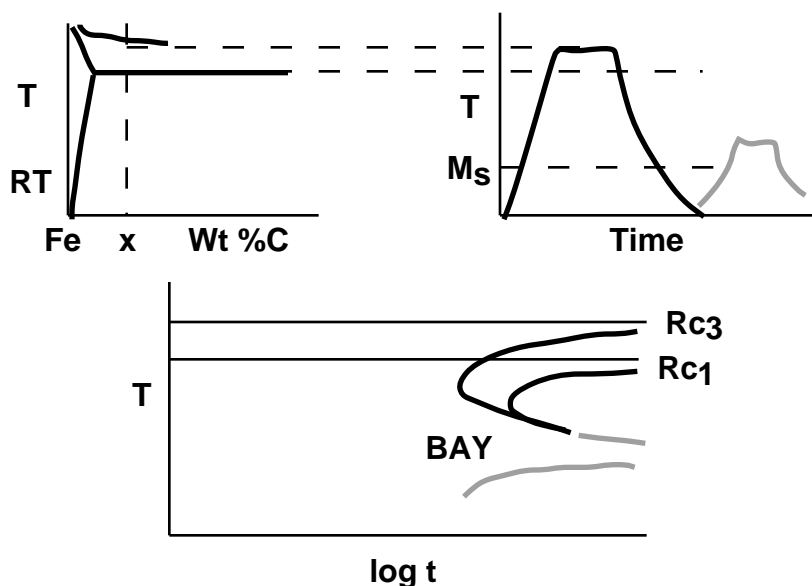
The first thought that comes to mind is that the dominant matrix phase should be ferrite because it is ductile above the DBTT. To obtain a high rate of work hardening during plastic deformation it is necessary to arrange for a rapid rate of increase in the dislocation density within the deforming grains. One way to lower the yield stress is to increase the grain size but that would adversely affect the ductility and lower the tensile strength. Fine grained ferrite is still desirable. A low applied stress for yield will arise if we can introduce residual stress concentrations that help to initiate slip. Thus we find that we find a single way to answer both questions. Because we want to accomplish all this during the production of the steel it makes sense to ask what can be done via the phase transformations that occur during heat treatments.

The production of ferrite/pearlite mixtures has already been ruled out. This leaves ferrite, bainite and martensite. Consider martensite. When some martensite forms in a steel which has a significant carbon content, it is hard and it generates localized strains around it due to its change in shape and volume. Such incompatibilities are generally disadvantageous in heat treatments designed to fully transform the steel because of the risk of the occurrence of distortion and quench-cracking. Now, however, we are searching for a way to produce residual stresses. If we can find a way to generate numerous small, separated, volumes of martensite dispersed throughout a ferritic microstructure we might have a solution our problem. The way to produce such a microstructure is first to produce a mixture of fine ferrite and austenite grains and then to quench it to convert the austenite to martensite. Thus the steel must be held in the  $\alpha/\gamma$  two phase field and then cooled such that the austenite transforms to martensite. If some more proeutectoid ferrite forms during the cooling it should have no particularly adverse effects; the formation of pearlite is undesirable. The final microstructure should then comprise a mixture of ferrite and martensite.

The general procedures described above have been successfully carried out. Because the product is a mixture of martensite and ferrite, the steels have been dubbed Dual Phase steels. A purist might complain that ferrite/pearlite steels also contain two phases- ferrite and cementite- and that a better name might be ferrimart or some such concoction. However, there we are.

In order to ensure that the martensitic or lower bainitic transformation does occur during natural cooling it is necessary to augment the hardenability. This can be done by adding Mn and Si. An example is 0.1 % C, 0.5 % -0.9% Si and 1 to 3 % Mn. In a typical process the sheet is passed through a continuous annealing furnace where it is heated into the alpha/ gamma range and then cooled again. Sometimes it is reheated to temper the martensite, but normally this is not done because it tends to anchor clean dislocations, reduce stress concentrations and lower the UTS which defeats the whole purpose. In some processes, the continuous annealing is preceded by cold rolling. In this case, the deformed ferrite recrystallizes during heating. With appropriate control of the rate of heating and the degree of cold work, a fine grained mixture of ferrite and austenite can be obtained. The time at the high temperature has to be short to retain these fine grains, so the austenite is inhomogeneous. Typically the aim is to produce about 15 to 20 % austenite.

Another production method is to finish the hot rolling stage so that 80 to 90 % ferrite forms and to allow the remaining austenite to transform later while the steel is being formed into a coil. For this to be successful, the steel must have suitable continuous cooling transformation characteristics. Alloying to produce a bay in the TTT diagram, creates a window so that the metastable austenite can be coiled before the martensite or bainite begins to form e.g. 0.06 % C, 0.9 % Si, 1.2 % Mn, 0.6 % Cr and 0.4 % Mo. Note that these compositions are similar to some of those of HSLA steels so the properties of both are being combined.



#### Deformation Behavior and Microstructure

The general microstructural constituents that can be present in dual phase steel after production are: a fine-grained ferrite matrix in which there is a relatively low dislocation content because of the high temperature excursion; some proeutectoid ferrite that formed from the austenite during cooling and is therefore more dislocated than the other ferrite; martensite or lower bainite whose microstructures depend upon the carbon content and the  $M_s$  temperature. These martensitic and bainitic volumes are associated with residual stresses because of the transformation shape

changes. Typically, the steels also contain some retained austenite and finally, when V or Nb are present there can be carbonitride particles embedded within the matrix.

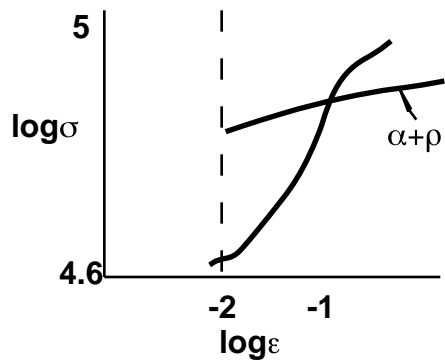
When these kinds of steels are deformed at room temperature, the precise behavior will depend on the microstructural details. Here, we consider the general types of behavior. The first objective to be satisfied by these steels is for them to yield smoothly and at low stresses. This is successfully achieved by the processing that has been described. Because the  $M_s$  temperatures for these steels are high, auto tempering should lock many of the dislocations generated during the transformation. The relative importance of residual stresses, stress concentrations and clean dislocations is not clear. It is clear, however, that the yield point phenomenon is absent. Consequently, the steel yields at relatively low stresses and work hardens rapidly. Initially, the plastic strain occurs in the ferrite that existed before cooling began because this is the softer ferrite due to its low dislocation content. When that ferrite has work hardened so that its flow stress is the same as the yield strength of the ferrite that formed during cooling, all the ferrite deforms. The retained austenite usually transforms to martensite early during the deformation. The associated shape change contributes to the dimensional strain occurring during the deformation and the transformation produces more of the hard phase. Electron microscopic studies have shown that eventually the martensite begins to deform and fracture. Voids open up at the martensite/ferrite interfaces and general failure ensues if the deformation is continued. The tensile strength varies approximately linearly with the % martensite or lower bainite. Typical results are 80 KSI for 10 % by volume rising to 110 KSI at 30 %. Elongations of about 20 % are obtained.

During the tensile deformation of ferrite/pearlite steels, the lower yield strength is typically 2/3 to 3/4 of the tensile strength. In contrast, the ratio in dual steels is 0.5-0.6. After the Luders extension is completed the stress strain curve for ferrite/pearlite steels can be quite well described by the equation

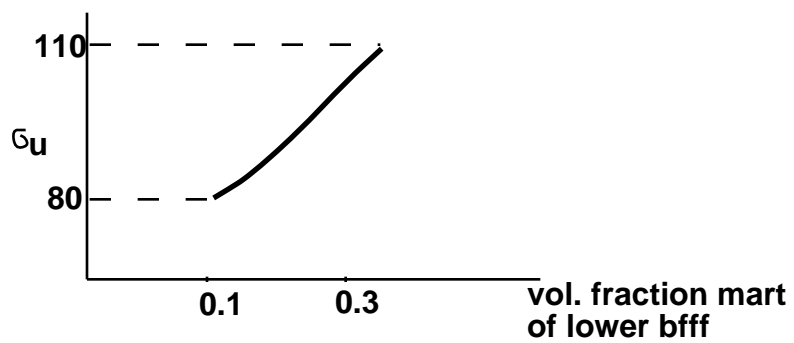
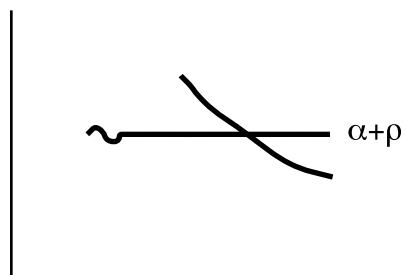
$$\sigma = K\epsilon^n$$

where  $K$  is a constant and  $n$  is called the strain exponent. The equation relates the true stress to the true strain. By taking logarithms of both sides, we see that this equation predicts a linear relation between  $\log \sigma$  and  $\log \epsilon$  with a slope  $n$ . This linear relationship is frequently, well obeyed as is shown by the curves marked alpha/P in the following sketches. Dual phase steels do not obey this kind of equation. Examples of the behavior that has been observed are shown, schematically in the sketches by the unlabeled lines.





$$\frac{d(\log \sigma)}{d(\log \epsilon)} = n$$

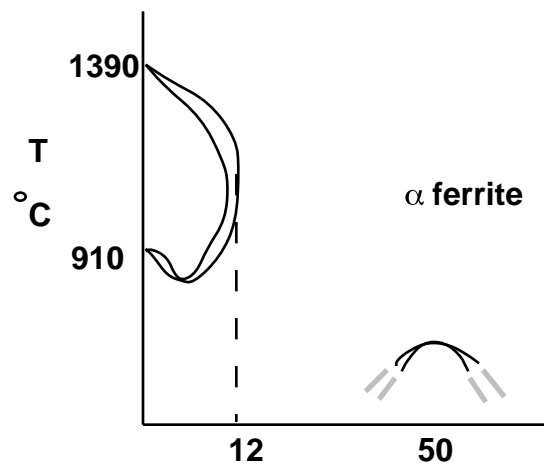


## Wrought Stainless Steels

Iron is not mined in its elemental form. It is extracted from ores in which it exists mainly combined with oxygen in oxides. After being extracted it is then used to manufacture steels. All the steels that we have considered so far are generally subject to degradation by forming oxides and hydroxides, either by oxidation when heated or by corrosion unless protected from environments that contain water and oxygen. Hence, once made and put into use in steels, iron attempts to return to its former state by forming rust or scale. Usually, with the occasional exception such as weathering steels, the corrosion product is not effective protection for the steel below it. Consequently the steel continues to rust as time passes. Oxidation occurs readily when carbon steel is heated. The oxide scale spalls off and oxidation continues as long as the steel is hot. This behavior along with other corrosion processes such as dissolution in dilute acids, imposes obvious limitations on the use of carbon and low alloy steels.

Many methods of combating rusting and corrosion have been and are still being used. These include protective coatings such as paint, plastic and tin that are intended to isolate the steel from the corrosive agent, sacrificial coatings such as zinc that corrodes preferentially, and the application of electrical potentials designed to provide protection by inhibiting the electrochemical reactions. Alloying elements such as silicon, molybdenum and copper are helpful for increasing lifetimes at ambient temperatures; weathering steels have already been mentioned. As the effects of alloying additions on the properties of steels became increasingly understood, it was discovered that Cr dramatically improves the corrosion and oxidation resistance of steel. Cr oxidizes and forms a thin, transparent, tightly adherent layer of oxide on the surface of the steel that prevents or minimizes further corrosion. Steels to which sufficient Cr has been added for this purpose, form the family of steels called stainless steels. The tonnage of stainless steels used annually is only a small fraction of that of carbon and low alloy steels. Its range of specialized uses, however, is very wide, spanning from knives and forks through brewing to aerospace applications.

According to the US steel Co. handbook, the AISI has defined a steel to be stainless if it contains more than 4 wt. % Cr. Most standard types, however, contain rather more chromium than four % so, for our purposes, we will consider stainless steels to be steels that contain at least 11.5 wt. % Cr. They are further classified by being divided into four main groups, viz. martensitic, ferritic, austenitic and precipitation-hardening stainless steels. The fourth group contains stainless steels in which strengthening is provided by precipitates of a second phase. There are minor classifications such as duplex stainless steels which contain significant quantities of both austenite

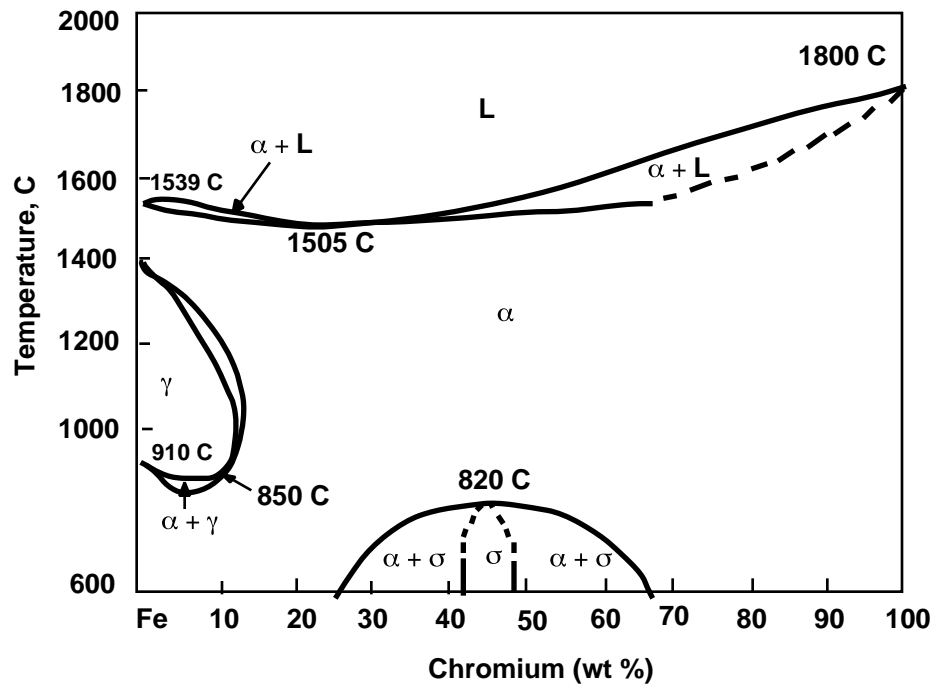


and ferrite. The four main types of stainless steel are further identified by a mixture of numerical and letter codes, see for example the ASM handbook, edition 9, volume 3.

