CHANGES IN OXIDE CHEMISTRY DURING CONSOLIDATION OF Cr/Mn WATER ATOMIZED STEEL POWDER

E. Hryha, L. Nyborg

Abstract
Modern water atomization methods allow industrial production of high-purity water atomized powder grades prealloyed with chromium and manganese. Surface coverage by oxide islands, formed by a variety of mixed oxides of chromium and manganese with higher thermodynamic stability, is below 10% which assumes good sinterability of such PM grades. However, there is still a risk of formation of oxides products on the powder surface during critical stages of powder consolidation, especially during the heating stage. Therefore present work is focused on the effect of alloying elements content on the possible scenarios of oxides’ reduction/formation/transformation in Fe-Cr-Mn-C powder systems. Accurate analysis of specimens, sampled during different stages of the sintering process, by advanced analysis techniques (HR SEM+EDX) was combined with thermodynamic modelling of oxides’ stability. Obtained results indicate that oxide transformation process is governed by thermodynamic stability of present oxide phases in the sequence $\text{Fe}_2\text{O}_3 \rightarrow \text{FeO} \rightarrow \text{Fe}_2\text{MnO}_4 \rightarrow \text{Cr}_2\text{FeO}_4 \rightarrow \text{Cr}_2\text{O}_3 \rightarrow \text{MnCr}_2\text{O}_4 \rightarrow \text{MnO}/\text{MnSiO}_x \rightarrow \text{SiO}_2$.

Keywords: alloyed sintered steels, surface analysis, surface oxide, sintering atmosphere, oxide reduction

INTRODUCTION
Increasing demands on structural parts’ performance, together with high price of the typically used alloying elements like Ni, Mo and Cu decrease competitiveness of high-performance Ni-Mo alloyed PM parts compared to products of conventional metallurgy. Therefore utilization of more effective, cheaper and environmentally friendly alloying elements like Cr, Mn and Si, commonly used in cast and wrought steels, is one of the most promising ways to decrease the price and at the same time increase performance of the structural PM steels.

However high activity to oxygen creates obstacles in utilization of Cr, Mn and Si in PM steels, due to the difficulties in powder manufacturing, risk of oxidation during handling and further consolidation. Recent improvement in production of water atomized steel powders prealloyed with Cr and Mn shows the possibility to obtain industrial high-quality prealloyed powder grades that allow reaching high mechanical properties in single press-single sintering route [1]. It is also important to note that, in terms of surface composition, some modern Cr and Cr-Mn alloyed powders are comparable with industrial Mo-alloyed grades [2-4]. Therefore remaining issue is to define sintering conditions to maintain, as a minimum, high powder cleanness during powder consolidation. This means that temperature profile and processing atmosphere conditions have to be adjusted in such a
way as to avoid powder oxidation and/or oxides’ transformation during the sintering process. Credible tailoring of the processing conditions for successful sintering of Cr-Mn alloyed PM steels relies on the thorough knowledge of oxide phases existing in the systems under view. The available thermodynamic data concerning stability of these phases under industrially feasible conditions and kinetics of the oxides transformation are rather scarce. Therefore evaluation of the stability of oxide phases present at different sintering stages and their transformation during sintering of Cr/Mn prealloyed PM steels was the main goal of this work.

EXPERIMENTAL

Water-atomized powder grades A and B were used as test materials. Powder A was prealloyed with 0.8 wt.% Cr and 0.4 wt.% Mn and powder B was prealloyed with 1.8 wt.% of Cr and also contained about 0.1 wt.% of Mn. Oxygen content of the used powders was in the range 0.10 to 0.14 wt.%. Powders were admixed with 0.5 wt.% of natural graphite (UF4 from Kropfmühl) and 0.6 wt.% of Kenolube as a lubricant. Modified Charpy impact test bars (5×10×55 mm³) were uniaxially compacted at 600 MPa to a green density of ~7 g·cm⁻³. Specimens were sintered in nitrogen/hydrogen blend (10% of H₂) in a laboratory tube furnace Entech with a flow rate around 12 l·min⁻¹ (~0.05 m·s⁻¹). Specimens for fractographic evaluation were sampled at different temperatures during heating: at 700, 800, 900, 1000, 1120 and 1200°C, as well as after sintering for 1 to 30 min at 1120 and 1200°C. Oxides’ amounts and compositions were evaluated on the fresh fracture surfaces by means of HR SEM+EDX (LEO Gemini 1550 equipped with INCA Energy analyzer).

