New Alloying Systems for Ferrous Powder Metallurgy Precision Parts

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Abstract:
Traditionally, the common alloy elements for sintered steels have been Cu and Ni. With increasing requirements towards mechanical properties, and also as a consequence of soaring prices especially for these two metals, other alloy elements have also become more and more attractive for sintered steels, which make the steels however more tricky to process through PM. Here, the chances and risks of using in particular Cr and Mn alloy steels are discussed, considering the different alloying techniques viable in powder metallurgy, and it is shown that there are specific requirements in particular for sintering process. The critical importance of chemical reactions between the metal and the atmosphere is described, and it is shown that not only \(O_2\) and \(H_2O\) but also \(H_2\) and even \(N_2\) can critically affect sintering and microstructural homogenization.

Keywords: Sintered steels, Sintering, Alloy elements, Atmosphere, Reduction.

1. Introduction

Manufacturing of ferrous powder metallurgy (PM) precision parts has increased significantly in the last decades, in particular for automotive applications [1]. The capability of PM to produce geometrically precise components in large numbers and with excellent reproducibility has been exploited esp. for engines and transmissions components. The limiting factor is the mechanical property profile of pressed and sintered parts which, mainly due to inherent porosity, exhibit lower tensile strength, impact resistance and fatigue endurance strength than comparable wrought steel grades [2, 3], although in service the differences play a less prominent role than would be supposed from laboratory tests.

One of the primary targets in PM parts production is therefore higher density either in the entire component or at the loaded surfaces [4], attained by e.g. warm compaction [5], high velocity compaction [6] or surface densification [7,8]. Densification during sintering, as common e.g. with hardmetals or PIM parts, plays a minor role with pressed and sintered components due to tolerance reasons, although also here the potential should not be underestimated.

In addition to the porosity, also the metal matrix can be modified to improve the mechanical properties. Traditionally, sintered steels containing Cu, Ni and in part Mo have been used, the choice of these alloy elements being due to the low stability of the respective oxides which can be reduced in almost any atmosphere. However, the drastic price increases

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of Ni, Cu and Mo in the last few years have rendered these elements less attractive, as has been the effect of health and safety regulations for Ni and recycling concerns for Cu. Standard alloy elements in wrought steels, in particular Cr, Mn and Si, offer better chances here, but these elements form quite stable oxides, which means that the sensitivity of green compacts to oxidation during sintering is higher, and also reduction of the natural oxide layers covering the powder particles is more difficult. Nevertheless, in particular Cr prealloyed steel powders are increasingly being used for parts production, although only parts producers experienced in sintering of tricky materials are successful here. The question if prealloyed or mixed powder grades is to be preferred is not yet answered, although in the case of Cr the low solution strengthening effect in ferrite [2] recommends this element for prealloying. In the case of Mn, prealloying would result in lower compactibility at least at contents >1%; here, mixing or using masteralloys must be regarded as an alternative [9-11].

In this work, the sintering behaviour of nonconventional PM steels is described with regard to alloying technique and chemical reactions during sintering as compared to more simple types such as Fe-C or Fe-Mo-C, and recommendations for sintering practice are given.

2. Degassing and reduction behaviour of standard PM steels

For assessing the sensitivity of a PM steel compact to oxidation, studying the degassing and reduction reactions during the initial stages of sintering is helpful [12] since both oxidation sensitivity and reducibility are affected by the same basic parameters. Thermal analysis through DTA, thermogravimetry (TG) and dilatometry are well suited, combined with chemical analysis through mass spectrometry (MS)[13, 14], which enables identifying the compounds formed during solid-gas reactions and thus the reactions themselves.