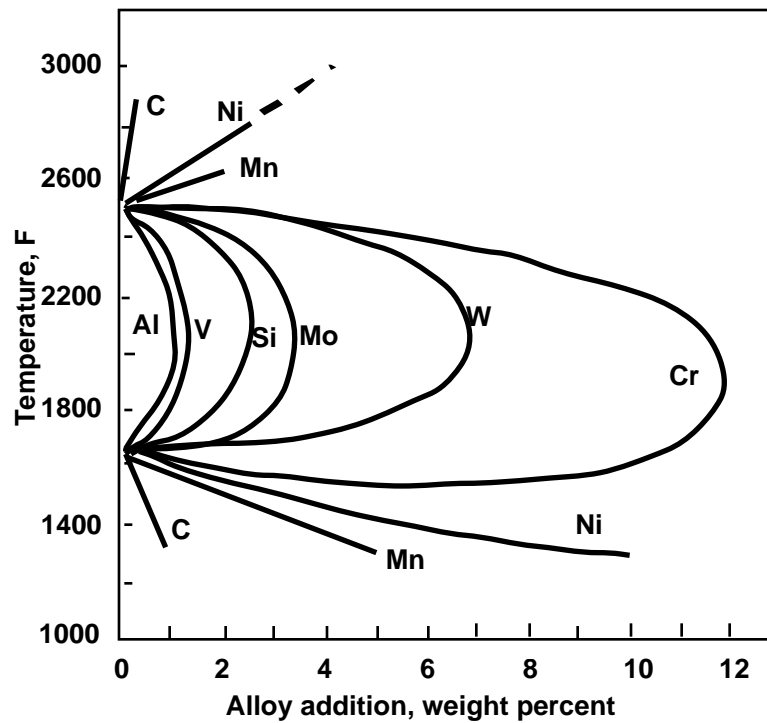
Because the most important alloying element in stainless steel is Cr, it is logical to begin a discussion of the physical metallurgy of these materials with a consideration of the binary Fe-Cr system.

As the binary phase diagram shows, the introduction of the ferrite stabilizing Cr forms a gamma loop in which resides those combinations of temperature and composition for which austenite is the stable phase.

After: Honeycombe, p251



After: Krauss, p353



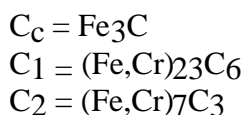
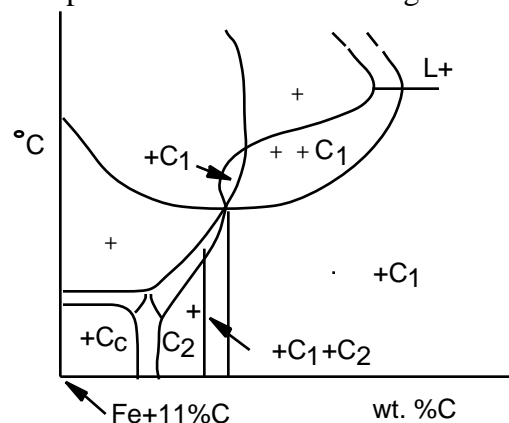
( Gamma loops formed in various binary systems of iron. )

This phase field is separated from the ferrite phase field by the two phase field. When the Cr content exceeds 12%, it is possible for ferrite to exist at all temperatures at which the binary alloys are solid. The binary system also contains the intermetallic, Fe-Cr, sigma phase. This is tetragonal and has a unit cell that contains 30 atoms. This phase diagram shows that for some compositions, the solid solutions of the alloy can be transformed into austenite by heating them into the gamma loop. It also shows that when the austenite is cooled it must transform to ferrite to attain equilibrium. We infer from this that if the cooling process is conducted in a manner that precludes this transformation from occurring by diffusion controlled nucleation and growth processes then a martensitic transformation is possible. Hence, the existence of martensitic stainless steels.

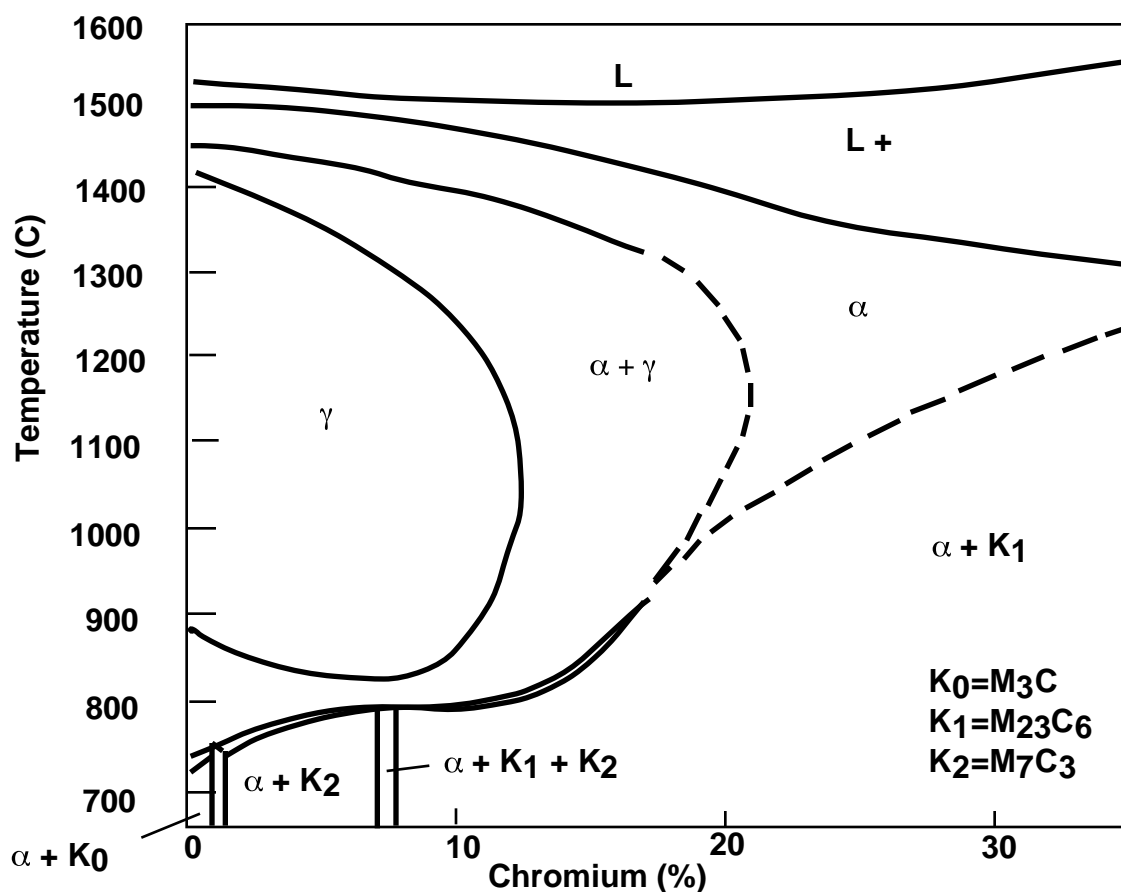
### Martensitic Stainless Steels.

Martensitic stainless steels are used in the quenched and tempered condition. The term quenched is somewhat of a misnomer because with such large alloying element contents parts made from these steels are often air-hardenable, i.e. the martensite forms when the part is removed from the austenitizing furnace and simply allowed to cool down in still air. Quenching in oil is sometimes used for thick sections. In either case, tempering is performed soon after the martensite has formed, especially when there is significant carbon present, in order to avoid delayed cracking. The binary Fe-Cr diagram indicates the compositional limits of those alloys that can be rendered into martensite. Because the Cr is to be kept as high as possible for anti-corrosion purposes, austenite stabilizers such as carbon, manganese and also nickel are added to expand the austenite phase field. These additions enable martensite to be produced in 11.5 wt. % Cr steels. As was true for the martensitic steels considered previously, the carbon dissolved in the martensite has a significant effect on its hardness.

When the carbon content becomes significant, the formation of chromium carbides becomes possible and the pertinent phase diagram becomes the ternary Fe-Cr-C diagram. An example of a section at 0.1 wt. % C is shown below. The complexity is obvious. Two important additional things can be recognized. First, a variety of chromium carbides can form. Also, certain heat treatments can form mixtures of ferrite and austenite in which cooling could convert the austenite to martensite. Thus we can have fully martensitic microstructures and ferrite/martensite microstructures. This implies that the classification of a particular steel as martensitic or ferritic cannot be done solely on composition but must also recognize the microstructure existing during use.

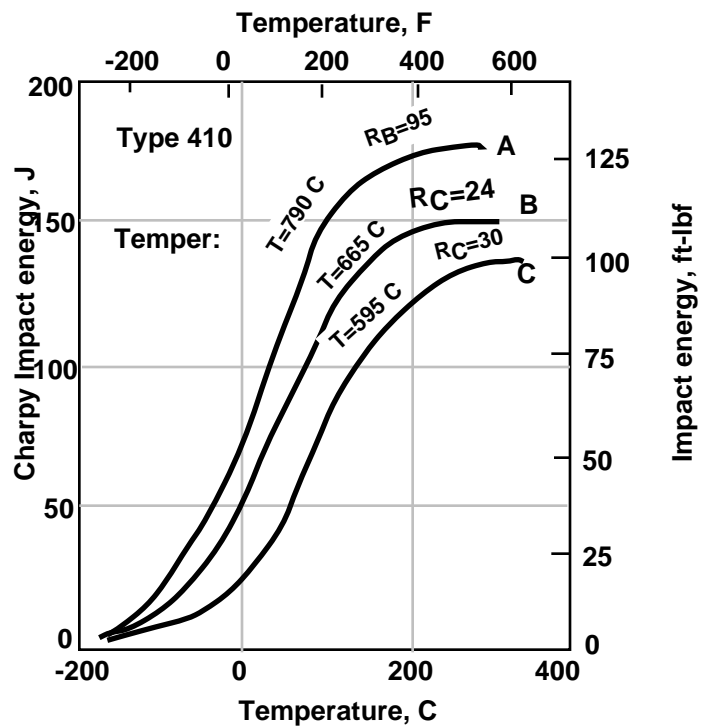
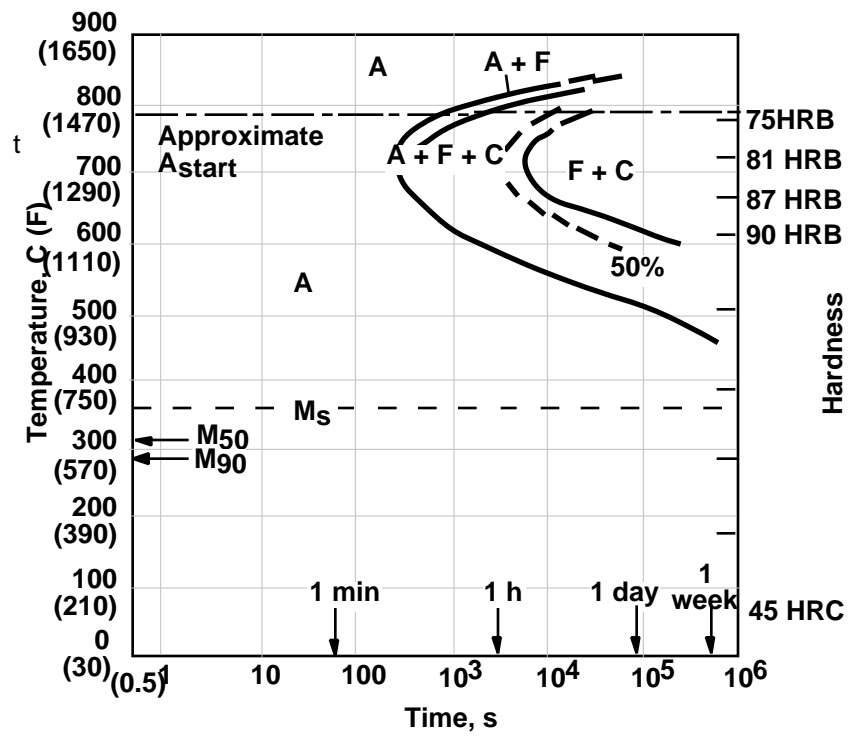


