EFFECT OF SINTERING ATMOSPHERE ON THE TRANSFORMATION OF SURFACE OXIDES DURING THE SINTERING OF CHROMIUM ALLOYED STEEL

D. Chasoglou, E. Hryha, L. Nyborg

Abstract
Chromium is the one of the most attractive alloying elements for PM steels. Nevertheless, its high affinity to oxygen during sintering, especially during the heating stage, has to be considered. The present study relates surface products formation and their transformation to the employed sintering atmosphere. The study consists of the investigation of the type, morphology and distribution of reaction products on the fracture surfaces of specimens pressed and sintered at different temperatures between 700 and 1200°C, for various times, as well as the evaluation of the metal surface – sintering atmosphere interactions in terms of gas composition and temperature. Specimens were sintered in three different atmospheres - nitrogen, nitrogen/10% hydrogen and vacuum. Fractographic investigation of fracture surfaces of specimens sampled at different temperatures, by means of HR SEM combined with EDX analysis, show that the presence of hydrogen has clearly a positive effect on the early reduction of surface iron oxide during the heating stage, which is reflected in lower amounts of oxides present as well as lower carbon loss after sintering. The amount of oxide inclusions is higher after high temperature sintering in the case of vacuum due to pronounced development of inter-particle connections during the heating stage, above 900°C, which led to enclosure of the surface oxide layer inside the necks. A change in the morphology and size of oxide inclusions was observed during the heating stage and after sintering the oxides were mainly encountered as small (<1 µm) spherical inclusions and rarely coalesced into larger agglomerates. At higher temperatures, inclusions are stoichiometric Cr-Mn spinel oxides that have among the highest thermodynamic stabilities for this system. Metallographic study of sintered specimens verifies the extent of the oxide reduction and the carbon dissolution.

Keywords: PM steel, chromium pre-alloyed powder, sintering, sintering atmosphere, surface oxide, oxide reduction, carbothermal reduction, spinel oxides.

INTRODUCTION
Powder metallurgy technique is a well established manufacturing route for the production of components with complex shapes that require strict dimensional tolerances for engineering applications [1-4]. Today’s challenge for the improvement of the mechanical properties of the final products can be achieved by e.g. minimizing the porosity,
optimizing the final microstructure and facilitating strong inter-particle necks. Therefore it is important to control the microstructure by careful alloying with elements such as Cr, Mo, Mn, V, Si etc. Chromium has been widely used in the wrought steel industry as an alloying element, because it increases hardenability, it is relatively inexpensive and is well recyclable [2,5]. On the other hand, in the PM industry the use of Cr means that care must be taken to sinter the material properly under appropriate clean conditions to make sure that thermodynamically stable oxides rich in Cr along with other strong oxide formers are controlled. It is important in this context to have proper understanding of the processes taking place in every stage of the processing route from powder to the final sintered product [6-10]. By adding the alloying elements such as Cr and Mn, in the pre-alloyed state it is possible to deal, up to a certain extent, with their high affinity to oxygen since the presence of these alloying elements in solid solution will lower their activity roughly down to their content [6-8]. However, pre-alloying with Cr is known to decrease the compressibility of the powders due to the ferrite solid solution strengthening, though the low content of chromium in pre-alloyed state does not provide any strong restriction on the powder compressibility [11,12]. Therefore, nowadays water atomized steel powder with low Cr content is widely used for the production of structural sintered parts.

In previous studies [13,14] it has been shown that even if the powders, after atomization, undergo an annealing treatment in reducing atmospheres the surfaces of the powder particles will be covered with an inhomogeneous oxide layer. The major part of the surface is covered by a thin Fe-oxide layer with a thickness of about 6 nm, but dispersed on the surface there are also small (~200 nm) spherical particulates, that are rich in strong oxide forming elements like Cr and Mn [13-16]. It is of paramount importance to reduce the surface oxides during the heating stage in order to facilitate strong sinter necks during sintering which will have a direct effect on the mechanical properties of the component.