![DTA/TG/DTG graphs of steel compacts in inert atmosphere. Heating/cooling at 10 K·min⁻¹, T_max = 1400°C, helium](image)

**Fig. 1** DTA/TG/DTG graphs of steel compacts in inert atmosphere. Heating/cooling at 10 K·min⁻¹, T_max = 1400°C, helium

When studying the reactions taking place during sintering of carbon containing steels, it can be observed that reactions take place within rather well defined temperature “windows”. In Fig.1, the DTA and TG graphs are given for plain carbon steel Fe-C and for an Mo prealloyed steel; for better visibility also the differential mass loss (DTG) is plotted. It can be seen that there is some slight mass loss in the temperature range 200-400°C, followed by a very pronounced mass loss peak that occurs at about 700°C in Fe-C and about 750°C in Fe-Mo-C, but in both cases within a narrow temperature interval. At higher temperatures,
another, much broader mass loss peak occurs that is less pronounced than that in the 700°C temperature range, but the total mass loss in this range is in fact higher.

![Graphs of steel compacts Fe-1.0%C in inert atmosphere](image)

**Fig. 2** MS graphs of steel compacts Fe-1.0%C in inert atmosphere. Heating/cooling at 10 K·min⁻¹, T_max = 1400°C, helium

For identifying the reactions responsible for these mass changes, mass spectrometry can be used to advantage. In Fig.2, mass spectra for several mass numbers are given for the plain carbon steel. As can be seen, the graph obtained for m28, which shows the highest intensity, is more or less an inverse replica of the DTG graph, at least at T>500°C. m28 is not an unambiguous signal, it might be N₂ or CO. However, since the signal for m12 (carbon) is virtually identical to that for m28, only at a lower intensity, it is clear that m28 must in this case be CO, indicating carbothermic reduction of oxides. This is also corroborated by the fact that the peak at 700°C is also found with m44 (CO₂). CO and CO₂ being linked by Boudouard’s equilibrium. At T<500°C there is a signal for CO₂ and not for CO, which is well in agreement with Boudouard’s equilibrium, but also a double peak for m18 (water). This indicates that the low temperature mass loss is due to desorption of water and decomposition of hydroxides, together with some carbothermic reduction effects (these reactions can be completely eliminated by e.g. a delubrication treatment, see [15]). The peaks at 700 and 950 to 1100°C are both due to carbothermic reduction of oxides; as shown by studies with different Fe powder fractions (PMP) and preoxidized powders [16], the 700°C peak indicates reduction of the surface oxides and the high temperature peak that of the internal oxides present within the powder particles. Since this latter reaction also involves diffusion, it is markedly slower than removal of surface oxides.

All the reactions observed here take place at temperatures below the standard sintering temperature for ferrous parts, which is >1100°C. In practice they have virtually been
ignored, since they are a natural part of the sintering process, and oxygen removal inadvertently takes place during sintering.

What must however be considered is the natural carbon loss through CO formation. Here it should be considered that in many cases, sintering occurs in H\textsubscript{2} containing atmospheres, and since H\textsubscript{2} is also a reducing agent, it competes with carbon in that role. There will be less carbon loss during sintering the more oxygen is removed through formation of H\textsubscript{2}O.

In order to assess the respective contributions of C and H\textsubscript{2} to the reduction process, impact test bars were sintered in the dilatometer under H\textsubscript{2} and Ar, respectively, the gases generated being analyzed by MS. The graphs are shown in Fig.3. Evidently, in Ar the reduction takes place as shown in the DTA/TG, with reduction peaks at 700-800 and 950-1150°C, respectively. (The peaks are broader here and also shifted to higher temperatures, since larger specimens have been used compared to the TG). When sintering in H\textsubscript{2}, however, there is a very significant m18 (H\textsubscript{2}O) peak at about 400°C; on the other hand, the m28 (CO) peak at 700-800°C is almost completely absent. This indicates that here, the reduction of the surface oxides is afforded through reaction with H\textsubscript{2}. The internal oxides, in contrast, are removed under formation of m28 and not m18, indicating that at the higher temperatures necessary to afford diffusion of oxygen to the particle surfaces, carbon is the more effective reducing agent. This is in agreement with the Richardson-Ellingham diagram which shows that at low temperatures the free energy of formation for H\textsubscript{2}O is more negative than that of CO or CO\textsubscript{2}, while with increasing temperature CO becomes significantly more stable, the reducing power of C thus exceeding that of H\textsubscript{2}.
This implies that there is always some loss of carbon through reduction with the natural oxide content of the metal powders although the loss is smaller when sintering in H₂ since in this case only the internal oxides consume C while sintering in inert atmospheres requires all oxygen to be removed by reaction with carbon.

