Part I

2

Thermodynamic conditions for the Mn–O system in sintering of manganese steels

2.1. Manganese in steelmaking

Manganese is the most widely used alloying element in the production of classic steels. Because of its possible application as an alloying element in the production of steels (this has not as yet been realised), it is necessary to discuss its physical–metallurgical characteristics which determine its irreplaceable role in classic steel production. In this connection, it is important to stress the fundamental difference between the production of classic manganese-alloyed steels and the production of sintered steels which influences the properties of final products. The classic and also manganese-alloyed steels are produced by melt metallurgy with the unlimited solubility of manganese in the melt. The production of a solid skeleton from a dispersed iron powder and its alloying with manganese and also with other alloying elements by sintering take place by diffusion mechanisms only in the solid state. This production is affected by a considerably larger number of mutually interacting factors in comparison with the production of classic steels. These factors must also be taken into account in the application of manganese as an alloying element in powder metallurgy with its physical–metallurgical characteristics, some of which are discussed later.

Due to its physical–metallurgical properties, manganese has a special position in ingot steel metallurgy, *i.e.* alloying and deoxidation. At the same time, manganese is the cheapest alloying

element. The density of manganese is 7.21 g cm^{-3}, melting point 1244°C.

Manganese is found in every classic structural steel. It comes from ore, and steels with the content of up to 0.4% Mn are not regarded as alloyed steels. The steels with the manganese content of 0.8–1% and with 0.4–1% C are characterised as low-alloy steels, the steels with 0.8–1.7% Mn and with 0.6-0.1% C belongs to quenched and tempered steels with the hardness of 300–350 HV and the steels with 0.9–1% C are classified in the group of steels with no deformability. Higher alloyed steels with 6–12% Mn are characterised as steels with high wear resistance, with the Hadfield steel (12% Mn, 1.2% C) being the main representative of this group of steels.

The highest solubility of manganese in α-iron is 3% and in γ-iron it is up to 55%. Manganese is present in four modifications, *i.e.* α, β, γ and δ. From the viewpoint of sintering it is necessary to ensure that manganese at the transformation points, *i.e.* at 727°C (α→β), 1100°C (β→γ) and 1136°C (γ→δ) expands and this expansion is the main reason for the growth of the dimensions of sintered manganese-alloyed compacts.

Like nickel, manganese forms the open γ-region and by this decreases the γ→α transformation temperature. Diffusion of manganese in α- and γ-iron is considerably slower than carbon diffusion. The manganese atoms can replace iron in the carbide and, consequently, it may be expected that the iron carbide will be greatly enriched with manganese. This phenomenon is more evident in low-carbon steels and vice versa.

When the manganese content is increased the pearlitic transformation point is shifted to the side with lower carbon content. Increasing manganese content also reduces the rate of transformation in both the pearlitic and bainitic ranges, and the maximum rate of transformation in the bainitic range and also the martensitic transformation are shifted to lower temperatures. A special feature of the diffusion processes in the manganese steels is that in certain systems the steel can contain simultaneously ferrite, bainite, martensite and austenite.

Alloying of pure iron with manganese has almost no effect on its notch toughness. At a carbon content of up to 0.2% no quenching of the steels takes place even after rapid cooling of the manganese steels from the γ-region in water. Consequently, these steels change their properties only slightly even after long-term tempering.
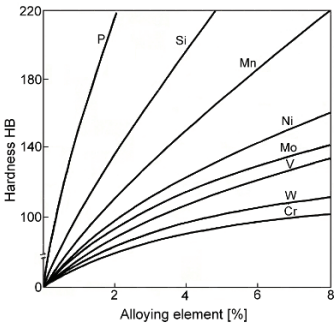
Fig. 2.1. Effect of alloying elements on hardness of ferrite [1].
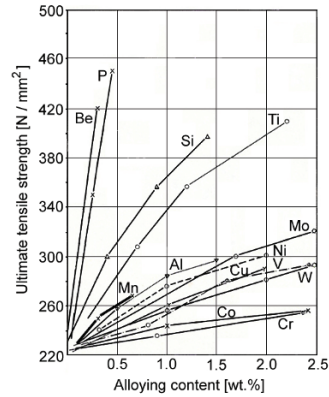
Fig. 2.2. Effect of alloying elements on tensile strength of ferrite.
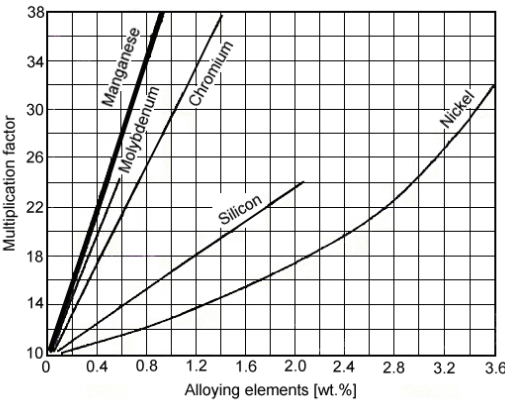
Fig. 2.3. Multiplication factor of alloying elements.

