SINTERING

Sintering is the process by which metal powder compacts (or loose metal powders) are transformed into coherent solids at temperatures below their melting point. During sintering, the powder particles are bonded together by diffusion and other atomic transport mechanisms, and the resulting somewhat porous body acquires a certain mechanical strength.
### TABLE OF CONTENTS

6.1  GENERAL ASPECTS

6.2  BASIC MECHANISMS OF SINTERING

6.3  SINTERING BEHAVIOR OF IRON POWDER COMPACTS

6.4  THE SINTERING ATMOSPHERE

REFERENCES
6.1 General Aspects

The sintering process is governed by the following parameters:
- temperature and time,
- geometrical structure of the powder particles,
- composition of the powder mix,
- density of the powder compact,
- composition of the protective atmosphere in the sintering furnace.

The practical significance of these parameters can be described briefly as follows:

**Temperature and time.**
The higher the sintering temperature, the shorter is the sintering time required to achieve a desired degree of bonding between the powder particles in a powder compact (specified e.g. in terms of mechanical strength).
This constitutes a dilemma: From the viewpoint of production efficiency, shorter sintering times would be preferable; but the correspondingly higher sintering temperatures are less economical because of higher maintenance costs for the sintering furnace.
In iron powder metallurgy, common sintering conditions are: 15 - 60 min at 1120 - 1150°C.

**Geometrical structure of the powder particles.**
At given sintering conditions, powders consisting of fine particles or particles of high internal porosity (large specific surface), sinter faster than powders consisting of coarse compact particles. Again, we have a dilemma: Fine powders are usually more difficult to compact than coarse powders, and compacts made from fine powder shrink more during sintering than compacts made from coarse powder. Particles of commercial iron powders (spongy or compact types) for structural parts are usually ≤ 150 μm (ref. Chapter 3).

**Composition of the powder mix.**
The components of powder mixes are selected and proportioned with a view to achieving desired physical properties and controlling dimensional changes during sintering (ref. Chapter 3). When mixes of two or more different metal powders (e.g. iron, nickel and molybdenum) are sintered, alloying between the components takes place simultaneously with the bonding process.
At common sintering temperatures (1120 - 1150°C), alloying processes are slow (except between iron and carbon), and a complete homogenization of the metallic alloying elements is not achievable. If the powder mix contains a component that forms a liquid phase at sintering temperature (e.g. copper in iron powder mixes), bonding between particles as well as and alloying processes are accelerated.
Density of the powder compact.
The greater the density of a powder compact, the larger is the total contact area between powder particles, and the more efficient are bonding and alloying processes during sintering. Furthermore, these processes are enhanced by the disturbances in the particles' crystal lattice caused by plastic deformation during compaction (ref. Chapter 1, § 1.2.3, § 1.2.4).

Composition of the protective atmosphere in the sintering furnace.
The protective atmosphere has to fulfill several functions during sintering which in some respects are contradictory. On the one hand, the atmosphere is to protect the sinter goods from oxidation and reduce possibly present residual oxides; on the other hand, it is to prevent decarbonization of carbon-containing material and, vice versa, prevent carbonization of carbon-free material.

This illustrates the problem of choosing the right atmosphere for each particular type of sinter goods. In iron powder metallurgy, the following sintering atmospheres are common:

- reducing-decarbonizing type: hydrogen (H$_2$), cracked ammonia (75% H$_2$, 25% N$_2$),
- reducing-carbonizing type: endogas (32% H$_2$, 23% CO, 0-0.2% CO$_2$, 0-0.5% CH$_4$, bal. N$_2$),
- neutral type: cryogenic nitrogen (N$_2$), if desirable with minor additions of H$_2$ (to take care of residual oxides) or of methane or propane (to restore carbon losses).

Proper choice and careful control of the sintering atmosphere are important but difficult because of circumstances which will be dealt with in some detail in paragraph 6.4.

6.2 Basic Mechanisms of Sintering

6.2.1 Solid state sintering of homogeneous material

Judging by the changing shape of the interspace between sintering particles, the sintering process passes through two different stages: 1) an early stage with local bonding (neck formation) between adjacent particles, and 2) a late stage with pore-rounding and pore shrinkage. In both stages, the bulk volume of the sintering particles shrinks - in the early stage, the center distance between adjacent particles decreases, in the late stage, the total pore volume shrinks. See schematic illustrations at Fig. 6.1.
The driving force behind these sintering phenomena is minimization of the free surface enthalpy \( \Delta G_{\text{surface}} < 0 \) of the particle agglomerate (ref. chapter 1, § 1.4.1.).

Bonding between powder particles requires transport of material from their inside to points and areas where they are in contact with one another. Pore-rounding and pore shrinkage require transport of material from the dense volume to the pore surfaces, as well as from softer to sharper corners of the pore surface.

In the absence of a liquid phase, five different transport mechanisms are possible:

- volume diffusion (migration of vacancies),
- grain-boundary diffusion,
- surface diffusion,
- viscous or plastic flow (caused by surface tension or internal stresses),
- evaporation/condensation of atoms on surfaces.

In order to find out which of these mechanisms is predominant in the sintering process, the growth of necks, formed between spherical particles during sintering, has been studied experimentally. See micrographs at Fig. 6.2.
According to a theoretical model developed by C.G. Kuczynski, the growth of these necks is governed by the following law:

\[
\left( \frac{x}{a} \right)^n \sim t
\]

(6.1)

\(a\) = particle diameter, \(x\) = neck width, \(t\) = sintering time

See schematic representation at Fig. 6.3. Kuczynski’s model predicts: \(n = 2\) for viscous or plastic flow, \(n = 3\) for evaporation/condensation, \(n = 5\) for volume diffusion, \(n = 7\) for surface diffusion.
The validity of formula (1) is confirmed by extensive experimental material. In the case of spherical metal particles, an exponent \( n = 5 \), and in the case of spherical glass particles, an exponent \( n = 2 \) was found to agree best with the experimental results. See diagrams at Fig. 6.4.

