

INFLUENCE OF THE PURITY OF THE SINTERING ATMOSPHERE ON THE REDUCTION OF OXIDES DURING SINTERING OF Fe-Cr-MO STEELS

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Abstract

The effect of the purity of the 10% H₂+N₂ sintering atmosphere and cooling rate on the reduction of oxides in Fe-3%Cr-0.5%Mo+0.5C% was investigated. Specimens with a density of 6.9 g·cm⁻³ were sintered at 1120°C for 30 min in the N₂-rich atmosphere with oxygen contents of 2.0 vpm (purity 5.0) and 0.5 vpm (purity 6.0), respectively. Two different cooling rates, 10°C/min and 50°C/min, were used. The contents of the active gases CO, CO₂, and H₂O were continuously monitored. It is shown that the iron oxide layer at particle surfaces is removed by hydrogen-reduction during the heating stage at 470°C. Thermodynamically stable oxides are removed by carbothermic reduction at temperatures higher than 820°C. The reducing processes were evaluated on the basis of oxygen-carbon balance in the sintered materials. The elimination of oxide contamination of interfaces results in higher mechanical properties.

Keywords: *Cr alloyed sintered steels, oxide reduction, monitoring of composition of the sintering atmosphere*

INTRODUCTION

The main obstacles of powder metallurgy processing of Cr alloyed steels, which offer attractive potential for the production of high-performance automotive components, is the high affinity of chromium to oxygen. However, there has been recent progress towards production of high-quality water atomized Cr pre-alloyed powders (e.g. Höganäs AB, Astaloy CrM and Astaloy CrL powders). Numerous studies performed on such powders reported that selective oxidation of strong oxide formers results in the formation of heterogeneous oxide layer distributed along the particle surfaces [1, 2]. Surface chemical analyses showed that more than 90% of powder particles is covered by easily reducible iron oxide layer (thickness of about 6 nm) with presence of spherical particulates, about 20-200 nm in size, formed by complex Cr-Mn-Si oxides. The surface iron oxide layer contains about 40-50% of the total oxygen content [2]. The rest is concentrated in particulate particles on the powder surfaces and a large part is present in complex internal oxides [3]. Reduction of surface oxides is necessary for achieving strong particle necks and thus high mechanical properties of sintered components [4]. The reduction of oxides is determined by their thermodynamic stability. Crucial roles in the reduction of oxides play the protective atmosphere and carbon added as graphite to the starting powder.

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 oxide ($p(O_2)^{atmosf} < p(O_2)^{oxide}$). If the sintering is carried

out in a hydrogen containing atmosphere, without 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, oxides reduction occurs through carbothermic reactions. Danninger et al. [5-8] experimentally studied the influence of carbon on the degassing and oxide reduction processes of several on Fe-based alloying systems containing admixed graphite. The generation of CO associated with mass loss observed at defined temperatures during heating of powder compact containing admixed carbon was taken as a basis for assumption that reduction of oxides takes place through the direct carbothermal reaction. Ortiz and Castro [9-10], Mitchell and Cias [11,12] proposed that chemical events 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 [11] this fact results in the formation of a specific "microclimate" inside the compact. In such micro-volumes the equilibrium state is established between local carbon, chromium, oxygen and water vapour contents. Self-generation of CO/CO₂ gas mixture by added graphite controls the reduction of oxides inside the compacts rather than the ratio H_2/H_2O [9-12]. The contents of CO, CO₂, H₂O and H₂ in the atmosphere depend on temperature. Mitchell and Cias [11] identified the critical reactions that take place in pores and are connected with CO generation, which improves CO/CO₂ ratio. There are the water gas reaction $C + H_2O = CO + H_2$ (thermodynamically favourable after 450°C) and the Boudouard reaction $C + CO_2 = 2CO$, effective from ~700°C.