Manganese has a higher hardening effect on ferrite compared with other alloying elements, for example, nickel and, in particular, chromium. The hardening effect of manganese has been and still is the main aim of research also in powder metallurgy in the production of sintered structural steels. Figure 2.1 shows the hardening effect of manganese on the hardness of ferrite in comparison with other elements, and Fig. 2.2 shows the effect on ultimate tensile strength. These data are valid only for carbon contents of up to 0.1%. The high hardening effect of manganese on ferrite is also shown by the multiplication factor in Fig. 2.3.

The parameters important for hardenability are the Grossman factor for 1 wt.% alloy, oxidation reaction enthalpies and diffusion coefficients as the additional data presented in the diagrams in the previous section for the elements used and researched most

Table 2.1. Grossman factor for 1 wt.% alloy (GF), diffusion coefficient of alloying element in γ-iron (D_x), self-diffusion coefficient of γ-iron (D_{Fe}) and free enthalpy of formation of oxide (ΔG) (kJ·g·atom) oxygen) [1]

Alloying element	GF	D_x / D_{Fe}	ΔG
Copper	1.3	1	−150
Nickel	1.4	0.5	−250
Molybdenum	3.7	5	−310
Iron			
Chromium	3.1	5	−540
Manganese	4.5	2.5	−500
Vanadium	–	5	−620
Boron	–	–	−650
Silicon	1.7	10	−680

extensively in powder metallurgy, are presented in Table 2.1. (The changes in the free enthalpy ΔG of oxide formation is a measure of how readily the material oxidises assuming that metal and oxide are present as the solid phase).

The deoxidation effect of manganese in the production of steel is evident as a result of its high affinity for oxygen. Manganese in the melt reacts with oxygen and also sulphur with the formation of oxides and sulphides which easily transfer into the slag and also evaporate and react with oxygen in the atmosphere above the melt surface.

2.2. Basic thermodynamic characteristics of protective atmospheres for sintering steels alloyed with manganese and other elements

The sintering of materials based on ferrous powders, which represent almost 80% in mass of total production of powder metallurgy, must be perfected under a protective atmosphere. The task of the protective atmosphere under the effect of the heat at elevated temperatures is the formation of a solid body from a dispersed powder system. The effect of the protective atmosphere expresses itself during the entire sintering process, *i.e.* yet in yearly stages of heating of the compacts at dewaxing, which adversely affects the quality of the atmosphere in spite of it that in most cases it occurs only during a relatively short time during this sintering stage.

The most important function of the atmosphere is the reduction of the oxide films covering the surface of the used powder components used for the preparation of the compacts (base and alloying powders stored in air), including the surface of interior pores in the compacts. The reduction of the atmosphere containing some amount of humidity to the equilibrium conditions for the given material system must guarantee satisfactory clean metal surfaces of the metal powder components in the compacts to form contacts (necks, bonds), so that the material transport during sintering between powder particles is not inhibited under contemporary protection of the compacts against the oxidation [2].

The further role of the atmosphere is to protect the system being sintered against oxidation during preheating, isothermal sintering and cooling up to the exit of the sintered parts from the furnace. The flowing gases used as protective atmospheres transport away also the gaseous products of the reduction. The protective atmosphere also guarantees during the isothermal sintering hold the growth of interparticle bonds as well as a substantial extent of alloying of the austenite matrix with additional elements with the impact on the homogeneity of the structure and required physical and mechanical properties of the material.

In the protective atmospheres used in powder metallurgy, pure hydrogen exerts a high reducing effect in most cases but due to some of its drawbacks (highly explosive, high cost), cracked ammonia is often used (75% H_2/25% N_2) as a proper protective atmosphere. At present, modern nitrogen-based atmospheres (nitrogen + hydrogen) are used in most cases. They are formed as a mix of two gases over a wide ratios up to (5–3)% H_2/(95–97)% N_2. Therefore, the ratio of these gases is prepared in loco adapted to the material systems being sintered. Nitrogen, N_2, as molecules, does not react with iron nor with oxygen. It is basically neutral or even beneficial for many ferrous alloys [3].

