THE EFFECTS OF HEAT TREATMENT ON THE MICROSTRUCTURE AND MECHANICAL PROPERTIES OF SINTERED Fe-2Cu-1.5Mo-0.5C AND Fe-0.2Mo-1.5Cr-1.5Ni-0.8Mn -0.4C STEELS

Ch. Fial, E. Dudrová, M. Kabátová, M. Kupková, M. Selecká, M. Sulowski, A. Cias

Abstract

Three types of heat treatment in nitrogen were carried out on Fe-2Cu-1.5Mo-0.5C, DH-1, and Fe-0.2Mo-1.5Cr-1.5Ni-0.8Mn-0.4C, 34HNM, steels-sintered in nitrogen in a semi-closed container at 1120°C: sinteraustempering at 350°C, 400°C and 500°C for 60 minutes; cooling at 60°C/minute and tempering at 200°C for 60 minutes; cooling at 10°C/minute (cooling rate used in industrial sintering). The effects of heat treatment on density, microstructure, mechanical properties and fracture of the steels were investigated. Preliminary results, now reported, indicate only minor differences between mechanical properties resulting from the different heat treatments. Currently the best combination of strength and plasticity was achieved after sinteraustempering of Fe-0.2Mo-1.5Cr-1.5Ni-0.8Mn-0.4C at 500°C: yield strength (0.2% offset proof stress) of 409 MPa, UTS of 753 MPa, TRS of 1414 MPa and A of 1.1%.

Keywords: semiclosed container sintering, sinteraustempering, microstructure, mechanical properties

INTRODUCTION

Recently two new techniques for production of sintered alloy steels have been introduced: sinterhardening [1] and sinteraustempering [2]. In the sinterhardening technology martensitic or martensitic+bainitic microstructure is obtained in the sintering furnace, thus eliminating subsequent quenching and tempering heat treatments. For sinteraustempering, the steel is cooled rapidly from the sintering temperature down to the bainitic region, then isothermally annealed to complete the bainitic transformation and subsequently cooled to the room temperature. A disadvantage of this process is the relatively high temperature (~ 500°C) of annealing, encouraging oxidation. To solve this problem vacuum processing has been proposed [2], alternatively, as is proposed in this communication, use of semi-closed container, Fig.1, with a getter addition. The possibilities of using semi-closed containers for conventional sintering in flowing gases (nitrogen, nitrogen-hydrogen, even air) have been recently explored by Cias [3,4] and this communication is a preliminary exploration of applying this technique for sinteraustempering and, for comparison, sinterhardening for two PM steels: Fe-2Cu-1.5Mo-0.5C and Fe-0.2Mo-1.5Cr-1.5Ni-0.8Mn -0.4C. In Figure 2 the explored heat treatments are shown on a schematic TTT diagram.
Fig. 1. The Cias semi-closed container [3,4]: a) with open seal, b) closed with samples, ready for sintering.

EXPERIMENTAL PROCEDURES

The starting powders were:
- Prealloyed iron powder Astaloy CrL (Hoganas),
- Prealloyed iron powder Distaloy DH (Hoganas),
- Graphite powder grade ultra fine (Hoganas),
- Norwegian low carbon ferromanganese powder (Elkem ASA/ Eramet / Comilog Manganese Co.),
- Elemental Ni powder.

From the powders, by Turbula mixing for 60 minutes two mixtures were prepared (Table 1):

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Fe</th>
<th>C</th>
<th>Cu</th>
<th>Mo</th>
<th>Cr</th>
<th>Ni</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>DH-1</td>
<td>96</td>
<td>0.5</td>
<td>2.0</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>34 HNM</td>
<td>95.6</td>
<td>0.4</td>
<td>-</td>
<td>0.2</td>
<td>1.5</td>
<td>1.5</td>
<td>0.8</td>
</tr>
</tbody>
</table>
The powders were single-action compacted into ISO 2740 dog-bone tensile test bars in a steel die with zinc stearate lubricated walls at 660 MPa. The green densities ($d_1$) of compacts were in the range of 6.66-6.67 g/cm$^3$ and 6.65-6.78 g/cm$^3$ for DH-1 and 34 HNM compacts, respectively. Isothermal sintering was carried out in semi-closed container (containing also lumps of ferromanganese), Fig.1b, in a laboratory horizontal tube furnace at 1120°C for 60 minutes with the flowing gas being dry (10 ppm moisture) nitrogen, employing convective (65°C/min.) cooling. The specimens were cooled from the sintering temperature according to the schemes in Fig.2. The as-sintered densities ($d_2$) were in the range of 6.63-6.73 g/cm$^3$ and 6.62-6.73 g/cm$^3$ for DH-1 and 34 HNM sintered steels, respectively. The samples were mechanically tested on a MTS tensile-testing apparatus at a rate of 1 mm/min. and in three-point bending on a ZD-10 tester using a jig with a span of 28.5 mm, at a crosshead rate of 2 mm/min. To examine microstructures and fractures, by light microscopy, a Leica DM LM instrument, and by scanning electron microscopy, a JEOL JSM 7000 F instrument, equipped with EDX, were employed. Hardness was measured on HPK-A/S tester.

