Interstitial chemistry in sintering of metallic materials – often overlooked but decisive

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ABSTRACT
Sintering is a process by which particulate materials – loose or compacted – are transformed into a body that may be fully dense or may still contain pores, but in any case has structural integrity and load-bearing capacity. The physical mechanisms – especially the transport processes – that are responsible for these changes have been studied since the 1950s. However, the chemical part of sintering also is of decisive importance in particular for metallic systems, especially concerning the interstitial elements O and C. Any metal powder that has ever been exposed to air bears oxygen on the surface, and this oxygen has to be removed in the early stages of sintering to enable the physical transport processes to become effective. In the present work, various chemical reactions involving oxygen and/or carbon are described, and it is shown how the alloying system selected as well as the starting powder grade affect these reactions and the properties of the final products.

Introduction
Sintering is a process that is – and has been – used to a large extent for producing solid components from disperse starting materials. ‘Firing’ of ceramics has been employed for many millenia to produce household goods (Wu et al., 2012), but also iron and steel products have been manufactured for many centuries through the particulate route. An
example of this is, for example, the Bloomery furnace technique, which yielded iron sponge that consisted more or less of iron particles sintered together during reduction (Kieffer & Hotop, 1948). Only in the thirteenth century, melting of iron in the blast furnace became feasible and quickly superseded the older (less productive) technique. Modern powder metallurgy (PM) then re-started with the production of ductile W filaments for incandescent lamps (Johnson, 2008) at the beginning of the twentieth century and received a further boost with the invention of WC-Co hardmetals by Schröter and Skaupy in the 1920s (Brookes, 1992; Ortner, Ettmayer, & Kolaska, 2014). From the 1930s, ferrous precision parts and porous bearings were increasingly manufactured by the press-and-sinter route, and nowadays the ferrous parts make up for the major tonnage of PM products (Silbereisen, 1984; Whittaker, 2015). This tonnage is still small when compared to steel production by the ingot metallurgy route, but the added value is significantly higher. The high material and energy utilization of the PM routes are important benefits, especially in times of CO₂ sensitivity. In the 1980s, metal injection moulding (MIM) was introduced into large-scale production, which combines the moulding capability of polymer injection moulding with the multitude of materials accessibly by powder metallurgy (German & Bose, 1997). In the recent years, the numerous variants of additive manufacturing (also called 3-D printing) were developed, and here in particular the ‘indirect’ or sinter-based versions depend on a sintering process after shaping (Danninger, de Oro Calderon, & Gierl-Mayer, 2017).

The sintering processes taking place in ceramic and metallic systems have been studied thoroughly from the 1950s, involving both solid state and liquid phase sintering (see, e.g. Cannon and Lenel, 1953; German, 1985; Kang, 2005; Petzow & Huppmann, 1976; Schatt, 1992). The focus of such studies has traditionally been on the processes within the metallic phase(s) that result in formation and growth of interparticle contacts and in densification. However, also the chemical part of sintering is highly relevant, in particular for sintering of metals. The major difference between sintering of metallic vs. ceramic systems is the environment. In contrast to the most ceramics, metals are thermodynamically unstable in air (except for a few noble metals) and are oxidized when heating to the elevated temperatures necessary for sintering. Therefore, sintering of metallic systems has to be performed in protective atmosphere – inert or reducing – that prevents undesirable reactions, in particular oxidation. Furthermore, all metal powders that have ever been exposed to air carry oxygen on the surface, adsorbed, as hydroxides, or as oxides. These have to be removed prior to sintering, since the oxide layers inhibit the transport mechanisms required to form solid metallic interparticle contacts.
Furthermore, the surface energy of oxides is much lower than that of metals, and therefore the tendency to decrease the surface – which is the main driving force for sintering- is accordingly lower. Therefore, in the most metallic systems, the removal of the oxide layers is an essential precondition for successful sintering, and several ways are feasible to achieve this goal. However, also parallel reactions – for example, transfer of interstitial elements – have to be considered, and may strongly affect the final outcome.

In addition to the reactions involving oxygen, also the formation of internal compounds such as carbides, may play a major role during sintering, as will be shown in this article for selected materials. From the multitude of powder metallurgy materials, low alloy sintered steels and hardmetals have been chosen as examples, as these are the most important PM products regarding both tonnage and revenue. The work focuses on the role and interaction of O, C and H. It should of course be considered that also nitrogen can play a major role in special cases, such as stainless steels, cermets, and Ti alloys, as well as for iron and low alloy steels, see, for example, Gierl and Danninger (2005) and Šalak (1971). However, for the materials described here, it is the other mentioned interstitials that are decisive. From the same reason, only high purity Ar and H₂ have been used as sintering atmospheres; for the effect of technical atmospheres, the reader is referred to the relevant literature (Beiss, 2009; Bergman, 2009; Bocchini, 2004; Danninger & Gierl-Mayer, 2002; Hryha, Dudrova, & Nyborg, 2012).

**Basic considerations**

Generally, the thermodynamic preconditions are the same for ingot metallurgy and for powder metallurgy. One difference is however the temperature applicable during processing, which for powder metallurgy is limited by the melting point of – at least – the major constituent. The second – very pronounced – difference is the specific surface, which is dramatically larger for components made from powders, resulting in very much higher reactivity with the environment. This surface is maximum at the onset of the sintering process and decreases significantly during sintering, but it still remains high for specimens that contain open porosity. For materials that become fully dense during sintering – or in which only closed pores remain – the final surface is the external surface of the component, which is the same as for a similar part from wrought material. Pore closing may cause problems if atmosphere constituents are trapped, which is to be considered in particular for insoluble gases such as Ar (German & Churn, 1984).
For the reactivity of a particulate compact with the atmosphere, also the different atmospheres have to be distinguished, as schematically shown in Figure 1. Outside the body, the atmosphere is more or less that one that is introduced into the sintering furnace from outside, with a fairly well controllable composition. However, inside the pore network, the local composition of the atmosphere is governed by the thermodynamic equilibria, which are rapidly established due to the short free paths. Shifting of these equilibria, for example, towards reduction of oxides, is possible only by influx of reactants or – which is usually dominating – removal of reaction products such as H₂O, CO or CO₂. Often it is rather the kinetics of transport of gaseous species through the pore network that determines the progress of a certain reaction, at least if thermodynamics are principally favourable. In the case of liquid phase sintering, the complex liquid–solid–gas interactions at high temperature will determine the ability of the liquid phase to wet the solid particles and penetrate the pore network to achieve an even distribution of the liquid phase (de Oro Calderon, Gierl-Mayer, & Danninger, 2021). Elimination of the oxides present on the different surfaces is of major importance also during liquid phase sintering. Such reduction can take place through reactions with the atmosphere (e.g. by reaction with H₂ or CO), with the carbon present in the compact, and also with oxygen-sensitive elements present in the liquid phase (e.g. silicothermic reduction of oxides in liquid phases containing Si) (Oro et al., 2016).