After: Honeycombe, p252

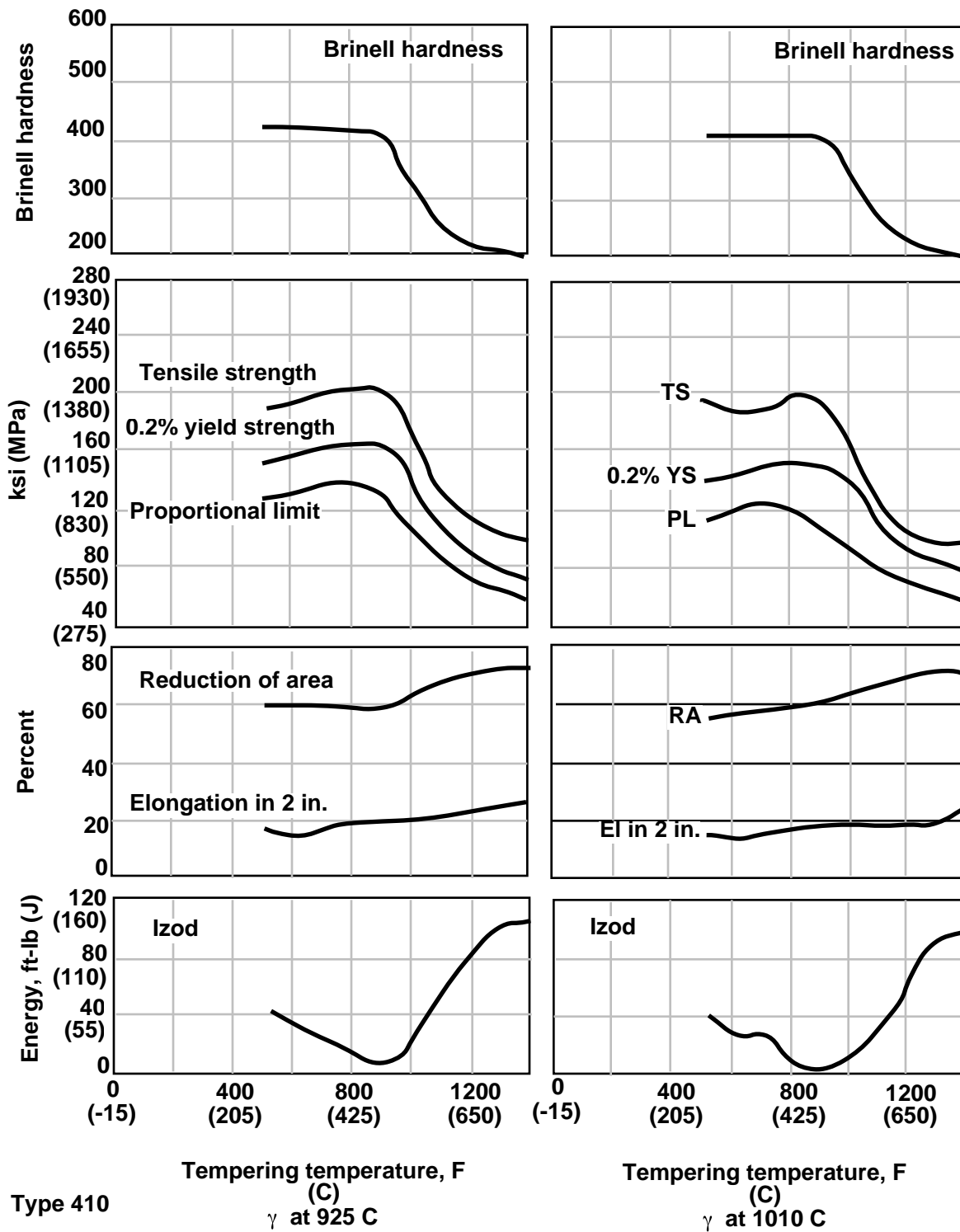


Compositions of AISI Type 400 Martensitic Stainless Steels.					
AISI	-----Nominal composition, %-----				
type no.	C	Mn	Cr	Ni	Others
403	0.15 max	1.0	11.5-13		
410	0.15 max	1.0	11.5-13		
416	0.15 max	1.2	12-14	...	0.15S min
420	0.15 min	1.0	12-14		
431	0.20 max	1.0	15-17	1.2-2.5	
440A	0.60-0.75	1.0	16-18	...	0.75 Mo max
440B	0.75-0.95	1.0	16-18	...	0.75 Mo max
440C	0.95-1.20	1.0	16-18	...	0.75 Mo max
Body-centered cubic, magnetic, heat treatable					

After: Krauss: p381



After: ASM-stainless steels, p17,39



After: ASM--Stainless steels, p18

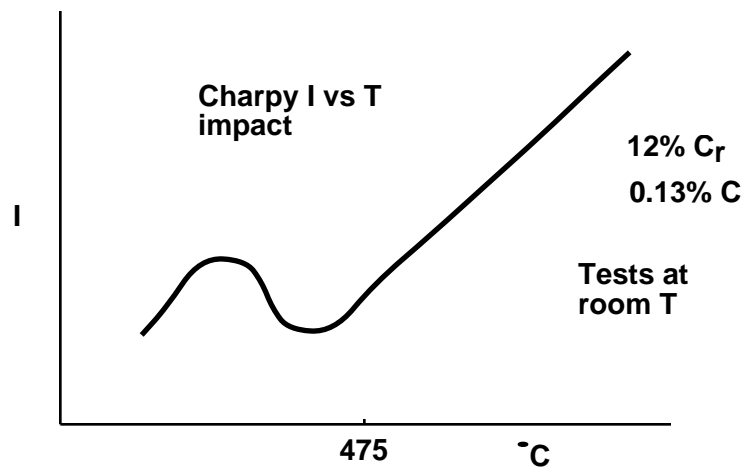
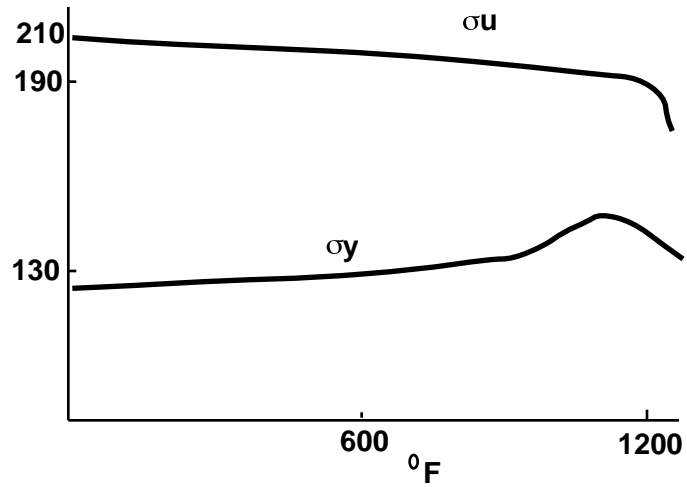
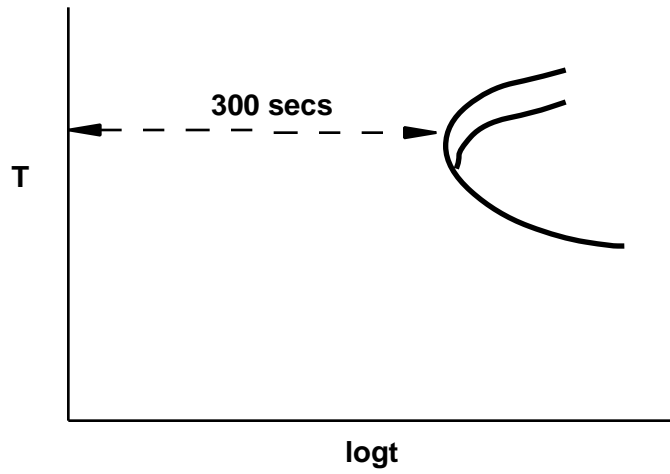
The martensitic steels are given 4xx numbers in the AISI numbering system. An example is 410 which has 0.15 % C, 1% Mn, 1 % Si, 11.5-13.5 % Cr. However, the ferritic steels which as we will soon see are mainly ferrite, are also described with 4xx numbers. 430 designates a ferritic steel while 431 refers to a martensitic steel. It is not, therefore, immediately obvious that a 4xx steel is martensitic or ferritic.

Let us consider the main roles of alloying elements in martensitic stainless steels with respect to properties other than corrosion resistance.

- a) The extent of the austenite phase field is usually controlled by the competition between the austenite stabilizers, Mn, C, N and Ni and the ferrite stabilizer Cr.
- b) During the decomposition of the austenite by diffusion controlled processes, the high concentration of Cr strongly retards the transformations and moves the nose of the TTT diagram to the right, increasing the time for the start of the transformations to over 300 seconds. This endows the steels with high hardenability. Indeed, many sections are air-hardenable. Another consequence of the sluggish rates of the diffusion controlled transformations is that martempering processes are readily conducted.
- c) The carbon endows the martensite with hardness and strength. The Cr contributes additional hardening.
- d) In a similar manner to its effects on the diffusion controlled reactions involved in the transformation of austenite, Cr strongly retards the rates of the processes that occur during tempering. One consequence of this is that stress relief can occur and residual stresses can be removed during tempering, before serious softening takes place. This is obviously of practical use.

The tensile yield stress and the tensile ultimate stress for samples of a 12 % Cr 0.1% C steel are depicted as a function of tempering temperature in one of the following sketches. It shows that secondary hardening due to the precipitation of chromium carbides can occur. The tempering temperatures were one hour in each case. These are fine properties and some enhancement is possible through additional alloying. Unfortunately, tempering in the vicinity of 885 °F (475°C), which corresponds to the initiation of the mild secondary hardening peak, produces hardening but reduces the impact toughness severely as is shown in the corresponding sketch. This embrittlement appears to be related to the beginning of the secondary hardening process in which sheets of carbides precipitate on boundaries. Besides this embrittlement problem, the DBTT's of these steels are around or barely below room temperature which means that they are not useful in cryogenic applications.





## Ferritic Stainless Steels

In the classical sense, ferritic stainless steels have been considered to be those that possess Cr contents that would place them to the right of the gamma loop on the binary Fe Cr phase diagram. The binary alloys of that composition would, indeed, be ferritic to the melting point. However, this ignores the effects of carbon and, as the Fe Cr 0.1 C diagram shows, mixtures of austenite and ferrite can form in these steels at high temperatures. Because of the high hardenability, the austenite can transform to martensite during cooling. Most of the commonly designated ferritic steels can behave in this manner, particularly those containing 17-18 % Cr. From the practical point of view, a better definition of a ferritic stainless steel is a steel that contains more than 12 % Cr and is used in a state in which its microstructure is mainly ferrite plus carbides.

Ferritic stainless steels have very good corrosion resistance in many environments. However, their mechanical properties are not very good. Being BCC they have a DBTT. In the common cases where the steel contains N, P, S and C, the DBTT can be higher than room temperature. AISI 446 (27 % Cr) has a DBTT around 150°C. Very pure steels have much better toughness but most normal, commercial alloys have a transition temperature near room temperature. Furthermore, because the grain size cannot be refined by heat treatment, large grains produced in the heat affected zones at welds can reduce the local strength. For these reasons, ferritic stainless steels have not been very popular for structural applications. An exception is 405 (11.5-14.5 % Cr, 0.08 % C, 1 % Mn, 1 % Si, 0.04 % P, 0.03 % S, 0.1-0.3 % Al) has been used in the petroleum industry.

The inherent problems of the BCC structure and irreversible grain coarsening are exacerbated by the existence of three forms of embrittlement that can arise during particular heat treatments.

### Sigma phase embrittlement

When ferritic stainless steels are aged for very long times between 540-750°C the sigma intermetallic phase is precipitated and the steel becomes brittle. The embrittlement is removed by heating the steel above 800 °C where the sigma phase is dissolved. This remedy is of little use if the heat treatment cannot be done. Fortunately, the kinetics of the precipitation process is very slow; several hundred hours are necessary for the embrittlement to occur. Hence it doesn't happen during the usual times of cooling or welding. It is important if the component is intended to operate in the relevant temperature range.

### 475 °C or 885 °F embrittlement

This is a loss of impact toughness that can be caused by holding the steel at temperatures between 400°C and 540 °C . The embrittlement is associated with the precipitation of a coherent chromium-rich phase throughout the grains. It can be cured by reheating the steel above 800 °C and cooling. Quenching is unnecessary because this form of embrittlement requires long times to form.

### High temperature embrittlement

When ferritic steels containing the usual contents of C, N, P and S are heated above 1000 °C and then cooled naturally as for example during welding, they can become severely embrittled and also lose their corrosion resistance near grain boundaries. The phenomenon is similar to sensitization in austenitic steels( to be considered later) and is considered to be caused by precipitation of Cr carbides and nitrides on grain boundaries.

**Compositions of AISI Type 400 Ferritic Stainless Steels.**

AISI	Nominal Composition, %			
type no.	C	Mn	Cr	Others
430.....	0.08 max	1	16.0-18.0	
430F.....	0.12 max	1.25	16.0-18.0	0.6Mo max
430F Se.....	0.12 max	1.25	16.0-18.0	0.15Se min
446.....	0.20 max	1.5	23.0-27.0	0.25N max
Body-centered cubic, magnetic, not heat treatable				

**Compositions of AISI Type 200 Austenitic Stainless Steels.**

AISI	Nominal Composition, %			
type no.	C	Mn	Cr	Others
201.....	0.15 max	7.5	16-18	
202.....	0.15 max	10.0	17-19	0.6Mo max
Face-centered cubic, nonmagnetic, not heat treatable				

**Compositions of Selected AISI Type 300 Austenitic Stainless Steels.**

AISI	Nominal Composition, %				
type no.	C	Mn	Cr	Ni	Others
301	0.15 max	2.0	16-18	6.0-8.0	
302	0.15 max	2.0	17-19	8.0-10	
304	0.08 max	2.0	18-20	8.0-12	
304L	0.03 max	2.0	18-20	8.0-12	
309	0.20 max	2.0	22-24	12-15	
310	0.25 max	2.0	24-26	19-22	
316	0.08 max	2.0	16-18	10-14	2-3 Mo
316L	0.03 max	2.0	16-18	10-14	2-3 Mo
321	0.08 max	2.0	17-19	9-12	(5x%C) Ti min
347	0.08 max	2.0	17-19	9-13	(10x%C) Nb - Ta min
Face-centered cubic, nonmagnetic, not heat treatable					

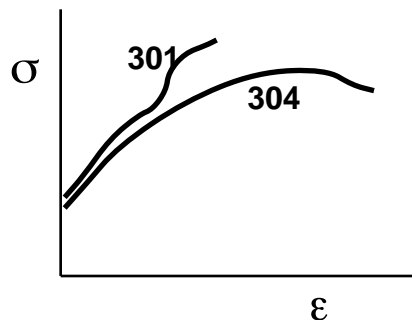
**After Krauss, p374,372,359**

The first two forms of embrittlement are of no great concern unless the steel can experience them during use. They do not arise otherwise and do not occur during welding because of the very sluggish rates at which the transformations occur. In contrast, however, the high temperature embrittlement has been a very serious problem for years. It has been of particular concern with respect to welding. In this case we already have the problem that there is no way to refine the grain size if it becomes large in the heat affected zone. This, combined with the embrittlement and the localized loss of corrosion resistance, has been very troublesome.