---

Fig. 6.4. Neck growth between spherical particles, examined experimentally as functions of sintering time and temperature; \( x \) = neck width, \( a \) = particle diameter; slope of curve (log-log scale) \( 1/n = 1/5 \) for silver particles (top), and \( 1/n = 1/2 \) for Na-K-Si-glass particles (bottom). [6-2], [6-3]
6.2 BASIC MECHANISMS OF SINTERING

From these results, it can be concluded that, in the early stage of sintering, volume diffusion is the predominant mechanism for metal particles, and viscous flow for glass particles. It is very likely but more difficult to confirm experimentally that, in the early stage of sintering, volume diffusion is predominant also in the case of non-spherical metal particles and metal powder compacts. In the late stage of sintering, volume diffusion is, no doubt, responsible for the phenomenon of pore rounding. The sketch at Fig. 6.5a shows schematically how vacancies migrate from the sharp corners to the flatter parts of the pore surface.

![Figure 6.5a](image)

**Figure. 6.5.** Vacancies migrating (a) from sharp corners to flatter parts of the pore surface, and (b) from smaller pores to near-by larger pores and grain boundaries (schematically).

But volume diffusion does not fully account for the observed rates of pore shrinkage and changes in the distribution of pore sizes. In actual fact, vacancies, emanating from the surface of a pore, do not migrate all the way to the outer surface of the sintering body. They either "condense" at the surface of nearby larger pores, or get trapped at grain boundaries where they are formed into rows or sheets which subsequently collapse owing to plastic flow. See schematic illustrations at Fig. 6.5b.

From the micrographs at Fig. 6.6, it can be seen how larger pores increase in size on account of smaller ones, and how small pores disappear in the neighborhood of grain boundaries.
6. SINTERING

6.2.2 Solid state sintering of heterogeneous material

When a mixture of particles of two different metals is being sintered, alloying takes place at locations where necks are formed between particles of different metallic identity. These two processes interact with one another: On the one hand, the growth rate of the neck now depends not only on the diffusion rates in the two pure metals but also on the
different diffusion rates in the various alloy phases being formed in and on either side of the neck. On the other hand, the neck width controls the rate of alloy formation. The outcome of this interaction varies with the chemical identity of the two metals: it may have an accelerating, a delaying or no effect at all on the growth rate of the neck. The schematic diagrams at Fig. 6.7 show the relationship between phase diagram and alloy formation at the neck between two different particles.

Figure 6.7. Relation between equilibrium diagrams and phase formation during sintering in the contact region between particles of different metallic identity. [6-6]

In commercial iron powder mixes, the particles of alloying additions are usually much smaller than those of the base powder. While the mean size of the iron particles is
approx. 100 μm, the particle size of alloying additions is usually below 20 μm or finer. In a compact made from such a powder mix, the distribution of alloying elements is very uneven at the beginning of the sintering process. During sintering, the alloying atoms diffuse from the surface to the center of the iron powder particles. The rate of homogenization depends on the respective diffusion coefficient which, in turn, depends on temperature. See diagram at Fig. 6.8.

Interstitial elements like carbon (added in the form of graphite) diffuse very rapidly in iron, while substitutional elements like nickel, copper and molybdenum diffuse much more slowly. Assuming that the alloying element consists of small spherical particles randomly dispersed in a dense iron matrix, the time \( t_p \) required to achieve a certain degree of homogenization \( p \) can be calculated from diffusion equations as described in chapter 1, § 1.3. The homogenization time \( t_p \) is given by the following expression:\(^7\)

\[
\frac{4}{\pi} \left( \frac{L}{R} \right)^2 \]

---

\(^7\) G. Bockstiegel, Tidsbehov för diffusionsutjämnning av inhomogent fördelade legeringsämnen i en grundmetall, Internal Höganäs-Report R 18/71 (1971).
6.2 BASIC MECHANISMS OF SINTERING

\[ t_p = \frac{a^2}{4\pi D} \left[ \frac{\pi C_o}{6 C_a (1-p)} \right]^{2/3} \] (6.2)

\( a \) = diameter of the alloying particles, \( D \) = diffusion coefficient, \( C_o \) = initial concentration of the alloying element in the dispersed alloying particles (usually 100%), \( C_a \) = average concentration of the alloying element in the base metal, \( p = C_{\text{min}} / C_{\text{max}} \) = degree of homogenization.

The diagram at Fig. 6.9 shows required homogenization times, calculated from (6.2), for 4% spherical nickel particles dispersed in an iron matrix at different temperatures and for different degrees of homogenization.

The diagram at Fig. 6.10 shows experimentally determined degrees of homogenization of nickel and carbon in sintered compacts made from iron powder admixed with 4 wt.% nickel powder and 0.6% graphite.
Figure 6.10. Homogenization of nickel and carbon during sintering at 1120°C in a compacted iron-4\%nickel-1\%graphite powder mix.
6.2 BASIC MECHANISMS OF SINTERING

6.2.3 Sintering in presence of a transient liquid phase

Consider a compact made from a mixture of particles of two different metals. If one component of the mixture melts at sintering temperature, the arising liquid phase is first being pulled by capillary forces into the narrow gaps between the particles of the solid component, creating the largest possible contact area between liquid and solid phase.

Then, alloying takes place and, if the initial proportion of the liquid phase is smaller than its solubility in the solid phase, the liquid phase eventually disappears. The bulk volume of the compact swells because the melting particles leave behind large pores, while the framework of solid particles increases in volume corresponding to the amount of dissolved liquid phase. See schematic illustration at Fig. 6.11.

![Figure 6.11. Sintering with a transient liquid phase (schematically);](a) initial heterogeneous powder compact, (b) one component of the powder mix melts and infiltrates the narrow gaps between the solid particles leaving large pores behind, (c) alloying takes place between liquid and solid phase, and the liquid phase gradually disappears again.

The micrographs shown at Fig. 6.12 demonstrate the swelling of a compact, made from a mixture of 90 wt.% Fe-powder and 10 wt.% Cu-powder, when sintered at a temperature above the melting point of copper (1086°C). It can be seen that the liquid copper not only infiltrates the gaps between the iron powder particles but also penetrates their grain boundaries.

