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THE STRUCTURE AND MECHANICAL PROPERTIES OF SINTERED ASTALOY-BASED STEELS PRODUCED UNDER DIFFERENT CONDITIONS

STRUKTURA I WŁASNOŚCI MECHANICZNE SPIEKANYCH STALI WYKONANYCH NA BAZIE PROSZKÓW STOPOWYCH ASTALOY CrL I ASTALOY CrM WYTWARZANYCH W RÓŻNYCH WARUNKACH

In the present paper an attempt has been made to work out a new chemical composition of sintered steel for sinter-hardening applications and to establish the most advantageous technology as far as mechanical properties and microstructure are concerned. Additions of alloying elements such as copper and nickel have traditionally been used in sintered steels for many years. Because of expensive and cancerogenic nickel and heavy-recycled copper it has been decided to replace these elements with molybdenum, manganese and chromium, in order to increase the mechanical properties of sintering manganese steels.

Mn-Cr-Mo PM steels (Fe-3%Mn-1.5%Cr-0.2%Mo-0.8%C and Fe-3%Mn-3%Cr-0.5%Mo-0.8%C) were investigated. Their chemical compositions were based on the pre-alloyed Höganäs Astaloy CrL and Astaloy CrM powders, containing 1.5% and 3% Cr, and 0.2% and 0.5%Mo, respectively. Manganese in the form of low-carbon ferromanganese and elemental carbon in the form of ultra fine graphite were added to the steel powders. Following mixing in a double cone laboratory mixer (60 rpm/30 minutes), the mixtures were pressed in a rigid die to achieve the green density of 6.8-7.0 gcm^{-3}.

The compacts were sintered at 1120°C and 1250°C for 60 minutes in either hydrogen or nitrogen atmosphere. To improve the local dew point (self-gettering effect) and to minimize the loss of manganese due to volatilisation, the specimens were sintered in a semi-closed stainless steel container. The cooling rate was approximately 65°Cmin^{-1}. After sintering, all specimens were tempered at 200°C for 60 minutes in air.

The mechanical properties and microstructures indicate that processing of the Mn-Cr-Mo alloy steels achieved its objectives. The optimized chemical composition, alloying technique and processing of PM Mn-Cr-Mo sinter-hardened steels result in the benefits if comparing the properties of Fe-Mn-Cr-Mo-C steels with both commercial sintered nickel steels and sinter-hardened PM manganese steels.

Keywords: powder metallurgy (PM), Mn steels, sinter-hardening, mechanical properties, Astaloy CrL and Astaloy CrM, manganese-chromium-molybdenum PM steels

W pracy podjęto próbę opracowania nowego składu chemicznego stali spiekanej przeznaczonej do obróbki typu sinter-hardening, z jednoczesnym wskazaniem najkorzystniejszej, pod względem własności wytrzymałościowych i mikrostruktury, technologii jej wytwarzania. Do niedawna głównymi składnikami stopowymi w tej grupie stali były nikiel i miedź. Jednak ze względu na rosnącą cenę i rakotwórcze działanie niklu oraz trudną do przetworzenia miedź, zdecydowano się na zastąpienie tych pierwiastków tańszymi oraz korzystnie wpływającymi na własności wytrzymałościowe, molibdenem, chromem oraz manganem.

Badaniom poddano stale o dwóch składach chemicznych: Fe-3%Mn-1,5%Cr-0,25%Mo-0,8%C oraz Fe-3%Mn-3%Cr-0,5% Mo-0,8%C. Mieszanki zostały sporządzone na bazie rozpylanych stalowych proszków stopowych Astaloy CrL (1,5% Cr i 0,2% Mo) oraz Astaloy CrM (3%Cr i 0,5%Mo), wyprodukowanych przez szwedzką firmę Höganäs. Mangan w ilości 3% mas. został wprowadzony do mieszanki w postaci proszku niskowęglowego żelazomanganu (1,3%C i 77%Mn), a węgiel w postaci proszku grafitu C-UF. Ze sporządzonych mieszanek proszków metodą prasowania jednostronnego w stalowej matrycy przygotowano wypraski (o średniej gęstości mieszczącej się w zakresie od 6,8 g/cm^3 do 7,0 g/cm^3), które następnie poddano spiekaniu w atmosferze azotu i wodoru w temperaturze 1120°C oraz 1250°C przez okres 60 minut. Po spiekaniu próbki chłodzono z prędkością około 65°Cmin^{-1}, a następnie poddano odpuszczaniu w powietrzu przy temperaturze 200°C przez czas jednej godziny.