RESULTS

Mechanical properties

The results of mechanical testing are shown in Tables 2 and 3. S+C refers to sintering and cooling at 10K/min, SAT to sinteraustempering and S + H to sinterhardening. Yield strength refers to 0.2% offset.

Metallographic investigations were carried out on 3% Nital etched samples. The characteristic microstructures are shown in Figs.3 and 4.

Tab.2. Mechanical properties of DH-1 sintered steels

<table>
<thead>
<tr>
<th>Processing Variant</th>
<th>Yield strength [MPa]</th>
<th>A [%]</th>
<th>UTS [MPa]</th>
<th>TRS [MPa]</th>
<th>HV30 (apparent)</th>
<th>HV30 (cross section)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAT 500°C</td>
<td>413±50</td>
<td>0.7 ± 0.1</td>
<td>514 ± 68</td>
<td>1548 ± 173</td>
<td>207 ± 14</td>
<td>195 ± 7</td>
</tr>
<tr>
<td>SAT 400°C</td>
<td>389±61</td>
<td>0.5± 0.2</td>
<td>483 ± 84</td>
<td>1571 ± 70</td>
<td>180 ± 16</td>
<td>171 ± 8</td>
</tr>
<tr>
<td>SAT 350°C</td>
<td>355±55</td>
<td>0.5± 0.2</td>
<td>446 ± 125</td>
<td>1360 ± 193</td>
<td>178 ± 13</td>
<td>167 ± 27</td>
</tr>
<tr>
<td>S+H</td>
<td>353±86</td>
<td>0.5 ± 0.2</td>
<td>439 ± 77</td>
<td>1460 ± 101</td>
<td>175 ± 23</td>
<td>166 ± 25</td>
</tr>
<tr>
<td>S+C</td>
<td>387±55</td>
<td>0.6 ± 0.2</td>
<td>489 ± 76</td>
<td>1474 ± 137</td>
<td>180 ± 28</td>
<td>188 ± 11</td>
</tr>
</tbody>
</table>

Tab.3. Mechanical properties of 34 HNM sintered steels

<table>
<thead>
<tr>
<th>Processing Variant</th>
<th>Yield strength [MPa]</th>
<th>A [%]</th>
<th>UTS [MPa]</th>
<th>TRS [MPa]</th>
<th>HV30 (apparent)</th>
<th>HV30 (cross section)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAT 500°C</td>
<td>409 ± 21</td>
<td>1.1 ± 0.2</td>
<td>753 ± 67</td>
<td>1414 ± 194</td>
<td>244 ± 28</td>
<td>272 ± 16</td>
</tr>
<tr>
<td>SAT 400°C</td>
<td>436 ± 22</td>
<td>0.9 ± 0.2</td>
<td>668 ± 60</td>
<td>1301 ± 274</td>
<td>213 ± 36</td>
<td>270 ± 18</td>
</tr>
<tr>
<td>SAT 350°C</td>
<td>403 ± 31</td>
<td>0.8 ± 0.3</td>
<td>636 ± 104</td>
<td>1292 ± 204</td>
<td>216 ± 20</td>
<td>252 ± 16</td>
</tr>
<tr>
<td>S+H</td>
<td>432 ± 38</td>
<td>0.8 ± 0.2</td>
<td>674 ± 92</td>
<td>1347 ± 139</td>
<td>223 ± 30</td>
<td>266 ± 14</td>
</tr>
<tr>
<td>S+C</td>
<td>393 ± 27</td>
<td>0.8 ± 0.2</td>
<td>604 ± 49</td>
<td>1361 ± 188</td>
<td>218 ± 25</td>
<td>290 ± 16</td>
</tr>
</tbody>
</table>
Fig. 3. Characteristic microstructures of DH-1 PM steel after heat treatment: a) SAT 500°C, b) SAT 400°C, c) SAT 350°C, d) sinterhardened, e) sintered and cooled.
Fig. 4. Characteristic microstructures of 34 HNM PM steel after heat treatment: a) SAT 500°C, b) SAT 400°C, c) SAT 350°C, d) sinterhardened, e) sintered and cooled.
Microstructure of DH-1 steel