Liquid copper can easily penetrate the grain boundaries of solid iron because the energy stored in the new interfaces between liquid copper and solid iron is smaller than the energy stored in the initial grain boundaries (minimization of the free enthalpy of interfaces).
6. SINTERING

Figure 6.12. Three stages in sintering at 1150°C: a compact made from a mixture of 90% iron powder (MH 100.24) and 10% copper powder. Curves at the left-hand side of the micrographs show the increase of temperature and of linear expansion of the compact (corrected for shrinkage without copper) [6-7]
If, in the example above, the pure iron particles are substituted with carbonized iron particles having a pearlitic microstructure, the liquid copper penetrates the interfaces between ferrite and cementite lamellae. This leads eventually to a partial disintegration of the pearlitic particles.

Consequently, the initially rigid framework of solid particles collapses locally, and the bulk volume of the compact shrinks. The micrograph at Fig. 6.13 shows beginning disintegration of pearlitic iron particles under the influence of liquid copper.

These examples explain why additions of copper to iron powder mixes result in less shrinkage or produce growth during sintering of structural parts, and why additions of carbon (graphite) to iron-copper powder mixes compensate the growth-producing effect of copper. (See diagrams at Fig. 6.18 further down).
6.2.4 Activated sintering

A special kind of sintering with a transient liquid phase is often referred to as activated sintering. Here, a base powder is admixed with a small amount of a metal or metal compound which, although having a melting point above sintering temperature, forms a low-melting eutectic together with the base metal. See Fig. 6.14.

![Figure 6.14. Activated sintering by creating a low melting eutectic between base metal and "activator".]

The added metal or metal compound is called the activator. During sintering, atoms from the activator diffuse into the particles of the base metal until the latter begin to melt superficially. This superficial melting enhances the formation of necks between adjacent particles of the base metal. As the activator continues to diffuse deeper into the particles of the base metal, the liquid phase (eutectic) disappears again. Activated sintering is utilized e.g. in the manufacturing of so-called heavy metals.

Here, an addition of only a few percent of nickel powder to tungsten powder produces a transient tungsten-rich eutectic at 1495°C which substantially accelerates the sintering process. The sintering of iron powder can be activated through small additions (e.g. 3 wt.%) of finely ground ferro-phosphorous (Fe₃P). As can be seen from the binary phase diagram shown at Fig. 6.15, Fe and Fe₃P form a eutectic at 1050°C.
During sintering at 1120°C, the phosphorous concentration at the surface of the iron powder particles temporarily exceeds 2.6 wt.%, and the particles melt superficially. But as the phosphorous diffuses deeper into the iron particles, its concentration at the surface drops below 2.6 wt.% again, and the liquid phase disappears.

Then, a second benefit of phosphorous becomes effective: Surface regions of the iron particles with phosphorous concentrations between 2.6 and 0.5 wt.% have changed from austenite to ferrite. As will be seen in the next paragraph, the coefficient of self-diffusion (volume diffusion) for iron is approx. 300 times greater in ferrite than in austenite. Consequently, at equal temperature, sintering proceeds faster in ferrite than in austenite.

Figure 6.15. Binary phase diagram Fe–Fe₃P with eutectic at 1050°C.
6. SINTERING

6.3 Sintering behavior of iron powder compacts

In powder metallurgy industry, the efficiency of the sintering process is judged by the quality of the physical properties it lends to the sintered parts in relation to its processing costs. Thus, in the manufacturing of structural parts based on iron powder, a prime interest is to achieve optimal strength and dimensional stability at lowest possible sintering temperatures and shortest possible sintering times.

The following paragraphs provide some general guidelines to a better understanding of the principle relationships between sintering conditions and resulting properties. Detailed information about the sintering behavior of a large variety of iron powders and iron powder mixes is available from HÖGANÄS AB in the form of special brochures and technical reports.

6.3.1 Plain iron powders

The influence of sintering time and temperature on density, tensile strength and elongation of iron powder compacts (NC100.24) has been examined under laboratory conditions. Tensile test bars were compacted (in a lubricated die) from NC100.24 (without lubricant addition) to a density of 6.3 g/cm³.

When examining the influence of sintering time, the test bars were sintered, one by one, under dry hydrogen in a narrow furnace muffle (ID = 25 mm) at different temperatures. The test bars were heated and cooled very rapidly. As can be seen from the diagrams at Fig. 6.16, tensile strength and elongation increase rapidly during the first few minutes of sintering but more and more slowly as sintering continues, while the density increases only moderately over the entire range of sintering times.
When examining the influence of sintering temperature, the test bars were sintered, five at a time, for one hour under dry hydrogen in a laboratory furnace. Heating-up time approx. 10 min; cooling time to below 400°C approx. 10 min.

Figure 6.16. Tensile strength, elongation and density of sintered iron (MH100.24) as functions of sintering time at two different temperatures. [6-9]
6. SINTERING

From the diagram at Fig. 6.17, two important features are apparent:

- Tensile strength and elongation adopt noticeable values first at sintering temperatures above 650 and 750°C respectively. From there-on, they increase almost exponentially until reaching an intermediate maximum at approx. 900°C. Just above 910°C, where the crystal structure of iron changes from ferrite to austenite, the values of tensile strength and elongation suddenly drop a little and then increase again, but more slowly than below 910°C.
- The temperature dependence of the self-diffusion coefficient of iron, drawn in the same diagram for comparison, drops dramatically as ferrite changes to austenite ($D_\gamma = D_a/300$).

Figure 6.17. Tensile strength and elongation of sintered iron (NC100.24, density: 6.3g/cm3, sintering: 1h in H2), and the self-diffusion coefficient of iron as functions of sintering temperature. [6-10]
The parallelism between these two features is not incidental. To the contrary, it is strong evidence of the predominant role which volume diffusion plays in the sintering process of iron. (Note: the coefficients of grain boundary diffusion and surface diffusion do not change substantially at the transition from ferrite to austenite). The effect of the drastic change of the diffusion coefficient on tensile strength and elongation is muffled by the following circumstance:

All test bars begin to sinter already during the heating-up period, while still in the ferrite state, and those which are heated up to higher temperatures have already acquired a certain level of strength before they change from ferrite to austenite.

### 6.3.2 Iron-copper and iron-copper-carbon powder mixes

In order to utilize the advantage of a transient liquid phase during sintering and to achieve higher strength properties, many commercial iron powder mixes contain copper. Copper additions to iron powder can produce undesirable dimensional growth during sintering.