Wyniki badań własności wytrzymałościowych oraz obserwacje zgładów metalograficznych, potwierdzają osiągnięcie zamierzonego celu pracy. Optymalny skład mieszanki oraz prawidłowo dobrany proces wytwarzania stali Mn-Cr-Mo pozwala otrzymać lepsze własności w porównaniu do komercyjnie wytwarzanych spiekanych stali niklowych oraz manganowych.

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1. Introduction

Over the last 60 years sintered manganese steels have been within the scope of interest of PM metallurgists worldwide. The work concentrated on [1]:

- the effect of manganese content and other alloying elements on the mechanical properties of sintered structural parts [1-5],
- the effect of alloying elements, which create a liquid phase at sintering temperatures, on the microstructure and mechanical properties of sintered manganese steels [1, 6],
- elimination of expensive and cancerogenic nickel and heavy-recycled copper by introducing manganese and chromium into sintered steels in order to increase mechanical properties of the materials [7, 8].

The changes in PM structural steels technology during the last fifteen years seem to be comparatively small. Major developments have taken place in the sophistication of manufacturing operations and in the application of the final product. However, there have been major advances in understanding the manufacturing processes and sintering mechanisms of PM manganese steels [4, 9]. Thus the alloys, have more consistent properties and offer substantially better performance [10, 11].

The main objective of this work was to substitute nickel, which has been shown to be a cancerogenic and allergic [12], with manganese. The second objective was to optimize the processing parameters in order to produce inexpensive, low-alloy, high-strength Mn-Cr-Mo PM structural steels.

2. Background

Manganese is an obvious choice for high strength application if it can be protected from oxidation during sintering [4]. Cias and co-workers [2, 5, 9, 13] overcame this problem under laboratory and pilot scale production conditions. It is widely recognised that mechanical properties and dimensional stability of sintered manganese steels depend on the iron powder grade, sintering temperature, and dew point of sintering atmosphere [10]. Manganese PM steels exhibit smaller dimensional scatter than those containing copper. A recently developed alloy, containing 3% Mn, can be processed in a belt furnace providing that careful control of the oxygen partial pressure is maintained. In another work [14], the same authors examined the influence of molybdenum on properties of steels containing 3-4% manganese. They suggest that when the oxygen content of the raw materials is minimised, fine ferromanganese powder is employed and the sintering conditions ensure reducing atmosphere, it is possible to obtain an acceptable microstructure and good mechanical properties of sintered Fe-3%Mn-(0.5%Mo)-0.7%C steel. These results lead to the current work focusing on properties of pre-alloyed Fe-Cr-Mo steels, with additions of fine ferromanganese powder, and mechanical properties of Fe-3%Mn-(0.5Mo)-0.6%C steels based on a plain iron powder, in order to isolate the effect of Cr on the microstructure and properties.

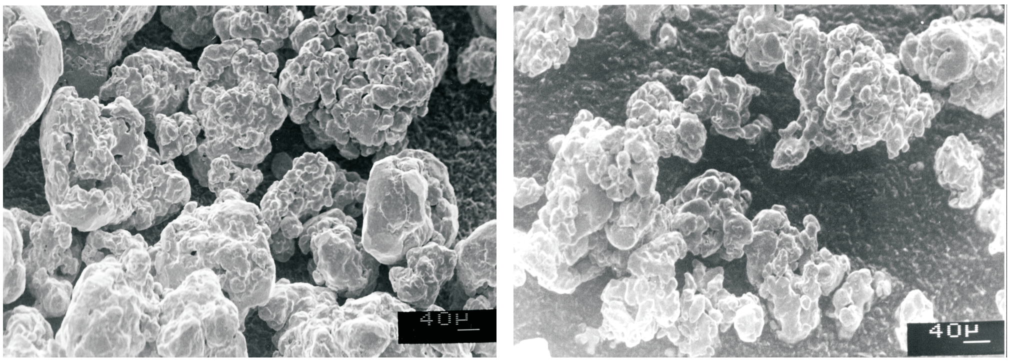
The reaction of manganese with various sintering atmospheres has been the subject of investigations [15-18]. Oxidation of manganese can be overcome by using an iron powder having low con-tent of oxygen and ferromanganese powder.