Therefore the role of the sintering atmosphere becomes very important since it must:
1. Reduce surface oxides in order to enhance the contact between neighboring powder particles;
2. Prevent oxidation of the sintered part;

For the reduction of the surface oxides it is known that careful control of the purity and composition of the sintering atmosphere is required [8-10,17-26].

During heating/sintering in vacuum or nitrogen atmosphere, the general reduction reaction – dissociation of oxide is:

\[ \frac{2}{y} \text{Me}_x\text{O}_y = \frac{2x}{y} \text{Me} + \text{O}_2 \] (1)

For a hydrogen containing atmosphere and taking also into account the graphite present in the compact the following reactions are taking place as well (*Me stands for metal):

Reduction by hydrogen: \[ \text{Me}_x\text{O}_y + y\text{H}_2 = x\text{Me} + y\text{H}_2\text{O} \] (2)

Direct carbothermal reduction: \[ y\text{C} + \text{Me}_x\text{O}_y = x\text{Me} + y\text{CO} \] (3)

Indirect carbothermal reduction: \[ y\text{CO} + \text{Me}_x\text{O}_y = x\text{Me} + y\text{CO}_2 \] (4)

Water gas reaction: \[ \text{H}_2 + \text{CO}_2 = \text{H}_2\text{O} + \text{CO} \] (5)
The reactions mentioned above depend on the temperature and pressure and of course on the thermodynamic stability of the metal oxides present [8-10,20-23,26]. The Fe-oxide can be easily reduced by hydrogen at lower temperatures (<500°C) according to reaction (2). More stable oxides like Cr- and Mn-oxides or spinels require higher temperatures for their reduction and this happens with the participation of carbon according to the reactions (3) and (4) with the last being the dominant reducing mechanism [6-10,17-24]. According to oxide reduction studies by thermoanalytical methods and mass-spectroscopy [18,19,25,26] and gas profiles on a material system with higher Cr content, carbothermal reactions begin at ~800°C and have a first maximum between 800-1000°C [8,10,18,19,21,26]. These peaks are related to the reduction of the surface iron oxide layer. For the reduction of oxides from internal pores that are at least partially open to the surface and more stable surface oxides, forming particulates, as well as mixed internal oxides, higher temperatures are required [8-10,17,19,21-26].

The aim of this study is to investigate the role of the temperature and atmosphere on the phenomena concerning the reduction of surface oxides, during the heating stage as well as during the sinter-holding for the given material system. With the information obtained along with previous studies, it is possible to have a clear picture of the chemical reactions occurring during the sintering cycle. The clarification of the process is very important from a scientific perspective as well as from the industrial since it gives the possibility to create a process mapping that which will help to optimize the sintering process in terms of atmosphere composition/control and sintering temperature and time, towards an efficient volume production of sintered parts.