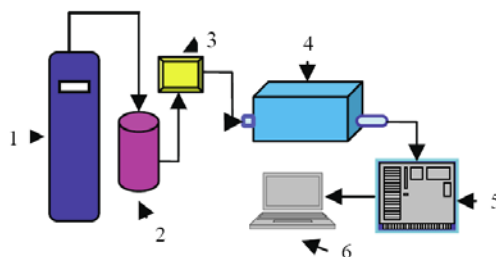
Oxide reduction processes in Cr-Mn pre-alloyed powders have been studied from different aspects, but a systematic study of the effect of oxygen content in the sintering atmosphere on reduction processes in Cr alloyed sintered steels has not been reported. Bocchini [13] analyzed the composition of controlled atmospheres for the proper sintering of carbon PM steels. He considered equilibrium constants of relevant reactions between CO₂ and H₂O, C and CO₂ and CO and H₂O. Mitchell et al. [11] considered the thermodynamic aspects of the reduction of stable oxides of Cr and Mn and calculated the maximum pressures of active gases in the sintering atmosphere that can be tolerated in the system. They showed that for oxides reduction by solid carbon it is necessary to consider the reducing effect of the partial pressure following the $2C + O_2$ reaction. In order to have reducing conditions for a iron pre-alloyed with 3% Cr and 0.5% Mo, thermodynamic calculations [11] showed that the oxygen partial pressure should be $<4.5 \cdot 10^{-20}$ bar at 1120°C. Bergman [14] reported that in system with graphite added to the starting powder, the sintering conditions are reducing also at higher partial pressure of oxygen (up to 10^{-16} bar) due to favourable local conditions in the material. Danninger et al. [5-8] using the DTA, DTG and mass spectroscopy (MS) analyzed the composition of the reaction products created during sintering of various powder systems. On the basis of chemical composition of reactive products and temperature of their generation, they proposed general correlations between reducing reactions and temperatures, chemical composition of starting powder, etc. Hryha, Nyborg et al. [3,15], on the basis of thermodynamic calculations, presented an algorithm of transformation of less stable to more stable oxide related to the temperature of reduction during the sintering cycle; this transformation was confirmed by HR SEM combined with EDX analysis.

The aim of this work was to study the influence of both atmosphere purity and cooling rate on the reduction processes during sintering of compacts from water atomized powder Fe-3 wt% Cr-0.5 wt% Mo with 0.5 wt.% added graphite at temperature 1120°C in N₂+10% H₂ atmosphere by continuously monitoring the sintering atmosphere composition. The composition of the sintering atmosphere is a very important technological parameter and its determination gives information about interactions between sintered material and furnace atmosphere during all stages of sintering.

EXPERIMENTAL PROCEDURES

The starting powder materials used were commercial water atomized pre-alloyed powder Astaloy CrM of nominal composition Fe-3%Cr-0.5%Mo with starting oxygen content of 0.197 wt.% and commercial graphite Kropfmühl UF4 added in the amount of 0.5 wt.%. Cylindrical specimens $\varnothing 10 \times 12 \text{ mm}^3$ with a density $\sim 6.9 \text{ g}\cdot\text{cm}^{-3}$ were compacted using only die-wall lubrication. The time-temperature profile applied in all experiments was the following: heating rate $10^\circ\text{C}/\text{min}$ up to 1120°C , isothermal sintering at 1120°C for 30 min and cooling to room temperature. Two different cooling rates were applied: $10^\circ\text{C}/\text{min}$ and 50°min , respectively. The sintering took place in a laboratory tube furnace ANETA1. The specimens (always 6 pieces) were kept in a special semi-closed low-carbon steel container in which the atmosphere composition in inner microvolumes was simulated. Therefore, the flow-rate of the inlet atmosphere used in the experiments was rather low - only 2 l/min.

In order to evaluate the effect of the oxygen purity of sintering atmosphere on reduction of oxides, mixtures of 10% H_2+N_2 with oxygen contents of 2.0 vpm (purity 5.0) and 0.5 vpm (purity 6.0), respectively, were used. Before entering the furnace atmosphere, the gases were dried by liquid nitrogen freezing. The dew point of the inlet atmosphere (monitored by Super-Dew SHAW) was $\sim -70^\circ\text{C}$. The dew point in the container with specimens was monitored using Michell Cermet II sensor.



1 - gas cylinder ($\text{N}_2 - \text{H}_2$ mixture), 2 - liquid nitrogen dryer; 3 - hygrog (inlet dew - point); 4 - furnace (ANETA), 5 - $\text{CO}/\text{CO}_2/\text{H}_2\text{O}$ analyzers, 6 - PC.