There have been three main methods used to combat this problem. The first is to pay stringent attention to the steel making process in order to ensure a very low interstitial solute content. The second is to add small amounts of very strong carbide and nitride formers e.g. V, Nb and Ti to scavenge these elements. These two methods can be successful. However, as the Cr content increases so does the minimum acceptable level of interstitial solutes. At 35 % Cr, the interstitial level can not be reduced low enough by these methods. In these cases the third method is via the addition of other substitutional solutes. It has been found that small additions of Al, Cu, Pt, Pd, Ag, V in the range of 0.1 -1.3 % can improve the as-welded ductility and corrosion even in the presence of relatively high quantities of interstitial solutes.

#### Austenitic stainless steels

This group of steels are iron chromium alloys to which enough Ni and Mn have been added to prevent the formation of significant amounts of ferrite. Because this is achieved by the austenite stabilization effects of the alloying elements (superimposed on those due to C and N) it is important to realize that different alloys comprise austenites of different stability's as reflected by them having different  $M_s$  temperatures. Accordingly, they can be subdivided into two groups depending on whether or not the austenite can be induced to transform martensitically when deformed at room temperature, i.e. when the  $M_d$  temperature is above room temperature. In these groups we have stable austenite which does not transform and metastable austenite which does form some martensite.



Consider the room temperature tensile stress-strain curves that are typical for tests on the two austenitic steels, 301 and 304. That of 304 shows the "normal" behavior of an FCC polycrystal while that of the 301 has an increased work hardening rate caused by the impedance to slip provided by the formation of martensite on the active slip planes.

301 16-18 % Cr 6-8 % Ni 0.15 % C 2 % Mn 1 % Si

304 18-20 % Cr 8-10 % Ni 0.08 % C 2 % Mn 1 % Si

The  $M_d$  temperature for a 304 steel is usually just below room temperature. This means that if the steel is refrigerated and then deformed, martensite can form in 304 and change the stress-strain curve accordingly.

A major reason for alloying so as to create an austenitic steel is to eliminate the DBTT and obtain good impact toughness over a wide range of temperatures. These steels are generally of good toughness and good corrosion resistance. Their tensile strengths can be varied by varying the grain size and the dislocation density. There are a couple of negative aspects that must be recognized.

#### Sensitization

When held at high temperatures and then slowly cooled through 600 °C these alloys can lose their corrosion resistance in the near vicinity of grain boundaries and become less tough. Because the loss of corrosion resistance is restricted to narrow strips at the grain boundaries, deep grooves are formed. Whole grains can "fall out". A similar phenomenon can occur in ferritic steels but it appears to have been more troublesome for austenitic steels. The treatment is said to have sensitized the steel. It has been established that the loss of corrosion resistance is associated with the precipitation of chromium carbides on the grain boundaries. As the temperature falls past 600 °C, these carbides nucleate heterogeneously on grain boundaries and grow for a while as the steel cools further. The chromium required for this growth must be supplied by substitutional diffusion which occurs slowly and more slowly as the temperature decreases. As a result, the chromium concentration near the boundaries on which the carbides grow is severely depleted. This has been confirmed by modern electron micro-analytical techniques. Hence a grain boundary has, on either side of it, a thin layer of steel in which the chromium content is not high enough to provide protection. Severe localized corrosion is the result.

Attempts to cure this problem when it is not easily possible to avoid the heat treatment that causes it, involve compositional modifications. The required modification is obvious. Eliminate the carbon and no carbides will precipitate. Elimination is not presently feasible but a reduction is. For example, modified 304 called 304L has 0.03 % C max. specified. An alternative approach is to try to combine the carbon into precipitates that do not easily dissolve at high (>950 °C) temperatures. For this purpose small additions of Nb, V and Ti are added to sequester the carbon. Obviously these two approaches can be combined. These modifications are similar to those employed in the case of ferritic steel.

#### Stress corrosion cracking

Stress corrosion cracking is a process in which cracks form and grow into a material that is simultaneously experiencing a stress and is in an appropriate corrosive environment. The stress need not be applied externally; residual stresses due to prior processes can be effective. The corrosive media are generally specific for the particular material. They are not necessarily particularly aggressive from the point of view of general dissolution and corrosion. Austenitic stainless steel is particularly susceptible to aqueous media that contain chlorine ions. In general, the process can take place at ambient temperatures and will occur more rapidly as the temperatures are raised. The cracks tend to branch frequently and propagate through the grains. Eventually sheets can be cracked completely through. Stress corrosion cracking is a serious problem for austenitic steels but ferritic stainless steels are immune to it.

To avoid this problem when it is desirable to use austenitic stainless steel, it is necessary to minimize residual stresses and to ensure that the environment does not contain those species such as chlorine that are known to be particularly potent for stress corrosion cracking. Often this is not

easy to do. Although the phenomenon has been known for many years, austenitic steel components (as well those made from numerous other alloys) continue to fail in the field from stress corrosion cracking.

### Precipitation Hardenable Stainless Steels

Under appropriate conditions it is possible to produce precipitation of intermetallic compounds that can cause precipitation hardening in stainless steels. The precipitates involve the alloying elements Mo, Ni, Ti and Al. There are three main classes of precipitation hardenable alloys : austenitic PH steels, martensitic PH steels and semi-austenitic PH steels.

Members of the first group have compositions that produce very stable austenite with respect to martensite. An example is Allegheny-Ludlum 's A-286: 14.75 % Cr, 25.25 % Ni, 0.05 % C, 1.45 % Mn, 1.3 % Mo, 0.15 % Al, 0.3 % V, 2.15 % Ti . The heat treatment is relatively simple: solution treat for 1 hour at 1000 Celsius, water quench and age at 730 Celsius. Yield strengths of 190 KSI can be obtained but these type of steels are not widely used.

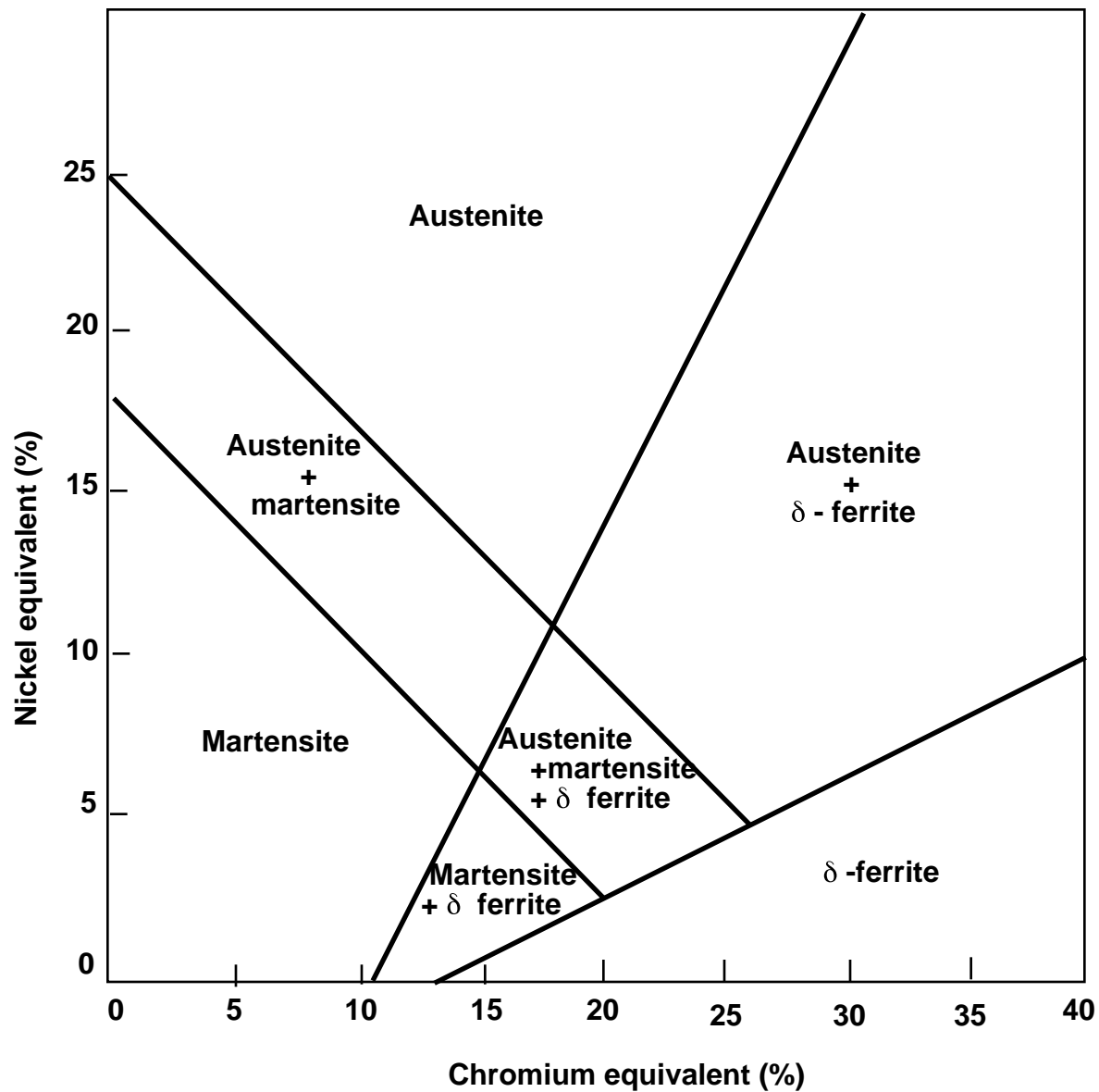
The martensitic precipitation hardenable stainless steels are similar to maraging steels. An example is the PH 13-8 Mo type. Here the PH indicates precipitation hardenable, the 13 denotes the chromium content (12.7 %), the 8 the nickel content (8 %) and the Mo indicates that it contains molybdenum (2.2 %). The alloy has a low carbon content and contains some aluminum. In this case the solution treatment produces homogeneous austenite that transforms to martensite on cooling. Precipitation occurs when the martensite is aged at 450-650 Celsius.

The semi-austenitic precipitation hardenable stainless steels are so named because in the annealed or solution treated condition they generally contain 5-20 % delta ferrite which persists. The metallurgy and heat treatment schedules for these steels are quite complex. The general procedure is as follows. After production the steel annealed at the Mill (called the Mill anneal) which puts the steel into its semi-austenitic state. It is then shipped to the customer who fabricates it into particular products. These products are then given a heat treatment known as conditioning. Conditioning involves heating to a particular temperature and maintaining the temperature for a specified time and air -cooling. The object of the conditioning treatment is to remove the microstructural effects of the fabrication process e.g. forming deformation and to adjust the composition of the matrix solid solution so that its  $M_s$  temperature is raised to close to room temperature from its earlier lower value. This is typically achieved by precipitating chromium and carbon from solid solution. Conditioning enables the steel to be transformed into martensite by refrigeration. Finally, the martensite can be precipitation hardened by an aging treatment.

The chemistry of these steels is chosen with the aim of balancing the ferrite and austenite stabilizing elements so as to control the  $M_s$  temperature. The steel must not be too stable as austenite because then the  $M_s$  temperature will be too low for convenience. On the other hand, if the  $M_s$  temperature in the steel after the mill anneal is too high, martensite might be produced during transit, specially during winter. An example of such a steel is Armco 17-7 PH, 17 % Cr, 7% Ni, 1.2 % Al, 0.5 % Mn, 0.04 % N, 0.3 % Si and 0.07 % C for which a mill anneal is, using Celsius, 1053 + or - 15; conditioning is at 953 + or - 8 for 10 minutes and an air-cool. The martensite is produced by refrigeration to -73 and precipitation occurs during an hour at 510°C.