EXPERIMENTAL PROCEDURE

Water atomized Cr-Mo alloyed powder of nominal composition Fe-1.5Cr-0.2Mo, provided by Höganäs AB, Sweden, was chosen as a base material. Initially, the surface chemical analysis of the base powder was performed using HR-SEM combined with EDX analysis in order to verify the composition of the powder particles surface. A powder mixture consisting of the Cr-Mo alloyed powder, 0.5 wt.% of natural graphite (UF4) and 0.6 wt.% of Kenolube as a lubricant was prepared and Charpy test bars (10x10x55 mm) were compacted to a green density of ~7 g/cm³. Prior to sintering, the compacts were de-lubricated at 450°C for 30 min in a N₂ atmosphere. In order to examine the effect of the sintering atmosphere composition, the sintering process was performed in N₂/10%H₂ blend, pure N₂ and vacuum. Sintering in nitrogen and nitrogen/hydrogen blends was performed in an Entech laboratory tube furnace; vacuum sintering was performed in a pilot vacuum furnace from Vacua Therm Sales. The dew point (DP) was monitored inside the tube furnace directly above the container with the samples. Before sintering, the furnace was purged with gas, used for sintering until a dew point of ~50°C was reached before starting every sintering process. The diameter of the tube furnace was 43 mm and the flow rate of the used atmospheres was approx. 12 l/min. The heating rate was kept constant at 10°C/min during all sintering trials and the specimens were sampled at different temperatures: 700°C, 800°C, 900°C, 1000°C, 1120°C (1, and 30 min) and 1200°C (30 min). The cooling rate was approx. 150-200°C/min for the specimens sintered in N₂/H₂ blend and in pure N₂. As for the sintering in vacuum, the cooling rate was approx. 100°C/min. All the samples after the heating/sintering were annealed at 200°C for 1 hour in a pure N₂ atmosphere. Fracture surfaces were obtained by impact testing and were examined under a LEO Gemini 1550 HR-SEM in combination with EDX (INCA) analysis. Additionally, bulk oxygen and carbon chemical analyses were performed in LECO instruments for all the specimens in order to track the changes of O- and C-content during the sintering process. Finally,
metallographic investigation was performed with a Leica LEITZ DSRX optical microscope in order to examine the obtained microstructures.

RESULTS
Previous studies [13-15] of powder surfaces by means of surface sensitive techniques like X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) indicate that in the case of iron-based alloys the surface of the powder is covered by a heterogeneous oxide layer, composed of a thin Fe-oxide layer and particulate features of thermodynamically stable oxides (Cr–Mn–Si). The HR-SEM micrographs along with the EDX analysis on the powder surfaces of the studied base powder, see Fig.1, verified the presence of randomly distributed spherical particulate features of ~200 nm size, that are rich in strong oxide forming elements like Cr and Mn as shown in the acquired EDX spectra. The XPS analysis of the powder surface [16] support that the powder is covered by a inhomogeneous oxide layer that consists of particulate features and a thin (~7 nm) Fe-oxide layer in between.

![Fig.1. High resolution SEM micrograph of powder surface and EDX analysis of observed particulate feature and the matrix.](image)

The results from the chemical analysis (O and C content) for the specimens sampled at different temperatures can be seen in Figs. 2(a) and 2(b).

![Fig.2. a) O-content and b) C-content for: the base powder, de-lubricated sample and specimens heated/sintered at different conditions and sampled at different temperatures.](image)
The oxygen content is always comparable in the cases of the specimens sintered/heated in vacuum and N$_2$/H$_2$ apart from those sintered at 1200°C for 30min, whereas in the case of N$_2$-processed samples there seems to be a higher O-content, see Fig.2a. During heating in all atmospheres the oxygen content is nearly at the same level up to ~1000°C. Above 1000°C, a pronounced reduction of the O-content is noted, with a steeper decrease registered during heating in vacuum. The lowest decrease in oxygen content during heating and sintering at lower temperatures was observed for specimens processed in pure nitrogen atmosphere. However, a considerable drop in oxygen content was observed after sintering at 1200°C, after which the oxygen content was even lower than for the vacuum sintered specimen. From the oxygen content values it is evident that the temperature range of the reduction is more extended for the specimens sintered in N$_2$/H$_2$ blend and vacuum compared to the N$_2$ atmosphere during the heating stage. In general it must be taken into consideration that there could have been slight oxidation of the samples during the cooling process after sintering in gaseous atmospheres.

As in the case of oxygen, the carbon content also remains constant during heating up to 1000°C for specimens processed in N$_2$/H$_2$ blend and N$_2$ atmospheres, whereas a decrease in carbon content was registered around 800°C for those heated in vacuum. This indicates the start of carbothermal reduction of surface oxides at lower temperatures for vacuum compared to the other two atmospheres. For nitrogen/hydrogen and nitrogen atmospheres decreased C-content was observed above 1000°C. This results in the highest carbon loss after sintering at both temperatures for vacuum, while the lowest final carbon loss was observed for N$_2$/H$_2$ series.