The carrier of oxidation of the sintered materials is the water vapour H_2O in the H_2/H_2O atmosphere. Due to a porous structure, pressed powder components react more readily with the surrounding atmosphere than fully dense materials and this affects the choice of the gas and its optimum mix and gas flow rate.

The susceptibility of an element to oxidation is indicated by the change of the free enthalpy of oxide formation. The temperature dependence of that and of oxygen potential for different metal oxides is shown in Fig. 2.4. This dependence is used to determine the partial
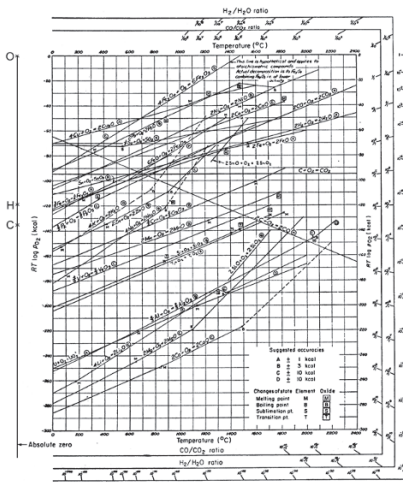
Fig. 2.4. Temperature dependence of enthalpy changes and oxygen potential of metal oxides (Richardson–Ellingham diagram) with the line for Mn at 1150°C [4].

pressure of oxygen which is in equilibrium with the oxide and the corresponding H_2/H_2O ratios at the given temperature for a specific metal. (The CO/CO_2 equilibrium ratios for the metals are in this case not considered because this atmosphere was not used for sintering of manganese steels described in this work). The values of this oxygen pressure for several metals, including corresponding dew points, are shown in more detail in Fig. 2.2. In general, the fraction of water vapour in a furnace atmosphere in a H_2/H_2O mixture is determined by the dew point measurements. The dew point is a measure of the water to hydrogen partial pressure ratio and tells the temperature at which water vapour will condense. It is a common measure of the atmosphere reduction potential. The dependence of the H_2/H_2O ratio in an atmosphere and the dew point is shown in Fig. 2.6.

The equilibrium data for interesting metals are those used in selecting the atmosphere for the given material system and sintering conditions. The use of equilibrium data to calculate compositional requirements for the protective atmosphere implicitly assumes that the system in question may be brought to an equilibrium or steady state condition. The steady state differs from a true equilibrium here in that only a partial, or local, equilibrium is established at the metal–vapour (atmosphere) interface. Supplying the atmosphere at a rate sufficient to overpower any compositional changes that might occur does this by reaction of the atmosphere with metal surfaces. It is readily obvious that this situation is not possible with porous metal materials since the surface extends well into the interior volume, the volume of pores and continuous rapid replenishment of atmosphere
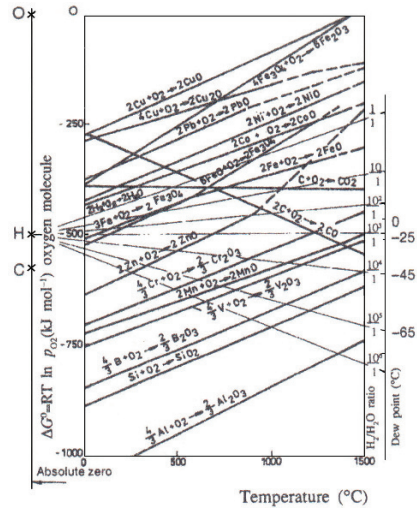
Fig. 2.5. Temperature dependence of enthalpy changes and oxygen potential of some selected metal oxides and corresponding dew points (Richardson–Ellingham diagram) [1,4].
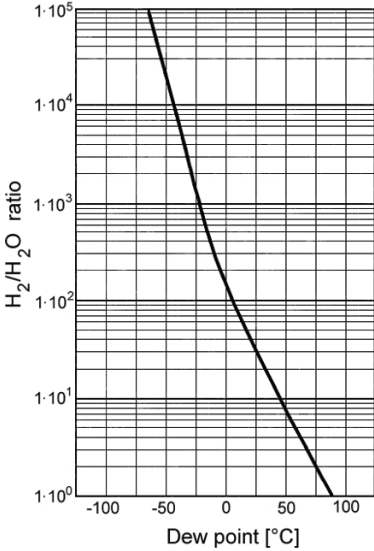
Fig. 2.6. Correlation between H_2/H_2O ratio and dew point [5].

in contact with their interior surfaces is physically impossible under normal furnace conditions.