RESULTS AND DISCUSSION

Surface analysis of the surface of powder A, typical appearance of which is presented in Fig.1, reveal presence of two types of surface oxides: homogeneous thin iron oxide layer, covering all powder surface, and spherical particulate oxides that size up to 200 nm. As in the case of Cr-alloyed powders [2, 4] and Mn-alloyed powders [3], iron oxide layer has a thickness of about 6 nm [5] and is formed by Fe₂O₃. Previous results [2-5] also indicate that particulate oxides are formed by a variety of simple oxides [Fe,Mn,Cr]ₓOᵧ as well as mixed oxides of spinel type like FeCr₂O₄, MnFe₂O₄, MnCr₂O₄ and [Fe,Cr,Mn]SiO₃. The fraction of the oxides of different type (simple or spinel) is dependent on powder composition and manufacturing. The HR SEM+EDX analysis of particulates on the surface of powder A also shows that they are complex mixed oxides with high fraction of Mn-Cr spinel oxide, see Fig.2. Hence most of the surface is covered by homogeneous iron oxide that is easy to reduce at typically applied sintering conditions. Calculations also show [3] that total coverage by particulate oxides is below 10% and about 40-50% of the total oxygen content is bonded in the surface iron oxide layer. Therefore such surface oxide characteristics (composition, amount and distribution) imply good sinterability. However, during the heating stage re-oxidation can occur [6-8], leading to the formation of more thermodynamically stable surface oxide if sintering conditions are not adjusted properly.
Fig. 1. SE images of particles of powder A showing morphology and distribution of particulate features on the powder surface.

Fig. 2. HR SEM+EDX analysis of particulate features on the surface of powder A.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>O</th>
<th>Si</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrum 1</td>
<td>30.2</td>
<td>0.5</td>
<td>8.2</td>
<td>4.7</td>
<td>56.4</td>
<td>100.0</td>
</tr>
<tr>
<td>Spectrum 2</td>
<td>38.0</td>
<td></td>
<td>12.1</td>
<td>7.1</td>
<td>42.8</td>
<td>100.0</td>
</tr>
<tr>
<td>Spectrum 3</td>
<td>5.7</td>
<td>1.5</td>
<td></td>
<td></td>
<td>92.8</td>
<td>100.0</td>
</tr>
<tr>
<td>Spectrum 4</td>
<td>0.0</td>
<td>1.5</td>
<td></td>
<td></td>
<td>98.5</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Onset of the inter-particle necks’ development is directly connected to the reduction of the surface iron oxide layer. Therefore careful tracking of the inter-particle necks’ development indicates efficiency of the surface oxides’ reduction. In the case of hydrogen containing atmosphere, applied in our experiments, reduction of the surface iron oxide layer takes place at lower temperatures in the range 350-550°C [3, 8-10]. Therefore first line branched inter-particle connections are observed even at 700°C in both studied powders, see Fig. 3, independently of alloying elements’ content. This fact confirms the same nature of the oxide layer on the surface of both powders. Careful analysis of the fracture surface of specimens sampled at higher temperatures clearly shows critical importance of efficient surface iron oxide layer reduction at the lowest possible temperature. The reason is that if the iron oxide layer is not fully reduced at low temperatures, intensive inter-particle necks development after about 900°C will lead to enclosure of residue of this iron oxide layer inside inter-particle necks. Indisputably presence of carbon leads to the active carbothermal reduction of iron oxide layer after Boudouard equilibrium (~720°C), however this reduction reaches its maximum at higher temperatures (>1000°C). Therefore, if the kinetics of inter-particle necks’ growth is higher
than the kinetics of surface oxide layer reduction, significant enclosure of residue of iron surface oxide can happen [11]. Inter-particle ductile fracture, initiated by point inclusions and cementitic lamellas is the main failure micro-mechanism for specimens sampled at the beginning of the sinter-holding at 1120°C. During heating up to this temperature almost all of the surface oxides on the free powder surface (pore surface), including surface oxide layer, as well as particulate features on the powder surface are reduced by carbon. Enclosed oxides inside inter-particle necks also undergo considerable changes (amount, size, morphology, chemistry, etc.) in this temperature region, see Fig.3.