3. Degassing and reduction of Cr-Mo prealloy steel grades

Prealloyed steel grades containing Cr have been available already in the 1980s, as oil atomized grades from Sumitomo [17] – which however disappeared from the market after about 2 years – and as water atomized and then vacuum annealed grades from Kawasaki Steel [18]. Significant impact on the market was attained however only later, when Cr-Mo alloyed grades became available from Höganaås AB at attractive prices [19, 20]. However, it was recognized quite soon that the sintering procedures had to be adapted, due to the specific sintering behaviour of these materials. Also here, thermal analysis is helpful for identifying the specific effects of Cr on sintering.

Fig. 4 DTA/TG/DTG/MS graphs of prealloyed steel compacts (Fe-3%Cr-0.5%Mo)-1%C in inert atmosphere. Heating/cooling at 10 K·min⁻¹, T_max = 1400°C, helium

If the DTA/TG/DTG plots of compacts prepared from 3%Cr-0.5%Mo prealloyed powder are studied, it stands out clearly that while there is some mass loss at T>400°C, the previously observed mass loss peak at 700°C is no more present. In its place there is a peak with its maximum at 1000°C. The high temperature peak has also been shifted to higher temperatures, exhibiting its maximum at about 1250°C. These mass loss peaks are also
replicated in the MS graph for m28 (and, once more for m12) while there is no m44 signal, indicating that at these temperatures Boudouard’s equilibrium has been completely shifted towards CO. Quite intense signals for m44 (CO₂) and m18 (H₂O) are found at about 400°C, which indicates that the degassing reactions at low temperatures depend not so much on the powder composition but rather on the “history” of the powder, esp. the storage conditions.

![Graph a) Argon](image)

**Fig.5:** Gas formation during sintering of (Fe-3%Cr-0.5%Mo)-0.5%C in different atmospheres. Dilatometer, 10 K·min⁻¹

Also for Cr-Mo prealloyed steels, sintering in H₂ containing atmosphere is common practice, and also here, the question of the effective reducing agent has to be answered. Therefore, dilatometric sintering runs with MS control were carried out. As shown in Fig.5, the degassing and reduction in Ar is similar to that observed in He, see Fig.4. (The less pronounced m28 reduction peak at 1000°C originates from different powder batches being used). Sintering in H₂ results in slightly more pronounced formation of H₂O at about 400°C, but the double peak for m28 at 1000 and 1250°C, respectively, is present also here, which indicates that the main reduction also of the surface oxides occurs through carbon. The fact that the m18 (H₂O) peak occurs at the same temperature in case of the Cr-Mo steel as for Fe-C indicates that the oxide reduced by H₂ is iron oxide at this temperature. This is in agreement with AES studies [21] indicating that the Cr-Mo prealloyed powder particles are covered in part by iron oxides. Since there is however no 700°C peak indicating carbothermic reduction of iron oxide it must be assumed that during heating from 400 to 700°C, the oxide is completely transformed to chromium oxide or at least to chromite FeCr₂O₄.

The fact that in any sintering atmosphere carbon is the primary reducing agent also implies that the carbon content of the powder compact plays a major role. This is of relevance mainly for case hardening steel grades, with inherently lower carbon content; in this case
there is at least some risk that the admixed carbon content is too low to afford sufficient deoxidation.

Therefore, thermoanalytical studies were carried out with Cr-Mo steel compacts containing different amounts of admixed graphite.