Fig.1. Scheme of atmosphere monitoring setup.

Figure 1 shows the layout of the sintering atmosphere monitoring setup, sintering furnace and PC processing the monitored data. The atmosphere was continually sampled directly from a container near the specimen surfaces. The contents of CO , CO_2 in the sintering atmosphere were recorded by non-dispersive infrared analyzers on base Gas Card II Plus sensor. All sensors were connected to a PC, and continuous monitoring of the CO , CO_2 , and H_2O contents was performed using special software. The microstructural analyses were performed using optical (Olympus GX 71) and scanning electron (Jeol JSM 7000F, equipped with INCA EDX analyzer) microscopy. Analyses of the oxygen and carbon contents in the sintered specimens were performed by LECO TC 36 instruments. The R_{FR} values were obtained using non-standard “button” tensile test. Button-shaped samples were machined from sintered cylindrical specimens. The shape of the specimens for this type of test is shown in Fig.2.

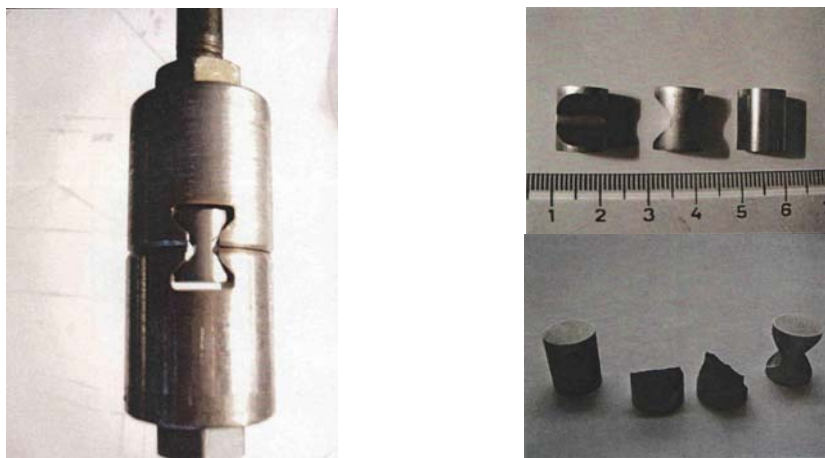


Fig.2. Tool and specimens for "button test".

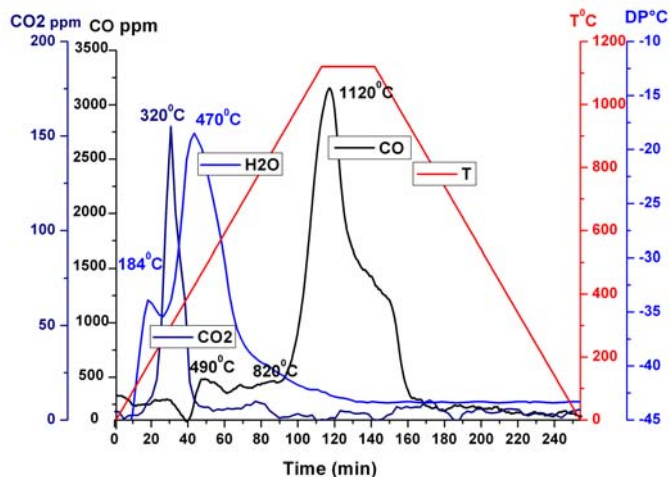
RESULTS

The results of the atmosphere composition monitoring during sintering of AstaloyCrM+0.5C powder compacts at 1120°C in atmosphere 10% H₂+N₂ of purity 5.0 and 6.0 are presented in Fig.3a, b. It is to be noted that there is no significant difference between the records obtained during sintering in both atmospheres containing 2 ppm or 0.5 ppm of oxygen, respectively.