In general, the main criterion for removal of oxygen compounds is the stability of their bonding to the metal surface. Adsorbed oxygen is quickly desorbed at slightly elevated temperatures. Hydroxides, in contrast, require higher temperatures to decompose, and they are transformed into H₂O - in part also H₂ - which evaporates, and oxides, which remain bonded to the particle surfaces. For oxides, the Gibbs free energy of formation of the respective oxide is the main indicator of how easily surface oxides can be removed. Here, the
Ellingham-Richardson diagram gives the information about the stability of the oxide at a given temperature. Furthermore, also the composition of the atmosphere in equilibrium with the oxide/metal system can be deduced, which depends on the reducing agent employed. The ratio \( H_2O/H_2 \) is relevant for a reduction process with \( H_2 \), the ratio \( CO_2/CO \) for the indirect carbothermal reduction, while for the direct carbothermal reduction the partial pressure of \( CO \) is the governing parameter. This equilibrium composition is however that of the ‘internal’ atmosphere; while the external one may differ significantly, especially if it is not a static but a flowing atmosphere as is common in sintering practice (even in vacuum sintering, as the gases formed are continuously pumped off) (Quadbeck & Schreyer, 2010).

There is one further parameter that is crucial for oxygen removal, the solubility of oxygen in the metal. In most cases, this is very low (Fromm & Gebhardt, 1976), which favours oxygen removal, but there are several metals, in particular Ti, Zr and Hf, which possess a high solubility for oxygen (and for nitrogen and hydrogen as well). This means that under reducing conditions, the oxygen concentration in the metal decreases but also its chemical activity, and at a certain level the reduction comes to a standstill. Typically, this occurs at an oxygen level that is still detrimental for the mechanical properties, in particular for the ductility and fatigue endurance strength (Amherd Hidalgo & Ebel, 2016). In this case, any oxygen introduced into the system that has formed stable oxides will remain there, and the strategy therefore must be different, simply focussing on keeping oxygen out by using low-oxygen starting powders and processing the material in such a way that pickup of oxygen (or other interstitials) is kept to a minimum. This is essential, especially not only for MIM Ti products (German, 2013), but of course also for additive manufacturing, where Ti products play a major role too.

With most other elements, however, oxygen solubility is low, and oxygen can be introduced into the reaction equation as solid oxide, with the chemical activity 1, which means that under favourable thermodynamic (and kinetic) conditions, virtually complete deoxidation is possible.

**Systems with a single metallic component**

For such systems, the chemical reactions for removing oxygen are fairly straightforward – at least in case of low O solubility in the metal – and depend on one hand on the stability of the respective oxides, and on the other hand on the reducing agent used. Standard agents are carbon – especially if this is already a constituent of the system – and hydrogen, which is mandatory if carbon is to be excluded, as for example, in
refractory metals. As can be derived from the Ellingham-Richardson diagrams, these reducing agents are different in their effectiveness, in particular regarding the temperature. At lower temperatures, the Gibbs free energy of formation is significantly more negative for H$_2$O than for CO. On the other hand, the equilibrium graph for H$_2$O becomes less negative at higher temperature while that for CO becomes more negative, because of the gain in entropy. Therefore, H$_2$ is the preferred reducing agent at lower temperatures, while C is more effective in the high temperature range.

This can be illustrated when comparing thermogravimetry (TG) graphs combined with mass spectrometry (MS) for iron–carbon, taken in different atmospheres (see Figure 2). In inert atmosphere – where only carbon is active as reducing agent – the first pronounced reduction is indicated by the peak in mass 28 (CO) in the MS graph, and another smaller one for m44 (CO$_2$). This peak in the MS is registered simultaneously to a pronounced mass loss observed at about 800°C. A similar process with a less sharp but wider m28 (CO) peak is observed in the range 1000–1200°C. When doing the same run in H$_2$, in contrast, the first reduction peak is observed already at around 400°C, and it is detected for mass 18 (H$_2$). However, the second reduction peak is again observed at 1200°C, and once more for m28 (CO). This confirms that even in H$_2$ atmosphere the dominating process at higher temperatures is carbothermal reduction, as it is also indicated by the drop of the H$_2$O signal in parallel with the increase of the CO signal.

The reason why the reduction does not occur in a single-temperature interval but in two is the presence of different sources of oxygen. The first peak indicates removal of the surface oxides, which occurs rapidly as soon as the thermodynamic conditions for reduction are fulfilled. The second peak indicates the removal of the internal oxides as well as those

![Figure 2. Thermogravimetry/mass spectrometry graphs for Fe–0.5%C, sintered in different atmospheres (99.999% purity). Water-atomized Fe powder, natural graphite. Heated at 20 K.min$^{-1}$.](image-url)
trapped in the pressing contacts. In both cases, oxygen has to diffuse to the surface for successful reduction, which is a comparatively slow process and results in a wider peak. This can be confirmed by using Fe powders with different particle sizes: the finer the powder is, the more pronounced is the first peak, and the more shifted is the second one to lower temperature (Danninger, 2006). For the very fine Carbonyl iron powder, the temperature interval between the two peaks is very narrow (Danninger & Gierl, 1998), because the diffusion path for the internal oxygen is rather short.

**Carbon control during sintering**

There is one inevitable consequence of the contribution of carbothermal reactions, and this is carbon loss. Carbon consumed for the reduction is removed as CO/CO$_2$ and is thus lost as alloy element. Sintering in reducing atmosphere may somewhat decrease this loss: less C is required because part of the oxygen is removed as H$_2$O. However, some carbon loss must always be considered because – as explained before – the reduction at high temperatures always takes place through carbothermal reactions. In contrast to the surface decarburization caused by impure – especially humid – atmospheres, carbon loss for reduction purposes is homogeneous and typically also regular and predictable. It can be compensated for, for example, by adding slightly more carbon carrier – typically fine, well-crystallized graphite powder, mostly high purity natural graphite – to the starting powder mix, or by applying a slightly carburizing atmosphere.

Another type of possible carbon loss is the recently described decarburization due to methane formation at intermediate temperatures (Danninger & Avakemian, 2014; Oro, Campos, Gierl-Mayer, Danninger, & Torralba, 2015). Also in this case a homogeneous decarburization is observed. The exact mechanisms are still not well understood, but it has been observed that the intensity of this process strongly depends on the alloying elements present in the steel, and in the way these elements are introduced (e.g. elemental powders vs. prealloyed powders).

In any case, when defining the carbon content of powder metallurgy products, it should always be stated if it is the *nominal* carbon content (e.g. the amount of graphite admixed) or the combined carbon, that is, that detected in the sintered product by combustion analysis, since these two values may differ considerably.

