INFLUENCE OF CARBON CONTENT ON OXIDES’ REDUCTION DURING SINTERING OF Cr-Mo-C PREALLOYED STEEL

M. Hrubovčáková, E. Dudrová, J. Harvanová

Abstract
This contribution deals with the effect of carbon content (0.5, 0.6 and 0.8 wt.%) on the reduction processes during the sintering of chromium pre-alloyed steel, Astaloy CrM, using continuous monitoring of CO, CO$_2$ and H$_2$O content in the sintering atmosphere. Specimens with a green density of 6.9 g·cm$^{-3}$ were isothermally sintered at 1120 and 1200°C for 30 min in a N$_2$+10% H$_2$ atmosphere. The results showed that iron oxides are removed by hydrogen reduction during the heating stage at ~470°C, direct carbothermal reduction of oxides starts at ~900°C. The carbon is an effective reducing agent and has a significant effect on the final microstructure composition of sintered compacts. Continuous monitoring of atmosphere composition showed that higher carbon content shifts the carbothermal reduction of stable chromium oxides to a lower temperature. It does not affect the final oxygen content and has a negative effect on fracture strength of sintered material due to the presence of a carbide phase at grain boundaries.

Keywords: chromium alloyed steel, sintering, continuous monitoring of sintering atmosphere, carbon content, oxidation/reduction processes

INTRODUCTION
The high price of Ni, Cu, and Mo, the traditionally used alloying elements for high-strength steels, is forcing producers to look for a new and cheaper alloying mode. Chromium, as an alloying element, has higher performance/cost ratio and it is therefore of great interest to the future of sintered structural steels. Modern powder grades pre-alloyed with chromium, Astaloy CrM and Astaloy CrL, produced by Höganas AB, Sweden, are attractive because they can replace the Fe-Ni-Cu-Mo alloyed sintered steels for medium and high strength structural parts, particularly used in the automotive industry [1].

The main obstacles of PM processing of Cr-alloyed steels is the high affinity of chromium for oxygen that results in higher sensitivity to oxidation during sintering and also a more difficult reduction of stable surface oxides present in the starting powder. Surface chemical analyses using XPS and AES techniques showed that more than 90% of the surface of powder particles is covered by an easily reducible iron oxide layer (with a thickness of about 6 nm) with the presence of spherical particulates, about 20-200 nm in size, formed by complex Cr-Mn-Si oxides [1-5]. Besides these surface oxides, there is a great amount of internal oxides [6]. Reduction of surface oxides is necessary to achieve strong particle necks and thus high mechanical properties of sintered components [7]. The reduction of oxides is determined by their thermodynamic stability. The sintering atmosphere, and carbon added as a graphite to the starting powder, play a crucial role in the
reduction [6, 8-11]. Careful control of the purity and composition of the protective atmosphere is required for the sintering of steels alloyed with elements having high affinity for oxygen [11-14]. For proper control of the sintering atmosphere composition it is necessary to understand the interactions between the sintered compact and the active components of the atmosphere. In accordance with the principles of thermodynamics, the reduction of a metallic oxide in an inert atmosphere occurs when the oxygen partial pressure of the atmosphere is lower than the dissociation pressure of the oxide \( p(O_2)_{\text{atm}} < p(O_2)_{\text{oxide}} \). If the sintering is carried out in a hydrogen-containing atmosphere, without a carbon presence, the partial pressure of oxygen is related to the ratio of partial pressure \( p(H_2)/p(H_2O) \). During the sintering of carbon-containing material, the oxides’ reduction occurs through carbothermal reactions. For a porous material, the chemical reactions taking place on the external surface of the powder compact may be quite different from those in its inner part, especially after pressing to relatively high green densities. According to Mitchell [10] this fact results in the formation of a specific “micro climate” inside the compact. In such micro-volumes an equilibrium state is established between local carbon, chromium, oxygen and water vapour contents. Self-generation of \( CO/CO_2 \) gas mixture by the added graphite controls the reduction of oxides inside the compacts, rather than the ratio \( H_2/H_2O \) of the sintering atmosphere [6, 8-10].