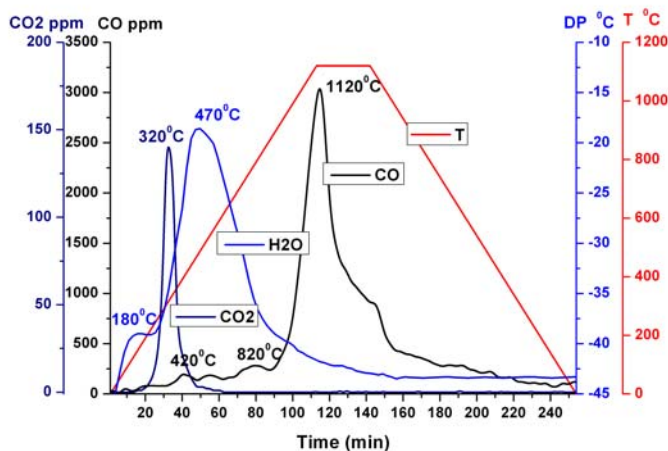
First peak on dew point (DP) profile, Fig.3, at ~180°C is connected with humidity removal from the specimens. The second peak with maximum at ~470°C corresponds to reduction of thermodynamically less stable surface iron oxides by hydrogen. The reducing activity of carbon increases with temperature, and at about 720°C carbon begins to play a dominant role in the reduction process due to carbothermic reduction [5-7]. On the carbon monoxide profile, the small peaks in the temperature range of 200-500°C are linked with lubricant decomposition and graphite oxidation. The peak with a maximum above 820°C is connected with carbothermic reduction of surface iron oxides by plain graphite in Fe/C contacts. Iron oxides present as FeO at this temperature are the result of partial reduction of the former iron oxide layer (Fe₂O₃) covering particle surface. At about 900°C the concentration of CO in sampled atmosphere rapidly increases. The CO peak with a maximum at 1120°C is connected with surface carbothermic reduction of thermodynamically stable Cr oxides and reduction of spinel iron containing oxides (Cr₂FeO₄) from internal pores, which communicate with the surface of the compact.

The largest peak identified on carbon dioxide profile with a maximum at ~370°C is connected with the decomposition of lubricant and also iron carbonate.

Figures 4 and 5 show the O₂ and C contents related to the sintering atmosphere purity and cooling rate. Oxygen content in specimens sintered at 1120°C in the atmosphere with the purity 5.0 decreased from 0.197 wt.% to 0.118 wt.% for the cooling rate of 10°C/min and to 0.098 wt.% for the cooling rate 50°C/min. In the case of specimens sintered in the atmosphere with purity of 6.0, the oxygen content for cooling rate of 10°C/min decreased to 0.095 wt.% and for cooling rate of 50°C/min to 0.089 wt.%. Higher cooling rate results in lower oxygen content.



a)



b)

Fig.3. Monitoring of atmosphere composition during sintering Astaloy CrM+0.5C at 1120°C for 30min in 10% H₂ +N₂ atmosphere with purity of a) 5.0, b) 6.0.

The reduction in oxygen content is equal to oxygen bound in surface oxides. The reduction of internal oxides from the kinetics point of view requires sintering temperature of about 1200°C [10,11]. Figure 5 shows the decrease in carbon content in sintered specimens as the consequence of the carbothermic reduction processes taking place. The carbon content in sintered specimens decreased from 0.5 wt.% to 0.38 wt.% in specimens sintered in the atmosphere of purity 5.0 for the cooling rate of 10°C/min and to 0.39 wt.% for the cooling rate of 50°C/min. For specimens sintered in the atmosphere of purity 6.0 and cooled at 10°C/min, the carbon decreased to 0.39 wt.% and to 0.41 wt.% of those cooled at 50°C/min.

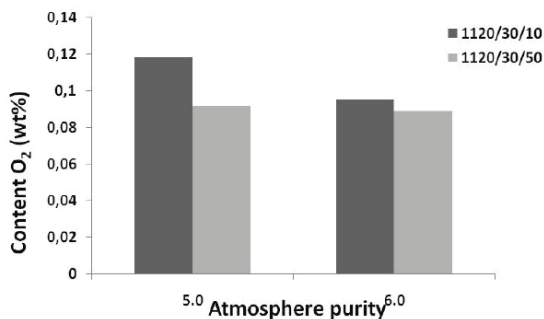


Fig.4. Oxygen content after sintering at 1120°C.