For carbon steels or low alloy steels, the carbon balance is important, but some tolerance is usually acceptable. For sintered high alloy steels – such as high speed steels – precise control of the carbon content is however essential. The reason is that they can be sintered to the required
full density only within a very narrow temperature interval, in some cases ±3 K (Bee & Wood, 1985; Beiss, Wählıng, & Duda, 1985; Grinder, Berglin, & Sporrong, 1985; Henry, Nurthen, & Brewin, 1987; Podob & Woods, 1981), and the exact temperature of this interval strongly depends on the carbon content. Therefore, precisely establishing the starting carbon content in the powder (considering the carbon loss for reduction of the oxygen content and other possible effects that affect the carbon balance) is an essential precondition for successful sintering. Typically, vacuum sintering is employed to ensure optimum carbon control. In vacuum conditions, the oxygen traces present in the furnace during sintering can be controlled better than in case of a flowing atmosphere, as even in case of high purity atmospheres oxygen is consistently introduced. Of course, also the continuous removal of the reaction products when processing in vacuum benefits a more effective reduction. Nevertheless, flowing atmospheres have also been investigated. Studies on sintering in nitrogen-containing atmospheres have shown, for example, that nitrogen pickup lowers the required temperature and slightly increases the useful temperature ‘window’ (Urrutibeaskoa & Jauregi, 1993; Urrutibeaskoa & Urcola, 1993) but also here carbon control remains the essential requirement.

The same, economically much more important, requirement towards carbon control holds for hardmetals. Sintered WC-Co hardmetals must be biphasic, consisting of the binder, typically Co with dissolved W and C, and the hexagonal WC phase. The tolerable ‘window’ for the carbon content is very narrow, in particular for hardmetals with low binder content (see the difference between Figure 3(a). WC–20 wt% Co and b.WC–4 wt% Co), and keeping large-scale industrial production within this window is an essential requirement for any producer, but is industrial standard today. Even slightly too low carbon contents – for example, by losing carbon for carbothermal reduction – would result in brittle eta-carbides, and too high C levels in inclusions of free graphite (Figure 4). In both cases, the materials are more or less (expensive) scrap. This extreme sensitivity of the product quality to the carbon balance, and therefore to all reactions during sintering involving carbon, is the reason why the first systematic studies of these chemical reactions have been done on hardmetals, starting in the early 1990s (Leitner, Heinrich, & Görting, 1995; Leitner, Hermel, & Jaenicke-Rößler, 1996). Currently, research is further boosted by the trend to replace Co by other, less critical binder metals, in particular Fe (Prakash, 1980; Prakash & Holleck, 1980; Schubert, Fugger, Wittmann, & Useldinger, 2015; Wittmann, Schubert, & Lux, 2002), because of environmental and health reasons (Svanehav, 2019). In the system WC-Fe the tolerable carbon ‘window’ is however significantly more narrow than for WC-Co (see
the difference between Figure 3(a). WC–20 wt% Co and c. WC–20 wt% Fe). In particular, rather characteristic of the Fe-binders is the so-called roofing of the 2-phase region. As can be seen in Figure 3(c), a broad part of the 2-phase region (where only WC and fcc phases are stable) is ‘roofed’ by a region in which eta carbides are stable at high temperatures. In praxis, this implies that dendritic eta carbides may precipitate during cooling. Often these carbides are, for kinetic reasons, never decomposed into WC + fcc at lower temperatures (as thermodynamics would dictate), and even when they transform, this results in heterogeneities in the binder distribution (Schubert et al., 2015]. The ‘effective’ carbon window is thus even smaller, that is, between points A and B in Figure 3(c). Carbon control is therefore even more demanding in Fe-based binders, which is a major obstacle against introducing these environmental-friendly hardmetals into large-scale production.

However, even if the carbon content is maintained within the tolerable window, there is still a difference if the carbon level is on the low-C or on the high-C side of the window, since this can have a considerable influence on the properties of the binder phase. At low carbon contents, higher amounts of W are dissolved in the binder phase, since both parameters are linked to the solubility product for

*Figure 3. Quasibinary polythermal sections of the systems WC-Co/Fe, (a) WC–4 wt%Co, (b) WC–20 wt%Co and (c) WC–20 wt% Fe)*
WC in liquid Co. Also the solubility of other alloying elements in the binder phase increases at decreasing carbon contents and reaches a maximum at the limiting carbon concentration, resulting in the formation of sub-stoichiometric carbides (typically eta-carbides, but also or kappa-carbides have been reported) (de Oro Calderon, Agna, Gomes, & Schubert, 2019; Steinlechner, de Oro Calderon, Koch, Linhardt, & Schubert, 2022). Solid solution of elements in the binder phase (in particular in the case of W) increase the lattice distortion and thus the binder hardness (presumably by solid solution strengthening) and the hardness of the hardmetal. Moreover, properties like corrosion resistance can be dramatically influenced by the degree of binder alloying (and thus also by the carbon content). As has been proved for hardmetals with Ni-based binders, significantly higher amounts of alloying elements like Cr, Mo and W can be dissolved at low carbon contents, as compared with high carbon contents. As a consequence, low carbon grades present superior corrosion behaviour (as compared with materials with higher carbon content) due to the higher amount of elements dissolved (W, Cr and Mo) that modify the nature of the protective layers formed under corrosive environments (Steinlechner et al., 2022).

The final W content in WC-Co hardmetals can be easily controlled nondestructively by measuring the magnetic saturation: lower W content means higher saturation. Measuring this property is therefore routine in hardmetals production (Roebuck, 1996).

**Multi-component systems**

For systems that contain more than one metallic element, the respective oxygen affinity of the various components has to be considered for oxygen removal during sintering. Furthermore, also the route how the elements are introduced is of high relevance. In contrast to ingot metallurgy, powder metallurgy offers various options here, as shown in

![Image](image-url)
Figure 5. The prealloyed variant is roughly equivalent to the situation in ingot metallurgy: all elements are present in each single powder particle in virtually the same concentration, and thus also the chemical activity, that is, the oxygen affinity, is rather constant.

In powder mixes or diffusion bonded variants (in which the alloy element particles are slightly sintered to the base powder to prevent segregation effects) two different scenarios are possible: In many cases, the oxygen affinity of the different elements present is rather similar (e.g. in case of classical Cu–Ni–Mo alloyed sintered steels or also in WC-Co hardmetals). However, the oxygen-sensitivity of the different elements present in the system may also differ considerably. This means that particles of metals with high oxygen affinity may be positioned closely adjacent to elements with lower oxygen affinity, as for example, in sintered steels containing Cr, Mn or Si. This difference in the oxygen affinity may be slightly alleviated when introducing the elements though the masteralloy route, that is, admixing to the base powder a prealloyed powder that contains all the alloying elements combined (typically with the base component) (Banerjee, 1981; Schlieper & Thümmler, 1979; Zapf & Dalal, 1977). In this situation, the chemical activity of the oxygen-sensitive elements is reduced, because they are alloyed with an element with lower oxygen affinity (de Oro Calderon et al., 2017). Nevertheless, differences of the oxygen affinity between the base powder and the admixed masteralloy powder will exist also here.