The objective of this contribution is studying the role of carbon content on oxide reduction processes in microstructure of the Fe-3%Cr-0.5%Mo+0.5-0.8%C steel sintered at 1120 and 1200ºC in \( N_2+10%H_2 \) atmosphere. To obtain information on oxidation-reduction processes, the sintering atmosphere composition (CO, CO\(_2\) and H\(_2\)O content) was continuously monitored during the entire sintering cycle.

**EXPERIMENTAL PROCEDURE**

The starting powder used was commercial water atomized Cr pre-alloyed powder - Astaloy CrM of nominal composition Fe-3%Cr-0.5%Mo (Höganäs AB, Sweden) and commercial graphite Kropfmühl UF4 added in the amount of 0.5, 0.6 and 0.8 wt.%. Cylindrical specimens Ø10x12 mm\(^3\) were compacted to the density 6.9 g·cm\(^{-3}\) using only die-wall lubrication. The specimens were sintered at 1120 and 1200ºC for 30 minutes; the heating rate was kept at 10ºC/min. The specimens were cooled to room temperature at 50ºC/min. The gas mixture \( N_2+10%H_2 \) of high purity (5.0) was used as a sintering atmosphere. Before entering the furnace, the sintering atmosphere was dried by liquid nitrogen. Therefore the dew point of the inlet atmosphere (monitored by Super-Dew SHAW) was ~ -70ºC. The flow-rate of the inlet atmosphere used in the experiments was 2 l/min. Sintering was carried out in a laboratory tube furnace ANETA 1. The specimens (always 6 pieces) were kept in a special semi-closed low-carbon steel container where, it can be assumed, that the atmosphere composition (in the container) can simulate the composition of the “micro climate” inside the compacts. The dew point of the atmosphere in the container with specimens was monitored using a Michell Cermet II sensor. The atmosphere was continually sampled directly from the container near the specimen surfaces. The CO and CO\(_2\) contents in the sintering atmosphere were recorded by non-disperse infrared analyzers on the basis of Gas Card II Plus sensor. All sensors were connected to a PC and continuous recording of the CO, CO\(_2\), and H\(_2\)O content was performed using special software. The microstructural analyses were performed using light and scanning electron microscopy (Olympus GX 71 and Jeol JSM 7000F equipped with INCA EDX analyzer), respectively. Analyses of oxygen and carbon contents in sintered specimens were performed using a LECO TC 36 instrument. The fracture strength \( R_{FR} \)
values were obtained using the non-standard “button” tensile test. Button-shaped samples were machined from sintered cylindrical specimens [15].

RESULTS AND DISCUSSION

Because carbon plays a crucial role in the reduction of oxides by carbothermal reactions, this work deals with the study of the influence of the graphite addition in the amount of 0.5, 0.6 and 0.8% on oxide reduction processes and microstructure of sintered Astaloy CrM steel. In order to distinguish the volatile and dissociating surface compounds from the reducible ones, the Astaloy CrM specimens without the addition of carbon were also investigated. The records of the atmosphere composition monitored during the sintering at 1200°C of the Astaloy CrM without any carbon and with 0.5, 0.6 and 0.8% of carbon addition are presented in Fig.1a-d. The reduction processes take place in two temperature intervals [15-19]. During the heating, the surface layer of iron oxides is reduced by hydrogen from the sintering atmosphere. Visible on the dew-point (DP) profile is the reduction of Fe oxides, starting at about 300°C and reaching maximum at ~470°C.

![Fig.1](image_url)

Fig.1. Records of atmosphere composition monitoring during the sintering of Astaloy CrM+0-0.8 wt.%C at 1200°C for 30 min in 10%H₂+N₂ atmosphere.