Additionally, any minor change of local temperatures can affect equilibrium ratios. The situation inside the parts is very different, indeed, in the regions equilibrium can be established only between local carbon content and in discussed case also local manganese and local oxygen or residual water vapor formed by reaction of hydrogen with iron oxide. The effect of the atmosphere inside the parts can be important at relatively low densities. For this reason, the ideal stages should be considered almost completely valid only for the 'skin' – surface of PM parts. What really happens, which reactions proceed in the core, strictly depends on porosity, pore structure, part volume and part size, and perhaps on the flow rate of the atmosphere. The porosity increases in a large amount the total reaction surface with the active gas of the sintered compact. For instance, at the total porosity of 12% of a sample the surface area of interconnected pores is around 130 times larger as its geometrical surface area [6]. For a better understanding of actual sintering conditions, definitely different from the classical equilibrium concept, it may be necessary to discuss from the thermodynamic point of view the different
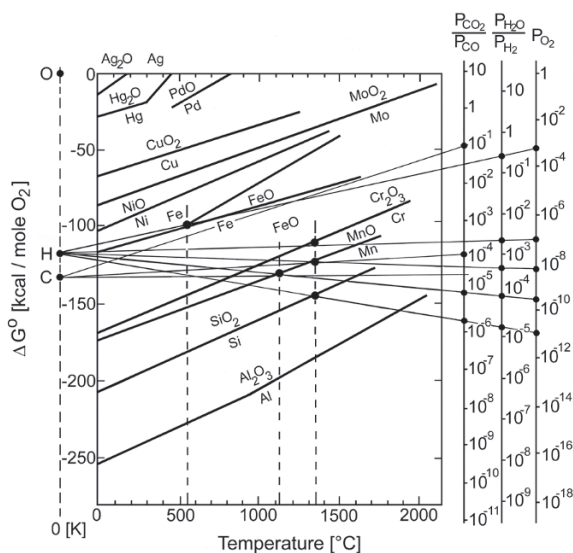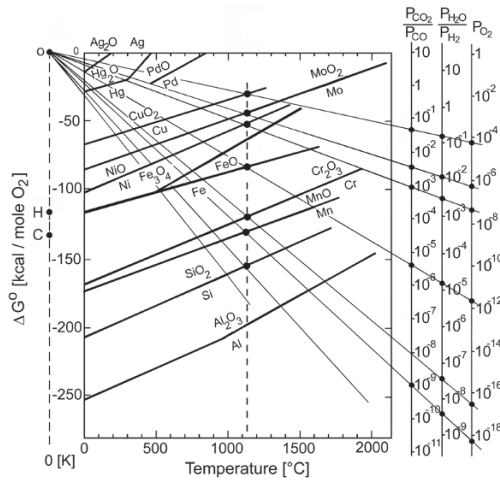
Fig. 2.7. Graphical determination of the equilibrium dissociation pressure P_{O_2}, $P_{H2O/H2}$ and $P_{CO2/CO}$ for FeO/Fe, Cr_2O_3/Cr, MnO/Mn and SiO_2/Si systems at various temperatures [1,2,7].

possible atmospheres separately for individual material systems, what the researchers tried and try to do especially for the Fe–Mn system.

Figure 2.7 illustrates the equilibrium oxygen dissociation pressure for FeO (550°C), MnO at 1120°C, the most common sintering temperature, and for Cr_2O_3, MnO and SiO_2 at 1350°C. The difference between these dissociation pressures is larger than by 6 orders of magnitude, *i.e.* it is very low for MnO. Figure 2.8 shows for comparison the determination of equilibrium temperatures for Cu, Mo, Fe, Cr, Mn and Si in the H_2/H_2O atmosphere.

Manganese belongs to the elements, which form the oxides reducible only with carbon not with hydrogen. The sintering of manganese and of manganese containing alloys and the reduction of its oxides with hydrogen should be possible only under the presence of some other element, which forms with it a solid solution. Iron is an excellent element for this application [9,10]. Manganese with oxygen forms the compounds Mn_2O_3, MnO_2, MnO_3, Mn_2O_7, Mn_3O_4 and MnO. The majority of them have also different modifications. MnO_2 and Mn_2O_3 easily decompose to Mn_3O_4 and oxygen and by this reason are easily reducible. MnO_2 (manganese dioxide, manganese ore – pyrolusite) dissociates at the temperatures of 400–500°C [11], and is reducible also with hydrogen was used therefore for

Fig. 2.8. Graphical determination of equilibrium temperatures for Cu, Mo, Fe, Cr, Mn and Si in the H_2/H_2O atmosphere [8].