Graphite additions to iron-copper powder mixes counteract the dimensional growth caused by the copper (see § 6.2.3). The carbonization of the iron caused by the graphite additions boosts the mechanical strength of the sintered parts.

The influence of varying additions of copper and graphite on tensile strength and dimensional changes achieved at different sintering temperatures can be seen from the diagrams at Fig. 6.18. Compacting and sintering procedures were the same as for the test bars of plain iron powder discussed in the preceding paragraph.

During sintering, approx. 0.2% of the added graphite was lost to the sintering atmosphere in the form of carbon monoxide (CO), and the microstructure of the carbon-containing test bars after sintering was pearlitic.
6. SINTERING

Figure 6.18. Influence of varying additions of copper and graphite and of sintering temperature on tensile strength and dimensional changes of sintered iron (NC100.24, green density: 6.3 g/cm³, sintering: 1h in H₂), at indicated temperatures. [6-11]
6.4 The sintering atmosphere

The main purpose of sintering atmospheres is to protect the powder compacts from oxidation during sintering and to reduce residual surface oxides in order to improve the metallic contact between adjacent powder particles. A further purpose of sintering atmospheres is to protect carbon-containing compacts from decarbonization.

6.4.1 General problematic

As has been mentioned already in paragraph 6.1, mainly three different types of sintering atmospheres are common in iron powder metallurgy: reducing-decarbonizing (e.g. hydrogen, cracked ammonia), reducing-carbonizing (e.g. endogas) and neutral (e.g. nitrogen).

At a cursory glance, the choice may seem obvious: A reducing atmosphere for carbon-free materials and a non-decarbonizing or neutral atmosphere for carbon-containing materials.

However, apart from economical considerations, there are some technical and thermodynamical problems which complicate both, the choice and the control of the proper atmosphere:

- **Technical problems** arise in connection with the proper control of flow rates and flow directions of the atmosphere in continuous sintering furnaces. A continuous furnace of modern design, for the sintering of iron powder structural parts, usually consists of four zones serving different purposes:
  1) the so-called burn-off zone, where the lubricants (contained in the compacts) are burned off between 250 and 700°C,
  2) the hot zone, where the iron powder parts are sintered at 1120 - 1150°C,
  3) the so-called carbon restoring zone, where superficially decarbonized parts can be recarbonized at 800 - 900°C, and
  4) the cooling zone, where the sintered parts are cooled down to approx. 250-150°C, before being exposed to air. See schematic drawing at Fig. 6.19. Ideally, each one of these zones would require its own specific combination of flow rate, flow direction and composition of atmosphere. However, ideal conditions are not achievable. To find practicable compromises and provide adequate furnace designs, is the business of the manufacturers of industrial sintering furnaces. Within the frame of this chapter, we cannot enlarge on problems of furnace design; instead, we refer to the competence and specific know-how of furnace makers.
Figure 6.19. Zones of a continuous sintering furnace (schematically).

Zone 1 = Burning-off lubricants, 2 = Sintering, 3 = Re-carbonizing, 4 = Cooling
G = Gas Inlet, S = Smoke and gas outlet
• **Thermodynamical problems** arise from the circumstance that a sintering atmosphere of given composition changes character with temperature. For instance:

- The character of endogas changes with rising temperature from carbonizing to decarbonizing, and the character of hydrogen (with traces of water vapor) changes with falling temperature from reducing to oxidizing. Furthermore, the atmosphere changes its composition while reacting with the sintered material. Reduction of residual oxides enriches the atmosphere with water vapor; decarbonization of sintered material enriches the atmosphere with carbon monoxide. In the following paragraphs, we will discuss these problems in more detail.

### 6.4.2 Thermodynamical processes during sintering

Sintering atmospheres usually contain, in varying proportions, several of the following components: N$_2$, O$_2$, H$_2$, H$_2$O (vapor), C (soot), CO, CO$_2$ (and in some cases also CH$_4$ or propane). Depending on the relative proportions of these components, the atmosphere is reducing, oxidizing, carbonizing, decarbonizing or neutral.

**Oxidation and reduction.**

Oxidation of metals or reduction of metal oxides in sintering atmospheres can proceed by either of the following three reactions:

\[
\text{metal} + O_2 \leftrightarrow \text{oxide} + \Delta H^O_1\quad (6.3)
\]

\[
\text{metal} + 2 \text{H}_2\text{O} \leftrightarrow \text{oxide} + 2 \text{H}_2 + \Delta H^O_2\quad (6.4)
\]

\[
\text{metal} + 2 \text{CO}_2 \leftrightarrow \text{oxide} + 2 \text{CO} + \Delta H^O_3\quad (6.5)
\]

Corresponding reactions take place between H$_2$ and H$_2$O and between CO and CO$_2$:

\[
2 \text{H}_2 + O_2 \leftrightarrow 2 \text{H}_2\text{O} + \Delta H^O_4\quad (6.6)
\]

\[
2 \text{CO} + O_2 \leftrightarrow 2 \text{CO}_2 + \Delta H^O_5\quad (6.7)
\]

$\Delta H^O_1, \Delta H^O_2, \Delta H^O_3, \Delta H^O_4, \Delta H^O_5$ are the amounts of heat released (per mole O$_2$) in the respective oxidizing reaction. The corresponding changes of free enthalpy are:

$\Delta G^O_1 = -\Delta H^O_1, \Delta G^O_2 = -\Delta H^O_2, \Delta G^O_3 = -\Delta H^O_3, \Delta G^O_4 = -\Delta H^O_4, \Delta G^O_5 = -\Delta H^O_5$
6. SINTERING

The free enthalpy of oxidation.
The change of free enthalpy (per mole $O_2$) $\Delta G^O_i$ during the oxidation of a metal (or other chemical element) in a gaseous medium is given by one of the following three equations, depending on the type of oxidizing agent:

if $O_2$ is the only oxidizing agent:

$$\Delta G^O_i = -RT \ln \left( \frac{P_{metal}}{P_{oxide}} \cdot \frac{P_{O_2}}{P_{O_2}} \right)$$  \hspace{1cm} (6.8)

if $H_2O$ is the only oxidizing agent:

$$\Delta G^O_i = -RT \ln \left( \frac{P_{metal}}{P_{oxide}} \cdot \frac{P_{H_2O}}{P_{H_2}} \right)$$  \hspace{1cm} (6.9)

if $CO_2$ is the only oxidizing agent:

$$\Delta G^O_i = -RT \ln \left( \frac{P_{metal}}{P_{oxide}} \cdot \frac{P_{CO_2}}{P_{CO}} \right)$$  \hspace{1cm} (6.10)

$R$ = universal gas constant, $T$ = absolute temperature. $P_{metal}$, $P_{oxide}$ = vapor pressures of the pure metal and of the oxide respectively. $P_{O_2}$, $P_{H_2O}$, $P_{CO_2}$ = partial pressures of the reacting components of the atmosphere.