It is economically advantageous to produce PM steels having the highest hardenability. Therefore several research workers have developed a low alloy PM structural steel with the addition of 2-4% wt.-% of manganese and 0.6-0.8 wt.-% of carbon. For such a composition, the M_s and M_f temperatures decrease significantly and temperature-time-transformation diagrams (TTT and CTT) are moved toward longer times [4, 11]. In the TTT diagram for Fe-3%Mn-0.8%C steel two noses exist; the upper pearlite nose and the lower bainite nose. In this steel it is possible to cool at a rate allowing to avoid the pearlite transformation completely and to obtain bainite by continuous cooling to room temperature. The high hardenability of the manganese steel results in a bainitic microstructure that is produced directly upon cooling from the sintering temperature without any subsequent thermal processing [19] such as austempering. In austempering, the steel is first quenched below the pearlite nose of the TTT curve to a temperature at which bainite formation is possible and held for a certain period of time to complete the transformation. For most highly stressed components it is advantageous to obtain a bainitic microstructure in the as-sintered condition [20].

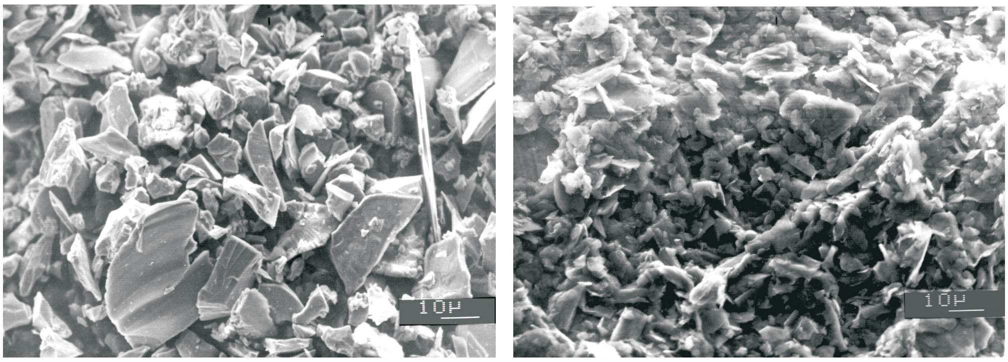
3. Materials and experimental procedures

The steels investigated in this study were based on the pre-alloyed Höganäs Astaloy CrL and Astaloy CrM powders (Figs. 1a and 1b). Manganese and carbon, in the form of low-carbon ferro-manganese (1.3%C, 77% Mn) and ultrafine graphite, were added to these powders (Figs. 1c and 1d) to obtain Fe-3%Mn-1.5%Cr-0.25%Mo-0.8%C and Fe-3%Mn-3%Cr-0.5%Mo-0.8%C steels. The powders were mixed without lubricant in a double cone laboratory mixer to achieve uniform particle distribution. Rectangular 55×10×5 mm bending specimens (according to PN-ISO 5754) and "dogbone" tensile test bars (according to ISO 2740) were prepared from both powders by cold pressing in rigid dies. The cold pressing pressure was adjusted individually to produce green compacts of nominally the same density.

The sintering operation was carried out in either dry nitrogen or hydrogen atmospheres, both having a dew point -60°C, at 1120°C and 1200°C for 60 minutes, and followed by convective cooling at a rate of 65°Cmin^{-1}. During sintering the temperature was controlled to ±2°C. After sintering all specimens were tempered at 200°C for 60 minutes in air To improve the local dew point, by the self-gettering effect, and to minimise the loss of manganese due to evaporation, all specimens were sintered in a semi-closed stainless steel container.



a) Astaloy CrL b) Astaloy CrM



c) ferromanganese d) graphite C-UF

Fig. 1. Microhardness of nitrided AISI 321 steel as a function of distance from the surface

All as-sintered specimens were tested for density, by the water displacement method, mechanical properties and analysed for the contents of oxygen and carbon.