alloying of sintered manganese steels. The oxides Mn_3O_4 and MnO exist at temperatures higher than 800°C, and should be reducible only with carbon at presence of the element with high solubility of manganese [12]. These Mn-oxides prove to be of greatest importance for powder metallurgy. Iron in this case can act as an activator at temperatures higher than the ordinary sintering temperature of 1120°C and, therefore, the analysis is always concentrated on MnO as the most hardly reducible Mn-oxide. The oxidation of metallic manganese in air starts at ~400°C under the formation of an active bright blue-grey Mn-oxide, which at 500°C transforms in air to a stable inactive green in colour MnO. At the increased temperature, over 900°C forms also an inactive dark grey form of MnO of non-stoichiometric composition [13].

All requirements concerning the formation and reduction of manganese oxides during the sintering of mixed manganese steel according to the Richardson–Ellingham diagram shown in Figs. 2.4 and 2.5 are related to MnO only. The basic reaction of manganese and oxygen expresses the equation:

$$2Mn + O_2 = 2MnO.$$
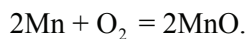
The thermodynamic conditions for reduction of MnO oxide by various hydrogen-containing atmospheres or by solid carbon are described below. They only particularize the oxygen potentials in

Table 2.2. Equilibrium data of Mn/MnO in O_2 (partial oxygen pressure) gas mixture of H_2/H_2O and corresponding water contents; d.p. – dew point [3,8]

	Temperature [°C]								
	600	700	800	900	1000	1100	1150	1200	1400
P_{O2} [Pa]	10^{-38}	10^{-34}	10^{-30}	10^{-26}	10^{-24}	10^{-22}	10^{-21}	10^{-20}	10^{-16}
H_2/H_2O	$1\cdot10^8$	$1\cdot10^7$	$3\cdot10^6$	$7\cdot10^5$	$2\cdot10^5$	$9\cdot10^4$	$5.0\cdot10^4$	$4.0\cdot10^4$	$2.7\cdot10^3$
P_{H2O} [Pa]	0.01	0.05	0.13	1.06	2.35	2.06	3.89	10.10	37.67
dew point [°C]	102	–90	–80	–75	–60	–57	–50	–40	–30
H_2O vol.[%]	$1\cdot10^{-6}$	$9\cdot10^{-6}$	$5.2\cdot10^{-5}$	$1.4\cdot10^{-4}$	$1.1\cdot10^{-3}$	$1.3\cdot10^{-3}$	$2.0\cdot10^{-3}$	$3.8\cdot10^{-3}$	$3.7\cdot10^{-2}$

the atmosphere under some sintering condition for MnO and partly for FeO. The calculated minimal dew points and oxygen potentials for H_2/H_2O atmospheres in the temperature range of 600 to 1400°C to reduce MnO or to prevent oxidation of manganese are listed in Table 2.2. These data correspond to the free enthalpy changes shown in Figs. 2.4 and 2.5 demonstrating high affinity of manganese for oxygen and hard reducibility of its oxides. It is possible to deduce

from this why manganese as a PM alloying element did not find up to the time none large scale application in production of sintered alloyed steels. These thermodynamic data were and in some cases are considered as a decisive factor against manganese in spite of the results obtained at sintering of manganese steels. It would be very hard up to impossible to fulfill these requirements for the purity of the atmosphere for sintering of manganese steel, namely under industrial conditions.

The thermodynamic requirements for the purity of a sintering atmosphere should be not constant during the entire sintering temperature range. The total preheating period and the cooling stage under laboratory and, in particular, under industrial sintering conditions need the atmosphere with higher purity than that for isothermal sintering. This is often decisive for the determination of the dew point of the atmosphere used. The preheating period in the sintering process is that in which dewaxing of the compacts occurs at which the lubricant melts and evaporates followed by burn-off requiring a humid atmosphere at the temperature below ~600°C [14]. On the other hand, the Mn-containing parts require for elimination of oxidation first the manganese carriers in the compacts an atmosphere with an extremely low dew point, as for instance of –102°C at 600°C, what is not realizable in practice.

In general, the fraction of water vapour in a furnace atmosphere in H_2/H_2O mixtures is determined by the dew point measurements. The relation between the dew point and moisture is listed in Table 2.3. However, on cooling, the compacts will again recross the oxidation-reduction boundary and be oxidized during cooling. If that occurs at a high temperature, then the compacts will be discoloured and possibly attacked.