The Ellingham-Richardson diagram.
A standard measure for the tendency of a metal (chemical element) to oxidize is the heat released when 1 mole of gaseous $O_2$ at 1 atm pressure combines with the pure metal (pure element) to form oxide. The corresponding change of the free enthalpy of the reacting system is designated by $\Delta G^O$.

The temperature dependence of $\Delta G^O$ follows directly from (6.8) when $P_{O_2} = 1$:

$$\Delta G^O = -RT \ln \left( \frac{P_{metal}}{P_{oxide}} \right)$$  \hspace{1cm} (6.11)

A very convenient way of presenting experimentally obtained values of $\Delta G^O$ for different metals is by means of Ellingham-Richardson diagrams. See example at Fig. 6.20.
The advantage of these diagrams is that they give the free enthalpy released by the combination of a fixed amount (1 mole) of the oxidizing agent. The relative affinity of the elements to the oxidizing agent is thus shown directly. The further down in the diagram the $\Delta G^0$ line of the metal is situated, the greater is its affinity to oxygen. For instance: the distance between the $\Delta G^0$ lines of iron and aluminum is 537.7 kJ/mole $O_2$ (128.3 kcal/mole $O_2$), i.e. aluminum is a very strong reducing agent for iron oxide. This circumstance is utilized e.g. in so-called thermit welding. Here, a proper mixture of
iron oxide powder and aluminum powder is ignited to the effect that the aluminum reduces the iron oxide, and the enormous amount of released reaction heat melts the metallic iron.

**Dissociation temperature.**

At the so-called standard dissociation temperature, the oxide is in equilibrium ($\Delta G^0 = 0$) with the pure metal and gaseous oxygen ($O_2$) at 1 atm pressure. As can be seen from the Ellingham-Richardson diagram at Fig. 6.20, metal oxides can in principle be reduced to metal simply by heating them in air at this temperature. Some values are: Au < 0°C, Ag 185°C, Hg 430°C, Pt-group metals 800 - 1200°C, Fe >4000°C. Apart from the noble metals, no other metal oxides can be reduced simply by heating in an industrial furnace without the presence of some reducing agent.

**Dissociation pressure.**

At any given temperature, a metal and its oxide are in equilibrium with a particular partial pressure of oxygen $P_{O_2}$. This pressure is called equilibrium dissociation pressure. Above this pressure, the metal oxidizes. Below this pressure, the oxide dissociates into metal and gaseous oxygen. This pressure is calculated as follows:

Combining equations (6.8) and (6.11) yields:

$$ \Delta G^0_1 = \Delta G^0 - RT \ln P_{O_2} $$

(6.12)

The reacting system is in equilibrium when $\Delta G^0_1 = 0$. Hence:

$$ P_{O_2} = \exp \left( \frac{\Delta G^0}{RT} \right) $$

(6.13)

In the Ellingham-Richardson diagram, the dissociation pressure for a metal oxide at a given temperature $T$ can easily be found by drawing a straight line from point "O" at the upper left corner of the diagram to the point with abscissa $T$ on the $\Delta G^0$ line of the metal in question. Extrapolating this straight line to the scale marked $P_{O_2}$ at the right-hand side of the diagram, one can directly read the dissociation pressure. For iron oxide (FeO) at 1120°C, for instance, we find $P_{O_2} = 10^{-12}$ atm. See diagram at Fig. 6.21.

This tells us that simple heating of iron oxide in conventional vacuum or inert gas of conventional purity is entirely unsatisfactory. A reducing gas has to be added to the furnace atmosphere.
6.4 THE SINTERING ATMOSPHERE

Höganäs PM-school

The influence of reducing agents.

The influence of reducing agents like gaseous mixtures of H₂ and H₂O or CO and CO₂ is governed by the pertaining equilibrium point. We derive the dependence of the equilibrium point on temperature and on partial pressure ratio \( \frac{P_{H₂O}}{P_{H₂}} \) or \( \frac{P_{CO₂}}{P_{CO}} \):

Combining equations (6.9) and (6.11) yields

\[
\Delta G_2^0 = \Delta G^0 - 2RT \ln \left( \frac{P_{H₂O}}{P_{H₂}} \right)
\]

(6.14)
6. SINTERING

The reacting system is in equilibrium when \( \Delta G^0_2 = 0 \). Hence:

\[
P_{\text{H}_2\text{O}} / P_{\text{H}_2} = \exp \left( \Delta G^0 / 2RT \right)
\]  

(6.15)

Combining equations (6.10) and (6.11) yields:

\[
\Delta G^0_3 = \Delta G^0 - 2RT \ln \left( P_{\text{CO}_2} / P_{\text{CO}} \right)
\]  

(6.16)

The reacting system is in equilibrium when \( \Delta G^0_3 = 0 \). Hence:

\[
P_{\text{CO}_2} / P_{\text{CO}} = \exp \left( \Delta G^0 / 2RT \right)
\]  

(6.17)

At any given temperature \( T \), a metal and its oxide are in equilibrium with a partial pressure ratio \( P_{\text{H}_2\text{O}} / P_{\text{H}_2} \) as given by (6.15) or with a ratio \( P_{\text{CO}_2} / P_{\text{CO}} \) as given by (6.17). Below this ratio, the oxide is reduced to metal. Above this ratio, the metal is oxidized.

A convenient way of finding the equilibrium temperature is by plotting the right-hand side of (6.14) or (6.16) against temperature in the Ellingham-Richardson diagram as shown at Fig. 6.22.