The tensile properties were evaluated on the "dog-bone" specimens according to PN-EN 10002-1. The resulting stress-strain curves were analysed to calculate the 0.2% offset yield strength ($R_{0.2}$), ultimate tensile strength (*UTS*) and % elongation at fracture (*A*). The transverse rupture strength (*TRS*) was determined by the three-point bending test according to PN-EN ISO 3325. Impact test was carried out on 55×10×5 mm un-notched specimens to measure impact strength (KC) with a 15 J Charpy impact tester according to PN-EN 10045-1. The hardness of specimens (HV30) was determined by the Vickers method according to PN-EN ISO 3878.

Metallographic studies were carried out on polished and nital-etched samples [21], using the Leica DM4000M light microscope.

4. Results

The green and as-sintered densities were 6.90 – 6.94 gcm^{-3} and 6.92 – 7.00 gcm^{-3}, respectively. The results of mechanical tests are summarised in Table 1.

TABLE 1

Mechanical properties of sintered Mn-Cr-Mo steels

<table>
<tr><td colspan="9">Fe-3%Mn-1.5%Cr-0.25%Mo-0.8%C</td></tr>
<tr><td rowspan="2">Sintering atmosphere</td><td rowspan="2">Sintering temperature (°C)</td><td rowspan="2">UTS (MPa)</td><td rowspan="2">$R_{0,2}$ (MPa)</td><td rowspan="2">A (%)</td><td rowspan="2">TRS (MPa)</td><td rowspan="2">KC (J/cm^2)</td><td colspan="2">Hardness (HV30) measured on:</td></tr>
<tr><td>Surface</td><td>Cross-section</td></tr>
<tr><td>N_2</td><td rowspan="2">1120</td><td>582</td><td>275</td><td>4.4</td><td>1138</td><td>12.0</td><td>186</td><td>213</td></tr>
<tr><td>H_2</td><td>612</td><td>292</td><td>4.2</td><td>1282</td><td>11.6</td><td>195</td><td>227</td></tr>
<tr><td>N_2</td><td rowspan="2">1200</td><td>723</td><td>267</td><td>4.2</td><td>1470</td><td>8.7</td><td>257</td><td>239</td></tr>
<tr><td>H_2</td><td>766</td><td>260</td><td>4.3</td><td>1554</td><td>14.5</td><td>229</td><td>265</td></tr>
<tr><td colspan="9">Fe-3%Mn-3%Cr-0.5%Mo-0.8%C</td></tr>
<tr><td rowspan="2">Sintering atmosphere</td><td rowspan="2">Sintering temperature (°C)</td><td rowspan="2">UTS (MPa)</td><td rowspan="2">$R_{0,2}$ (MPa)</td><td rowspan="2">A (%)</td><td rowspan="2">TRS (MPa)</td><td rowspan="2">KC (J/cm^2)</td><td colspan="2">Hardness (HV30) measured on:</td></tr>
<tr><td>Surface</td><td>Cross-section</td></tr>
<tr><td>N_2</td><td rowspan="2">1120</td><td>613</td><td>273</td><td>4.2</td><td>1184</td><td>8.7</td><td>213</td><td>232</td></tr>
<tr><td>H_2</td><td>671</td><td>284</td><td>4.2</td><td>1356</td><td>10.8</td><td>214</td><td>255</td></tr>
<tr><td>N_2</td><td rowspan="2">1200</td><td>761</td><td>281</td><td>3.6</td><td>1529</td><td>12.0</td><td>248</td><td>250</td></tr>
<tr><td>H_2</td><td>720</td><td>280</td><td>3.4</td><td>1470</td><td>18.0</td><td>249</td><td>241</td></tr>
</table>

As shown in Table 1, for higher concentrations of Cr and Mo, sintering at 1200°C in nitrogen atmosphere has to be employed to improve strength properties. The *UTS*, *TRS*, and *A* figures evaluated on specimens sintered at 1200°C were by 6%, 4% and 6% higher than the figures obtained for specimens sintered at 1120°C. For lower Cr and Mo concentrations better properties were achieved after sintering in hydrogen than in nitrogen, irrespective to the sintering temperature.