A detailed view on the oxygen potential in the sintering atmospheres previously and nowadays commonly used in powder metallurgy, *i.e.* endothermic gas (endogas), dissociated ammonia, hydrogen and on nitrogen-based atmospheres at different dew points for Cr and Mn is shown in Fig. 2.9. It follows from the diagram that H_2/H_2O and temperatures are the critical factors determining whether oxidation or reduction will occur. It was stated in [15] that none of the analyzed atmospheres can, according to these calculations, reduce the oxides or avoid further oxidation of Cr and Mn at 1120°C. The equilibrium values of the H_2/H_2O ratio and the dew points in H_2/H_2O atmospheres for selected metal–oxide systems are better shown in Fig. 2.6. It is necessary to note the differences in oxygen

**Table 2.3.** Relation between dew point and moisture content of gases [1]

Dew point		Moisture		Dew point		Moisture	
(°C)	(°F)	mg/l	vol.%	(°C)	(°F)	mg/l	vol.%
30	86	30.2	4.18	−15.6	4	1.54	0.18
25.6	78	23.7	3.22	−20	−4	1.08	0.125
20	68	17.3	2.31	−25.6	−14	0.675	0.076
15.6	60	13.3	1.75	−30	−22	0.455	0.0503
10	50	9.4	1.21	−35.6	−32	0.272	0.0294
7.8	46	8.15	1.04	−40	−40	0.178	0.0189
5.6	42	7.05	0.895	−45.6	−50	0.107	0.0112
0	32	4.8	0.6	−50	−58	0.064	0.0065
−5.6	22	3.28	0.4	−56.7	−70	0.029	0.0028
−10	14	2.35	0.282	−62.2	−80	0.014	0.0014
−13.3	8	1.83	0.216	−65	−85	0.009	0.0008
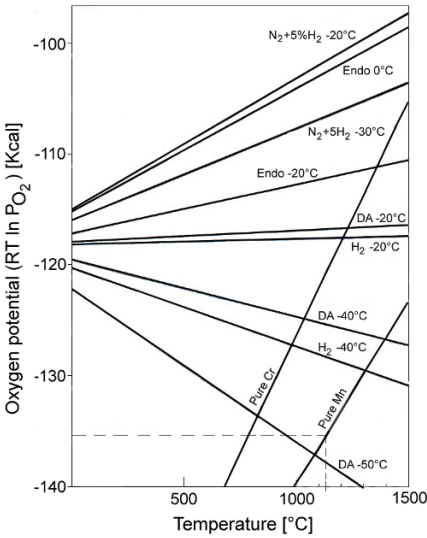
Fig. 2.9. Oxygen potential in endogas, dissociated ammonia, hydrogen and N_2-based atmospheres at different dew points (indicated temperatures refer to the dew point of the atmosphere [8,15,16].

potentials in H_2/H_2O atmospheres for sintering with Mo and Ni alloyed steels compared to that alloyed with Cr and Mn. Low requirements for the purity of the atmosphere for industrial sintering of pressed iron based parts were perhaps the main starting reason for alloying of sintered steels mainly with Ni and Cu as elements
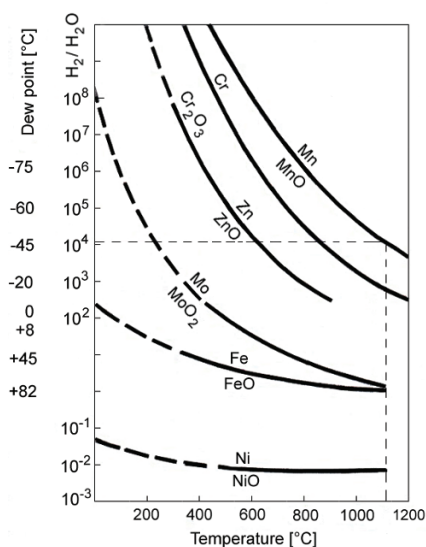
Fig. 2.10. Equilibrium values of H_2/H_2O ratio and the dew points in H_2/H_2O atmospheres for selected metal-oxides systems [4,7].

with low affinity for oxygen, *i.e.* low requirements o the purity of the sintering atmospheres [2], Fig. 2.10.

All mentioned reactions for Mn–O–H systems from the thermodynamic point of view are calculated for the unit activity of the system. They refer to chemically pure compounds, including hydrogen. In the real systems, the chemical activity of, for example, all manganese carriers as, for instance, ferromanganese grades and/or some special Mn-containing master alloys, is much lower because they contain different impurities, mainly iron. Accordingly, FeO and vice-versa (unlimited solid solubility) can substitute the places in the lattice of MnO.