We draw a straight line from point "H" or from point "C" to the applying ratio on the \( P_{\text{H}_2\text{O}} / P_{\text{H}_2} \) scale or on the \( P_{\text{CO}_2} / P_{\text{CO}} \) scale of the diagram respectively. Where this straight line crosses the \( \Delta G^0 \) line is the equilibrium point. Below this temperature the metal is oxidized; above it is not.

Three examples may illustrate the method:

1. Fe does not oxidize at temperatures above approx. 550°C when the \( P_{\text{H}_2\text{O}} / P_{\text{H}_2} = 25/100 \) (dew point +60°C); neither do Cu, Mo and Ni.

2. Fe does not oxidize at any temperature when \( P_{\text{CO}_2} / P_{\text{CO}} = 1/10 \) (=10% CO2); neither do Cu, Mo and Ni.

3. Cr oxidizes at temperatures below 1300°C even when \( P_{\text{CO}_2} / P_{\text{CO}} = 1/1000 \) (=0.1% CO2).
6.4 THE SINTERING ATMOSPHERE

Figure 6.22. Graphical determination of equilibrium temperatures for Fe in an H₂O/H₂ and in a CO₂/CO atmosphere, and for Cr in a CO₂/CO atmosphere.
Decarbonization and carbonization.
The following reactions are involved in the decarbonization or carbonization of carbon-containing iron powder compacts:

When carbon is present in the form of graphite:
1. \[ 2 \text{C} + \text{O}_2 \leftrightarrow 2 \text{CO} + \Delta H^0_{6} \]  
2. \[ \text{C} + \text{CO}_2 \leftrightarrow 2\text{CO} + \Delta H^0_{7} \]  
3. \[ \text{C} + 2 \text{H}_2\text{O} \leftrightarrow 2 \text{CO} + 2 \text{H}_2 + \Delta H^0_{8} \]  

When carbon is present in the form of cementite:
1. \[ 2 \text{Fe}_3\text{C} + \text{O}_2 \leftrightarrow 6 \text{Fe} + 2 \text{CO} + \Delta H^0_{9} \]  
2. \[ 2 \text{Fe}_3\text{C} + 2 \text{H}_2\text{O} \leftrightarrow 6 \text{Fe} + 2 \text{H}_2 + 2 \text{CO} + \Delta H^0_{10} \]  
3. \[ \text{Fe}_3\text{C} + \text{CO}_2 \leftrightarrow 3 \text{Fe} + 2 \text{CO} + \Delta H^0_{11} \]  
4. \[ \text{Fe}_3\text{C} + 2 \text{H}_2 \leftrightarrow 3 \text{Fe} + \text{CH}_4 + \Delta H^0_{12} \]  

\( \Delta H^0_{6}, \Delta H^0_{7}, \ldots, \Delta H^0_{12} \) are the amounts of heat released (per mole \( \text{O}_2 \)) in the respective decarbonizing reaction.

The dependence of these reactions on temperature and partial pressure ratios of the involved gas components can, in principle, be presented by means of Ellingham-Richardson diagrams in a similar fashion as has been demonstrated.

For practical purposes, however, it is more convenient to study the influence of temperature and partial pressure ratios from a type of diagrams presented in the following paragraph.

6.4.3 Equilibrium diagrams: iron - sintering atmosphere

Ellingham-Richardson diagrams are useful for the understanding of the thermodynamical basis of chemical reactions between metals and atmospheres. However, in the particular case of iron, special phase diagrams present more conveniently the influence of temperature and gas composition upon the equilibrium between iron, iron oxides, and iron carbide (cementite).
6.4 THE SINTERING ATMOSPHERE

The system: Fe - FeO - Fe$_3$O$_4$ - H$_2$ - H$_2$O.

In the diagram at Fig. 6.23, the equilibrium lines (phase boundaries) between Fe, FeO and Fe$_3$O$_4$ are drawn as function of reaction temperature and percentage of H$_2$O (water vapor) relative to H$_2$. The most important feature of this diagram is the slope of the border line that separates Fe from FeO and Fe$_3$O$_4$. It indicates that water vapor is more oxidizing at lower than at higher temperatures. This means that a fairly low content of water vapor – which is harmless at maximum temperature in the sintering furnace – might very well be oxidizing in the cooling or in the pre-heating zone. In actual fact, at temperatures below 200°C, a water vapor content of as low as 2% is still oxidizing.

![Equilibrium diagram: Fe - FeO - Fe$_3$O$_4$ - H$_2$ - H$_2$O.](image)

Figure. 6.23. Equilibrium diagram : Fe - FeO - Fe$_3$O$_4$ - H$_2$ - H$_2$O.

The system: Fe - FeO - Fe$_3$O$_4$ - Fe$_3$C - CO - CO$_2$.

In the diagram at Fig. 6.24, the equilibrium lines (phase boundaries) between Fe, FeO and Fe$_3$O$_4$ are drawn as function of reaction temperature and percentage of CO$_2$ relative to CO.
6. SINTERING

Also drawn, in the same diagram, are the almost parallel equilibrium lines for the Boudouard reaction:

\[2 \text{CO} \leftrightarrow \text{C} + \text{CO}_2\]

and for the cementite reaction:

\[3 \text{Fe} + 2 \text{CO} \leftrightarrow \text{Fe}_3\text{C} + \text{CO}_2\]

At lower temperatures, the Boudouard reaction is generally the most prevalent and results in the deposition of soot on the sintering parts. However, at temperatures above 700 - 800°C, the carbonizing reaction is dominant. Deposition of soot is suppressed by fast heating and cooling in the sintering furnace. Note that carbon monoxide is more strongly reducing at lower than at higher temperatures while, above 800°C, its carbonizing action gets gradually weaker with increasing temperature.

Figure 6.24. Equilibrium diagram : Fe - FeO - Fe$_3$O$_4$ - CO - CO$_2$. 

