PREDICTION, FORMATION AND ANALYSIS OF MICROSTRUCTURE OF HIGH CHROMIUM-ALLOYED PM STAINLESS STEEL SINTERED IN DIFFERENT ATMOSPHERES

R. Shvab, E. Hryha, P. Shykula, O. Bergman, S. Bengtsson, E. Dudrová

Abstract
Analysis of the microstructure of high chromium alloyed PM stainless steel was performed in several stages. The equilibrium phase diagrams and mass fractions of phases for alloy Fe-20%Cr-17%(Ni,Si,Mn)-C were calculated using Thermo-Calc and JMatPro software. All calculations were done for two nitrogen content levels, which correspond to compositions of material sintered in N₂-H₂ and atmosphere without nitrogen (pure H₂ and argon), respectively. According to calculations, austenite and chromium carbides are in equilibrium if sintering is an in atmosphere without nitrogen, and austenite with chromium carbonitrides and carbides for material sintered in N₂-H₂ atmosphere. The microstructure of the materials is affected by the sintering atmosphere, especially at the surface. The influence of sintering atmospheres on microstructure was analyzed. The results showed that the predicted microstructure is in good agreement with observed real microstructure.

Keywords: high chromium alloyed steel, sintering atmosphere, nitrogen, microstructure

INTRODUCTION
High Cr-alloyed stainless steels have been widely used in automotive, biomedical, food, pharmaceutical and marine industries due to their high strength and ductility, fatigue strength, corrosion and wear resistance [1-6]. The main advantages of the powder metallurgy (PM) process, in comparison with conventional metallurgy, are high material utilization, low energy consumption, short overall production time and the ability to tailor microstructures [7]. When using PM materials, one important variable must be considered, namely, porosity [8]. Sintering is a very important stage of PM processing for achieving minimal porosity and decreasing its influence on mechanical properties of material. Using such alloying elements as manganese, silicon and chromium leads to more demanding sintering conditions. These elements have very high affinity to oxygen and create stable oxides on the surface of powder particles [9-12]. Information about powder particle surface oxides plays the most important role in choosing the optimal sintering conditions in terms of providing strong metal bonding between the metal particles during sintering. One more important aspect should be taken to account during sintering is the atmosphere. During the whole sintering cycle a large number of reactions between furnace atmosphere and sintered material take place. They are strongly associated with chemical composition of the
atmosphere and sintered material, but also with the time-temperature sintering regime. Therefore, it is necessary to pay attention to the complex reactions between the furnace atmosphere and sintered material, especially in terms of nitrogen and carbon content in the surface of sintered parts [13-15].

Computational thermodynamics is a powerful tool for calculating equilibria and predicting microstructure and properties of materials. The most popular of them, the Thermo-Calc and JMatPro softwares, were used in this work. Metallography identifies the microstructure, which serves to explain how composition and processing dictate the properties and performance of metals and alloys. In particular, static and dynamic mechanical properties, including fracture and the degradation of metals and alloys by corrosion, can be predicted and understood in terms of microstructure. Thus, a quantitative characterization of microstructure is a necessary ingredient in the development of metals and alloys with enhanced properties [16].

Prediction, formation and analysis of the microstructure of high Cr-alloyed PM steel and the influence of sintering atmosphere on the microstructure and mechanical properties were investigated in the present contribution.

**EXPERIMENTAL MATERIAL AND METHODS**

The material studied in this work is sintered high chromium alloyed austenitic steel Fe-20%Cr-17%(Ni, Si, Mn)-C. Cold compaction at pressure of 600 MPa was applied for all samples. Sintering was performed at 1250°C for 30 min in pure hydrogen and N₂-H₂ atmospheres, respectively, in a Carbolite laboratory tube furnace. Sintering in argon atmosphere was performed using a Netzsch 402C dilatometer at TU Vienna. All the gases were of 5.0 purity, and the inlet dewpoint was lower than -60°C. Sintering was followed by cooling of 10°C/min. Density of sintered samples was ~ 7.4 g·cm⁻³ which corresponds to porosity of ~ 4%.

Theoretical prediction of microstructure of the material was done using Thermo-Calc and JMatPro software. The equilibrium phase diagrams and mass fractions of phases were calculated by Thermo-Calc Classic version S with utilizing TCFE6 database and “JMatPro the Materials Property Simulation Package Public Release Version 6.2.1” software with stainless steel database for this version.

Microscopical observations of sintered microstructures were performed on JEOL JSM-7000F scanning electron microscope equipped with INCAx-sight EDX analyzer, and the results were compared with theoretical predictions.