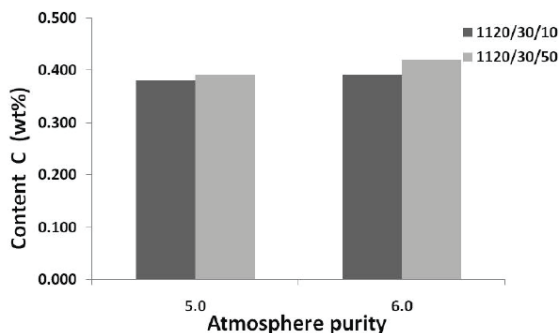


Fig.5. Carbon content after sintering at 1120°C.

Microstructural observations of sintered specimens correspond to the results of chemical analyses. In non-etched microstructure of starting powder, Fig.6a, one can see a high amount of oxide particles distributed along grain boundaries and within the powder particles. Due to the reduction processes which take place during sintering, the amount and size of oxide inclusions rapidly decreases, Fig.6b.

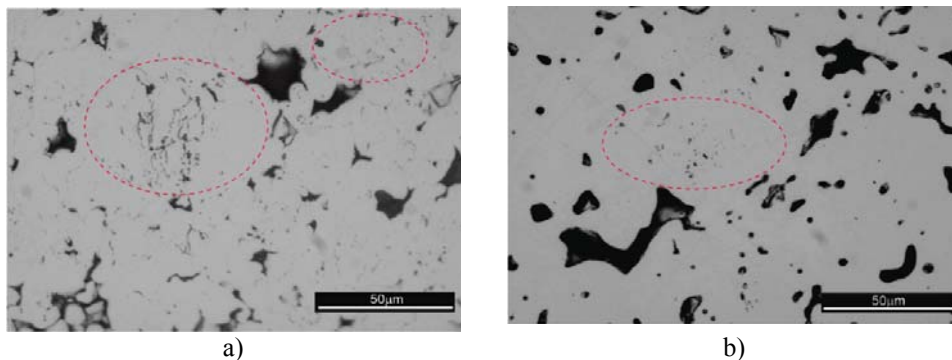


Fig.6. Non-etched microstructure of Astaloy CrM+0.5%C steel: a) green compact; b) sintered at 1120°C for 30 min in 10% H₂+N₂ (6.0), cooling rate 50°C/min.

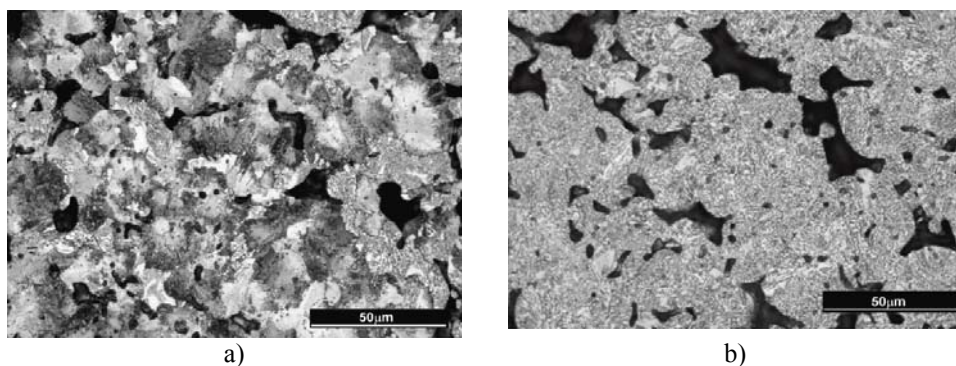


Fig.7. Etched microstructure of Astaloy CrM+0.5%C steel sintered at 1120°C in 10% H₂+N₂ (6.0) for 30 min cooled at a) 10°C/min and b) 50°C/min.

A higher amount of oxide inclusions was observed in microstructure of specimens sintered in the atmosphere with lower purity and in those with the slower cooling rate. Remaining oxide particles are distributed along former particle surfaces and/or as small agglomerates within the powder particles. Etched microstructure of slow cooled specimens, Fig.7a, is more heterogeneous and consists of ferrite, pearlite and bainite, while the microstructure of specimens cooled at the higher cooling rate, Fig.7b, comprises bainite and some small amount of ferrite.