![Fig.3. Impact energy values for specimens from the different sintering/heating runs.](image)

For all series, the impact energy increases with increasing temperature and sintering time as seen in Fig.3. For the lower temperatures, all the specimens from all the series show similar values of impact energy with the N$_2$/H$_2$ heated ones displaying slightly higher values. For samples heated in vacuum at 900°C there is a sudden increase in impact energy (8 J), the values are at least 2 times higher than the respective ones for the N$_2$/H$_2$ and N$_2$ series. Between these last two series, specimens heated in N$_2$/H$_2$ still show higher impact energy. As soon as the sintering temperature is reached, the resulting impact energy values for specimens heated in vacuum and N$_2$/H$_2$ atmospheres are nearly the same (13.4 and 13.2 J respectively). The same trend is observed after low-temperature sintering, however the specimens sintered at 1200°C in N$_2$/H$_2$ atmosphere show the highest impact values (21.6 J). For the N$_2$ series, there seems to be a delay in the increase in impact energy.
with increasing temperature compared with results from the other series. However, after sintering at 1200°C for 30 min, the samples processed in vacuum and nitrogen exhibited similar impact energy values (17.3 and 17.8 respectively).

No visible oxidation was observed after de-lubrication of the samples, see Fig.4. The fracture surface of a de-lubricated sample (Fig.4a) shows relatively good purity and does not reveal any changes in powder surface appearance compared with the loose powder [13-16]. The particulate features did not change up to this temperature, 450°C (Fig.4b) and they can be categorized in two groups i) individual spherical features with size below 200 nm and ii) rarely observed larger agglomerates with size up to 1 μm.

Fig.4. Fracture surface of sample de-lubricated at 450°C at different magnifications.

Fig.5. Typical appearance of fracture surfaces of samples sintered at different temperatures/times in N₂/H₂ atmosphere.
As an example, the fracture surfaces at low magnifications of the samples sintered at different combinations of temperature and time in \( \text{N}_2/\text{H}_2 \) are presented in Fig.5. For all atmospheres, the specimens processed during the first stages of heating show rough fracture surfaces; the individual metal particles or their agglomerates can be easily distinguished for all specimens processed up to the sintering temperatures. Interparticle ductile fracture is the main failure micro-mechanism for all specimens. With increasing temperature, point and short line connections between the metal particles are changed to a more developed network of branched lines; dimple ductile fracture is evident for processing at increasing temperature. The character and strength of inter-particle connections are strongly determined by temperature and sintering time as well as by sintering atmosphere composition, as seen from the results in Fig.6.

Fig.6. Typical appearance of inter-particle necks on the fracture surfaces of specimens heated to different temperatures in \( \text{N}_2/\text{H}_2 \), \( \text{N}_2 \) and vacuum.