![Fracture surface of A+0.5%C and B+0.5%C compacts](image)

Fig.3. Fracture surface of A+0.5%C and B+0.5%C compacts, heated to 700, 900 and 1120°C and sintered at 1200°C for 30 min.

Experiments indicate that, even after sintering for 30 min at 1120°C, specimens reveal considerable decrease in the amount of observed inclusions and a clean fracture surface. However, the importance of good sintering process control for obtaining almost oxide-free sintered steels after low-temperature sintering has to be emphasized. Undoubtedly high-temperature sintering in high-purity reducing atmospheres allows reducing of almost all of the oxide inclusions inside the inter-particle necks, see Fig.3. Only rarely some inclusions can be found inside dimples of ductile fracture. Inclusions after
sintering at high temperature are spherical solitary particles with a size below 1 µm in the case of both studied sintered steels. Nevertheless, due to the low kinetics of reduction of thermodynamically stable oxide inclusions inside inter-particle necks, it is important to minimize surface oxide enclosure during the heating stage by early reduction of iron oxide layer.

Presented in Fig.4 micrographs of inter-particle connections at high resolution allow us to trace changes in morphology and size of oxide inclusions. The, enclosed at low temperatures, residue of iron oxide layer acts as a source of oxygen inside inter-particle necks. Increasing the temperature leads to an increase in activity of carbothermal reduction. At the same time intensity of mass-transfer of the elements with high oxygen activity (like Mn, Cr and Si) on the powder surface increases, which leads to transformation of oxide inclusions. With increasing temperature to ~900°C enclosed residues of iron oxide shrink in size, reaching now up to 0.5 µm and take an irregular shape, see Fig.4. Additionally enclosed oxides become enriched in chromium and manganese, as is shown by SEM+EDX analysis, see Fig.5. It is important to emphasize that the same ratio between Cr and Mn of 2:1 (marked in red) was detected, as it was observed for the base powder, see Fig.2. Traces of MnS were registered for powder A as well.

Fig.4. Particulates evolution during heating and sintering of A+0.5%C material.
The most significant change in oxide inclusions’ amount is observed between 1000 and 1120°C, when inclusions take a spherical shape and decrease in size considerably. Another important observation during heating up to high temperatures (>1120°C) is
coalescence of fine inclusions inside inter-particle necks, forming larger agglomerates up to 1-2 µm in size.

Even during the heating up to 1200°C the highest stability was detected for Cr-Mn spinel oxides. After sintering at low temperature (1120°C), the amount of oxide inclusions decreased considerably and they became enriched in silicon. In specimen sintered at 1200°C oxide inclusions can be found very seldom, are characterized by spherical shape and size up to couple of hundred nano-meters. At this stage Cr-Mn spinel oxides are reduced and observed inclusions are Si-based oxides, see Fig.5. It is important to note that the same trend in oxide development concerning oxide inclusions’ morphology, as well as their chemical composition, was detected for the powder B as well, see Fig.6 [7, 11]. The difference is that, depending on alloying elements’ content, higher amount of Mn or Cr was detected in Si-based oxide, respectively, see Figs 5 and 6. This leads to the important conclusion that the ratio between Cr and Mn in the base powder (2:1 for powder A and 18:1 for powder B) does not influence considerably stability of oxide phases present at low level of alloying elements’ content and applied processing conditions.