The oxygen and carbon concentrations in the investigated steels are given in Table 2.

TABLE 2

Oxygen and carbon concentration in Fe-Mn-Cr-Mo-C PM steels

<table>
<tr><td rowspan="2">Sintering atmosphere</td><td rowspan="2">Sintering temperature (°C)</td><td colspan="2">Fe-3%Mn-3%Cr-1.5% Mo-0.8%C</td><td colspan="2">Fe-3%Mn-1.5%Cr-0.25% Mo-0.8%C</td></tr>
<tr><td>C (%)</td><td>O_2 (%)</td><td>C (%)</td><td>O_2 (%)</td></tr>
<tr><td>N_2</td><td rowspan="2">1120</td><td>0.770</td><td>0.587</td><td>0.724</td><td>0.569</td></tr>
<tr><td>H_2</td><td>0.707</td><td>0.594</td><td>0.645</td><td>0.313</td></tr>
<tr><td>N_2</td><td rowspan="2">1200</td><td>0.628</td><td>0.385</td><td>0.612</td><td>0.401</td></tr>
<tr><td>H_2</td><td>0.618</td><td>0.410</td><td>0.527</td><td>0.498</td></tr>
</table>

As shown in Table 2, for higher Cr and Mo concentrations there is negligible influence of sintering atmosphere on oxygen and carbon contents in the sintered steels. There is slightly stronger effect of the hydrogen atmosphere on decarburization of the steel as compared to nitrogen one. As it is evident from Table 2, higher sintering temperature promotes oxide reduction in the Fe-3%Mn-3%Cr-0.5%Mo-0.8%C steel [18, 22].

The microstructure analysis of Fe-Mn-Cr-Mo-C PM steels was carried out on nital etched metallographic specimens under bright field (BF) and differential interference contrast (DIC) conditions. The light microscopy images show evidence of decarburization and higher porosity in the subsurface layer of specimens irrespective of the sintering conditions (Fig. 2).

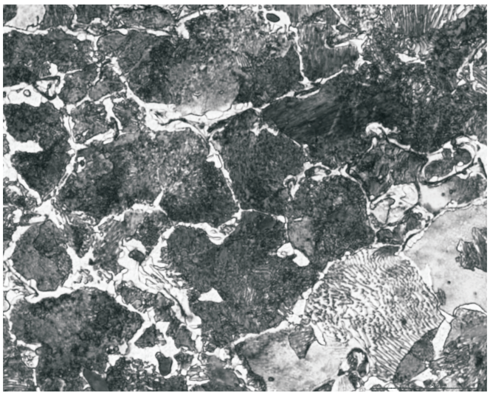


Fig. 2. Microstructure of subsurface layer of Fe-3%Mn-3%Cr-0.5% Mo-0.8%C steel, sintered at 1120°C in N_2, mag. 1000×, BF

The steel containing 3% Cr and 0.5% Mo, sintered at 1120°C in nitrogen has a microstructure which consists of pearlite and bainite. There are few big clusters of tempered martensite and retained austenite (Figs. 3-4), and undissolved particles of ferromanganese and slag inclusions disspersed in a fine-grained structure (Figs. 5-6).