---

36
At a sintering temperature of 1120°C, a ratio of 25% CO₂ / 75% CO is strongly decarbonizing but still sufficiently reducing. To maintain carbonizing conditions at this temperature, the content of CO₂ in the sintering atmosphere has to be decreased to a very low value. However, with decreasing contents of CO₂, the control of the carbon content in the sintering parts gets increasingly difficult. At 1120°C, an increase of the CO₂ content from 0,1 to 0,2% can change the action of the CO/CO₂ – atmosphere from carbonizing to decarbonizing. This means that, in this atmosphere, a satisfactory control of the carbon content in the sintering parts is practically impossible at 1120°C.

The system: Fe - Fe₃C - C - H₂ - CH₄.

When compacts of iron powder with admixed graphite are sintered in an atmosphere containing H₂, the following two reactions take place:

\[ C_{\text{graphite}} + 2 \text{H}_2 \leftrightarrow \text{CH}_4 \]

and

\[ 3 \text{Fe} + \text{CH}_4 \leftrightarrow \text{Fe}_3\text{C} + 2 \text{H}_2 \]

The equilibrium lines of these reactions are presented as functions of temperature and CH₄ - content in the phase diagram at Fig. 6.25.
6. SINTERING

The effect of CH₄ (methane) is different from that of CO. In contrast to carbon monoxide, methane acts increasingly reducing and carbonizing with increasing temperatures. Even very small amounts of methane in the sintering atmosphere cause carbonization or, above a certain temperature limit, carbon deposition. At 1120°C, methane contents as small as 0.1 to 0.2% are sufficient to produce or maintain a carbon content of 1% in iron powder parts. At 1120°C, methane contents exceeding approx. 0.3% cause carbon deposition on the iron parts and in the furnace.

Mixed systems.
In mixtures of several gases (e.g. such as endogas), very complex temperature-dependent interactions take place between the various gas components. The diagram at Fig. 6.26 shows how various gas mixtures are oxidizing, reducing, carbonizing or decarbonizing, depending on partial pressure ratios $P_{H₂O}/P_{H₂}$, $P_{CO₂}/P_{CO}$, and $P_{CH₄}/P_{H₂}$.

From the diagram emerges clearly that it is practically impossible to control the carbon content in the sintered parts at common sintering temperatures (1120 - 1150°C). At these temperatures, even extremely small changes of the partial pressure ratios $P_{CO₂}/P_{CO}$ and/or $P_{CH₄}/P_{H₂}$ are sufficient to switch the gas mixture from being carbonizing to being decarbonizing. On the other hand, carbon control is unproblematic at temperatures around 800°C. This is a strong argument for equipping continuous sintering furnaces with a re-carbonizing zone, operating at approx. 800°C, between sintering and cooling zone.
6.4 THE SINTERING ATMOSPHERE

6.4.4 Industrial sintering atmospheres

Local workshop conditions, the type of material to be sintered and economic considerations govern the selection of a suitable sintering atmosphere. The correct choice is of great importance not only for the achievement of optimal product quality but also for good economy.
6. SINTERING

**Hydrogen and cracked ammonia.**
Pure hydrogen, electrolytically or cryogenically produced, is the most unproblematic atmosphere for sintering carbon-free iron powder parts. As a rule, however, it is not economical, except in combination with high priced products such as alnico magnets and stainless steel parts.

An excellent substitute for pure hydrogen is cracked ammonia which consists of 75% H₂ and 25% N₂. The strong reducing action of this gas mixture is favorable in eliminating residual oxides which are present in all commercial iron powders. It is easy to handle and, although it is not the most economic atmosphere, it eliminates many production problems and yields a uniform and high quality sintered product.

Because of their strong decarbonizing action, neither pure hydrogen nor cracked ammonia can be used in the sintering of carbon-containing iron powder parts. Hydrogen and cracked ammonia form explosive mixtures with air. Thus, sintering in these gases can only be conducted in furnaces equipped with a gas-tight muffle.

**Endogas.**
Relatively inexpensive sintering atmospheres are produced in a special generator by incomplete combustion of a mixture of fuel gas and air, using a catalyst. Common fuel gases are e.g. methane (CH₄), propane (C₃H₈), or natural gas. The combustion product contains H₂, H₂O, CO, CO₂, N₂ and CH₄. Its composition varies with the air/fuel ratio and can be reducing, carbonizing, decarbonizing, inert, or even oxidizing.

The generated gas is called endogas when produced endo-thermically with low air/fuel ratios, and exogas when produced exo-thermically with high air/fuel ratios. See diagram at Fig. 6.27.
In iron powder metallurgy today, the use of exogas is less common, but endogas is widely used in the sintering of carbon-containing iron parts. When leaving the generator, normal endogas may contain up to 4% water vapor (H$_2$O) which makes it strongly decarbonizing. To make it suitable for the sintering of carbon-containing iron powder parts, it has to be dried (e.g. by means of a refrigerant cooler and a desiccant agent) to at least below 0.2% H$_2$ (dew point: -10°C). The strong influence of the dew point on the carbon potential of endogas is shown in the diagram at Fig. 6.28.
In endogas, very complex interactions take place between the various gas components. The temperature varies throughout the sintering cycle, and the gas composition changes due to reactions with residual iron oxides, mixed-in graphite, or leaking air. This makes
it very difficult to calculate, on the basis of any diagram, a suitable gas analysis for a given carbon content in the finished product. The diagrams are, however, important for the understanding of the behavior of various gas mixtures.

Endogas is poisonous and forms explosive mixtures with air. Endogas is harmful to the heating elements of the furnace when getting into contact with them. It can cause disastrous soot deposition when leaking into the brick-work of the furnace. Thus, sintering in endogas can only be conducted in furnaces equipped with a gas-tight muffle.

**Nitrogen.**

Compacts made from graphite-containing iron powder mixes can very well be sintered in (cryogenic) nitrogen. The graphite present in the compacts, reacting with residual oxides in the iron powder and with leaking air, produces sufficiently reducing and carbonizing conditions in the furnace. If necessary, the reducing action of this atmosphere can be controlled by bleeding-in very small amounts of wet or dry hydrogen into the hot zone of the furnace.

Correspondingly, its carbonizing action can be controlled by bleeding-in very small amounts of methane into the re-carbonizing zone of the furnace. Nitrogen, although being somewhat more expensive, has several advantages over endogas.

Nitrogen is neither poisonous nor does it form explosive mixtures with air. It does not react with the heating elements or any other parts of the furnace. Thus, sintering in nitrogen can be conducted in furnaces without gas-tight muffle.