The surface hardness HV10 of the samples was measured using HECKERT hardness tester.

**RESULTS AND DISCUSSION**

**Prediction of microstructure by Thermo-Calc and JMatPro**

Prediction of microstructure by Thermo-Calc software was realized by calculation of the equilibrium phase diagram of studied system in the temperature range of 500 to 1200°C for nitrogen content from 0 up to 1 wt.% (Fig.1) and by JMatPro calculation of mass fractions of phases (Figs.2, 3). The mass fraction of phases were calculated for two nitrogen contents – 0.08 wt.% and 0.8 wt.%. The sintered microstructure of the studied material depends strongly on the sintering atmosphere. During sintering in pure hydrogen and argon atmospheres the nitrogen content does not increase, and the sintered material contains about 0.08 wt.% of nitrogen. Sintering in N₂-H₂ atmosphere results in intense nitrogen pick-up due to high chromium content, increasing nitrogen content by up to 0.8 wt.%.
Fig. 1. Equilibrium phase diagram for the studied material, showing dependence of the phase composition on nitrogen content and temperature.

Figure 1 gives information about phases in dependence of temperature. At the temperature of about 500°C, a presence of austenite with $M_{23}C_6$ carbides and $M_2(CN)$ (HCP_A3#2) carbonitrides for sintered material it can be expected. $M_{23}C_6$ are complex chromium-iron carbonitrides. [17]. The $M_2(CN)$ are complex chromium-iron carbonitrides. [17]. $M_{23}C_6$ carbides (Cr,Fe)$_{23}$C$_6$, nucleate at grain boundaries in the temperature range 450-900°C [18], but the formation of $M_{23}C_6$ carbides is retarded by the presence of nitrogen. Nitrogen is not soluble in $M_{23}C_6$ and the carbide is destabilised as soon as a small amount of carbon is substituted by nitrogen. At high carbon contents, the $M_7C_3$ carbides are created at higher temperatures than $M_{23}C_6$ [19].

According to calculated diagrams, the formation of $M_2(CN)$ can be expected up to ~1000°C for material sintered in pure hydrogen and argon and up to 1200°C for material sintered in the $N_2-H_2$ atmosphere.

Thermo-Calc calculation gives information about equilibrium state, but for PM materials, reaching the equilibrium is quite problematic even at sintering temperature. It means that sintered microstructure would have composition close to that at the sintering temperature. According to Thermo-Calc equilibrium phase diagram for powder compacts sintered in pure hydrogen and argon, presence of austenite and $M_7C_3$ carbides in the microstructure can be expected. For compacts sintered in $N_2-H_2$ atmosphere, it is austenite with $M_2(CN)$ (HCP_A3#2) carbonitrides and $M_7C_3$ carbides. The mass fractions of phases were calculated by JMatPro, Figs. 2 and 3.
It is obvious that both the softwares used give similar results. According to JMatPro, the materials sintered in pure hydrogen and argon contain about 95 wt.% of austenite and 5 wt.% of $M_7C_3$ carbides. For powder sintered in mixed $N_2-H_2$ atmosphere the microstructure would contain about 90 wt.% of austenite, 8 wt.% of $M_2(CN)$ carbonitrides and 2 wt.% of $M_7C_3$ carbides.

**Metallographic observation**

Metallographic observations of sintered microstructures were performed in the etched state. The etchant of 1ml HF+5ml HNO$_3$+44ml distilled water was used. Figures 4 a, b present an example of microstructure of the investigated material sintered in the argon atmosphere.
The microstructure consists of austenite grains (with a size up to 30 µm) and network of carbides along grain boundaries. Some small carbides and “holes” left by dissociated carbides are inside austenite grains. At the sintering temperature, carbides dissolve and carbon is removed from the sample, because atmosphere does not contain any carbon. Removal of carbon occurs preferably along austenite grain boundaries. The austenite grain boundaries without carbides can move, which leads to grains growth.

**EDX analysis:**

- Cr, at% Fe, at% C, at%
  - 56 12 32
- Cr, at% Fe, at% C, at%
  - 55 14 31

Semiquantitative EDX analysis showed that carbides contain iron and chromium. Stoichiometry showed closeness of carbides to $M_7C_3$. 

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**Fig.4 a, b** Microstructure of investigated material, sintered in argon.

**Fig.5.** Microstructure and EDX analysis of precipitates, material sintered in argon atmosphere.
Fig. 6 a, b Microstructure of investigated material, sintered in pure hydrogen atmosphere.