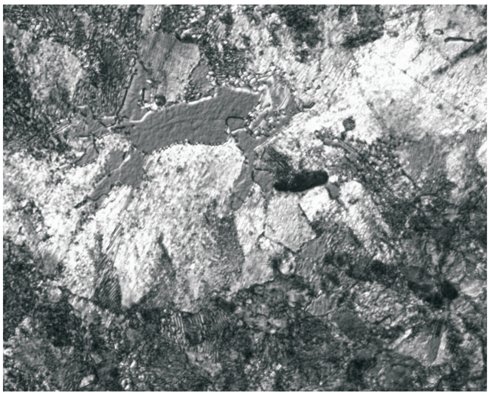


Fig. 3. Microstructure of Fe-3%Mn-3%Cr-0.5%Mo-0.8%C steel, sintered at 1120°C in N_2, mag. 1000×, DIC

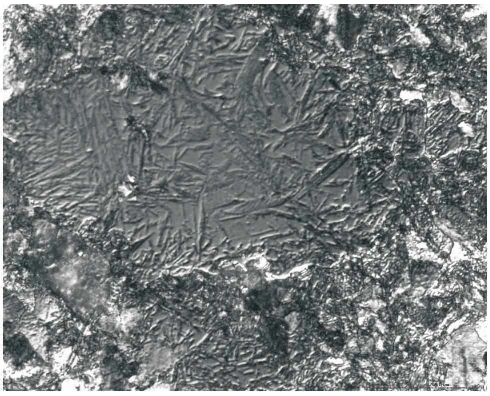


Fig. 4. Microstructure of Fe-3%Mn-3%Cr-0.5%Mo-0.8%C steel, sintered at 1120°C in N_2, mag. 1000×, DIC

The steels sintered at 1200°C contained mainly acicular bainite, tempered martensite and retained austenite, although pearlitic/bainitic regions and undissolved particles of ferromanganese were also observed.

The steels containing 1.5% Cr and 0.25% Mo have more homogeneous microstructure. The subsurface ferritic/pearlitic regions are presented in Fig. 6, whereas the core of the specimens contains fine pearlite and bainite is shown in Figs 7 and 8. Steels sintered in hydrogen show coarser microstructure containing pearlite, bainite and troostite (Fig. 9), as well as tempered martensite and retained austenite (Fig. 10).

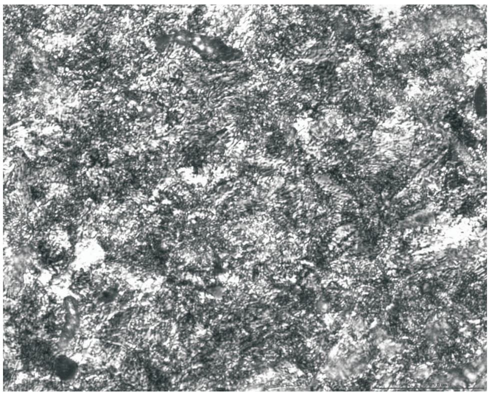


Fig. 5. Microstructure of Fe-3%Mn-3%Cr-0.5%Mo-0.8%C steel, sintered at 1120°C in N_2, mag. 200×, DIC

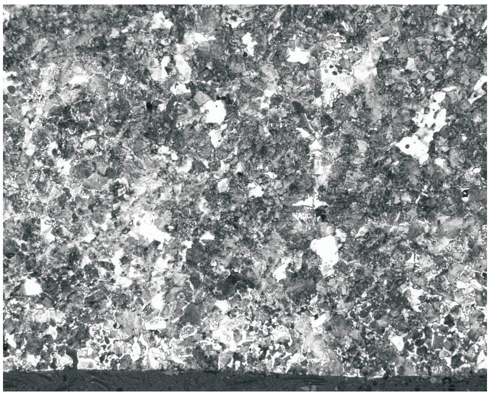


Fig. 6. Microstructure of subsurface layer of Fe-3%Mn-1.5% Cr-0.25%Mo-0.8%C steel, sintered at 1120°C in N_2, mag. 200×, BF

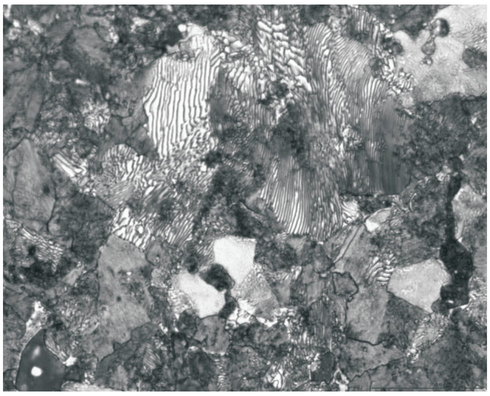


Fig. 7. Microstructure of Fe-3%Mn-1.5%Cr-0.25%Mo-0.8%C steel, sintered at 1120°C in N_2, mag. 1000×, BF