Inter-particle oxygen transfer reactions

Multi-component systems can be divided into such where the oxygen affinity is homogeneous – that is, the prealloyed variant – and such where the oxygen affinity varies among powder particles. If the oxygen
affinity does not vary too much, and particularly if that of the additives is lower than that of the base powder, then the system is uncritical insofar as the deoxidation is determined by the main constituent. This is the case for the conventional sintered steels mentioned above that contain Cu, Ni and/or Mo. All these elements have an oxygen affinity that is lower than that of Fe, and it is therefore the reduction of the iron oxide that controls the deoxidation process (Danninger, Wolfsgruber, & Ratzi, 1997). Any condition that grants the removal of oxygen from the Fe powders will also remove the oxygen from the alloy element particles, and typically this latter reduction will go unnoticed, the reduction profiles being very similar to those shown in Figure 2. The same holds for WC-Co hardmetals: W oxides are the most stable ones and are therefore reduced last, the onset of shrinkage being triggered by the removal of oxygen from the WC particle (Leitner et al., 1996).

If however the oxygen affinity of the additive is significantly higher than that of the base component, that is, if ΔG is markedly more negative, this will have a pronounced effect on oxygen removal. This is plainly evident when comparing the MS graphs of plain Fe–C (Figure 2) with those of Fe–C mixes containing 4 wt.% admixed electrolytic Mn, as shown in Figure 6. Here, it is clear that the characteristic very pronounced m28 peak visible in Figure 2(a) at about 800 °C has completely disappeared. There is just one distinctive peak with the maximum at about 1200 °C, that is, at even higher temperature than that for the internal oxides in Figure 2(a). When sintering in H2, there is a minor peak of m18, significantly smaller than in Fe–C – as also indicated by the very slight mass loss – but the main reduction occurs carbothermally also here, as indicated by the pronounced mass loss above 1000 °C combined with a major m28 peak.

![Figure 6](image-url)

Figure 6. Thermogravimetry/mass spectrometry graphs for Fe–0.5%C + 4% Mn admixed, sintered in different atmospheres (99.999% purity). Water-atomized Fe powder, natural graphite and electrolytic Mn. Heated at 20 K/min−1.
In these materials, the main proportion of oxygen is introduced via the base iron powder. Assuming that the base Fe powder contains 0.08%O (as typical for water-atomized powders, according to the supplier information (Online Hoganas Handbook-0_interactive_version:_Iron and Steel Powders for Sintered Components_2017) as well as numerous analyses done by the authors) and the admixed Mn powder contains 1%O, the oxygen in the mix originates to about 66% from the Fe powder. Therefore, in inert atmosphere, a pronounced m28 peak at 800 °C would be expected, as shown in Figure 2(a). However, the disappearance of this peak proves that the reduction product generated – CO – cannot be detected by MS since it is unable to leave the ‘internal atmosphere’ in the pore network, being immediately gettered by the Mn particles present. Here, it should be considered that an atmosphere with an increased CO content – CO is generated by the equilibrium Fe oxide/Fe/C/CO at a given temperature – is strongly oxidizing for elements with high oxygen affinity such as Mn, Cr or Si (Figure 7(a)) (Vattur Sundaram, Hryha, & Nyborg, 2014; Wendel, Manchili, Hryha, & Nyborg, 2020). In fact, in this case, the net reaction is an oxygen transfer from the Fe base powder to the alloy element, strictly speaking a metallothermic reduction of iron by the alloy element through the gas phase (de Oro Calderon et al., 2017; Gierl-Mayer, de Oro Calderon, & Danninger, 2016). This ‘internal getter’ effect can be schematized as shown in Figure 7(b): oxygen transfer being short-circuited within the very narrow pore channels in which it is much more probable to contact an alloy element particle than to reach the external atmosphere, where it could be detected analytically.

The fact that in the H₂ atmosphere some H₂O is detected at about 400 °C indicates that at this temperature the reactivity of Mn is still too low to fully getter the water vapour generated by reduction of iron oxide.
with H\textsubscript{2}. However, the amount of oxygen thus removed is marginal, as indicated by the very low mass loss compared to the second reduction at T>1000 °C. In principle, it might be possible to hold the specimen at 400 °C for some time to remove as much oxygen as possible through reduction with H\textsubscript{2} (Chasoglou, Hryha, & Nyborg, 2011). In practice, however, this would interfere with the delubrication process, mandatory for pressed and sintered compacts, which typically requires temperatures of around 600 °C, at which the internal getter effect is already active, as visible in Figure 6(b) from the very low m18 signal.

Summarizing, it can be stated that in powder compacts consisting of components with different oxygen affinity, the removal of the oxides is inhibited by internal oxygen transfer – the ‘internal getter’ effect – and the conditions required for effective oxygen removal, in particular the temperature, are those that hold for that alloy element that forms the most stable oxide.

**Intra-particle transfer reactions**

Transfer reactions that change the chemistry of the oxides occur not only in mixes but have been shown to take place also in prealloyed powders containing, for example, Cr or Mn. As shown by Karamchedu, Hryha, and Nyborg (2015) and Karlsson and Nyborg (2001), such powders contain about 50% of the oxygen as a thin, continuous iron oxide layer in which islands of complex Cr–Mn–Si oxides are embedded. Therefore, it would be expected that the reaction process would result in one peak for iron oxides – 700 … 800 °C in inert atmosphere – and another one at higher temperature, for the complex oxides. Thermoanalytical study however shows that there is in fact a double peak, but the first one is shifted to considerably higher temperatures, typically >1000 °C, while in the lower temperature range only a marginal signal is present (see Figure 8(a)). In the H\textsubscript{2} atmosphere, the typical m18 peak at 400 °C is present(see Figure 8(b)), but as in the previous cases, only a minor amount of oxygen is removed this way. It might also be noted when comparing Figure 8(b) from prealloyed Fe–3Cr–0.5Mo with Figure 2(b) from a plain iron powder, that the reduction of the iron oxides with H\textsubscript{2} occurs at slightly lower temperatures (i.e. ~350 °C instead of ~400 °C) in the case of prealloyed powders. The probable reason is that the iron oxide layer formed in the case of powders prealloyed with Cr is on the one hand thinner, and on the other hand of a higher purity. The reason for its higher purity could be that the more oxygen affine elements (always present in small amounts as impurities) are preferentially present in the form of particulate oxides in the case of prealloyed powders. This explanation is corroborated by the fact that in case of very high purity iron powder, such as Carbonyl
iron powder, the first m28 peak, which indicates carbothermal reduction of the surface oxides, is also observed at lower temperatures than in case of the less pure water-atomized powders described in the present study (see Danninger & Gierl, 1998). Also for Mn and Mn–Cr prealloyed steels, it has been observed that this first m28 peak occurs at the lower temperatures, the higher the content of these alloy elements is (Hryha, Gierl, Nyborg, Danninger, & Dudrova, 2010).

Figure 8(a) indicates that there are no more original iron oxides that would be reducible when the temperature threshold is reached above which iron oxides can be carbothermally reduced. From Figure 8(b) can be derived that some iron oxides are reduced by H₂ but only in a rather narrow temperature interval. If the upper temperature boundary is exceeded, the reduction slows down decisively, although of course for iron oxides the conditions for reduction by H₂ should become more favourable with higher temperature.