As it was mentioned above, considerable decrease in inclusions content was observed when sintering temperature (1120°C) was reached. Most of the observed inclusions have spherical shape and size up to 200 nm. However, agglomeration of fine particulates into larger agglomerates up to 1-2 µm in size was clearly observed, extension of which is determined by the sintering conditions during heating – amount of enclosed oxides. Therefore the most extended agglomeration was detected in case of sintering in pure nitrogen atmosphere [7], due to the larger amount of enclosed iron oxide inside inter-particle necks. HR SEM observation of oxide agglomerates reveals their nano-crystalline structure [7, 11], consisting of very fine (<200 nm) regularly-shaped ‘crystalline phase’ enclosed into some ‘glassy phase’, see Fig.7.

Fig.7. SEM+EDX analysis of inclusion on the fracture surface of specimen B+0.5C, sintered in nitrogen atmosphere at 1120°C for 30 min.
With increasing sintering time and/or temperature, reduction of the agglomerates take place, especially close to the pores and specimen surface, due to improved transport of reduction products in such locations. Due to the partial reduction of the agglomerates, the ‘glassy phase’ is reduced and only a fine crystalline phase left, especially after high-temperature sintering [11].

Based on the experimental results it can be concluded that oxide transformation in Cr-Mn low-alloyed PM steels occurs in accordance with thermodynamic stability of oxides, see Fig.8.

The dominant component of the oxide layer on the powder surface, Fe$_2$O$_3$ [3], reduces to metallic iron and partially to FeO-oxide. Transformation to iron-based spinel oxides Fe$_2$MnO$_4$ and Cr$_2$FeO$_4$ is also taking place to some extent. Experiments show that iron part of spinel oxides is reduced with increasing temperatures (above ~1000°C). At the same time, due to mass-transfer of Mn and Cr during the heating stage, formation of more stable MnCr$_2$O$_4$ spinel oxide is taking place. One of the mechanisms of this spinel formation is the substitution of Fe by Mn and Cr in iron-based spinel oxides Fe$_2$MnO$_4$ and Cr$_2$FeO$_4$. Lack of experimental and thermodynamic data for MnCr$_2$O$_4$ resulted in disregarding this oxide during previous studies of oxidation/reduction behaviour of prealloyed PM steels. Stability of this compound was experimentally confirmed more than two decades ago [12], but thermodynamic assessment of this phase was performed only very recently [13, 14]. Addition of Mn to a Fe-Cr system increases the stability region of the spinel oxide due to higher stability of Mn-Cr spinel than corresponding Fe-Cr spinel. Based on data from [13] the stability of the spinel oxides lies between those of the monolithic oxide components, as is plotted in Fig.8. With increasing sintering temperature and time, reduction of Mn-Cr spinel oxide is taking place and seldom observed oxides are Si-based with presence of Cr or Mn in some sites. Therefore transformation of oxides during heating and sintering of Cr-Mn- low-alloyed powder material occurs in accordance with the thermodynamic stability of oxides: Fe$_2$O$_3$ → FeO → Fe$_2$MnO$_4$ → Cr$_2$FeO$_4$ → Cr$_2$O$_3$ → MnCr$_2$O$_4$ → MnO/MnSiO$_x$ → SiO$_2$.
CONCLUSIONS

Heating between 800 and 1000°C was identified as the most critical region during sintering of Cr-Mn PM steels due to the risk of surface oxide enclosure inside inter-particle necks and further transformation of iron-based oxides into stable Cr-Mn-oxides. Agglomeration of fine oxides into larger agglomerates (up to 1 µm in size) was observed close to the sintering temperatures. Critical importance of balance between thermodynamics and kinetics of oxide reduction/transformation has to be taken into account. Results indicate that oxide transformation processes occur in accordance with the thermodynamic stability of oxides in the sequence $\text{Fe}_2\text{O}_3 \rightarrow \text{FeO} \rightarrow \text{Fe}_2\text{MnO}_4 \rightarrow \text{Cr}_2\text{FeO}_4 \rightarrow \text{Cr}_2\text{O}_3 \rightarrow \text{MnCr}_2\text{O}_4 \rightarrow \text{MnO/MnSiO}_x \rightarrow \text{SiO}_2$. MnCr$_2$O$_4$ spinel oxide was identified as the most stable oxide phase at applied sintering conditions in alloyed with Cr and Mn sintered steels.

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