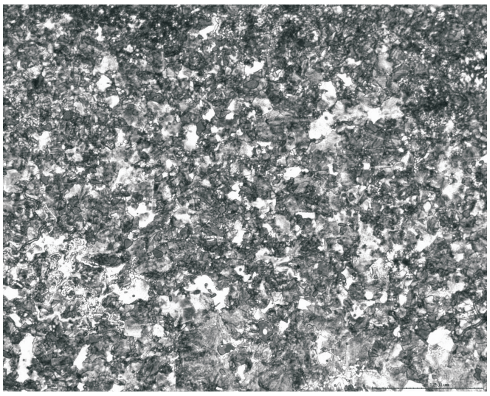


Fig. 8. Microstructure of Fe-3%Mn-1.5%Cr-0.25%Mo-0.8%C steel, sintered at 1200°C in N_2, mag. 200×, BF

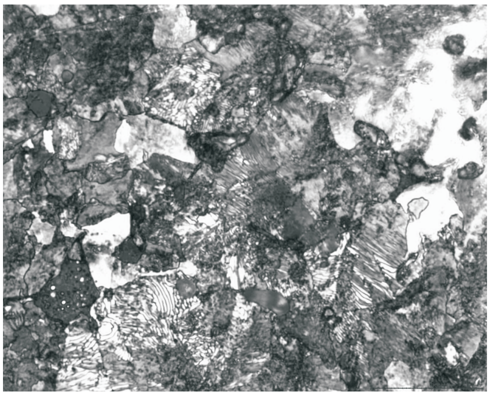


Fig. 9. Microstructure of Fe-3%Mn-3%Cr-0.5%Mo-0.8%C steel, sintered at 1120°C in H_2, mag. 1000×, BF

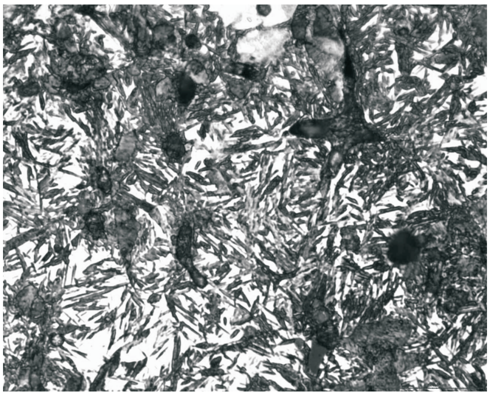


Fig. 10. Microstructure of Fe-3%Mn-3%Cr-0.5%Mo-0.8%C steel, sintered at 1120°C in H_2, mag. 1000×, BF

5. Discussion an conclusion

The qualitative metallography confirmed that manganese has been dissolved in the chromium-molybdenum alloy during sintering and has affected the microstructure formation on cooling.

The mechanical strength results showed negligible effect of the sintering atmosphere. Results obtained from both the tensile and bending test showed a measurable effect of the sintering temperature on strength and ductility of the sintered steel, irrespective of the alloy composition and sintering atmosphere.

The results can be concluded as follows:

1. The optimised chemical composition, alloying technique and processing of PM Mn-Cr-Mo sinter-hardened steels result in relatively high mechanical properties of the material, which can be improved by increasing the sintering temperature from 1120°C to 1200°C. The need for a secondary quench-hardening treatment is thus eliminated.
2. For Fe-3%Mn-1.5%Cr-0.25%Mo-0.8%C steel the best combination of high mechanical strength and good ductility was obtained after sintering at 1200°C in dry hydrogen.
3. It is possible to produce PM Mn-Cr-Mo steels in dry nitrogen atmosphere without decreasing their mechanical properties.
4. For Fe-3%Mn-3%Cr-0.5%Mo-0.8%C steel the highest mechanical strength combined with satisfactory ductility was achieved after sintering at 1200°C in dry nitrogen.

Acknowledgements

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