Compositions of Selected Precipitation-Hardening Stainless									
AISI		Nominal Composition, %							
type no.	Trade name / producer	C	Cr	Ni	Mo	Cu	Al	Ti	Other
Martensitic grades									
635	Stainless W								
	(U.S. Steel)	0.06	16.75	6.25			0.2	0.8	
630	17.4 PH								
	(Armco Steel)	0.04	16	4.2		3.4			0.25Cb
.....	PH 13-8 Mo								
	(Armco Steel)	0.04	12.7	8.2	2.2		1.1		
Semiaustenitic grades									
631	17.7 PH								
	(Armco Steel)	0.07	17	7.1			1.2		
633	AM 350								
	(Allegheny Ludlum)	0.05	16.5	4.25	2.75				0.10N
Austenitic grades									
600	A-286								
	(Allegheny Ludlum)	0.05	14.75	25.25	1.3		0.15	2.15	0.30V, 0.005B

After: Krauss, p386

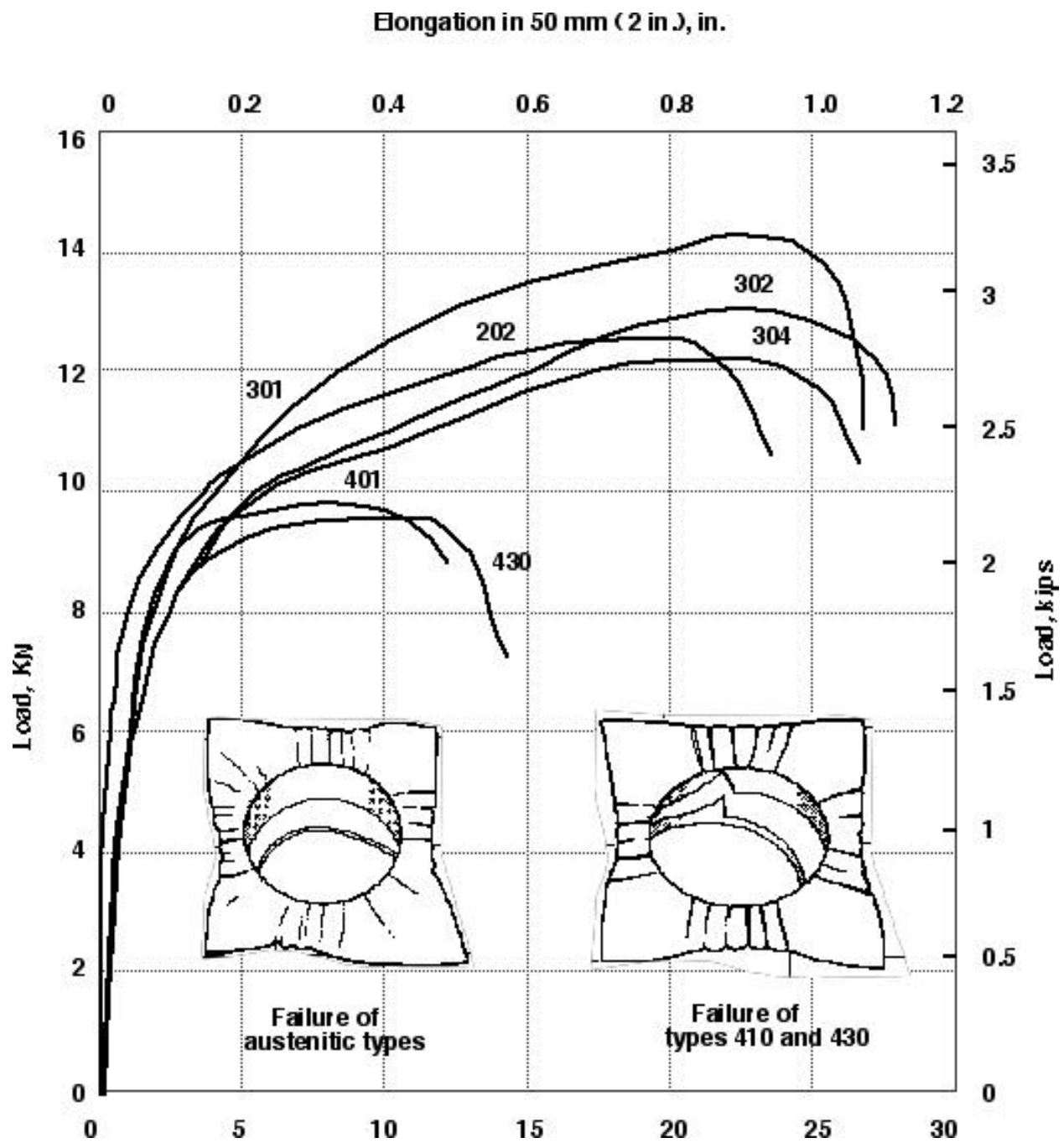


**Schaeffler diagram. Effect of alloying elements on the basic structure of Cr-Ni stainless steels (Schneider and Climax Molybdenum Co., Foundry Trade J. 108,562,1960).**

$$\text{Cr equivalent} = (\text{Cr}) + 2(\text{Si}) + 1.5(\text{Mo}) + 5(\text{V}) + 5.5(\text{Al}) + 1.75(\text{Nb}) + 1.5(\text{Ti}) + 0.75(\text{W})$$

$$\text{Ni equivalent} = (\text{Ni}) + (\text{Co}) + 0.5(\text{Mn}) + 0.3(\text{Cu}) + 25(\text{N}) + 30(\text{C})$$





From ASM Stainless Steels, p259

## Tool Steels

Tool steels are obviously those steels from which tools are made. There are many such steels ranging from relatively simple plain carbon steels to complex, highly alloyed steels. This is a reflection of the enormous variety of operations that are performed by tools. To begin a survey of tool steels, let us first consider the range of operations in which tools are used. We begin with procedures in which items or other material are moved. For these, we require tools such as screw drivers, wrenches, pliers, spades, post-hole diggers, bull-dozer blades etc.. Then there are numerous operations in which materials are cut or fractured; for these we require knives, axes, saws, scissors, mower blades, farming implements, chisels, razor blades and jack-hammers and tools for drilling, broaching, reaming, milling and lathes. Then there are the processes in which materials are formed into different shapes by deformation in hot or cold working operations such as stamping, forging, rolling and extrusion. These processes involve the forming machines themselves and various cold and hot work dies that interact directly with the work pieces. And, lest we forget, we need tools with which to make tools.

It is clear that there is an enormous range of applications for tool steels. For some tools, such as a chisel, a simple plain carbon steel can be perfectly adequate. In other cases such as high speed machining, during which the cutting tool can become red hot, a much more sophisticated steel is necessary. A factor that is common to tools is that they are used on some type of work piece. Usually the shape or form of the work-piece is changed by plastic deformation, material removal or fracture. Therefore, there is a common requirement for tools. The work-piece should have a minimum effect on the form of the tool in order for the tool to do its job successfully and for it to have a reasonable lifetime. With this background in mind let us list those properties of materials that should be important with respect to selecting or designing a material for a tool.

- (1) Strength. In general the tool should be stronger and harder than the work piece.
- (2) Edge retention. In many applications the tool material must be capable of being sharpened and then be able to resist becoming blunt rapidly.
- (3) Wear resistance. Wear removes material from tools and thereby changes their shapes. This property often determines the useful lifetime of the tool.
- (4) Shock resistance. In many operations tools are loaded rapidly and must therefore be capable of sustaining stresses created during shock loading.
- (5) High temperature stability. During operations conducted at elevated temperatures such as hot forming and high speed cutting it is important that the tool material retain its properties at those temperatures rather than rapidly undergoing microstructural changes that cause undesirable changes in its properties.

Now let suppose that we have materials that possess some or all of these properties. It is then necessary that tools can be manufactured from them. Obviously, tools made of a material with superior properties can be used to make tools from materials of inferior properties (referring, of course, to relevant properties), but how are the first kind of tools made? Diamond is an example of a material that has excellent properties from the view point of a variety of tools. For example, it is extremely hard. It is used in a number of abrasive tool applications but it does not lend itself easily to being manufactured into monolithic tools. In contemplating this situation, the value of the fact that the properties of steels can be changed by heat treatments becomes evident. This enables tools to be fabricated into shapes close to their final physical form from steels that are initially easily formed and/or machined. Then when they have been made, they can be heat treated in order to endow them with the properties required for operation as a tool. It is this versatility that accounts for

the wide use of steel to make tools. There are many different kinds of tool steel. This is partly because of the many different applications of tools. For any particular application, the steel chosen should have adequate properties to perform properly and also be an economical choice. Usually the steel is delivered in the annealed or spheroidized condition; the customer is responsible for subsequent heat treatments.

Inspection of the list of desirable properties leads us to conclude that in many cases the heat treatment will involve austenitization, cooling rapidly enough to form martensite and then a tempering treatment. Often, then, the tool or the working parts of it will consist of tempered martensite. When the desired properties can be obtained by using plain carbon steels then they are the most economical choice. Otherwise alloy steels are required. Let us consider the main alloying elements that we might predict to be important in tool steels.

a) Hardenability is an important consideration because it controls the sizes that can be heat treated throughout or the depth of case hardening. The hardenability also dictates the necessary quench rates. This is particularly important because the incidence of quench cracking, distortion and dimensional change can be minimized by reducing the rate of cooling required to produce martensite. This suggests the use of Mo, Cr and Mn.

b) A high carbon concentration dissolved in the austenite is required to obtain tempered martensite that has a high hardness. Furthermore, wear resistance at the surface of the tool is enhanced by the presence of hard particles of second phases. The obvious second phase is a carbide. The stable alloy carbides coarsen more slowly than does cementite and are therefore more effective than cementite at higher temperatures. We predict the use of carbide formers such as Cr, Mo, W and V and sufficient carbon to provide these alloy carbides while also endowing the martensite with enough hardness. When the most important role of the alloy carbides require that they be finely distributed within the steel, then they should precipitate during tempering as opposed to being inherited from the austenite. Therefore, it is to be expected that heat treatments involving high austenitization temperatures and long times will be required to form austenite in which the appropriate amount of the relevant alloying elements is dissolved. This creates the risk of excessive grain growth during austenitization. As always, a favorite hedge against that problem is grain boundary pinning by very strong carbides such as vanadium carbide.

c) Very often it is the properties of the material at the surface of the tool that determine the performance of the tool. These can deteriorate rapidly unless the material resists oxidation and decarburization. In this respect, we predict that Cr should be an effective alloying element.

We conclude that Cr, Mo, W, V, C and Mn should be important alloying elements in tool steels.

There is a large number of different tool steels. At first, one might attempt to organize them by classifying them chemistry or by their intended application. Unfortunately, there does not seem to be an easy method whereby they can neatly classified. Often many different steels can be used for the same application, so a classification in terms of use is not clear. Although, some steels can be grouped together according to their compositions, many steels contain the same alloying elements and, again, it is often possible for a major element in one steel to be partially or entirely

# AISI classification and nominal compositions of major tool steels

		Identifying elements, %								
AISI	UNS No.	C	Mn	Si	Cr	V	W	Mo	Co	Ni
Water-hardening tool steels										
W1	T72301	0.60-1.40(a)	...	...	...	...	...	...	...	...
W2	T72302	0.60-1.40(a)	...	...	...	0.25	...	...	...	...
W5	T72305	1.10	...	...	0.50	...	...	...	...	...
Shock-resisting tool steels										
S1	T41901	0.50	...	...	1.50	...	2.50	...	...	...
S2	T41902	0.50	...	1.00	...	...	...	0.50	...	...
S5	T41905	0.55	0.80	2.00	...	...	...	0.40	...	...
S6	T41906	0.45	1.40	2.25	1.50	...	...	0.40	...	...
S7	T41907	0.50	...	...	3.25	...	...	1.40	...	...
Oil-hardening cold-work tool steels										
O1	T31501	0.90	1.00	...	0.50	...	0.50	...	...	...
O2	T31502	0.90	1.60	...	...	...	...	...	...	...
O6(b)	T31506	1.45	0.80	1.00	...	...	...	0.25	...	...
O7	T31507	1.20	...	...	0.75	...	1.75	...	...	...
Air-hardening, medium alloy cold-work tool steels										
A2	T30102	1.00	...	...	5.00	...	...	1.00	...	...
A3	T30103	1.25	...	...	5.00	1.00	...	1.00	...	...
A4	T30104	1.00	2.00	...	1.00	...	...	1.00	...	...
A6	T30106	0.70	2.00	...	1.00	...	...	1.25	...	...
A7	T30107	2.25	...	...	5.25	4.75	1.00 (c)	1.00	...	...
A8	T30108	0.55	...	...	5.00	...	1.25	1.25	...	...
A9	T30109	0.50	...	...	5.00	1.00	...	1.40	...	1.50
A10(b)	T30110	1.35	1.80	1.25	...	...	...	1.50	...	1.80
High-carbon, high-chromium cold-work steels										
D2	T30402	1.50	...	...	12.00	1.00	...	1.00	...	...
D3	T30403	2.25	...	...	12.00	...	...	...	...	...
D4	T30404	2.25	...	...	12.00	...	...	1.00	...	...
D5	T30405	1.50	...	...	12.00	...	...	1.00	3.00	...
D7	T30407	2.35	...	...	12.00	4.00	...	1.00	...	...
Low-alloy special-purpose tool steels										
L2	T61202	0.5-1.10 (a)	...	...	1.00	0.20	...	...	...	...
L6	T61206	0.70	...	...	0.75	...	...	0.25 (c)	...	1.50
Mold steels										
P2	T51602	0.07	...	...	2.00	...	...	0.20	...	0.50
P3	T51603	0.10	...	...	0.60	...	...	...	...	1.25
P4	T51604	0.07	...	...	5.00	...	...	0.75	...	...
P5	T51605	0.10	...	...	2.25	...	...	...	...	...
P6	T51606	0.10	...	...	1.50	...	...	...	...	3.50
P20	T51620	0.35	...	...	1.70	...	...	0.40	...	...
P21	T51621	0.20	1.20 (Al)	...	...	...	...	...	...	4.00
Chromium hot-work tool steels										
H10	T20810	0.40	...	...	3.25	0.40	...	2.50	...	...
H11	T20811	0.35	...	...	5.00	0.40	...	1.50	...	...
H12	T20812	0.35	...	...	5.00	0.40	1.50	1.50	...	...
H13	T20813	0.35	...	...	5.00	1.00	...	1.50	...	...
H14	T20814	0.40	...	...	5.00	...	5.00	...	...	...
H19	T20819	0.40	...	...	4.25	2.00	4.25	...	4.25	...
Tungsten hot-work tool steels										
H21	T20821	0.35	...	...	3.50	...	9.00	...	...	...
H22	T20822	0.35	...	...	2.00	...	11.00	...	...	...
H23	T20823	0.30	...	...	12.00	...	12.00	...	...	...
H24	T20824	0.45	...	...	3.00	...	15.00	...	...	...