These results clearly indicate that the composition of the surface oxides changes during heating, and that more stable oxides are progressively formed that require higher temperatures for reduction. As indicated by the Ellingham-Richardson diagrams, reduction becomes progressively carbothermal as the temperature increases. It has been shown by Hryha and Nyborg (2015) that in these types of steels the oxides are enriched with Cr, but the temperatures for these studies were significantly higher, in the range of 1000 °C and above, while the present results indicate that much lower temperatures are already sufficient to transform the oxides.

This was also corroborated by thermoanalytical runs with prealloyed materials that were differently treated before (Danninger, de Oro Calderon, & Gierl-Mayer, 2018). Evidently, the m18 (H₂O) signal observed at 400 °C in H₂ indicates the presence of iron oxide on the powder surfaces. If powder compacts are pre-treated in inert environment – Ar – at 400 °C, 

![Thermogravimetry/mass spectrometry graphs](image-url)

**Figure 8.** Thermogravimetry/mass spectrometry graphs for prealloyed (Fe–3.0%Cr–0.5%Mo)–0.5%C, sintered in different atmospheres (99.999% purity). Heated at 20 K min⁻¹.
the m18 peak is visible as with the untreated reference. If, however, pre-treatment is done by heating up to 650°C at 10 K/min and then immediate cooled at the same rate, in the following run in H₂ the m18 peak disappears almost completely. This confirms that the original iron oxides are transformed into more stable oxides in the temperature interval between 400°C and 650°C.

This can be explained to be another variant of the ‘internal getter’ effect, in which however not oxygen migrates but the alloy element. Since the chemical activity of the alloy element, for example, Cr, is much lower in the oxidic than in metallic state, Cr diffuses towards the surface and reacts there with the iron oxide – in principle once more a metallothermic reduction of iron oxide. This is schematically shown in Figure 9. It might seem surprising that alloy elements can diffuse sufficiently at those low temperatures to cause this effect, but extrapolated diffusion data from Handbook of Chemistry and Physics (1987) indicate that distances of 50 nm can be covered under these conditions which are sufficient to transform the very thin (a few nm) iron oxide layers into, for example, chromite FeCr₂O₄ or, as proposed in Hryha and Nyborg (2015), MnCr₂O₄.

Also here the consequence is that deoxidation is governed by the most stable oxide present in the system, which once more is not present from the beginning but is formed at least in part during the heating process. Since, however, the oxygen is in part already present as stable oxides from the beginning – which would require higher reduction temperatures anyhow – for industrial practice this internal getter effect is rather insignificant; it is just an interim process in the course of sintering that may even go unnoticed.

**Carbon transfer during sintering**

Transfer of interstitials holds however not only for oxygen; also carbon can be redistributed as a consequence of different affinities of the metallic components. In addition to the carbon effects on hardmetals as mentioned above, also in other systems the initial chemical inequilibrium in powder mixes can result in redistribution of carbon during the sintering process, either as unintended intermediate process or as a way to obtain a desired...
microstructure that would not be accessible through ingot metallurgy routes.

An interesting example is the redistribution of carbon in Cr alloy steels prepared from mixed powders, which can also be described as ‘internal decarburization’ of the ferrous matrix (see Figure 10).

If the composition is properly set, then a pearlitic microstructure is to be expected in case the ferrite-austenite transformation temperature has been exceeded, that is, when the dissolution of carbon has occurred. In plain Fe–C, such dissolution is complete at 1000 °C maximum, if suitable graphite grades are used (Danninger, Frauendienst, Streb, & Ratzi, 2001; Danninger & Gierl, 2001). However, when elemental Cr powders are admixed, the resulting matrix microstructure is not pearlitic but ferritic-pearlitic with fairly high ferrite content that would rather indicate a carbon content in the matrix of 0.3–0.4 wt.% (Figure 10(a) and (c)) as compared to the 0.7% of graphite added. On the other hand, the Cr particles exhibit a carbide shell that grows with increasing temperature until only carbide is left. The core of the original Cr particles remains hollow due to the Kirkendall effect, as a consequence of the widely differing diffusion coefficients of Cr in austenite vs. Fe in Cr (at 1200 °C: 4.5E-10 cm²/s vs. 7.3E-13 cm²/s (Handbook of Chemistry and Physics

Figure 10. Powder compact Fe-2%Cr–0.7%C, heated at 10K/min to defined temperature, then rapidly cooled. Cr introduced as elemental powder by admixing. Nital etched.
As shown already in Danninger, Kara, Ruhnow, and Ullrich (1990), this is a mixed Cr–Fe carbide, the Cr content decreasing from the core to the interface carbide-matrix.

This is however an intermediate effect: as soon as the critical temperature is reached at which transient liquid phase is formed between the ferrous matrix and the Cr carbide (Danninger, Pöttschacher, Bradac, Šalak, & Seyrkammer, 2005), both Cr and also the carbon contained in the carbide are rapidly dissolved in the matrix. This results in a microstructure that is in part martensitic – in the Cr-alloyed regions – but the remaining microstructure is pearlitic (Figure 10(d)), indicating that all carbon has been released back into the ferrous matrix.

Generally, it has been observed that the intermediate formation of carbides is characteristic for all PM steels prepared through the mixing route that contain carbide-forming elements. This process considerably slows down the homogenization of the alloy elements in the matrix by solid state diffusion. Also the transient liquid phases that enhance homogenization of these elements during sintering – above a given temperature – are typically formed between the austenitic matrix and the alloy metal transformed into carbide, not directly with the metal. This has been shown for Cr, Mo, W (Danninger et al., 2005) and also for V. In the latter case, carbides are formed in H₂ or vacuum, while in N₂ atmosphere, carbonitrides are generated which are even more stable in contact with the matrix. Thus, the formation of transient liquid phase requires still higher temperatures than in case of carbides (Danninger & Gierl, 2008).

The in-situ carbide formation can however be used also to obtain specific microstructures. In particular if low carbide contents are aimed at, powder metallurgy offers the chance to produce carbide-containing microstructures that would not be accessible by ingot metallurgy. A typical example are valve seat inserts containing Mo (Danninger, Wolfsgruber, & Dalal, 1994). Here, admixing elemental Mo powder and sintering under conditions at which the powder particles are transformed into carbides – but dissolved only to a minor degree - results in a carbide-reinforced steel microstructure.