a) Sintering and cooling 10°C/\text{min.}/\text{air}
Microstructure consists of areas of coarse bainite surrounded with fine bainite areas (higher content of Cu, EDS: 0.8-1 at.\% Mo, 4-9 at.\% Cu, 77-79 at.\% Fe). The microstructure has a “network” character (Fig.3c).

b) Sinterhardening: Sintering + rapid cooling (1°C/s) + tempering 200°C/60min/N\textsubscript{2}
Microstructure consists of coarse bainite (EDS: 1 at.\% Mo, 88 at.\% Fe, C), fine bainite (EDS: 1 at.\% Mo, 7 at.\% Cu, 78 at.\% Fe, C), some martensite (up to ~10\%) and areas with precipitated epsilon phase (EDS: 9 at.\% Cu, 80 at.\% Fe, C) (Fig.3d).

c) Sinteraustempering at 500°C
The mixed microstructure consists of upper bainite (90-84 at.\% Fe, C), areas of very fine bainite (EDS: 1-1.7at.\% Mo, 78-92 at.\% Fe, C) and relatively large Cu-rich areas with precipitated epsilon phase (EDS: 0.8 at.\% Mo, 10 at.\% Cu, 77 at.\% Fe, C), mostly surrounded by very fine bainite (Fig.3a).

d) Sinteraustempering at 400°C
Microstructure is mixed, consisting of coarse and fine upper bainite (higher concentration of copper) and some areas of polygonal ferrite with epsilon phase (EDS: 5-9 at.\% Cu, 1-1.3 at.\% Mo, 62-72 at.\% Fe, C) (Fig.3b).

e) Sinteraustempering at 350°C
Microstructure is similar to that of samples sinteraustempered at 500°C, but contains slightly finer bainite and smaller Cu-rich areas (EDS: 5.5-6 at.\% Cu, 0.8-1 at.\% Mo, 68-76 at.\% Fe) (Fig.3c).

Microstructure of 34 HNM steel

a) Sintering and cooling at 10°C/\text{min.}/\text{air}
The microstructure is heterogeneous, consisting of areas of pearlite/ferrite (low or not alloyed), bainite and austenite/martensite/bainite alloyed with Ni and Mn (Fig.4e).

b) Sinterhardening: Sintering + rapid cooling (1°C/s) + tempering 200°C/60min/N\textsubscript{2}
The microstructure is heterogeneous, consisting of bainitic matrix, austenite/martensite/ bainite areas alloyed with Ni, and areas alloyed with Mn. The remnants of the FeMnC particles and secondary phase particles on the surfaces of the original particles (oxides) and along the boundaries of the original austenite grains (carbides) are visible in the unetched state (Fig.4d).

c) Sinteraustempering at 500°C
The microstructure is heterogeneous, consisting of a bainitic matrix, areas alloyed with nickel (Ni-austenite, Ni martensite), areas alloyed with Mn (FeMnC) and remnants of ferromanganese particles. As Ni was added as a carbonyl powder, it became agglomerated and so austenite/martensite areas are relatively large. In the unetched microstructure fine and coarser oxide particles are visible. It seems that the boundaries of original austenite grains are “marked” with carbides (Fig.4a).

d) Sinteraustempering at 400°C
The heterogeneous microstructure of samples sinteraustempered at 400°C is similar to that after sinteraustempering at 500°C - consisting of bainitic matrix with some polygonal ferrite, fine bainite (often located near Ni-rich structures), areas alloyed with nickel (Ni-austenite and Ni martensite) and areas alloyed with Mn (the remnants of ferromanganese) (Fig.4b).

e) Sinteraustempering at 350°C
Microstructure of samples sinteraustempered at 350°C is similar to those observed after processing at 400 and 500°C - the microstructure is heterogeneous, consisting of bainitic, sometimes fine, matrix with some ferrite (slightly higher amount than for sample after SAT at 400°C), austenite/martensite/bainite areas alloyed with Ni, and areas alloyed with Mn (the remnants of ferromanganese particles are visible) (Fig.4c).