![Graphs](image-url)

**Fig.6:** MS/TG/DTG graphs m28 of prealloyed steel compacts (Fe-3%Cr-0.5%Mo)-x%C in inert atmosphere. Heating/cooling at 10 K·min⁻¹, T_max = 1400°C, helium

In Fig. 6, the MS graphs for m28 are given, as the most typical indicator for carbothermic reduction. Evidently, the material containing no admixed graphite at all does not show any significant mass loss or CO formation, only a few small CO “bumps” being observed at 600° and 850°C, respectively (apparently due to the natural C content of the metal powder). If however some graphite is added – even small amounts, as e.g. 0.2% - the mass loss and reduction behaviour immediately change to that already observed for high C levels. As can be seen from Figs.6b-d, there is virtually no difference between 0.2%C and 0.7%C, indicating that even the former content is sufficient to afford complete reduction. It must however be considered that the carbon loss due to the reduction process makes up for a quite significant proportion of the total carbon content. Assuming that the Cr-Mo prealloy powder contains about 0.13%O, the carbon loss can be assumed to be 0.1%, or 50% of the admixed graphite. Therefore, in particular at low C levels the carbon lost through reduction of oxides has to be considered and eventually compensated for by admixing accordingly more graphite.

From the practical viewpoint it might be assumed that since the reduction process for the surface oxides – which is that one relevant for the mechanical properties, see [22] – occurs at about 1000°C, sintering in standard mesh belt furnaces at about 1120°C would be successful also here. It must however be considered that the thermoanalytical studies are
carried out under almost ideal conditions, i.e. with small fragments of compacts and in high purity atmosphere. This is commonly not the case in industrial furnaces, and therefore Cr-Mo steels should be sintered at higher temperatures, at which the carbothermic reduction is thermodynamically favoured. Furthermore it has been found that the Cr-Mo steels benefit from high temperature sintering in particular at higher density levels, exhibiting quite significantly improved impact and fatigue strength [22].

4. Manganese alloyed steels

In contrast to Cr and Mo, Mn results in considerable solid solution hardening of ferrite, Fe-Mn prealloyed steel powders thus being less compactible than Fe-Cr- or Fe-Cr-Mo grades. Therefore, introduction of Mn through prealloying is attractive only at low Mn contents, typically <1% [23], at higher levels admixing being preferable. In this case the compressibility of the basic Fe powder is retained – also low prealloyed Fe-Mo powders being suitable, see [24] - , but homogeneous distribution of the Mn in the steel matrix has to be afforded during the sintering process.

In contrast to other elements which in case of admixing are homogenized either through solid state diffusion, as e.g. Ni and in part Cr, or through transient liquid phase such as Cu, Mo and in some cases Cr [25], the homogenization of Mn occurs predominantly through the gas phase (e.g. [10, 26, 27]). This holds both for admixed elemental manganese and for high Mn ferromanganese grades. The reason is the fairly high vapour pressure of Mn already at moderate temperatures [28]. This has considerable implications on the sintering process. Since at any given temperature the vapour pressure of Mn is several orders of magnitude higher than that of Fe, Mn is transported through the gas phase to the Fe surfaces but the reverse, gas phase transport of Fe to Mn, cannot occur. Therefore, Mn forms solid solution with Fe, expanding the Fe particles, and on the sites of the Mn carrier particles, pores remain that are either empty (if elemental Mn has been used) or filled with Fe sponge (in case of ferromanganese). The consequence of this one-way transport is macroscopic expansion. This can be seen to advantage in the dilatometric graphs given for Fe-Mn-C in Fig.7a. As a reference, similar graphs are given for Fe-Mo-C in Fig.7b.
Typically, in the case of Fe-Mn-C the expansion starts already at temperatures well below the ferrite-austenite transformation and consistently increases up to the isothermal sintering temperature. In Fe-Mo-C, however, the dimensional behaviour is virtually the same as in Fe-C up to a critical temperature at which transient liquid phase is formed and a very abrupt expansion occurs [29]. This effect is well known from Cu ("copper swelling") (e.g. [30]) but occurs also in systems in which a ternary liquid phase involving C is formed; in this case the critical temperature depends on the C content. The essential differences between the mechanisms is that in the case of transient liquid phase the expansion occurs above a given, well defined temperature threshold while with Mn it is a function of the vapour pressure and thus is quite effective also at moderate temperatures as employed e.g. in belt furnaces. Mn might thus be a replacement for Cu in its function for compensating the natural shrinkage during sintering, "Mn swelling" occurring already at even lower temperatures than Cu swelling.