Also here, both the sintering parameters and the carbon content play a major role, the latter influencing the type of carbide generated. In Figure 11, microstructures of a Co–Mo steel grade – as used for automotive valve seat inserts (Danninger et al., 1994) – are shown. The materials have been prepared with different starting C content. In case of lower C level, 0.6% admixed, the Mo particles are transformed first to binary carbide Mo₂C and then progressively to the ternary eta-carbide M₆C (typically Fe₃Mo₃C, turned yellow by Murakami’s reagent), resulting first in an intermediate core-rim structure and then, at longer times, in
complete transformation to eta-carbide (Figure 11(a)). In case of 1.0 wt% C admixed, in contrast, this carburizing process stops at the Mo₂C stage (Figure 11(b)), which is preferable in this case since Mo₂C enhances the wear resistance but is much less abrasive to the counter material than would be, for example, Cr carbides. This dependence of the carbide formed on the carbon content can also be derived from the respective ternary phase diagram Fe–Mo–C which shows that at lower C levels austenite is in equilibrium with M₆C, while at higher levels is in equilibrium with Mo₂C (Smith & Watanabe, 1977).

Internal carbon transference is also a relevant mechanism in hard-metals, in particular when elements with a high carbon affinity are added (e.g. Cr is commonly added as grain growth inhibitor or to improve the corrosion resistance of Ni-based binders). This can be very well illustrated, for example, when considering the possible use of stainless steel as binder in WC-based cemented carbides. In de Oro Calderon, Agna, et al. (2019), AISI 316 stainless steel powder (Fe–18 wt% Cr–13 wt% Ni–3 wt% Mo) was used with this purpose. After sintering samples with different carbon contents, Cr-rich carbides were observed in all samples, that is, no 2-phase (WC + Binder) materials could be produced, independently of the carbon content. Furthermore, as most of the Cr was present as carbide, the amount of Cr in the
binder phase after sintering was only 4 wt.%Cr, so no improvement in corrosion resistance can be expected in this material (normally Cr contents above 12 wt.% are needed to provide corrosion resistance in steels). It has been proved in WC-Co materials with increasing amounts of Cr that the precipitation of such Cr-rich carbides (see Figure 12) leads to a significant increase in hardness, accompanied however by a dramatic decrease in toughness (Suzuki & Tokumoto, 1984). The possibilities in terms of new binder compositions are thus limited and must be investigated for every particular combination of alloy binder and hardphase. Most of the well-studied high entropy alloys (HEAs) are, for instance, not an option when considering WC as a hardphase, as these alloys present rather high amounts of Cr that will be inevitably transformed into carbides. When considering multi-component alloying systems, thermodynamic software tools can be used to predict phase formation in different systems and thus speed up the research on novel binder compositions.

**Conclusions**

When studying the sintering of metallic powder compacts, not only the material transport processes – that lead to growth of sintering contacts and to densification – but also the chemical processes – especially those involving interstitial elements – have to be considered. This holds in

![Figure 12. Light microscopic image of alloy WC–Co15Cr, demonstrating the presence of M,C₃ grown around the WC, forming a carbide network. The Co-FCC binder was removed by etching with diluted HCl. The carbide can be coloured by Murakami etching.](image)
particular for the phenomena occurring at the surfaces of the powder particles, which contain oxygen in various compounds. This oxygen has to be removed in the early stages of sintering. When studying the interactions between the substrate and the atmosphere, also the difference between the external atmosphere, outside the compact, and the internal one, within the pore network, has to be considered. The composition of the latter is determined by the local chemical equilibria. Removal of oxygen is typically performed by reduction with \( \text{H}_2 \) or carbothermally, the latter reaction dominating the reduction in the higher temperature range. In this case, carbon loss is involved which has to be controlled and compensated for, this control being particularly crucial with WC-Co hardmetals and even more so if other binder metals are employed.

In case of components containing several metallic elements, the alloying route is highly important: for powder mixes that contain elements with different oxygen affinity, reduction of the less stable surface oxides results in the ‘internal getter’ effect, that is, oxygen transfer to that element that forms the most stable oxides. Final deoxidation thus requires conditions that enable reduction also of these oxides, which in practice means sufficiently high temperatures. Similar transfer reactions are observed also with prealloyed powders, although in this case the oxide-forming element diffuses to the powder surface, transforming originally less stable oxides into more stable ones. Once more, the final oxygen removal is determined by these latter oxides. Finally, such redistribution processes may involve not only oxygen but also carbon, heterogeneous carbon affinity resulting in ‘internal decarburization’, that is, carbide formation from alloy elements at the expense of C dissolved in the matrix. This in-situ carbide formation may be an intermediate process in the early stages of sintering, but may also be used to generate inequilibrium microstructures that would be inaccessible by conventional metallurgy.

**Disclosure statement**

No potential conflict of interest was reported by the author(s).

**Funding**

The research leading to these results has received funding from the People Programme (Marie Curie Actions) of the Seventh Framework Programme FP7/2007-2013/ under REA grant agreement n° 625556. The work was also supported by funding from the Austrian Science Fund (FWF) through the Lise Meitner programme.
References

Amherd Hidalgo, A., Ebel, T. (2016). Fundamental understanding of the influence of oxygen on the fatigue behaviour of Ti–6Al–7Nb alloys. *Proc. Powder Metall. World Congress 2016 Hamburg*. Shrewsbury: Epma.

Banerjee, S. (1981). New results in the master alloy concept for high strength sintered steels. *Modern Developments in Powder Metallurgy, 13*, 143–157.

Bee, J. V., & Wood, J. V. (1985). Phase distribution during the sintering of high speed steel powders. *Progress in Powder Metallurgy, 41*, 217–233.

Beiss, P. (2009). *Sintering atmospheres for PM steels*. Högananäs Chair in Powder Metallurgy, Workshop Sintering Atmospheres, Vienna.

Beiss, P., Wähling, R., & Duda, D. (1985). Toughness of vacuum sintered P/M high speed steels. *Modern Developments in Powder Metallurgy, 17*, 331–357.

Bergman, O. (2009). Analysis of oxide reduction during sintering of Cr-alloyed steel powder through photoacoustic spectroscopy measurements. *Proceedings of Euro PM2009, Copenhagen, Denmark* (Vol. 3, pp. 239–245). Shrewsbury, UK: EPMA.

Bocchini, G. F. (2004). Influence of controlled atmospheres on the proper sintering of carbon steels. *Powder Metallurgy in Progress, 4*, 1–34.

Brookes, K. J. A. (1992). *Hardmetals and other hard materials* (2nd ed.). East Barnet, UK: International Carbide Data.

Cannon, H. S., & Lenel, F. V. (1953). Some observations on the mechanism of liquid phase sintering In F. Benesovský (Ed.), *Proc. 1st Int. Plansee Seminar* (pp. 106–121). Reutte: Metallwerk Plansee GmbH.

Chasoglou, D., Hryha, E., Nyborg, L. (2011). Effect of atmosphere composition on the surface interactions during sintering of chromium-alloyed PM steels. *Proceedings Euro PM2011 Congress and Exhibition on Powder Metallurgy, Barcelona* (Vol. 3, pp. 111–117). Shrewsbury UK: Epma.

Danninger, H. (2006). *Moderne Legierungs systeme für PM-Formteile – Konsequenzen für das Sintern*. In H. Kolaska (Ed.), *Pulvermetallurgie in Wissenschaft und Praxis Bd*. (Vol. 22, pp. 21–47). Fachverband Pulvermetallurgie Hagen.