Maximum on CO₂ profile at about 320°C during the sintering of samples with added carbon, and also without any carbon, is connected with the decomposition of both surface hydrocarbons and lubricant used for die-wall lubrication. Carbon as a reducing agent becomes more effective at higher temperatures. Carbothermal reduction of oxides starts after the Boudouard equilibrium at ~720°C. A small maximum, visible at 820°C on the CO profile, is connected to carbothermal reduction of surface iron oxides by plain graphite in the Fe/C
contacts. Iron oxides, present as FeO at this temperature, are the result of a partial reduction of the former iron oxide layer (Fe₂O₃) covering the powder particle surface. The concentration of CO in the sampled atmosphere rapidly increases at about 900°C. The CO peak with a maximum at 1120°C is connected with carbothermal reduction of thermodynamically stable surface Cr-based oxides and a reduction of spinel iron-containing oxides from internal pores. The maximum at 1200°C is connected with a reduction of stable surface oxides and internal oxides. In terms of oxide reduction, the carbon content in sintered material may play an important role. From the kinetic point of view, higher carbon activity should have a positive effect on reduction processes. The carbon content of 0.6 and 0.8 wt.% shifts carbothermal reduction to lower temperatures when compared with 0.5 wt.% of carbon. Carbothermal reduction of thermodynamically stable Cr-based oxides and iron containing oxides from internal pores during the sintering of Astaloy CrM+0.6%C reached a maximum at 1100°C. In the case of Astaloy CrM+0.8%C the peak for reduction of stable surface Cr oxides is at 1074°C. On the CO profile for carbon-free specimens, small peaks at about 300-500°C are linked with absorbed gases, graphite oxidation, as well as die-wall lubricant decomposition. A maximum at 1200°C indicates that the small amount of carbon present in atomized powder (~0.019%) may have some reduction effect. A similar effect was observed by Danniner et al. [16]. Chemical analysis of oxygen and carbon contents in sintered specimens with different graphite additions, Table 1, showed the relatively small effect of the starting carbon content on reduction processes, which is in good agreement with the results reported by Danninger et al. [17].

<table>
<thead>
<tr>
<th>graphite addition [wt.%]</th>
<th>sintering temperature [°C]</th>
<th>C content [wt.%]</th>
<th>O₂ content [wt.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1120</td>
<td>0.42</td>
<td>0.097</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>0.34</td>
<td>0.027</td>
</tr>
<tr>
<td>0.6</td>
<td>1120</td>
<td>0.51</td>
<td>0.110</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>0.42</td>
<td>0.030</td>
</tr>
<tr>
<td>0.8</td>
<td>1120</td>
<td>0.68</td>
<td>0.110</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>0.56</td>
<td>0.031</td>
</tr>
</tbody>
</table>

The positive effect of higher sintering temperature on the reduction of oxides is well known from previous studies [6, 8-9, 16-19]. During the sintering of Astaloy CrM+0.5%C at 1120°C the oxygen content in specimens decreases by ~50%, from 0.197% to 0.097%, and by ~90% in the case of sintering at 1200°C, from 0.197% to 0.027%. It should be noted that internal oxides were removed during sintering at 1200°C.

Carbothermal reduction processes result in decreasing carbon content. The higher loss of oxygen content associated with more effective oxide reduction results in a higher loss of carbon.

Microstructural observations of sintered specimens are in good agreement with the results of chemical analyses. Small oxide inclusions are observed in non-etched microstructures of all specimens sintered at 1120°C, the oxides are located mainly at prior particle surfaces, some of them are inside the grains. In the case of specimens sintered at 1200°C, there are only some traces of oxides. The etched microstructure of specimens CrM+0.5-0.6%C consists mainly of bainite and martensite, Fig.2a. Increasing carbon content increases the amount of martensite; the content of 0.8% leads to the formation of the network of carbides at grain boundaries, Fig.2b.
The use of the non-standard "button test" allows us to obtain information about the quality of material in terms of the of the rupture strength values, $R_{FR}$, that are in the range of 240-945 MPa, Fig.3. It is seen that increasing carbon content leads to decreasing fracture strength.