**Fractography**

The fracture surfaces of the variously processed and tensile tested steels are shown in Figs.5 and 6.

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Fig.5. Characteristic fractographs of DH-1 PM steel after heat treatment: a) SAT 500°C, b) SAT 400°C, c) SAT 350°C, d) sinterhardened, e) sintered and cooled.
Fig. 6. Characteristic fracture of 34 HNM PM steels after different heat treatment: a) SAT 500°C, b) SAT 400°C, c) SAT 350°C, d) sinterhardened, e) sintered and cooled.

Fractography of DH-1 steel
a) Sintering and cooling at 10°C/min/air
   Failure was by interparticle ductile fracture with fine shallow dimples and large dimples initiated by MnS inclusions (EDS: 25-26 at.% S and 27-38 at.% Mn, rest Fe). Sporadic occurrence of cleavage facets was detected. After TRS test the same type of fracture was observed, but without cleavage. Probably, as in later similar SEM
observations, this is due to examining fields close to the surface, where there was higher porosity (Fig.5e).

b) Sinterhardening: Sintering + rapid cooling (1°C/s) + tempering 200°C/60min/N₂. The failure was by interparticle ductile fracture with fine shallow dimples and relatively large cleavage facets – probably in areas of very fine bainite or martensite. Coarse shallow dimples were initiated by spherical MnS inclusions (EDS: 25 at.% S, 24 at.% Mn, rest Fe). After TRS testing similar fractures, including cleavage facets, were observed (Fig.5d).

c) Sinteraustempering at 500°C
Fractography revealed interparticle ductile fracture with fine shallow dimples. Failure took place along surfaces of bainite packets when fine shallow dimples were initiated by fine carbides. Cu-rich areas with epsilon phase failed in a ductile mode with fine dimples and with local plastic flow. Coarse shallow dimples were initiated by spherical MnS inclusions (EDS: 41 at.% S and 42 at.% Mn, rest Fe). Rare transgranular cleavage facets were very small, up to 5 microns in size. Pores and fine particulates, e.g. FeMoC carbides, were detected. After TRS testing very similar fracture behaviour was observed (Fig.5a).

d) Sinteraustempering at 400°C
Fracture of the steel is very similar to that sinteraustempered at 500°C. Failure in fine bainitic areas was probably also through the epsilon phase. After TRS testing cleavage was not detected (Fig.5b).

e) Sinteraustempering at 350°C
Interparticle ductile fracture was observed with fine shallow dimples and sporadic occurrence of cleavage facets in fine bainite. TRS testing resulted in similar observations, but not of cleavage (Fig.5c).

**Fractography of 34 HNM steel**

a) Sintering and cooling at 10°C/min/air
In tensile failure, predominant was interparticle ductile fracture with fine and coarse shallow dimples. The development of local plastic flow was also detected. After TRS testing, the same fracture behaviour was observed (Fig.6e).

b) Sinterhardening: Sintering + rapid cooling (1°C/s) + tempering 200°C/60 min/N₂
Fractures after tensile and TRS testing exhibit ductile failure with fine and coarse shallow dimples initiated by oxide particles, and fine shallow dimples along bainite packets. The development of local plastic flow was observed (Fig.6d).

c) Sinteraustempering at 500°C
In tensile and bend fractures, predominat was the interparticle ductile failure with fine and coarse shallow dimples, failure along prior particle surfaces initiated by oxide particles (complex Cr, Mn,[Si] oxides) and areas with fine shallow dimples, when the failure along bainite packets is initiated by carbides (Fig.6a).

d) Sinteraustempering at 400°C
After tensile and bend testing, again the predominat was interparticle ductile fracture with fine and coarse shallow dimples. In the vicinities of the remnants of original FeMnC particles, intergranular fracture facets were detected, typical feature of alloying through FeMnC particles. Such sites give rise to large defects, in this case up to 300 microns. Development of local plastic flow was observed (Fig.6b).

e) Sinteraustempering at 350°C
The tensile and bend fractures were similar to those of other SAT specimens, i.e. interparticle ductile fracture with fine and coarse shallow dimples initiated by oxide particles, areas with fine shallow dimples (along bainite packets). Cleavage fracture was observed more often than for sample after SAT at 400°C. Development of local plastic flow was observed (Fig.6c).