Fig. 8 Section of Fe-Mn-C, compacted at 600 MPa, sintered for 10 min at 1120°C

The Mn vapour condenses on the surfaces of the Fe particles, alloying them. Finally, intragranular homogenization has to occur through solid state diffusion but since the diffusional cross section in the case of vapour alloying is much larger than if diffusion has to come from admixed particles, accelerated homogenization occurs. This can be seen to advantage in metallographic sections. In Fig. 8, short time sintered Fe-Mn-C is depicted, and the Mn alloyed rims at the particle surfaces are evident. In Fig. 9, fully sintered microstructures are shown, and here it can be seen that after sintering at 1120°C most of the microstructure is alloyed with Mn, only the cores of the largest particles being unalloyed (= ferritic). Sintering at 1250°C results in fully homogeneous microstructure and in a degree of homogeneity that is not accessible e.g. with Ni alloyed sintered steels even after high temperature sintering. This indicates the effect of the vapour transport mechanism since the volume diffusion in austenite is not faster for Mn than it is for Ni (Diffusivity in austenite at 1250°C: $1.60 \times 10^{-10}$ cm$^2$.s$^{-1}$ for Mn vs. $1.73 \times 10^{-10}$ cm$^2$.s$^{-1}$ for Ni) [28].

Since however the gas phase, i.e. the internal pore space, is essential for Mn homogenization, it is not surprising that at very high green density levels Mn homogenization is retarded. It has even been shown that compacting at 1200 MPa results in lower elongation to fracture than at 600 MPa, which is very uncommon for sintered steels; usually higher density means better mechanical properties. The reason is that at the high green density there are insufficient pore space and internal pore surface for Mn homogenization.

As shown by Salak [26, 27], Mn vapour also leaves the pores of the compact, forming a Mn vapour shell around the body that acts as a getter. Salak states that the risk of oxidation when sintering Mn alloyed steels has been grossly overestimated in the past; the compacts
virtually protect themselves by the Mn vapour shell. The price to be paid for this protection is of course some Mn loss at the surfaces, i.e. in those places where the positive effect of Mn on the hardness and hardenability would be most welcome.

![Images of Fe-x%Mn-0.3%C, compacted at 600 MPa, sintered for 90 min in H₂](image1)

**Fig. 9** Sections of Fe-x%Mn-0.3%C, compacted at 600 MPa, sintered for 90 min in H₂

It has however been observed that the Mn loss is much more serious in the laboratory, where single or a few compacts are sintering in flowing atmosphere and the ratio Mn vapour-atmosphere is very much shifted towards the latter. In industrial production, however, there is apparently a steady state of Mn transport, i.e. the Mn removed from one compact is deposited on another one “downstream”, resulting in fairly low net loss of Mn.

![Images of near-surface regions of Mn alloyed sintered steels](image2)

**Fig. 10** Sections of the near-surface regions of Mn alloyed sintered steels
In Fig.10, cross sections through the surfaces are shown for a laboratory specimen and an industrially sintered part; evidently, Mn loss is much less pronounced in the latter case.

5. Effect of reactions with “inert” atmospheres

Conventionally, it has been assumed that reactions between powder compacts and the atmosphere during sintering take place through transfer of oxygen and/or carbon. The standard N$_2$-H$_2$ atmospheres have been regarded as being moderately reducing, and high purity N$_2$ by itself is thought to be an inert gas in sintering of ferrous compacts. By careful thermal analysis it has been shown that there is some nitrogen pickup when sintering plain iron or steels in N$_2$ atmosphere [31], but the amount of N introduced is rather low and, except for soft magnetic materials, does not play a major role. Also the classical alloy elements Ni, Cu and Mo are not reactive to nitrogen.