Changes in the free powder surface purity are clearly evident during the heating stage up to 1000°C in comparison with the de-lubricated condition, see Fig.6. An efficient reduction of surface iron oxides by hydrogen, providing metal-metal contact between adjacent particles, results in the presence of point and short-line inter-particle connections already at 700°C. No such inter-particle connections were registered for specimens processed in nitrogen and only point connections were found for the vacuum-heated specimens. The difference between the specimens is more evident after heating to 800°C, where samples heated in \( \text{N}_2/\text{H}_2 \) show the appearance of inter-particle dimple ductile fracture with very shallow dimples, while for the samples heated in \( \text{N}_2 \) these connections are just starting to develop. The vacuum-heated samples show better point and line connections compared to those heated in \( \text{N}_2 \), but the contacts are still less developed.
compared to the ones from the N₂/H₂-heated sample. The major improvement in the amount of the inter-particle connections and their strength appears at 900°C for vacuum sampled specimens; there is then a well developed inter-particle ductile fracture with deep dimples, initiated at enclosed oxide particles. It is important to emphasize the enclosing of unreduced surface oxide inside the inter-particle connections at this stage, especially in the case of vacuum-heated specimens. In the case of samples heated in N₂ a lower portion of dimple ductile fracture sites is registered. This change in inter-particle connections strength is reflected in the impact energy values, see Fig.3. For samples heated at 1000°C, the main failure mechanism for all sintering atmospheres is inter-particle dimple ductile fracture initiated by bridge porosity and point inclusions. The strength of the inter-particle contacts can be evaluated by the amount and appearance of the dimples. For the samples heated in N₂ and N₂/H₂ the dimples are shallower (and their amount is lower for the heated in N₂ sample) with larger inclusions inside. This indicates weaker connections in comparison with vacuum-processed samples, which in turn suggests comparatively stronger inter-particle connections and thus higher impact energy values. The free powder surfaces are slightly oxidized for specimens processed in gaseous atmospheres (especially nitrogen) and residues of the oxide layer are present at the inter-particle connections. Graphite flakes were present during the heating stage up to 1000°C. It is also important to note the better developed inter-particle necks close to the edges of the specimens across the fracture surface. However, the difference in dimple characteristics between edges and center of the specimen disappears for samples heated at around 1000°C for all atmospheres.

During this study special attention was devoted on the change of particulate oxide inclusions and other enclosed oxide residues inside inter-particle necks. The particulate features observed on the initial powder surface are present without changes up to about 800°C; they have the same size and shape as documented during powder analysis [16]. Growth of the particulates features in size (up to 500 nm) with increasing temperature was observed, their amount becomes larger and they take a more irregular shape in some cases. The amount, size and morphology of particulates are strongly determined by temperature and sintering atmosphere composition. A comparatively larger amount of bigger inclusions, enclosed inside inter-particle necks, is observed in the range 900-1000°C for samples heated in nitrogen and vacuum. The SEM+EDX analysis (Fig.7) shows that these oxide inclusions are rich in Cr and Mn and the respective concentration ratio is 2:1. This ratio was kept constant throughout all the experimental series.

As soon as the sintering temperature of 1120°C is reached, all the free powder particles surfaces are clean with no traces of oxide layer, see Fig.8. Especially for the high sintering temperature (1200°C) this is evident. Graphite flakes were not observed in samples heated at 1120°C or higher, indicating the complete dissolution of carbon into the matrix. For all the sintered specimens the main failure mechanism was a mixture of inter-particle and trans-particle dimple ductile fracture. However, for the samples processed in N₂/H₂ and N₂ there were also some sites with trans-particle cleavage fracture due to the bainitic/martensitic microstructure of sintered specimens. For the vacuum processed samples, such cleavage facets appeared only after sintering for 30 min at the respective sintering temperature due to the bainitic microstructure, but they were fewer in number. The reason for this was the different cooling rates applied (~3°C·s⁻¹ for N₂/H₂ and N₂, ~1.7°C·s⁻¹ for vacuum).

For the specimens sampled at the beginning of the isothermal sinter holding, unreduced surface oxide was still encountered inside the inter-particle connections. Inclusions can be found inside dimples as small spherical ones with size up to 0.5 µm, but also now they tend to start to form larger agglomerates (up to few micrometers in size).
Additionally, it is possible to find irregularly shaped inclusions that have the tendency to form larger agglomerates of a few micrometers in size inside inter-particle necks as well.

Fig. 7. SEM+EDX analysis of particulate features observed on the fracture surface of interrupted sintered specimens at 700 and 900°C, heated in N\(_2\)/H\(_2\) blend.

After increasing the dwell time to 30 min, the size and amount of inclusions inside the inter-particle necks seems to be reduced but agglomerates are still observed. The samples sintered in N\(_2\) show a higher amount of inclusions compared to the other two
materials. It is important though to keep in mind that the appearance of the inclusions depends on the local conditions present during the sintering process. Additionally, for these sintering conditions (and for higher temperatures) the presence of MnS was registered, but not in the inter-particle necks, thus implying that it would not play any significant role in the properties of the sample. With a further increase of the sintering temperature to 1200°C, inclusions inside the inter-particle necks are still encountered along with rarely observed larger agglomerates, their number and size is further reduced, but their morphology and size depends on the sintering atmosphere. SEM+EDX analysis of particulate inclusions inside inter-particle necks (Fig.9) surprisingly shows that the Cr:Mn ratio remained at 2:1.