DISCUSSION

Among the metallurgical features of DH-1 and 34HNM steels, probably the most important are high bainitic hardenability and formation of stable and competing alloy carbides. A high bainitic transformation means that steel transforms to a fully bainitic microstructure over a wide range of cooling rates. This feature makes the steel suitable for sinteraustempering. In 34HNM the well-balanced chromium and molybdenum contents of the steel stabilize various alloy carbides such as $M_2C$, $M_7C_3$, and $M_{23}C_6$.

One of the most striking features of the TTT diagrams for DH-1 and 34HNM steels is the wide range of transformation temperatures over which bainite is the predominant austenite transformation product. A convenient parameter for expressing the bainitic hardenability is the critical cooling rate for polygonal ferrite and pearlite formation. This is the lowest rate at which the steel can be cooled and still attain a structure free from polygonal ferrite. The critical cooling rate for polygonal ferrite formation of DH-1 steel is about 60°C/min. Modified Astaloy CrL steel, such as the one containing Ni and Mn at the high side of the specified ranges and 0.4C (34HNM) exhibit a fully bainitic microstructure in sinteraustempered specimens. The tensile strength of the DH-1 steel is satisfactory for MPIF grade FLN2-4405: 0.8Mo-2.0Ni-0.7Cr-0.1Mn, and even FL-4205-HT, FL-4605-HT, FD-0205-HT, and FD-0405-HT.

Raising the austenitizing temperature of steel 34HNM from 900 to 1120°C leads to an increase of the initial bainitic transformation temperature and an associated increase in the amount of lower bainite after isothermal transformation, which is manifest in higher bainitic hardenability [5].

It is reassuring that all the specimens, regardless of heat treatment variations, exhibited ductility. This demonstrates that use of semi-closed containers can be extended from conventional sintering technology to sinter-hardening and sinteraustempering. It is of particular importance for the latter, since it would not require expensive vacuum processing. On the basis of these preliminary data, it appears that mechanical properties of 34 HNM are marginally better than of DH-1. The various heat treatments either did not produce large property differences, though the indication is that sinteraustempering at 500°C gave marginally the best combination of strength and plasticity for both steels. More work is needed to optimise processing. One of the surprising features are the very high TRS/UTS ratios for DH-1. Again, detailed analysis of mechanical properties and failure mechanisms is called for. Such experiments are in train.

The most relevant literature set of results for comparison are those of Girardini et al. [2] who similarly experimented with Fe-3% Cr-0.5 Mo -0.35/0.5 C steels, but by vacuum processing. They reported that, once the cooling strategy has been set up, austempering was combined to sintering in a single sinteraustempering process aimed at obtaining a fully lower bainitic microstructure. Their mechanical properties were slightly lower than those attainable with sinterhardening, but pieces did not require any tempering. They concluded that a further improvement of properties may be expected. The preliminary set of results on further two steels now reported on indicates that the properties now attained are slightly higher. The authors join Girardini et al. in anticipating that further experimentation will lead to a further improvement in properties.
CONCLUSIONS

1. Semi-closed container processing is a satisfactory technique, on a laboratory scale, for sinter-hardening and sinteraustempering.

2. Fe-2Cu-1.5Mo-0.5C, DH-1 and Fe-0.2Mo-1.5Cr-1.5Ni-0.8Mn -0.4C, 34HNM, have been processed successfully, all specimens exhibiting ductility, using conventional PM, sinter-hardening and sinteraustempering experimental procedures.

3. The preliminary results did not detect marked differences between various heat treatments, but the indications are that, for both steels, sinteraustempering is the optimum (so far explored) processing procedure.

4. The best combination of strength and ductility was recorded for sinteraustempered Fe-0.2Mo-1.5Cr-1.5Ni-0.8Mn -0.4C steel at 500°C: yield strength of 409 MPa, UTS of 753 MPa, TRS of 1414 MPa and A of 1.1%.

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