Microfractographic observation of the fracture surfaces of “button” specimens showed that the prevalent failure mode is interparticle ductile dimple fracture, Fig 8a. The inclusions inside necks are small, quite spherical, particulates with sizes up 0.5 μm or bigger agglomerates of these particulates.

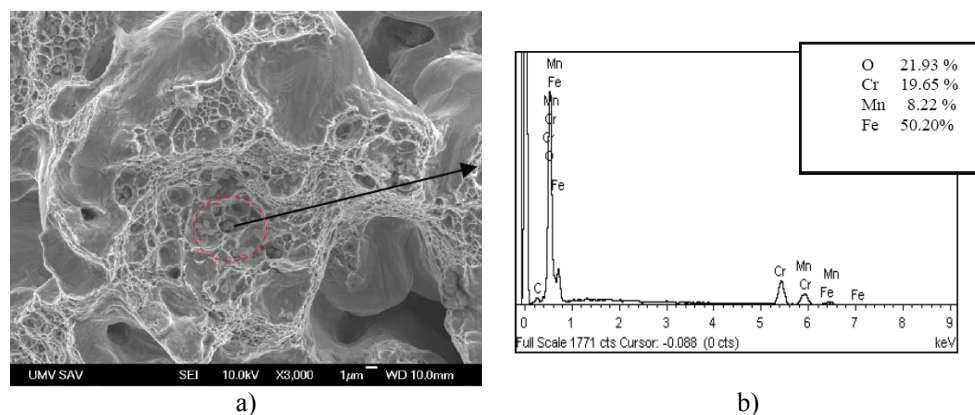


Fig.8. Fracture surface of Astaloy CrM+0.5%C sintered at 1120°C in 10% H₂+N₂ (6.0) for 30 min: a) SEM image, b) EDX analysis.

EDX microanalyses, Fig.8b, of oxide inclusions showed the presence of Cr and Mn. The ratio Mn:Cr is close to 2, which indicates that there are thermodynamically stable spinel oxides corresponding to MnCr₂O₄ type. Small dimples are initiated by fine oxide inclusions, larger and more shallow dimples are frequently initiated by small residual pores and/or larger inclusions or their agglomerates. It should be noted that the free surfaces of

former particles are clean, without any visible oxide layer. The presence of oxide particles at the free surfaces of particles was only sporadic.

The non-standard "button test" provides information on the quality of material and enables us to compare the influence of the applied processing parameters on the strength properties of the materials studied. The values of rupture strength R_{FR} , Fig.9, obtained by "button test" are in the range 566-753 MPa.

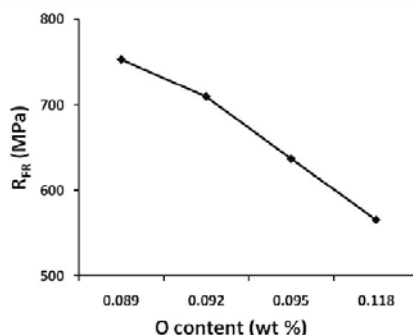


Fig.9. Rupture strength vs. oxygen content of CrM+0.5C sintered at 1120°C in 10% H_2+N_2 .

DISCUSSION

As mentioned above, the surface of atomized Cr pre alloyed powder is covered by heterogeneous surface oxides, composed of thin Fe-oxide layer and particulate features rich in strong oxide forming elements [1-2]. A necessary condition for achieving high mechanical properties of sintered material is the reduction of surface oxides during sintering and the creation of sufficiently strong necks between particles. Hydrogen from the sintering atmosphere and carbon added as graphite play a crucial role in the reduction processes.

Monitoring of the composition of the sintering atmosphere showed that the reduction of surface iron oxides by hydrogen starts at $\sim 300^\circ\text{C}$ and maximum of reduction is reached at $\sim 470^\circ\text{C}$. The reduction of iron oxide surface layer (Fe_2O_3), which contain about 40-50% of total oxygen at lower temperature is of great importance in terms of strengths of interparticle necks.