![Fig.2. Etched microstructure of: a) Astaloy CrM+0.5%C, b) Astaloy CrM+0.8%C; sintering at 1200°C.](image)

![Fig.3. Rupture strength of sintered material.](image)

![Fig.4. Theoretical phase diagram of Astaloy CrM-C steel.](image)
It is well known that carbon content has a significant influence on both microstructure and mechanical properties. According to theoretical phase diagram, Fig.4, the eutectoid point for Astaloy CrM-C material corresponds to 0.35 wt.% C at 786°C.

This means that at a carbon content above 0.35 wt.% C the formation of cementite film at grain boundaries can be assumed, particularly at slow cooling rates. Using a cooling rate of 50°C/min, the carbide phase precipitation was clearly identified in specimens with an addition of 0.8% C (at combined C of 0.56 and 0.68%). It is obvious that the formation of cementite film at grain boundaries also occurred at an addition of 0.6 wt.% C (0.42 and 0.51% C combined), as confirmed by the decrease in fracture strength of sintered specimens compared to the values for the 0.5% C addition (0.38 and 0.42% C combined), Fig.3.

The fracture surface analysis of all the specimens sintered at 1120°C indicated that free surfaces of former particles are clean, without the presence of oxides; the oxides’ inclusions are present occasionally in the fractured necks.

Inclusions inside the sintered necks are small spherical particulates with a size up to 0.5 µm or they create bigger agglomerates only a few microns in size. The EDX microanalysis showed that the ratio Cr:Mn is near to 2, which indicates that they are thermodynamically stable spinel oxides corresponding to the MnCr$_2$O$_4$ type. In the case of specimens sintered at 1200°C, the oxide inclusions were very rarely found on the fracture surfaces. The oxides entrapped in specimens sintered at 1200°C also have a Cr:Mn ratio close to 2 with the presence of a small amount of Si. EDX analysis of residual oxides confirmed the transformation from less stable Fe-oxides to the more stable spinel-type oxides according to the algorithm thermodynamically predicted by Hryha et al [3, 20]. The fracture surfaces of the specimens sintered at 1200°C with carbon contents of 0.5 and 0.6 wt.% C consist of fine and shallow ductile dimples, corresponding to failure along the surface of bainite packets. Some small amount of cleavage fracture facets also occurred, Fig.5a. In the case of specimens with a carbon content of 0.8 wt.% C the dominant was intergranular fracture corresponding to the presence of a carbide phase at grain boundaries, Fig.5b.
CONCLUSION

- The continuous monitoring of atmosphere composition during sintering of Astaloy CrM + (0.5-0.8)% C showed that higher carbon content shifted the carbothermal reduction to lower temperatures. Carbon content of 0.8% shifted the carbothermal reduction of thermodynamically stable surface Cr-based oxide 50ºC lower when compared to the carbon content 0.5%.
- Increasing the sintering temperature from 1120 to 1200ºC is beneficial for oxide reduction processes, which results in lower oxygen content.
- The results confirmed that a different carbon content has a small effect on reduction processes, corresponding to the result previously reported by Danninger [16].
- Increasing carbon content in the Astaloy CrM+C system, to the value when there is formation of carbide phase at the grain boundaries, is detrimental to mechanical properties. When the cooling rate 50ºC min was used, the negative effect was reflected at the graphite addition of 0.6%, corresponding to combined carbon content of 0.42-0.51%.
- It is well known that carbon content has a significant effect on microstructure. To achieve the desired performance, the carbon content in Astaloy CrM has to be limited. The optimal carbon content for Astaloy CrM is 0.4-0.45 wt.% [21]. Higher C content has a negative impact on mechanical properties due to the presence of cementite networks along grain boundaries, which results in a decrease in mechanical properties, rather for fatigue strain than monotonic strain.
- The presence of carbide networks along grain boundaries in specimens with 0.8 wt.% carbon content resulted in an embrittlement of the material, with its negative effect on mechanical properties.

Acknowledgements

The authors are thankful for financial support of the research by the Grant VEGA 2/0103/09 of the Slovak Grant Agency.

REFERENCES