The phase stability diagrams Mn–O–H and Mn–O–C for 800, 1200 and 1300°C, elaborated on the basis of mentioned thermodynamic analyses for reduction and conversion reactions of manganese oxides with $H_{2(g)}$, $CO_{(g)}$ and $C_{(s)}$ for the Mn–O–H and Mn–O–C systems, made it possible to deduce comprehensively the following results [8]:

- reduction of MnO → Mn by neither $H_{2(g)}$, $CO_{(g)}$ nor $C_{(s)}$ occurs below 1280°C
- reduction of MnO is possible only with $C_{(s)}$ at temperature above 1280°C
- conversion of MnO_2 to Mn (MnO_2 is not stable) is possible, the highest step of conversion reaches the reaction with $C_{(s)}$
- reduction both of Mn_2O_3 → Mn at >1000°C and of Mn_3O_4 → Mn at >1100°C with $C_{(s)}$ can take place
- reduction of $MnO_{(g)}$ in $H_{2(g)}$ and $CO_{(g)}$ can take place.

According to [17], the reduction of MnO to Mn occurs with carbon (solid) as graphite at a temperature over 1200°C evenly only through the Mn-carbide (Mn_5C_2) as follows from the overall reduction reactions for this process:

$$5MnO + 7C = Mn_5C_2 + 5CO$$
$$2MnO + Mn_5C_2 = 7Mn_{(g)} + 2CO.$$
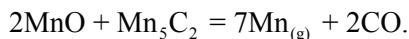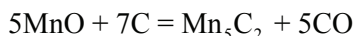
During the sintering of manganese steel, the conditions for the reduction with solid carbon do not form because at the temperature over 900°C, solid carbon (graphite) in sintered steel cannot be present due to its dissolution in austenite.

In term of the mentioned thermodynamic calculations, the presence of MnO in being admixed sintered Fe–Mn compacts is apriori assumed because the all calculations start with this Mn-oxide. The presence of some manganese oxides introduced or during sintering formed in sintered manganese containing systems in the literature was not observed and therefore also not analyzed. The surface of the starting manganese carrier particles (electrolytic manganese, ferromanganese grades, and/or special Mn-containing master alloys) should be covered with some layer formed at milling in which could be some manganese oxide or Mn–O oxide film. The MnO, which is green in colour and by this easy discernible also by look, is possible to exclude due to its reducibility only at the temperature exceeding the common sintering temperatures as follows from the previous data. Beside it, there are no data in the literature regarding the Mn-oxides on the particles of the manganese carriers. There is only the possibility for oxidation of manganese particles in the compacts during preheating period as well under laboratory as under industrial sintering conditions up to the temperature at which the equilibrium occurs at the dew point of the atmosphere used. For instance, by the use of the H/N sintering atmosphere with a dew point of –50°C, the equilibrium conditions for the Mn–O system corresponds to the temperature of 1150°C. This purity of the atmosphere does not fulfill the requirements for the preheating period over the temperature 400°C, at which manganese starts to oxidize, Table 2.2.

These data show that the sintering of manganese-alloyed steels in accordance with the thermodynamic requirements on the purity of the protective atmosphere cannot be realised without taking into account the stage of preheating to sintering temperature. In addition to this, all the thermodynamic criteria for the Mn–O system take into account only the possible reduction of MnO. There are no data

indicating whether this manganese oxide should be introduced into the Fe–Mn system as a layer on the manganese carrier powder, or whether the manganese particles in the compact should oxidise in the atmosphere with insufficient purity. Under no conditions can the MnO be reduced to such an extent that it would be capable of alloying the iron matrix of the compact in some actual sintering conditions. On the basis of these data it should be accepted that the sintering of manganese-alloyed steels takes place under different physical–metallurgical conditions.

2.3. Influence of protective atmospheres on proper sintering of carbon containing steels

In general, the task of the protective gas is to prevent oxidation of the compacts during sintering and reduce any oxide skins remaining from the powder processing, so that the contact between particles, and therefore, material transport during sintering are not inhibited [5]. In the sintering of carbon-containing steels, the protective atmosphere should prevent the decarburisation of the compacts.

To obtain the required high strength and other functional properties for greatly differing technical applications, the sintered steels always contain carbon mostly in combination with the additions of suitable alloying elements. It is well-known that the optimum properties of the sintered steels in combination with the additions of suitable alloying elements can be achieved only by a precise control of carbon control, what is a further requirement for the atmosphere. A comparison between the ranges of carbon content of fully dense wrought steel versus sintered porous steel is strongly unfavourable to PM. A precise control of carbon content is always a critical factor for elimination the decarburisation and by this for achieving, systematically, the highest required properties. The controlling role of the shielding atmosphere is discussed briefly in Table 2.4.