**Control of sintering atmospheres.**

The composition of sintering atmospheres should preferably be monitored, not only at room temperature outside, but also at residing temperatures inside the various zones of the furnace. Interesting points where gas samples may be taken are:

- after the gas generator (or storage tank),
- inside the re-carbonization zone,
- at the point of maximum temperature in the furnace,
- at outlet points.

From the preceding paragraphs, it is evident that the two most crucial properties of a sintering atmosphere are its dew-point \( \frac{P_{H_2O}}{P_{H_2}} \) and its carbon potential \( \frac{P_{CO_2}}{P_{CO}} \) and \( \frac{P_{CH_4}}{P_{H_2}} \).

Several dew-point meters are on the market; completely automatic or hand-operated, with or without auxiliary equipment for recording and regulating the dew-point of the atmosphere.
Among the different principles of dew-point measurement, the following three may be mentioned:

Method 1.
If a compressed gas is allowed to expand, its temperature drops and, at the dew-point of the gas, water vapor (if any) precipitates as a mist.

Method 2.
The instrument is fitted with a mirror which can be cooled down to a known temperature. When the gas is allowed to pass the mirror, a film of water condenses on the mirror at the dew-point.

Method 3.
Many salts have different electrical resistivities at different moisture contents and temperatures. If the temperature is kept constant, a dew-point meter can be based on the electrical resistivity of the salt.

Modern automatic devices for monitoring and recording the amounts of carbon dioxide, carbon monoxide and methane are based on the absorption of infra-red radiation by the gas. The principle is that each of these gases absorb different wave lengths of the infra-red light, and the absorption is proportional to the concentration of the gas in the mixture.

The oxygen content in the sintering atmosphere can be measured in situ by means of a ZrO₂-cell which operates on the principle that the partial pressure of oxygen in the atmosphere is compared with that of a well defined test gas. The gas to be analyzed is in contact with one side of the cell, the test gas with the other side. The difference of the partial pressures creates an electrical potential which is monitored and can be utilized to steer automatic measures for correcting the composition of the atmosphere.

In all cases, gas samples should be collected in the flowing gas stream; they should never be collected in dead corners. To protect the instrument from dust and soot in the gas, it is often recommendable to use a filter through which the gas sample is drawn. The filter may, for instance, be made from glass wool. Gas samples must be large enough, and the flow of gas through the tubes maintained for so long a time that all remaining gas from earlier tests is cleaned out.

6.4.5 Cracking of iron powder compacts during lubricant burn-off

Cracked and blistered sintered iron parts are an ill-famed phenomenon which sporadically pops up and disappear again seemingly without any comprehensible cause. See photographs at Fig. 6.29.
It has often been assumed that this harmful phenomenon is caused by a too rapidly decomposing lubricant in the burn-off zone of the sintering furnace. Thorough systematic investigations have since shown that this assumption is wrong.

It is not the decomposing lubricant that cracks the parts; it is the solid carbon which inside the pores of the parts precipitates from the carbon monoxide in the endogas, according to the Boudouard reaction 8:

$$2 \text{CO} \leftrightarrow \text{C} + \text{CO}_2$$

The rate of this reaction is highest between 500 and 700°C and is catalyzed by metallic iron, nickel and cobalt.

---

The diagram at Fig. 6.30 shows the thermodynamical limits for carbon precipitation at different temperatures in different artificial gas mixtures containing varying amounts of CO, CO₂, CH₄, H₂, H₂O, O₂, and N₂. Carbon precipitation occurs only to the left of the temperature curves. It is evident that carbon precipitation occurs in all common endogas compositions (shaded area) below approx. 650°C.

Figure 6.30. Calculated composition limits for carbon precipitation from gas mixtures containing CO, CO₂, CH₄, H₂, H₂O, O₂, and N₂. [6-12]
The obvious conclusion is that carbon precipitation can be prevented or substantially reduced by heating the iron powder compacts as rapidly as possible to a temperature above 650°C. Practical experience with the so-called Rapid Burn-Off technique (RBO) confirms this conclusion, i.e. iron powder compacts which are sintered in furnaces equipped with an efficient rapid burn-off zone do not crack or blister.

The diagram at Fig. 6.31 shows the influence of the gas composition at low heating rate (4°C/min) on carbon precipitation in iron powder compacts. By means of a thermobalance, the weight changes of the iron powder compacts were registered as a function of temperature. On the registered curves, we notice a weight loss due to escaping stearates between 250 and 400°C.

![Graph showing influence of gas composition on carbon precipitation and cracking of sintered iron powder parts.](image)

Figure. 6.31. Influence of gas composition on carbon precipitation and cracking of sintered iron powder parts. [6-12]
In dry endogas, the weight loss is followed by a substantial weight increase between 500 and 600°C due to carbon precipitation inside the compacts causing severe cracking and blistering. The weight increase and the blistering phenomenon is reduced by adding water vapor (H₂O) to the endogas. In a gas mixture of 10 % H₂ + 90 % N₂, no weight increase and no blistering or cracking occurs. The diagram at Fig. 6.32 shows the influence of the heating rate in dry endogas on carbon precipitation in iron powder compacts. At different heating rates, weight changes of the iron powder compacts were registered as described above. On the registered curves, we notice again a weight loss due to escaping stearates (beginning at approx. 250°C) followed by a weight increase due to carbon precipitation inside the compacts.

![Diagram](image)

**Figure 6.32. Influence of heating rate in dry endogas on carbon precipitation and cracking of sintered iron powder parts [6-12]**
At a heating rate of 4°C/min, this weight increase is very substantial in the temperature range between 500 and 600°C and causes severe blistering and cracking of the compacts. With increasing heating rates, the weight increase is more and more reduced, and the cracking and blistering phenomenon disappears gradually.

Based on these findings, the following practical measures to avoid cracked and blistered sintered iron powder compact seem adequate:

1. prefer gas mixtures of nitrogen and hydrogen to endogas. If this is not opportune,
2. use rapid burn-off technique, and/or
3. enrich endogas with water vapor in the burn-off zone.
References


[6-8] G. Bockstiegel, see ref. [7].