Fig.9. SEM+EDX analysis of particulate features observed on the fracture surface of specimens sintered at 1120 and 1200°C in N₂ atmosphere.

A more efficient reduction of the surface iron oxide layer during the heating stage of the sintering process in hydrogen-containing atmosphere was confirmed by metallographic studies of interrupted sintered specimens. This gave information about the microstructure development which can be linked to the surface reactions taking place. The first appearance of bainite close to the edges was observed for samples heated at 800°C in N₂/H₂ blend; indicating earlier reduction of the iron oxide layer during heating in this atmosphere. The metallographic cross-sections from samples heated in all three conditions at 900°C and after sintering for 30 min at 1200°C are presented in Fig.10. From the optical micrographs of materials heated up to 900°C it can be verified that there is better carbon dissolution in the samples processed in a hydrogen-containing atmosphere and in vacuum. In the first case bainite occurs, and in the latter pearlite is found. A pre-requisite for the starting of the dissolution of the carbon is that the surface oxide layer is reduced to a significant extent. Furthermore, the surface oxide layer is also better reduced in areas close to the surface of the samples since the purity of the local microclimate there is much better due to continuous sintering atmosphere interchange with flowing atmosphere in the case of
flowing gases, or the better ‘sucking out’ of reaction products during vacuum sintering. It can be seen that the reduction in vacuum is more efficient compared with the other conditions; for the gas-containing atmospheres, the extent of the bainite at the surface signifies the extent of the reduction occurring. Thus, it is obvious that the conditions for the N₂/H₂ atmosphere are far more reducing. Concerning the micrographs of materials sintered at elevated temperatures, these just show the final microstructure, consisting of a bainite-martensite mixture in the case of N₂/H₂ and N₂ sintering and bainite in the case of vacuum sintering, as seen in Fig.11. These observations are consistent with the appearance of the fracture surface for the studied materials.

![Fig.10. Microstructures of Cr-Mo material+0.5% C after heating to 900°C showing the presence of bainite in the case of the gas containing atmospheres and pearlite in the case of vacuum. From the upper row of micrographs the extent of surface oxide reduction is evidenced by the microstructure development following the carbon dissolution.](image)

![Fig.11. Microstructure of Cr-Mo material+0.5% C after sintering at 1200°C for 30 minutes.](image)