This however changes when shifting to other, less common, alloy elements. For high Cr stainless steels, nitrogen pickup during sintering is well known; for low alloy steels, such effects have mostly been neglected. If however strong nitride formers are used as alloy elements, the reactivity with the atmosphere may significantly affect the sintering process.

![Dilatometric graphs for Fe-1%V-0.7%C sintered in different atmospheres. Ferro-V90-125 μm, 10 K·min$^{-1}$, 60 min 1370°C isothermal](image)

It has been shown that the well known sintering activator boron is ineffective in N$_2$ containing atmospheres, being transformed into inert boron nitride [12, 32].

![Metallographic sections of dilatometric specimens as in Fig.11, sintered in different atmospheres](image)
A similar effect can be observed when sintering steels containing admixed vanadium. V is an expensive alloy element with rather high sensitivity to oxygen, and therefore its use in low alloy sintered steels has been limited. V addition via a complex master alloy has been proposed [9], and some Cr prealloyed powders contain a small amount of V [33]. If however steels of the type Fe-V-C are prepared and V is added as admixed ferrovanadium, there is a significant effect of the atmosphere on the homogenization during sintering, as shown in Figs. 11, 12 for V alloy steels in which relatively coarse Ferro-V has been admixed, to reveal the effects more clearly. Here it is evident that when sintering in really inert atmospheres, there is a pronounced expansion in the dilatometric graphs, typical for formation of transient liquid phase (“copper swelling”), as found also e.g. for Mo (see Fig. 7b). When sintering in \( \text{N}_2 \), in contrast, there is no such expansion up to a temperature of 1370°C but rather very regular shrinkage.

Metallographic sections reveal that after sintering in vacuum (or in argon) large, rounded secondary pores are found in the places of the former Ferro-V particles, as typical for transient liquid phase. After sintering in \( \text{N}_2 \), the Ferro-V particles are still in place but exhibit a typical core-rim structure as has been observed also with Cr particles in Fe-C matrix [34]. Here it can be assumed that when sintering in inert atmospheres, V is transformed into carbide before liquid phase is formed, but when sintering in \( \text{N}_2 \), carbonitride is generated that is more stable, forming a liquid phase only at higher temperatures. In fact, 1420°C have been necessary to generate transient liquid phase also in \( \text{N}_2 \).

6. Conclusions

Sintered low alloy steels containing Cr and/or Mn as alloy elements offer improved mechanical properties at significantly lower powder cost, thus extending the range of applications for PM precision parts. Cr, due its low hardening effect on ferrite, can be introduced through prealloying, several powder grades being commercially available. Because of the higher oxygen affinity of Cr compared to more traditional alloy elements such as Cu, Ni and Mo, careful atmosphere control during sintering is essential, and the natural oxide layers covering the powder particles are more difficult to remove, significantly higher temperatures being necessary. The main reducing agent in the Cr prealloyed steels is carbon, even when sintering in \( \text{H}_2 \), while in the case of Fe-C or Fe-Mo-C at least the surface oxides are reduced by hydrogen. High temperature sintering is beneficial both for complete reduction of the Cr steels and for optimum mechanical properties.

Prealloying of manganese is limited to low contents, due to its adverse effect on the compressibility, and admixing of elemental Mn or ferromanganese is preferable if contents >1% are desired. Homogenization of Mn thus has to be attained during sintering, and this process is however strongly supported by the unique gas phase transport mechanism that distributes Mn at the surfaces of the matrix particles. Some Mn loss through evaporation from the compacts may occur but this seems to be much less critical in industrial practice than in the laboratory. Finally it must be considered that less common alloy elements may also exhibit different chemical behaviour, as does vanadium, which exhibits retarded homogenization when sintering in \( \text{N}_2 \) compared to vacuum or argon.

It can thus be summarized that new alloying systems offer challenges with regard to the sintering process. If however equipment and sintering procedures are suitably adapted, PM precision parts with excellent mechanical properties are accessible that can significantly extend the range of applications for PM parts.
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