The sintering of material in pure hydrogen atmosphere, Figs. 6 a, b, resulted in microstructure similar to sintering in argon. It consists of large austenite grains, size of 10-30 µm, with carbide network along grain boundaries. The material contains less carbides inside the grains in comparison with sintering in the neutral argon atmosphere. Higher decarburization of material sintered in pure hydrogen is a consequence of methane formation, which is supported by alloying elements like Si, Cr and Mn [20].

EDX analysis:

<table>
<thead>
<tr>
<th></th>
<th>Cr, at%</th>
<th>Fe, at%</th>
<th>C, at%</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>57</td>
<td>12</td>
<td>31</td>
</tr>
<tr>
<td>b</td>
<td>54</td>
<td>13</td>
<td>33</td>
</tr>
</tbody>
</table>

Fig. 7. Microstructure and EDX analysis of precipitates, material sintered in pure hydrogen atmosphere.

Similarly to argon atmosphere, semiquantitative EDX analysis of material sintered in pure hydrogen showed that carbides contain iron and chromium. Stoichiometry showed closeness of carbides to $M_7C_3$. 
The microstructure of material sintered in \( \text{N}_2-\text{H}_2 \) atmosphere, Figs. 8 a,b, consists of austenitic matrix and carbides/carbonitrides dominantly precipitated along austenite grain boundaries. The grain size is 3-5 μm, and the carbide/carbonitride precipitates have sizes of 1-2 μm.

**EDX analysis:**

<table>
<thead>
<tr>
<th>Element</th>
<th>Cr, at%</th>
<th>Fe, at%</th>
<th>C, at%</th>
<th>N, at%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig. 8 a</td>
<td>51</td>
<td>12</td>
<td>18</td>
<td>19</td>
</tr>
<tr>
<td>Fig. 8 b</td>
<td>53</td>
<td>11</td>
<td>18</td>
<td>18</td>
</tr>
</tbody>
</table>

Fig. 9. Microstructure and EDX analysis of precipitates, material sintered in pure hydrogen atmosphere.

Semiquantitative EDX analysis of material sintered in \( \text{N}_2-\text{H}_2 \) atmosphere showed presence of nitrogen in precipitates, Fig. 9. Carbonitrides also contain iron and chromium. Stoichiometry showed closeness of carbonitrides to \( \text{M}_2(\text{CN}) \).

As it is visible from the examined microstructures, the sintering atmosphere has a big influence on the final microstructure. The absence of carbon in atmospheres of argon and hydrogen led to strong decarburization and grain growth. Sintering in \( \text{N}_2-\text{H}_2 \) atmosphere resulted in nitrogen pick-up and small austenite grains in the material. The sintering atmosphere also affects the mechanical properties of the sintered materials.
Hardness of the materials sintered in argon and pure hydrogen is lower than of material sintered in N₂-H₂ atmosphere, Table 1.

<table>
<thead>
<tr>
<th>Sintering atmosphere</th>
<th>Hardness, HV10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon</td>
<td>181±5</td>
</tr>
<tr>
<td>pure hydrogen</td>
<td>174±6</td>
</tr>
<tr>
<td>N₂-H₂</td>
<td>239±7</td>
</tr>
</tbody>
</table>

Strong nitrogen pick-up has a beneficial effect on hardness of the material studied. N₂-H₂ atmosphere is better than argon and pure hydrogen for sintering of the investigated powder.

CONCLUSIONS

Theoretical calculations of the microstructure by both Thermo-Calc and JMatPro software predicted presence of austenite with M₇C₃ carbides for powder sintered in argon and pure hydrogen atmosphere and austenite with M₂(CN) carbonitrides and M₇C₃ carbides for material sintered in mixed N₂-H₂ atmosphere. Metallographic observations of materials sintered in argon and pure hydrogen showed that the microstructure contains large austenitic grains, size of 10-30 µm, with carbide network along grain boundaries. Fine carbides (~1 µm) situated inside the grains were observed in the material sintered in argon. Due to stronger decarburization of material sintered in pure hydrogen, carbides inside the grains were absent. The microstructure resulting from sintering in N₂-H₂ atmosphere contains smaller austenite grains, size of 3-5 µm, with fine (1-2 µm) carbides and carbonitrides distributed mostly on grain boundaries. Metallographic observations of the microstructure confirmed theoretical predictions. Semiquantitative EDX analysis showed that carbides and carbonitrides have complex structure and contain iron and chromium.

Acknowledgement

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