Taking into account manganese, to these tasks with the special reference to the purity atmosphere it is necessary to add protection against oxidation of manganese particles as the alloying element during preheating, including the dewaxing zone, and also throughout the entire sintering process. This requirement follows from the thermodynamic considerations for the Mn–O system.

The mentioned 'unit' stages of sintering can proceed partly in other temperature ranges in relation to the starting base and alloy elements used, they can overlap each other. This can be, for example,

Table 2.4. 'Unit' stages occurring during the sintering of steels under the influence of a controlled atmosphere [18]

No.	Unit stage	Temperature range [°C]
1	Lubricant removal in the liquid state	150–200
2	Lubricant removal by gaseous decomposition	300–600
3	Refining (reduction of iron oxides)	750–1000
4	Carbon diffusion	900–1050
5	Diffusion of alloy additions	1050–1300
6	Carbon pick-up by atmosphere (in some cases)	1000–1300
7	Carbon restoration	1050–800
8	Microstructure formation	950 – 600
9	Final cooling under reducing or inert conditions	600 – 50

reduction of iron oxides. All starting powder particle surfaces used in powder metallurgy are commonly clean, not covered with stoichiometric oxides. It can therefore be assumed that the powders are covered with chemisorbed oxygen. Similarly, the alloying of iron matrix with some alloy element can proceed at lower temperature in dependence on mutual diffusivity of the elements.

The possible atmospheres, considering only the sintering of carbon-containing steels, which depend also on the type of alloy addition, may be:

• endogas from gaseous hydrocarbons (usually methane or propane)
• synthetic endogas (mixtures of methanol and nitrogen)
• cracked ammonia
• nitrogen-based mixes (N_2 + H_2) without carburising addition
• nitrogen-based mixes (N_2 + H_2) with carburising addition
• highly diluted endogas
• vacuum.

The most often used carburising addition is 0.5% of natural gas (methane, CH_4) to the atmosphere. This is especially important if the sintering atmosphere is required to have a certain 'carbon potential' to prevent decarburisation, *e.g.* during the sintering of steels containing C, or in other cases to promote carburisation. The water will combine with the carbon in the methane to form CO or CO_2, leaving the carbon in the iron unattacked.

Laboratory sintering of carbon-containing steels under a getter (alumina + graphite) is a common method to prevent the decarburisation of the parts. The amount of graphite addition must eliminate supercarburisation. The use of some controlled atmosphere depends on the local source of the base gas. The same atmospheres and methods to protect the sintered steels against the decarburisation are valid also for manganese steels.

In respect to carbon in the compacts, pure hydrogen as a protective atmosphere at sintering is the most common of commercially pure gases because it provides the most effective reducing atmosphere, but does not ensure decarburizing. The same character has also pure nitrogen as a cheap and explosion-safe inert gas or purging gas, especially for metals such as iron and copper which do not react readily with the furnace gas. On contrary, in this case carbon acts as a reduction agent to the oxygen introduced in the system with the base powders. Nitrogen-based protective atmospheres are produced by mixing inert, dry nitrogen with small, carefully controlled amounts of 'active' ingredients to control oxide reduction, carbon potential and strict dimensional accuracy, microstructure and mechanical and other required properties. Cracked (dissociated) ammonia is relatively a low-cost reducing atmosphere to sinter many metallic materials, is free from CO, CO_2 and water, and does not contain another oxygen or sulphur compound. The dissociation reaction occurring near 1000°C gives a pure, low moisture content atmosphere. The residual ammonia content is typically below 250 ppm, and as long as the moisture content is low the atmosphere is nearly neutral with respect to carbon. Due to its high H_2 content, the gas is decarburising and is therefore not suitable for sintering carbon-containing steels [5].

Decarburisation of manganese steels could be prevented by the same methods as for other steels, but no experimental knowledge applied in practice is available. Regarding the effect of some alloying element on the carbon activity in austenite, for instance Si or Ni, this element originates a decrease of the carbon content of saturated austenite and also of pearlite, whereas alloying additions, like Cu, Mn and Cr, decrease carbon activity. For this reason, the addition of more than 0.7% C to nickel-alloyed PM steels should be avoided to prevent any possible formation of brittle carbides at the grain boundaries [18]. As can be deduced from this, the addition of more than ~0.6% C to the sintered manganese steels should be studied in more detail regarding the characteristics of manganese in wrought steels, Chapter 2.1.