Danninger, H., Avakemian, A. (2014). Methane formation through substrate-atmosphere interaction during sintering of Si containing steels. *Proc. EuroPM2014 Salzburg*, paper EP14038, on CD, 2014 Shrewsbury, UK: Epma.

Danninger, H., de Oro Calderon, R., & Gierl-Mayer, C. (2017). Powder metallurgy and sintered materials. In: *Ullmann's Encyclopedia of industrial chemistry*. (pp. 1–57). Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA.

Danninger, H., de Oro Calderon, R., & Gierl-Mayer, C. (2018). Chemical reactions during sintering of PM steel compacts as a function of the alloying route. *Powder Metallurgy, 61*(3), 241–250.

Danninger, H., Frauenendienst, G., Strebl, K.-D., & Ratzi, R. (2001). Dissolution of different graphite grades during sintering of PM steels. *Materials Chemistry and Physics, 67*(1–3), 72–77.

Danninger, H., & Gierl, C. (1998). De-gassing during sintering of different Fe and Fe-C powder compacts. V. Arnhold & A. Romero (Eds.), *Proc. PM’98 Powder Metall. World Congress & Exhib., Granada* (Vol. 2, pp. 342–347). Shrewsbury: EPMA.

Danninger, H., & Gierl, C. (2001). Processes in PM steel compacts during the initial stages of sintering. *Materials Chemistry and Physics, 67*(1-3), 49–55.
Danninger, H., & Gierl, C. (2008). Reaction of nitrogen atmospheres with PM steel compacts during sintering. *Preprints PM2008 Powder Metallurgy World Congress* (pp. 336–344 [on CD]). Washington, DC: Princeton, NJ: MPIF.

Danninger, H., & Gierl-Mayer, C. (2002). Degassing and deoxidation processes during sintering of unalloyed and alloyed PM steels. *Powder Metallurgy Progress*, 2, 125–139.

Danninger, H., Kara, T., Ruhnow, M., & Ullrich, H.-Jr. (1990). Microprobe analysis of low alloyed sintered steels. *Mikrochimica Acta*, 101(1-6), 219–229.

Danninger, H., Pötschacher, R., Bradac, S., Šalak, A., & Seyrkmmer, J. (2005). Comparison of Mn, Cr and Mo alloyed sintered steels prepared from elemental powders. *Powder Metallurgy*, 48(1), 23–32.

Danninger, H., Wolfsgruber, G., & Dalal, K. (1994). Sintering and microstructure of PM valve seat insert materials. *Proc. PM’94 Powder Metall. World Congress* (Vol. II, pp. 875–878). SF2M, EPMA eds., Paris.

Danninger, H., Wolfsgruber, E., Ratzi, R. (1997). Gas formation during sintering of PM steels containing carbon. *Proc. "EURO PM’97" 1997 Europ. Conf. on Adv. in Structural PM Component Production*, Munich, Germany (pp. 99–106). Shrewsbury: EPMA.

de Oro Calderon, R., Agna, A., Gomes, U. U., & Schubert, W.-D. (2019). Phase formation in cemented carbides prepared from WC and stainless steel powder – an experimental study combined with thermodynamic calculations. *International Journal of Refractory Metals and Hard Materials*, 80, 225–237.

de Oro Calderon, R., Edtmaier, C., & Schubert, W.-D. (2019). Novel binders for WC-based cemented carbides with high Cr contents. *International Journal of Refractory Metals and Hard Materials*, 85, 105063.

de Oro Calderon, R., Gierl-Mayer, C., & Danninger, H. (2017). Application of thermal analysis techniques to study the oxidation/reduction phenomena during sintering of steels containing oxygen-sensitive alloying elements. *Journal of Thermal Analysis and Calorimetry*, 127(1), 91–105.

de Oro Calderon, R., Gierl-Mayer, C., & Danninger, H. (2017). Master alloys in powder metallurgy: the challenge of exploring new alloying compositions. *Powder Metallurgy*, 60(2), 86–96.

de Oro Calderon, R., Gierl-Mayer, C., & Danninger, H. (2022). Fundamentals of sintering: Liquid phase sintering. In F.G. Caballero (Ed.), *Encyclopedia of Materials: Metals and Alloys* (pp. 481–492). Oxford: Elsevier.

Fromm, E., & Gebhardt, E. (1976). *Gase und Kohlenstoff in Metallen*. Berlin: Springer.

German, R. M. (1985). *Liquid phase sintering*. New York: Plenum

German, R. M. (2013). Progress in titanium metal powder injection molding. *Materials (Basel, Switzerland)*, 6(8), 3641–3662.

German, R. M., & Bose, A. (1997). *Powder injection molding of metals and ceramics*. Princeton, NJ: MPIF.

German, R. M., & Churn, K. S. (1984). Sintering atmosphere effects on the ductility of W-Ni-Fe heavy metals. *Metallurgical Transactions A*, 15(4), 747–754.

Gierl, C., Danninger, H. (2005). Thermal analysis of plain iron – the effect of “inert” atmospheres. *Proc. EuroPM2005*, Prague (Vol. 3, pp. 3–8). Shrewsbury, UK: EPMA.

Gierl-Mayer, C., de Oro Calderon, R., & Danninger, H. (2016). The role of oxygen transfer in sintering of low alloy steel powder compacts: A review of
the “internal getter” effect. *Jom Journal of the Minerals Metals and Materials Society*, 68(3), 920–927.

Grinder, O., Berglin, L., & Sporrong, M. (1985). High temperature sintering of high-speed steel P/M-parts. *Modern Developments in Powder Metallurgy*, 17, 407–425.

*Handbook of Chemistry and Physics*. (1987). Vol. 67. Baton Rouge, LA: CRC Press.

Henry, R. J., Nurthen, P. D., & Brewin, P. R. (1987). Studies on sintering high speed steels to full density. *Progress in Powder Metallurgy*, 43, 399–414.

Hryha, E., Dudrova, E., & Nyborg, L. (2012). On-line control of processing atmospheres for proper sintering of oxidation-sensitive PM steels. *Journal of Materials Processing Technology*, 212(4), 977–987.

Hryha, E., Gierl, C., Nyborg, L., Danningher, H., & Dudrova, E. (2010). Surface composition of the steel powders pre-alloyed with manganese. *Applied Surface Science*, 256(12), 3946–3961.

Hryha, E., & Nyborg, L. (2015). Thermodynamic and kinetic aspects of oxide transformation during sintering of Cr prealloyed PM steels. *International Journal of Powder Metallurgy*, 51(3), 35–46.

Johnson, P. K. (2008). Tungsten filaments: The first modern PM product. *International Journal of Powder Metallurgy*, 44(4), 43–48.

Kang, S.-J. L. (2005). *Sintering*. Oxford: Elsevier-Butterworth Heinemann.