**DISCUSSION**

Previous studies [10-16] showed for ferrous powder pre-alloyed with chromium that the surface of the powder is covered by a thin (~6-7 nm) Fe-oxide layer along with randomly distributed particulate features that are rich in strong oxide forming elements such as Cr, Mn and Si [10-16]. It is well established that efficient development of strong sinter necks requires the previous removal of the surface oxide layer. Therefore, in this context the oxide reduction mechanisms present are of major importance. From the fractographic investigations the positive effect of the presence of H₂ on the reduction of surface Fe-oxide (in the temperature range 350°C-530°C [8,10,18,19]) is registered with a
better developed point and line inter-particle connections for the low temperature (700°C-800°C) sampled specimens. For the N₂ and vacuum heated samples the absence of a reducing agent, effective at lower temperatures, is proved by the lack of inter-particle connections. Direct oxide dissociation is not so pronounced at low temperatures, even for iron oxide, and the reducing activity of carbon is still very low. At 800°C, the added graphite becomes more active and first iron oxide in contact with graphite is reduced by direct carbothermal reduction (eq. 3) and further by indirect reduction mechanism (eq. 4) [8-10,17-26]. Another possible process is the reaction of graphite with oxygen produced from oxide dissociation at high temperatures (eq. 1). Considerable oxide reduction in the temperature range of 800-900°C is confirmed by the pronounced formation of inter-particle necks at around 900°C. This development is much more intensive in vacuum sintering due to better ‘microclimate’ inside the compact than during processing in the gaseous atmospheres. The dynamic vacuum during heating ‘sucks out’ gases produced by surface oxide dissociation and reduction (oxygen, carbon monoxide and carbon dioxide), that shifts both CO/CO₂ ratio and oxygen partial pressure to reducing conditions. Better developed inter-particle necks close to the specimen edges and much more intensive inter-particle necks development for vacuum-processed samples in comparison with those run in pure nitrogen atmosphere, where reduction mechanisms are the same as in vacuum, confirm the above mentioned assumption. Another important process observed for this temperature is the enclosure of the surface oxide layer between the developed inter-particle connections. At this stage the particulate features observed on the original powder surface are starting to grow in size at the expense of the thermodynamically less stable Fe-oxide layer by consuming released oxygen (in any form). Intensive mass-transfer of strong oxide forming elements (Cr and Mn) with increasing temperature, from inside the powder to its surface, is an important contributing factor to the growth of these particulates [13]. However, a net transfer of surface bound oxygen connected with Fe-oxides to a more stable particulate is also possible. The balance between these two kinds of scenarios is supposed to depend decisively on the heating rate. As soon as 1000°C is reached it seems that the inter-particle connections are well developed in terms of both strength and contact area. The vacuum heated sample shows better developed inter-particle connections and this can be reflected in the “depth” of the dimples observed in the ductile fracture compared to the other atmospheres. At this stage local microclimate conditions provide reduction of surface oxides on the free powder surface for all atmospheres and the enclosure of the surface oxide residues inside the developed inter-particle connections is completed [8,17-19,22-24]. The parts of the surface oxide enclosed inside the inter-particle connections will become the inclusions observed later inside the dimples of sinter necks.

Free powder particle surfaces from the samples heated up to 1120°C are clean with no sign of surface oxide layer, indicating that complete reduction has occurred even in internal pores that were partially open to the surface. Even particulate features on the free powder surface, composed of thermodynamically-stable Cr-Mn oxides, are reduced in all atmospheres by the carbothermal reduction. The appearance of cleavage facets at this point is connected with the developed microstructure, consisting of a mixture of bainite and martensite with the portion of martensite increasing with increasing time and temperature. From point of view of the neck area, they look the same at the beginning of sintering at 1120°C as after sintering, but shallow dimples indicate weaker connections before sinter-holding. With an increase in time no major differences were observed apart from the better developed inter-particle connections. The inclusions encountered now inside the sinter necks could vary in shape and size depending on the conditions present in their vicinity. In more detail these features can acquire a more spherical shape but somewhat smaller size
(<1µm), these type of inclusions are mainly observed inside small dimples. The same inclusions can also coalesce and form larger agglomerates of a few micrometers in size. Finally, the inclusions can be encountered in a more irregular shape but mainly in larger voids after sintering, which implies that their evolution is governed by the local conditions.

One surprising fact is the relative content of strong oxide forming elements found for the particulate features throughout the heating stage as well as after sintering. The Cr:Mn ratio is always 2:1 which implies that these oxides are probably MnCr₂O₄ spinel oxides, the presence of which was shown for Cr-Mn-alloyed powders [27]. At low temperatures, presence of iron in the particulate inclusions in the form of FeCr₂O₄ spinel is assumed [10,27]. The iron part of this compound is reduced at above 900°C. In this context, it should be remembered that the total Cr and Mn levels are underestimated when performing EDX point analysis on an oxide inclusion; there is a strong contribution from the iron matrix under the particulate even at adjusted conditions for fine particulate analysis (lowest possible acceleration voltage and current). However, the stoichiometric ratio (Cr/Mn) was the same for all analyses throughout the experimental series. This underlines the thermodynamic stability of the specific spinel oxide at applied sintering conditions. The description of the system Cr-Mn-O in terms of thermodynamics for the spinel oxide was only recently presented [10,27-29] and revealed that the thermodynamic stability of the spinel MnCr₂O₄ lies between those of Cr₂O₃ and MnO, see Fig.12.