After Boudouard equilibrium ($\sim 700^\circ\text{C}$) carbothermic reduction becomes the dominant reduction mechanism. Monitoring of composition of the atmosphere during sintering of the CrM+0.5%C powder showed that the direct carbothermic reduction connected with generation of CO starts at about 800°C . The first maximum at 820°C on the CO profile is linked with a reduction of surface iron oxides, carbothermic reduction of chromium oxide and iron oxides on surfaces of internal pores occurs at 1120°C . The results are in good agreement with results presented by Jaliliziyaieian et al. [16] which study reduction behaviour of Cr-Mo and Mn pre-alloyed steels during sintering. EDX analysis of residual oxides confirmed the transformation of the less stable oxides FeO, MnO and Cr_2O_3 to he more stable spinel-type oxides according to the algorithm thermodynamically predicted by Hryha et al [3, 15].

This work was focused on a study of the influence of both atmosphere purity and cooling rate on reduction processes during sintering the Fe-3Cr-0.5Mo powder with 0.5 wt.% added graphite. It should be noted that there was no significant difference between the

records obtained during sintering in both the atmospheres used: containing 2 ppm or 0.5 ppm of oxygen, respectively. However, the analysis of final oxygen content showed that in specimens sintered at 1120°C in the atmosphere with purity of 6.0, the oxygen content for cooling rate of 50°C/min decreased from 0.197 wt.% to 0.089 wt.%, while in specimens sintered in atmosphere with purity 5.0, it decreased to 0.098 wt.%. The results showed that the sintering at the temperature of 1120°C in an atmosphere of higher purity leads to the removal of more than 50% oxygen content present in the starting powder. During cooling, the system passes the critical temperature range and re-oxidation of specimens can occur. The chemical analyses confirmed that re-oxidation of specimens with slow cooling rate is significantly higher in comparison to those cooled at a higher rate. When these results are compared with those presented by Bergman [14], who studied the influence of oxygen partial pressure in the sintering atmosphere on the properties of Cr-Mo alloyed PM steel, it is apparent that flow rate of atmosphere is an important factor influencing the total oxygen content in sintered specimens. Bergman in his experiments used higher flow rate (4 l/min) and reported that cooling rate does not impact on total oxygen content of the sintered specimens. The using of the atmosphere with a low flow rate caused a worsening of purity of the local atmosphere generated in a semi-closed container because all exhaust gases formed during sintering cannot be sufficiently “blown off”.

Carbothermic reduction reactions lead to decreasing final carbon content, additionally, the results showed that as-sintered carbon content is influenced by atmosphere purity. The relatively high carbon loss may have been caused by the purity deterioration of the atmosphere in a semi-closed container.

The strength properties expressed by the fracture strength („button test“) confirmed a positive effect of atmosphere with higher purity on lower final oxygen content, in accordance with the hypothesis that lower oxide contamination of the material corresponds to a higher strength of the sintered material. The oxide inclusions participate in failure as dimple formation initiators. The greater number of large inclusions results in lower strength characteristics. A positive effect of bainitic microstructure on strength properties is evident from the comparison of the strength values for specimens processed with slow and accelerated cooling rates from the sintering temperature.

CONCLUSIONS

Continuous monitoring the composition of the sintering atmosphere confirmed thermodynamic predictions of reduction conditions of Cr alloyed steel at conventional sintering temperatures. The results showed that the surface iron oxides are reduced by hydrogen at ~470°C; direct carbothermic reduction connected with generation of CO starts at about 800°C and at 1120°C carbothermic reduction of chromium oxide and surface iron oxides from internal pores occurs. The oxygen purity of both atmospheres used (5.0 and 6.0 corresponding to oxygen content of 2 ppm and 0.5 ppm) has no significant effect on the monitored composition of sintering atmosphere and also characteristic temperatures of reduction processes. However, the results confirmed that both purity of sintering atmosphere and cooling rate are important factors which affect reduction processes during sintering. A decrease in oxygen content, more than 50%, in comparison with starting state (from 0.197 to 0.089 wt.%) was achieved in specimens sintered in the atmosphere with purity 6.0 and cooled at 50°C/min. The higher oxygen content in slowly cooled specimens indicates re-oxidation processes. The strength properties, expressed by the values of the rupture strength, increase with decreasing oxygen content in sintered specimens and higher cooling rate of 50°C /min, due to the microstructure consisting of bainite.

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