Karamchedu, S., Hryha, E., & Nyborg, L. (2015). Changes in the surface chemistry of chromium-alloyed powder metallurgical steel during delubrication and their impact on sintering. *Journal of Materials Processing Technology*, 223, 171–185.

Karlsson, H., & Nyborg, L. (2001). Surface product formation on chromium alloyed steel powder particles. *Proc. EuroPM2001 Nice* (Vol. 1, pp. 22–27). Shrewsbury: EPMA.

Kieffer, R., & Hotop, W. (1948). *Sintereisen und Sinterstahl*. Vienna, Austria: Springer.

Leitner, G., Heinrich, W., & Görting, K. (1995). Thermoanalytical simulation of the sintering behaviour of hard metals. *Advanced Powder Metallurgy & Particle Mater. -1995 Part 4* (pp. 259–266), compiled by M. Phillips, J. Porter, Princeton, NJ: MPIF.

Leitner, G., Herrmel, W., & Jaenicke-Rößler, K. (1996). In-situ optimization of sintering by gas phase analysis. *Advanced Powder Metallurgy & Particle Mater. -1996 Part 11* (pp. 435–444), compiled by T. M. Cadle, K. S. Narasimhan, Princeton, NJ: MPIF.

Online Hoganas Handbook-0_interactive_version:_Iron and Steel Powders for Sintered Components,_2017; downloaded 2022-1-11; pp. 106, 132. https://www.hoganas.com/en/services/handbooks/.

Oro, R., Bernardo, E., Campos, M., Gierl-Mayer, C., Danningher, H., & Manuel Torralba, J. (2016). Liquid phases tailored for introducing oxidation-sensitive elements through the master alloy route. *Journal of the Japan Society of Powder and Metalurgy*, 63(4), 172–184.

Oro, R., Campos, M., Gierl-Mayer, C., Danningher, H., & Torralba, J. M. (2015). New alloying systems for sintered steels: critical aspects of sintering behavior. *Metallurgical and Materials Transactions A*, 46(3), 1349–1359.

Ortner, H. M., Ettmayer, P., & Kolaska, H. (2014). *The history of the technological progress of hardmetals*. *International Journal of Refractory Metals and Hard Materials*, 44, 148–159.
Petzow, G., & Huppmann, W. J. (1976). Flüssigphasensintern–Verdichtung und Gefügeausbildung. *International Journal of Materials Research, 67*(9), 579–590.

Podob, M. T., & Woods, L. K. (1981). The mechanism of sintering high speed steel to full density. *Modern Developments in Powder Metallurgy, 13*, 71–92.

Prakash, L., & Holleck, H. (1980). The influence of the binder composition on the properties of WC-Fe/Co/Ni cemented carbides. *Modern Developments in Powder Metallurgy, 14*, 255–268.

Prakash, L. (1980). *Development of tungsten carbide hardmetals using iron based binder alloys* (PhD thesis), Institut für Material und Festkörperforschung, Kernforschungszentrum, Karlsruhe KFK 2984.

Quadbeck, P., & Schreyer, B. (2010). In-situ monitoring of gas atmospheres during debinding and sintering of PM steel components. *Proc. PM2010 World Congress* (Vol. 2, *Sintering* (EPMA, Edt.). Shrewsbury: EPMA.

Roebuck, B. (1996). Magnetic moment (saturation) measurements on hardmetals. *International Journal of Refractory Metals and Hard Materials, 14*(5/6), 419–424.

Šalak, A. (1971). Saturation of iron compacts with nitrogen during sintering in a nitrogen-containing atmosphere. *Kovove Materialy* (in Slovak, translation by British Iron and Steel Industry Translation Service, The Iron and Steel Inst., London UK), 1971(4), 345–353.

Schatt, W. (1992). *Sintervorgänge*. Düsseldorf: VDI-Verlag.

Schlieper, G., & Thümmler, F. (1979). High strength heat-treatable sintered steels containing manganese, chromium, vanadium and molybdenum. *Powder Metallurgy International, 11*, 172–176.

Schubert, W. D., Fugger, M., Wittmann, B., & Useldinger, R. (2015). Aspects of sintering of cemented carbides with Fe-based binders. *International Journal of Refractory Metals and Hard Materials, 49*, 110–123.

Silbereisen, H. (1984). Zur Geschichte der Sinterstahlfertigung in Deutschland. *Powder Metallurgy International, 16*(2), 65–69.

Smith, Y. E., & Watanabe, H. (1977). Premixing ferromolybdenum in alloy sintered compacts with the aid of a liquid phase. *Modern Development In Powder Metallurgy, 9*, 277–300.

Steinlechner, R., de Oro Calderon, R., Koch, T., Linhardt, P., & Schubert, W. D. (2022). A study on WC-Ni cemented carbides: Constitution, alloy compositions and properties, including corrosion behaviour. *International Journal of Refractory Metals and Hard Materials, 103*, 105750.

Suzuki, H., & Tokumoto, K. (1984). Microstructures and mechanical properties of WC-Cr3C2-15Co cemented carbide. *Journal of the Japan Society of Powder and Metalurgy, 2*, 18–21.

Svanehav, T. (2019). Cobalt-related regulatory actions and the potential impact on the cemented carbide (hardmetal) industry. *International Journal of Powder Metallurgy, 55*(3), 39–43.

Urrutibeaskoa, I., & Jauregi, S. (1993). Improved sintering response of vanadium-rich high speed steels. *International Journal of Powder Metallurgy, 4*, 367–378.

Urrutibeaskoa, I., & Urcola, J. J. (1993). Sintering behaviour of grade m water atomised high speed steel powders under vacuum and nitrogen rich atmosphere. *Powder Metallurgy, 36*(1), 47–54.

Vattur Sundaram, M., Hryha, E., & Nyborg, L. (2014). XPS analysis of oxide transformation during sintering of chromium alloyed PM steels. *Powder Metallurgy Progress, 14*(2).
Wendel, J., Manchili, S. K., Hryha, E., & Nyborg, L. (2020). Reduction of surface oxide layers on water-atomized iron and steel powder in hydrogen: Effect of alloying elements and initial powder state. *Thermochimica Acta, 692*, 178731.

Whittaker, D. (2015). Innovation drives Powder Metallurgy structural components forward in the automotive industry. *Powder Metallurgy Review, 4*(2), 35–53.

Wittmann, B., Schubert, W.-D., & Lux, B. (2002). WC grain growth and grain growth inhibition in nickel and iron binder hardmetals. *International Journal of Refractory Metals and Hard Materials, 20*(1), 51–60.

Wu, X., Zhang, C., Goldberg, P., Cohen, D., Pan, Y., Arpin, T., & Bar-Yosef, O. (2012). Early Pottery at 20,000 Years Ago in Xianrendong Cave, China. *Science (New York, N.Y.), 336*(6089), 1696–1700.

Zapf, G., & Dalal, K. (1977). Introduction of high oxygen affinity elements manganese, chromium, and vanadium in the powder metallurgy of P/M parts. *Modern Developments in Powder Metallurgy, 10*, 129–152.