(continued)

(a) Available with different carbon contents. (b) Contains graphite. (c) Optional

## AISI classification and nominal compositions of major tool steels

		Identifying elements, %								
AISI	UNS No.	C	Mn	Si	Cr	V	W	Mo	Co	Ni
Tungsten hot-work tool steels (continued)										
H25	T20825	0.25	...	...	4.00	...	15.00	...	...	...
H26	T20826	0.50	...	...	4.00	1.00	18.00	...	...	...
Molybdenum hot-work tool steels										
H42	T20842	0.60	...	...	4.00	2.00	6.00	5.00	...	...
Tungsten high-speed tool steels										
T1	T12001	0.75(a)	...	...	4.00	1.00	18.00	...	...	...
T2	T12002	0.80	...	...	4.00	2.00	18.00	...	...	...
T4	T12004	0.75	...	...	4.00	1.00	18.00	...	5.00	...
T5	T12005	0.80	...	...	4.00	2.00	18.00	...	8.00	...
T6	T12006	0.80	...	...	4.50	1.50	20.00	...	12.00	...
T8	T12008	0.75	...	...	4.00	2.00	14.00	...	5.00	...
T15	T12015	1.50	...	...	4.00	5.00	12.00	...	5.00	...
Molybdenum high-speed tool steels										
M1	T11301	0.80(a)	...	...	4.00	1.00	1.50	8.00	...	...
M2	T11302	0.85-1.00(a)	...	...	4.00	2.00	6.00	5.00	...	...
M3, class 1	T11313	1.05	...	...	4.00	2.40	6.00	5.00	...	...
M3, class 2	T11323	1.20	...	...	4.00	3.00	6.00	5.00	...	...
M4	T11304	1.30	...	...	4.00	4.00	5.50	4.50	...	...
M6	T11306	0.80	...	...	4.00	2.00	4.00	5.00	12.00	...
M7	T11307	1.00	...	...	4.00	2.00	1.75	8.75	...	...
M10	T11310	0.85-1.00(a)	...	...	4.00	2.00	...	8.00	...	...
M30	T11330	0.8	...	...	4.00	1.25	2.00	8.00	5.00	...
M33	T11333	0.90	...	...	4.00	1.15	1.50	9.50	8.00	...
M34	T11334	0.90	...	...	4.00	2.00	2.00	8.00	8.00	...
M36	T11336	0.80	...	...	4.00	2.00	6.00	5.00	8.00	...
Ultradhard high-speed tool steels										
M41	T11341	1.10	...	...	4.25	2.00	6.75	3.75	5.00	...
M42	T11342	1.10	...	...	3.75	1.15	1.50	9.50	8.00	...
M43	T11343	1.20	...	...	3.75	1.60	2.75	8.00	8.25	...
M44	T11344	1.15	...	...	4.25	2.00	5.25	6.25	12.00	...
M46	T11346	1.25	...	...	4.00	3.20	2.00	8.25	8.25	...
M47	T11347	1.10	...	...	3.75	1.25	1.50	9.50	5.00	...

(a) Available with different carbon contents. (b) Contains graphite. (c) Optional

**After: "Tool Steels" by G. Roberts, G. Krauss, and R. Kennedy, ASM International, 5<sup>th</sup> edition, pp8-9, 1998**

replaced by another element without creating much of a change in the properties of the steel. The AISI classifies tool steels into seven major categories. These are: water-hardening tool steels, cold work tool steels, hot work tool steels, high speed tool steels, shock-resisting tool steels, mold tool steels and special purpose tool steels. Here we see a classification by a mixture of use and heat treatment. These seven major classes are then subdivided into numbered classes ranging from the 100 class to the 600 class. I can see no simple way deducing the details of the classification. For selecting and identifying tool steels one should consult manuals on the subject. A fine reference is the ASM's publication "Tool Steels", 4<sup>th</sup> edition, by George A. Roberts and Robert A. Cary. What I propose to do here is to select a number of particular tool steels and consider their compositions, treatments and properties in the light of the fundamental relations between composition and phase transformations that we have examined hitherto.

#### Water hardening tool steels.

These steels are so named because they have relatively low hardenability so that they are hardened by being austenitized and quenched in water. They are basically plain carbon steels and are also called carbon tool steels. They contain from 0.6 wt. % to 1.4 wt. % carbon with a manganese content of usually 0.25 wt. %. Some of them contain small amounts of chromium or vanadium and a few contain both vanadium and chromium and, therefore, the group is sub-divided according to such details. The additional alloying elements, however, always comprise a fraction of a wt. %. Examples are:

W 1...0.6% to 1.6 % C, 0.25 % Mn and 0.25 % Si

W 5...1 % C, 0.25 % Mn and Si and 0.5 % Cr

W7....Same as W 5 except that the Cr level is 0.35 % and 0.2 % V is present.

There are some applications of carbon tool steels for which they are used when having a pearlitic microstructure. Most commonly, however, the intended microstructure in the tools made from these steels is tempered martensite where it is needed and softer, tougher microstructures elsewhere. Indeed, it is probably true to say that this class of tool steels is widely used because the relatively low hardenability of the steels enables water-quenching to produce tools as cores of fine pearlite encased within hard martensite. Typically, the working hardness in the case is in the range of HRC 58-65 and the core hardness is in the range of HRC 38-43. The hardness of the tempered martensite is primarily controlled by the carbon dissolved in the austenite prior to the quench. As we have seen, the hardness increases approximately linearly with carbon content in freshly formed martensite until about 0.6 wt. % C; thereafter it varies slowly and is essentially constant by 0.8 %. Because of this, we recognize that hypereutectoid tool steels are not selected for use because their high carbon contents endow the martensite with additional hardness but because the volume fraction of carbides in them is greater and this provides increased wear resistance. Therefore, it is unnecessary for all of the carbon to be dissolved in the austenite during austenitization.

The full story of the heat treatment of carbon tool steels begins with the forging process that produces the desired stock e.g. bars. Forging is carried out at temperatures well in the austenite phase field but below those which would cause dissolution of the vanadium carbides present in some steels. The steel is air cooled after forging. Then it is annealed, sometimes after a normalization treatment, to produce a suitable microstructure for delivery to the customer. The purpose of the annealing treatment is to enhance the machinability of the steel, eliminate any residual stresses and to provide a microstructure that will respond uniformly to subsequent hardening heat treatments. The desirable type of microstructure that achieves this purpose is either a

finely spheroidized microstructure or a mixture of fine spheroidite and pearlite. It is important to avoid the formation of films of cementite along austenite grain boundaries or a coarse spheroidal microstructure. These microstructures are produced by heating to and holding at temperatures within the austenite/cementite two phase field followed by slow cooling ( maximum rate 50°F per hour) to 1000°F. The steel is protected from excessive scaling and decarburization during annealing, often by being embedded in inert substances such as sand.

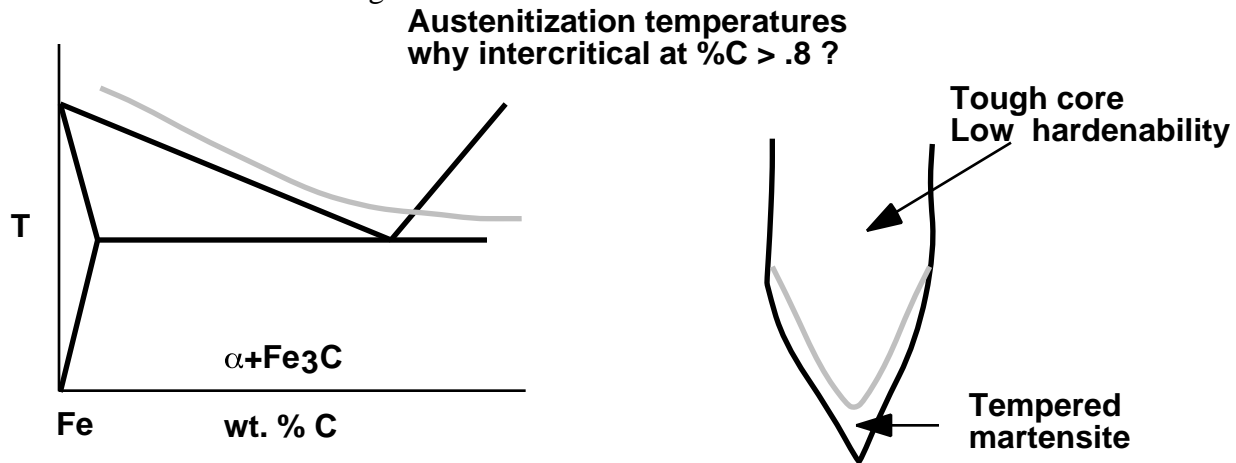
For hardening, these steels are austenitized above the  $A_1$  line but below the  $A_{cm}$  line. The microstructure before the quench comprises austenite grains in which proeutectoid cementite particles and possibly vanadium carbides are embedded. These carbides restrict grain growth during austenitization and are retained within the martensite when quenching is complete. The austenitization temperatures are high enough for the Cr to be dissolved. This is desirable partly because it then is helpful in resisting oxidation and decarburization. However, these degradation processes should also be minimized by using protective atmospheres or baths during heat treating. Another important contribution of the dissolved chromium is that it retards the rate of tempering reactions which enables some residual stress relief to be accomplished without too much softening. Finally, the chromium that becomes incorporated in the cementite improves the wear resistance provided by the carbides.

The microstructure in the case of carbon tool steels austenitized as above and then water-quenched to room temperature is not 100 % martensite even very near the surface. Retained austenite is usually present because the  $M_s$  temperature drops below room temperature as the carbon content rises. For example, samples of W1 steel austenitized at 1450°F begin to transform to martensite at approximately 400°F and will continue to transform, if continuously cooled, until the temperature is about -250°F where there is typically 1 % retained austenite present. If the quench is to room temperature the hardness of the mixture of martensite and retained austenite is typically above HRC 65 and roughly 90 % of the microstructure is martensite.

It is time now to elaborate on the martensitic transformation in these steels. When we first broached the subject of the martensitic transformation in plain carbon and the standard low alloy steels, I defined it as usually being an athermal transformation during which the quantity of martensite produced was dependent on the temperature to which the steel was cooled and not on the time spent at that temperature. This was to emphasize the difference between its kinetics and those of diffusion controlled nucleation and growth transformations. For hypoeutectoid plain carbon and low alloy steels this definition is fine because it is close to the truth and, also, for practical purposes, quenching to room temperature generally means continuously cooling to below the  $M_f$  temperature. It is, however, a definition that is not exactly true. Let us consider the behavior of W1 in greater detail. If a sample is quenched to room temperature, the transformation to martensite is incomplete with typically 12 % of the sample being retained austenite. If the sample is immediately cooled further, the transformation continues as if the cooling was continuous. If, however, the sample is held at room temperature for significant times, some of the austenite does transform. For example, Cohen in "Retained Austenite", Trans. ASM, Vol. 41, 35, (1949), shows that another 1% or so of martensite forms in an hour and about 2 or 3 % in 50 hours. During this isothermal hold, the remaining austenite also becomes more resistant to the athermal transformation because when cooling is resumed martensite does not form until the temperature has decreased on the order of a hundred degrees and much less of it forms. These subtleties become important now. If it is desired to transform as much austenite as possible then cooling should not be interrupted for significant delays. It is well known that tool steel articles can suffer delayed cracking if stored for periods of time after being quenched. Very likely, the volume changes produced by the continuation of the

transformation during storage contributes to this delayed cracking phenomenon. It is particularly important that such steels be tempered immediately after being quenched.

The phenomenon of delayed cracking was mentioned in the foregoing paragraph. This is related to quench cracking which refers to cracking that occurs during the quenching process. The risk of quench cracking increases as the carbon content of the austenite increases and as the severity of the quench increases. It is also true that quench cracking becomes more likely to occur as the austenitic grain size increases. This is another reason that vanadium is added to the higher carbon steels to refine the austenitic grain size.



### Cold Work Die Steels

This is a very important family of tool steels. The steels are used in a wide variety of applications involving tool and die work. Of these, the compositions that require quenching in oil are probably the most commonly used but when larger parts are used or when smaller dimensional changes are desirable during heat treatment, compositions that enable air hardening to occur are used.

As was summarized by Roberts and Cary, the major properties of these steels are:

- 1) small dimensional changes ( called movement) during hardening, hence small finishing work required;
- 2) high as-quenched hardness, due primarily to carbon dissolved in the austenite;
- 3) high hardenability when austenitized at low austenitization temperatures;
- 4) reasonably good resistance to quench-cracking in intricate shapes;
- 5) good retention of a keen cutting edge during use.

These are good properties, however, the steels are limited to cold work because they soften when heated and have no “red-hardness” i.e. they do not retain hardness when red-hot.

Examples are:

- 01 0.95 % C 1.2 % Mn 0.25 % Si 0.5 % Cr 0.2 % V 0.5 % W  
 07 1.2 % C 0.25 % Mn 0.25 % Si 0.6 % Cr 0.2 % V 1.6 % W 0.25 % Mo



We see that the amounts of alloying elements are not high and that most of them are carbide formers and, if dissolved in the austenite, will raise the hardenability. These steels typically undergo forging processes that are conducted around 1000 to 1100 degrees Celsius and are then annealed around 850 before being austenitized. Austenitization temperatures are in the range of 840 degrees where some of the alloy carbides except the vanadium carbides dissolve. The vanadium carbides and the low austenitization temperatures resist grain growth. When the Mn content is high, the permissible austenitization temperature is at the lower end of the range because Mn is an austenite stabilizer. The ability to austenitize the tool at relatively low temperatures reduces the dimensional changes that occur subsequently. Any elastic shape changes that occur because of differential expansion/contraction while the temperature is changing, are eliminated when the temperature of the tool is uniform. If the stresses associated with these changes are large enough to cause plastic deformation before the temperature becomes uniform then the shape changes are not recovered and are superimposed on those due to the phase transformations. Reducing the austenitization temperature is helpful for retaining prior dimensions. One should note that because of the high carbon content and the effects of the dissolved alloying elements, quenching to room temperature usually leaves a significant quantity of retained austenite in the steel, typically around 10 % by volume.