Fig.12. Ellingham-Richardson diagram showing the thermodynamic stability of oxides of interest (HSC Chemistry 6.1).

It has to be mentioned though that the amount of agglomerates and inclusions was considerably reduced after the sintering at 1200°C, which in turn implies that at this temperature the reduction of the Mn-Cr-spinel oxide takes place readily for the sintering conditions applied. Additionally, at these temperatures one has to take into consideration the possible reduction of internal oxides [9,18,24]. These phenomena are reflected in the low oxygen content after sintering, see Fig.1. Clearly, provided that proper sintering conditions are applied, reduction of a major amount of surface oxides of all kinds is realized. Finally, it must be mentioned that among the three different atmospheres employed when sintering for 30 min at 1200°C, the samples processed in N₂/H₂ showed the lowest amount of oxide inclusions of any kind in comparison with the samples processed in other atmospheres. This fact is also reflected by the lowest oxygen content. The highest oxygen content after high-temperature sintering was observed for vacuum-sintered specimen, which is also evident from the amount of inclusions on the fracture surface. This at first unexpected observation is connected with the higher amount of surface oxide being enclosed during heating in vacuum due to rapid inter-particle connections development already at around 900°C. The difference in location of oxides being accessible for e.g.
indirect carbothermal reduction is then a possible reason for the better reduction for high temperature sintering in nitrogen atmosphere in comparison with vacuum. This comparison further emphasizes the positive effect of hydrogen at lower temperatures as an important means for enhancing the high temperature sintering performance alongside also with lower carbon-loss.

CONCLUSIONS

From the fractographic investigations of Cr-Mo-alloyed material sintered at different temperatures between 700 and 1200°C, for various times, there is a clear positive effect of the hydrogen presence on early Fe oxide reduction with respect to the developed inter-particle connections up to 800°C. Better microclimate inside the compact along with the increase of the reducing activity of carbon with increasing temperature results in earlier and better developed inter-particle connections during heating in the case of vacuum heated samples, which in turn leads to the enclosure of surface oxide inside the necks already at 900°C. This early enclosure of surface oxide residues is reflected in the high temperature vacuum-sintered specimens that showed a larger amount of oxide inclusions of any kind, and thus also lower impact energy values.

The relative content of strong oxide forming elements in the particulate oxide stays the same with increasing temperature, showing a Cr:Mn ratio equal to 2:1 even after sintering at 1200°C. This in turn implies that these oxide inclusions are Cr-Mn spinel oxides which have among the highest thermodynamic stability for the system. Their morphology and size however changes with temperature and after sintering they are mostly spherical and small (<1µm). Additionally, as soon as 1120°C is reached the coalescence and agglomeration of these inclusions is registered for all three conditions but with their partial reduction occurring with increasing time and temperature.

The obtained microstructures depended on the extent of the reduction of the surface oxide which is connected with the carbon dissolution. Graphite was encountered up to 1000°C, especially in the interior of the samples.

This study verifies that the presence of hydrogen as a reducing agent is important for the heating stage during sintering and that this therefore assists in the reduction processes and the development of inter-particle connections. The study also underlines the fact that the local microclimate conditions play a vital role in the final characteristics of sinter necks.

Acknowledgements

This work has been carried out in the Department of Materials and Manufacturing Technology at Chalmers University of Technology with the support of Höganäs AB, Sweden and KK foundation as funding organizations within the framework of the CAPE (Centre for Advanced Production Engineering) industrial PhD school. The Master Thesis student E. B. Quejido is also acknowledged for her contribution in the SEM and EDX analysis of a number of specimens.

REFERENCES