Tempering is typically carried out below 300 Celsius, so the principal role of dissolved alloying elements is then to retard softening while residual stresses are relieved.

When even greater dimensional stability than that which can be obtained in intricate parts during quenching in oil is desirable, the logical thing to try is to increase the hardenability so that the martensitic transformation will occur during very slow cooling rates that eliminate serious temperature gradients in the work piece. This leads us to air hardenable tool and die steels in which greater amounts of Mo and Cr are present. The increased amount of Cr also adds the benefit of increased resistance to oxidation and decarburization. An example is A2 which contains:

1 % C 0.6 % Mn 0.25 % Si 5 % Cr 0.25 % V and 1 % Mo

Now, in order to raise the hardenability by means of the increased alloy content it is necessary to dissolve more of the alloying elements into the austenite. These steels are thus austenitized at higher temperatures than are the oil hardening types. Typically they are austenitized at about 1000 Celsius, air cooled and tempered. Heating to the austenitization temperature is carried out in stages to minimize distortion. It is common to heat to 750 - 800, hold at that temperature and then to continue up to the final temperature. The intermediate hold allows some of the phase transformations to be performed which reduces the time required at the highest temperature. This is beneficial because the effects due to decarburization etc. are more serious the longer the steel is at the elevated temperature, even though it is usually packed in protective materials. Another reason for the intermediate hold is that it provides a means of bringing the times spent at the maximum temperature by the surface and the interior closer together so that their microstructures are more similar.

With the increase in the dissolved alloy content comes an increase in the volume fraction of retained austenite because of the reduction in the  $M_s$  temperature. 18 % is typical. This retained austenite can transform during tempering. Indeed chromium carbides can form within it thereby reducing its carbon and chromium content such that its  $M_s$  temperature is raised above its former value causing martensite to form during cooling after tempering ( similar to conditioning in stainless steels). Double tempering might then be necessary. Sometimes A2 is refrigerated to reduce the amount of retained austenite within it.

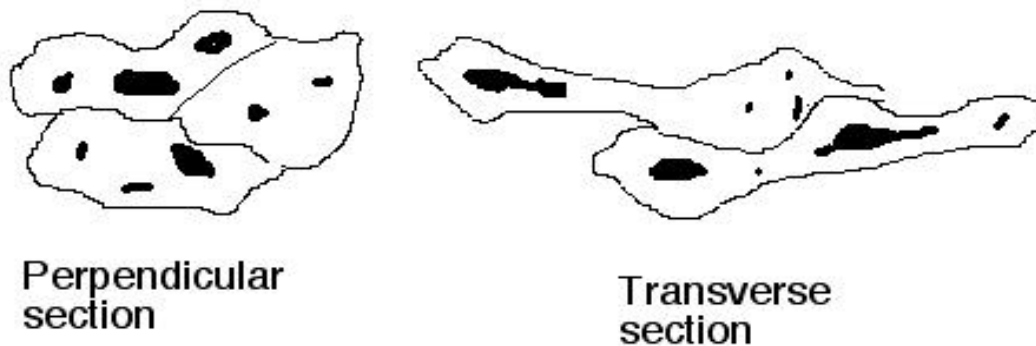
High chromium, high carbon, cold-work tool and die steels.

So far we have considered cold work tool steels that are of relatively low alloy content. Because chromium and chromium carbides give these steels good properties it follows that the effects of increasing the amounts of these two elements are worth examining. This results in the high chromium, high carbon, cold work steels. An example is D2:

1.5 % C 12 % Cr 0.8 % Mo 0.6 % V 0.3 % Mn 0.25 % Si.

It is clear from this composition that the steel will be rich in alloy carbides and have good resistance to oxidation. In fact the alloy content is so great that there are very significant departures from the behavior of carbon steels that are important to note. The as-cast microstructure of the steel following its manufacture, consists of primary grains surrounded by a eutectic mixture. As solidification begins, marked coring occurs as Cr and C are rejected from the solid. It is irrelevant whether the primary nuclei are delta ferrite or austenite; the eutectic constituents that solidify are austenite and carbides. Austenite transforms to ferrite as the casting cools and it is possible for martensite to form. Forging serves not only to produce the steel in suitable forms but also modifies the microstructure creating a more uniform mixture of matrix and carbides which, in turn, endows the material with more uniform properties. There is, however, a tendency for artifacts such as carbide stringers to arise. Forging is carried out from about 1000°C to 1100°C. Higher temperatures are not used because the eutectic constituent can melt. These steels have lower thermal conductivity than low alloy steels so that a pre-heat soak and slow heating rates are necessary. Also, very slow cooling rates are needed to avoid the formation of martensite.

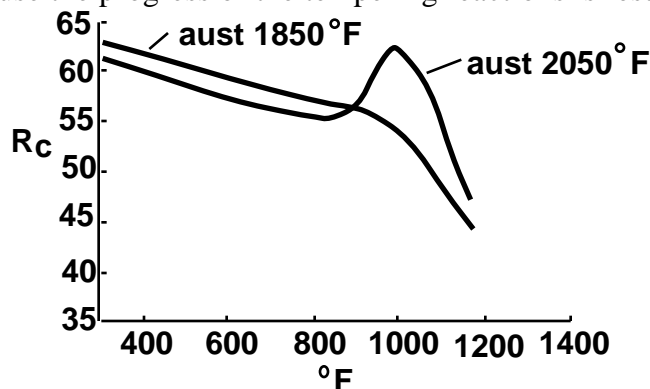
The forged steel is annealed before it is machined into tools. A typical annealing process is to heat to about 875°C in a controlled atmosphere, hold for two hours and then to slowly cool to 775°C, hold there for 2-4 hours and air-cool. The final microstructure is a mixture of large and small alloy carbides in a ferrite matrix.



Again the tools are hardened after they have been machined to shape. To ensure minimum dimensional changes and to avoid scaling, heating is done slowly in baths or protective atmospheres. Typically the tools are preheated to and soaked at an intermediate temperature and then heated to about 980°C. Some of the steels are oil-quenched but the molybdenum in D2 makes it air-hardenable in large sizes. The actual final “austenitization” temperature is quite important because, of course, complete austenitization does not occur. The steel will be austenite plus alloy carbides and the volume fractions of these phases will vary with the temperature. More of the carbides dissolve the higher the temperature that is used. This increases the concentration of solute

dissolved in the austenite which lowers the  $M_s$  temperature. This, in turn, causes an increase in the volume fraction of retained austenite which reduces the as-quenched hardness.

The variation of hardness during tempering is also dependent upon the austenitization temperature because of the effects of the composition of the austenite. In general, the rate of softening is low because the progress of the tempering reactions is restrained by the high alloy



content. Furthermore when the higher austenitization temperatures are used, secondary hardening can arise due to carbide precipitation and the formation of martensite in the “conditioned” retained austenite. The “conditioning refers to the rise in the martensitic start temperature of the retained austenite caused by the precipitation of carbides therein during tempering.

We have considered the main types of cold work tool steels but there are variations of these. For example, special wear resistant cold work die steels. What do we need for improved wear resistance? The answer is: hard, wear resistant carbides and lots of them. Vanadium and tungsten carbides are harder than chromium and iron carbides, so the an improvement should be obtained by replacing some of the chromium carbides with these. Hence D7:

2.3 % C 0.5 % Mn 0.5 % Si 5.25 % Cr 4.75 % V 1.1 % W 1.1 % Mo

Hot work die steels.

There are many applications in which the work piece is hot. For example, many of the parts that are made from aluminum alloys are made by hot working operations. During hot working operations the dies are often cooled by water or air blasts but the tool still becomes hot, particularly at its surface in contact with the work-piece. Commonly temperatures can range above 1000°F. The following are some of the important properties that should be possessed by hot-work tools steels.

1) They should resist being deformed at the working temperatures. The main reason that high carbon, low alloy tool, steels are unsuitable for hot working processes is that although they can be produced to have high hardness and strength at room temperature, they soften rapidly at elevated temperatures. It is true that the hot work steels that are used also soften when heated, but they do so slowly and retain enough strength to have a significant working life. For this to be so, the steels have medium to high contents of alloy element.

2) They should be shock resistant. This implies a resistance to mechanical and thermal shocks, both of which are encountered in service. Good notch toughness is desirable to avoid catastrophic crack propagation. To satisfy this requirement most hot work tool steels have low to

medium carbon contents e. g. 0.25-0.6 wt.%. The increase in toughness has to be a compromise of course because it is necessary to maintain adequate hardness and strength and also to avoid rapid wear or erosion. Wear rates tend to increase as toughness increases.

3) As is usually the case for tools, it is desirable that dimensional changes and warping are minimized when they are heat treated. This is particularly true when the tool is intended to produce a part as close as possible to its required net shape as is the case for dies. An obvious reason is that this will reduce the need for subsequent machining and thereby the cost of the tool. Hot work steels can develop a protective surface film during heat treatment. If, however, this film is removed during grinding processes required to adjust dimensions after heat treatment then the useful life of the tool will be less. The most common method of minimizing dimensional changes during heat treating is to use high alloy contents that raise the hardenability so that rapid temperature changes are unnecessary. This is beneficial with respect to undesirable effect caused by thermal shocks and thermal gradients.

4) Tools used in hot work operations experience cyclic variations in the surface temperature as they heat up and cool down. These temperature excursions generate cyclic stresses with the result that thermally induced fatigue is very common. This phenomenon generally manifests itself by the development of a network of fine cracks on the surface of the tool. The cracks are usually along the traces of grain boundaries and grains can even be pulled out of the surface. The phenomenon is known as “heat checking” or “craze cracking”. This is a common practical problem and its occurrence is often the limiting factor in the life of a die.

The hot-work tool steels can be divided into three broad classes: those in which Cr is the principal alloying element, those which contain W or Mo as the principal alloying element and those which contain about equal quantities of Cr and W. Most of them contain V which is combined with carbon and is not taken into solution during the normal heat treatments.

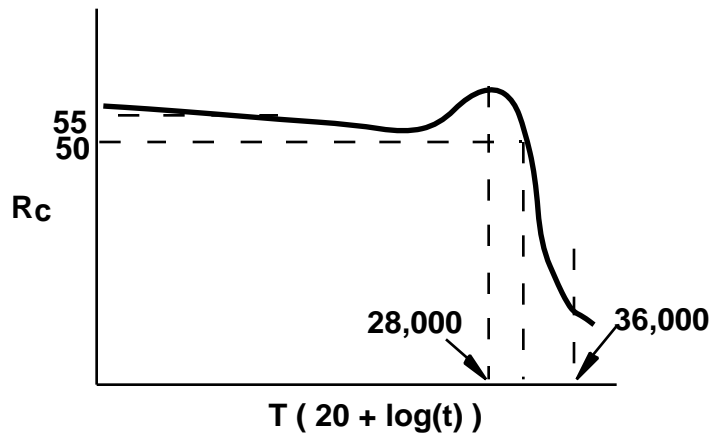
#### Examples

S7 0.5 % C 0.7 % Mn 0.3 % Si 3.25 % Cr 1.4 % Mo

H11 0.4 % C 0.92 % Si 5.1 % Cr 1.5 % Mo 0.4 % V

H14 0.4 % C 0.3 % Mn 1 % Si 5 % Cr 0.25 % V 5 % W

An interesting aspect of the metallurgy of hot work die steels is the use of master tempering curves. An example is shown below and refers to an H11 steel that was austenitized at 1850°F, air-cooled and tempered at various temperatures and times. The diagram was constructed from the experimental data as a plot of hardness (HRC) versus the parameter  $T(20 + \log t)$  where T is °F + 460 and t is the tempering time in hours. The hardness measurements were, of course made at room temperature; typical hardness values of 44-50 are used for working tools. The curve is used to estimate the combination of temperatures and times for which the tool can be used before it becomes too soft. For example, for a hardness of HRC 50 a horizontal line drawn across the diagram at that hardness intersects the curve at a particular value of the abscissa parameter. Then knowing the value of  $T(20 + \log t)$  it is possible to determine the various combinations of t and °F for which the hardness will be at least HRC 50.



### High Speed tool steels

Cold and hot work dies are tools that are designed to form the work piece into a desired shape and size. In contrast, the basic function served by the tool during many machining processes is to change the form of the work piece by cutting pieces (chips or swarf) from its surface. The tool is in contact with the work piece and the two move relatively. The cutting process generates heat which can raise the temperature of the working part of the tool. Accordingly, liquid coolant streams are commonly used in machining processes to lengthen the tool life by minimizing heat induced deterioration of its properties. Heat is created at greater rates the faster the machining is carried out and this imposes a limit on production rates. An increase in the rate at which a particular machining process can be performed is economically desirable. Faster machining rates are possible if the cutting tools can be made of a material that resists softening when heated. Tool steels which possess this property are called high speed, tool steels. Their major function is cutting and their major property is hot hardness, i.e. they retain a high hardness when heated to a red heat. Typically a HRC of 52 at 1000°F and HRC 48 at 1100°F can be achieved.

The first thing that comes to mind when contemplating making a steel hard is the martensitic transformation. So the steel should contain carbon and be of such a composition that it can be converted largely to martensite by a heat treatment. In order for it to have good wear resistance and to maintain a good cutting edge it should contain a high volume fraction of alloy carbides. Then for it to have “red hardness” undesirable changes in the microstructure should not occur or should occur slowly when the tool is hot. This means that the rates of tempering reactions and carbide coarsening processes should be small at the temperatures concerned. Indeed, some secondary hardening during use would be useful provided overaging is not rapid. The alloying elements that are suggested by these requirements are moderate to strong carbide formers that have low rates of diffusion in ferrite. This suggests elements like W, Mo and V. These elements along with cobalt are the important alloying elements in high speed tool steel. Tungsten was the first major element explored for this class of steel and the classic 18-4-1 high speed steel emerged around 1910. This steel is capable of cutting while at a visible red heat. Its composition is:

0.75 % C 0.3 % Mn 0.3 % Si 18 % W 4 % Cr 1 % V 0.7 % Mo

In general, high speed tool steels can be grouped as tungsten based, molybdenum based, and molybdenum-tungsten based. Vanadium and cobalt are the other important alloying elements. Although the original tool steels were tungsten based, each now has a molybdenum counterpart

which has come to be more widely used in this country as a result of strategic materials limitations during wars. We may simply note that the steels are rich in these elements and the metallurgy of the various alloys is quite similar. One should note that tungsten is roughly twice as heavy as molybdenum when comparing weight percentage compositions. Some other examples are;

T4 The 18-4-1+5 % Co  
M2 0.8 % C 5 % Mo 6 % W 2 % V 4 % Cr  
M10 0.9 % C 0.3 % Mn 0.3 % Si 4 % Cr 2 % V 8 % Mo

In general, these steels have high levels of carbide formers which produce excess carbides in the tempered martensite; i.e. the martensitic transformation occurs in austenite that contains alloy carbides so that these carbides are inherited by the martensite. Because of the high content of ferrite stabilizers, austenite isn't formed after holding at temperatures suitable for low alloy steels. For example heating to 1650°F and quenching doesn't produce martensite because austenite doesn't form. When the steel is heated to within 150°F of its melting point, austenite forms and dissolves sufficient carbon and other alloying elements so that it can then be hardened to HRC 63 or higher by cooling in air in thick sections. Secondary hardening by the precipitation of fine alloy carbides occurs during tempering and during use.

#### Microstructural constituents and treatments

The cast steel is extremely cored due to the segregation that occurs during solidification. It is irrelevant whether or not delta ferrite or austenite is the nature of the initial nuclei because the first portion to solidify is relatively lean with respect to its alloy content and is ferrite at room temperature. Embedded within it are some carbides and usually an amount of lamellar pearlitic-like constituent. During the solidification process, the enrichment of the liquid results in the formation of a skeleton-like, eutectic constituent in the final volumes to freeze. The first step after casting is to break down the eutectic network and to produce an array of ferritic grains containing alloy carbides. This is accomplished by hot forging or rolling and annealing at 1650°F. Typically these steels contain 0.25 -0.3 volume fraction of carbides.

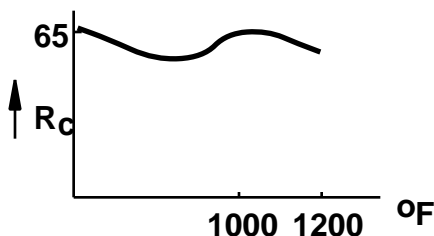
The carbides have been extracted (i.e. the ferrite has been dissolved away using appropriate chemical reagents) and identified (e. g. by electron diffraction) as follows:

M<sub>6</sub>C.....Fe<sub>3</sub>W<sub>3</sub> ; Fe<sub>4</sub>W<sub>2</sub>C. Cr, V and Co dissolves in the former and Mo replaces the tungsten in the latter in Mo steels.  
M<sub>23</sub>C<sub>6</sub>.....Chromium rich, dissolves Fe, V, Mo and W  
MC.....Vanadium rich  
M<sub>2</sub>C.....Tungsten or molybdenum rich carbide

The matrix contains some of the alloying elements in solid solution and very little carbon. Roughly half of the chromium content is in solution which is beneficial for corrosion resistance. It is possible for intermetallic compounds to form when the total carbon is low e.g. Fe<sub>3</sub>W<sub>2</sub>.

The heat treatment used to harden these steels first produces a mixture of austenite and alloy carbides. Initially the microstructure is an array of ferrite grains and alloy carbides. When the austenite begins to form the microstructure contains austenite, ferrite and carbides. Both the ferrite grains and the carbide particles restrict the grain growth in the austenite. Then M<sub>23</sub>C<sub>6</sub> begins to dissolve and the dissolution is complete when 2000°F is reached during slow heating. Then partial

solution of the other carbides occurs until the austenite typically contains about 7-12 % alloy carbides of the types MC and  $M_6C$ . On cooling there is an immediate tendency for the carbides to re-precipitate. Some precipitation occurs, especially on austenite grain boundaries. However, the rates of diffusion of W and Mo are very low and it requires very slow cooling for significant carbide precipitation to occur on the grain boundaries and within the grains. More rapid cooling yields bainite and then martensite plus carbides plus retained austenite. A typical tempering response is indicated in the sketch.



The starting material is 60-80% BCT martensite, 15-30 % FCC austenite and 5-12 % MC and  $M_6C$ . It is very hard and also very brittle with much residual internal stress. The usual tempering range is 950 to 1100°F but for the sake of completeness we will note that three stages of tempering have been observed.

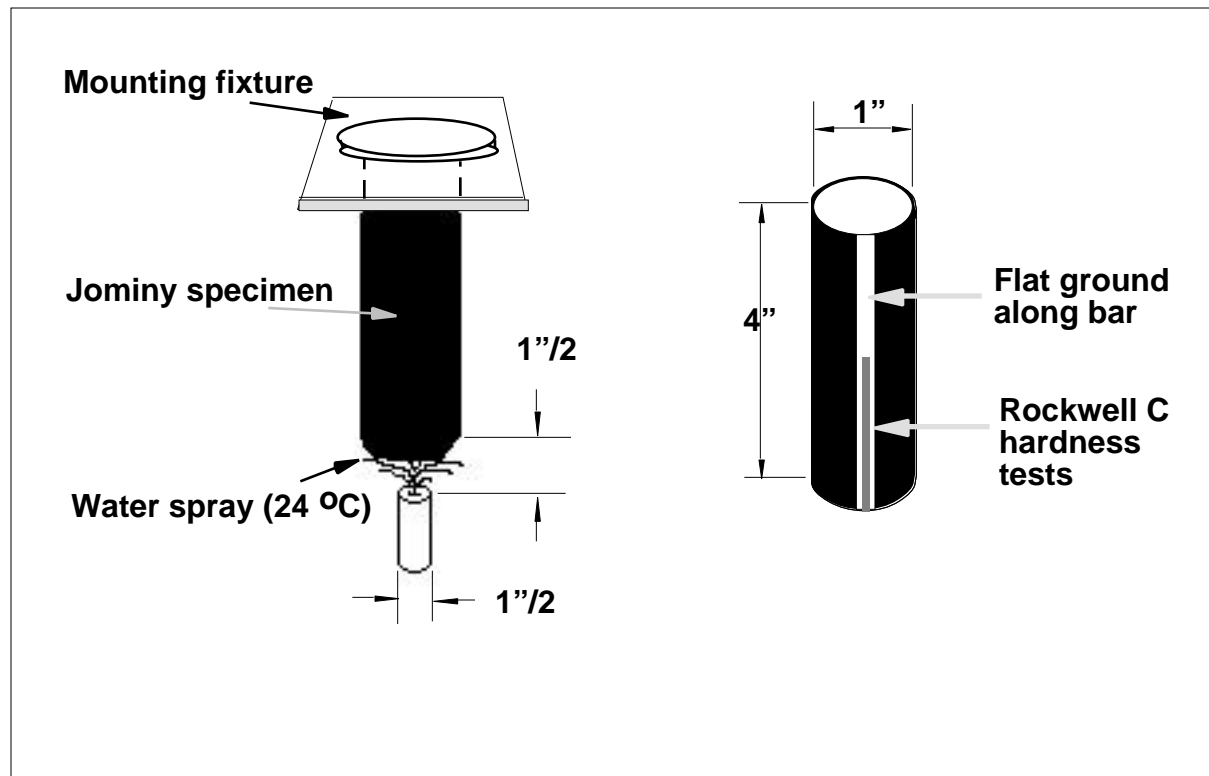
- 1) Up to 270°C, BCT martensite transforms to BCC plus epsilon carbide.
- 2) In the range 300-400°C BCC plus epsilon carbide goes to BCC plus cementite.
- 3) From 400- 560°C, BCC plus cementite changes to BCC with less cementite and the formation of alloy carbides occurs.

While these transformations are taking place at the higher temperatures in the martensite, precipitation of alloy carbides also occurs in the retained austenite which is also supersaturated. This reduces the concentration of dissolved alloying elements in the austenite which raises the  $M_s$  temperature. This causes more martensite to form when the tool is cooled after being tempered. Often double or even multiple tempering is necessary to eliminate the retained austenite. The red hardness is due to the reluctance of the carbides to coarsen because of the slow rates of diffusion and also because secondary hardening can occur while the tool is hot.

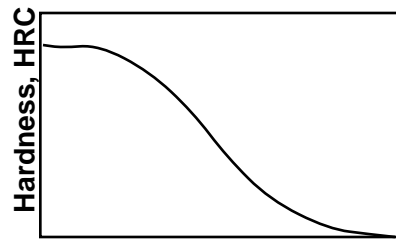
Once a high speed tool steel has been hardened by such a heat treatment they cannot be re-hardened by a straight forward repetition of the same heat treatment because discontinuous grain growth occurs. During the heating process used to austenitize the steel, the small acicular BCC crystals transform to austenite but their intercrystalline boundaries are pinned by fine carbides. These carbides restrict grain growth until high temperatures are reached whereupon, as the carbides dissolve, some crystal boundaries become unpinned before the others. Then a few grains are able to grow rapidly at the high temperatures and consume their neighbors. This process leads to exaggerated grain growth in which a few grains become very large. The effect is inherited in the tempered martensite that is formed subsequently causing very poor toughness. The elimination of this tendency requires special treatments such as long term cyclic heat treatments.

This completes our dash through part of the kingdom of tool steels.

## Additional Pictures:

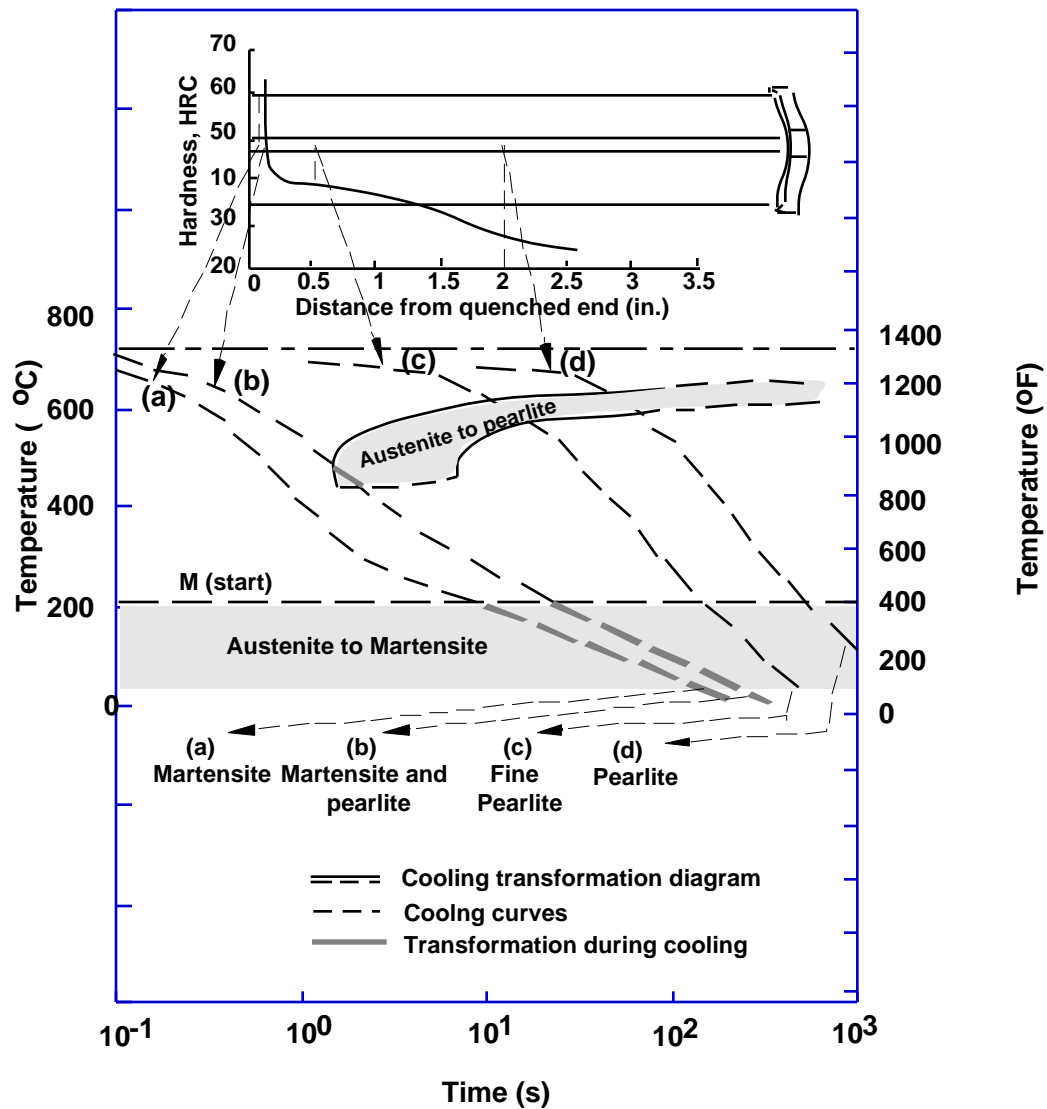






Typical hardenability plot of Rockwell C hardness as a function of distance from the quenched end.

Distance from quenched end



Correlation of hardenability and continuous cooling information for an iron-carbon alloy of eutectoid composition. (Adapted from H.Boyer, Editor, Atlas of Isothermal Transformation and Cooling Transformation Diagrams, American Society for Metals, 1977, p376)

