PERFORMANCE OF SINTER-HARDENED P/M STEELS

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ABSTRACT
Cost reduction with maintained mechanical properties is the key to preserve the strong growth of the P/M industry. Heat treatments have since long time been used to achieve a martensitic structure either at the surface or throughout a part. By combining tailor made alloying systems with sinter-hardening the required amount of martensite can be obtained directly after sintering. Pre-alloyed materials like Astaloy A, Astaloy Mo with copper additions and Astaloy CrM are suitable for sinter-hardening. In this paper mechanical properties and performance of sinter-hardened materials are discussed. It is found that different materials are to be used depending on the process route. Material selection is of importance to benefit the most from sinter-hardening.

KEYWORDS: sinter-hardening, steel, high strength, rapid cooling, powder metallurgy

INTRODUCTION
Sinter-hardening refers to a process where the cooling rate experienced in the cooling zone of the sintering furnace is fast enough that more than 50% martensite forms. The amount of martensite present in a material is dependent not only on the cooling rate, but also on the alloying element content, mass, density and geometry of a part. Alloying elements such as chromium, molybdenum, manganese, nickel and copper increase the hardenability or the ability of a material to form martensite when cooled from a temperature in the austenitic region. For larger parts either higher cooling rates or higher amount of alloy content are needed to get a given amount of martensite. For P/M steels the sintered density is an additional variable, which influence the hardenability as it influences thermal conductivity and therefore the cooling rate of the part (1).

In this paper the influence of cooling rate, alloying element content and density on hardenability and mechanical properties of different P/M materials is investigated.

EXPERIMENTAL PROCEDURE
Materials
Four materials based on the prealloyed powder grades Astaloy Mo, Astaloy CrM, Astaloy A and Astaloy B were investigated. Astaloy Mo is prealloyed with Mo, Astaloy A and Astaloy B are prealloyed with Ni, Mo and Mn while Astaloy CrM is prealloyed with Cr and Mo. See table 1. All powder grades, except for Astaloy CrM were admixed with 2% Cu and Kropfmühl graphite UF4 (96/97% C).

Table 1: Chemical composition of the base powders investigated

<table>
<thead>
<tr>
<th>Grade</th>
<th>Ni %</th>
<th>Mo %</th>
<th>Cr %</th>
<th>Mn %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Astaloy Mo</td>
<td>1,5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Astaloy A</td>
<td>1,90</td>
<td>0,5</td>
<td>0,2</td>
<td></td>
</tr>
<tr>
<td>Astaloy B</td>
<td>0,45</td>
<td>0,6</td>
<td>0,3</td>
<td></td>
</tr>
<tr>
<td>Astaloy CrM</td>
<td></td>
<td>0,5</td>
<td>1,5</td>
<td></td>
</tr>
</tbody>
</table>
Processing conditions
Design of experiment methodology was used to plan and evaluate the experiments. The influence of variations in cooling rate, density and carbon content on the apparent hardness HV10, tensile and yield strength were evaluated. The investigated materials were tested for densities in the range 6,9-7,2 g/cm³, cooling rates in the range 1-6 °C/s and carbon contents in the range 0,45-0,9% for the Astaloy A, Astaloy Mo and Astaloy B based materials and carbon content in the range 0,35-0,55% for the Astaloy CrM based material.

The specimens, tensile testing bars according to ISO standard 2470-1986 with a length of 90 mm were compacted in a Tonitechnik semiautomatic laboratory press. The parts were compacted at different pressures to achieve three different density levels 6,9, 7,0 and 7,2 g/cm³. The density levels 6,9 and 7,0 g/cm³ were achieved by cold compaction of mixes containing 0,8% Amide-wax as a lubricant. The highest density level, 7,2 g/cm³ was achieved by using warm compaction in combination with Densmix™ powders containing 0,6% Lube. As the base powders investigated have different compressibility different compacting pressures are needed to achieve a given green density. Table 2 summarises the green density of Astaloy A, Astaloy Mo, Astaloy B and Astaloy CrM admixed with 0,6% Kenolube when compacted at 600 and 800 MPa.

Table 2: Compressibility of the investigated materials. Compacting pressure 600 and 800 MPa with 0,6% Kenolube.

<table>
<thead>
<tr>
<th>Material</th>
<th>GD 600 MPa (g/cm³)</th>
<th>GD 800MPa (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Astaloy Mo</td>
<td>7,10</td>
<td>7,32</td>
</tr>
<tr>
<td>Astaloy A</td>
<td>6,98</td>
<td>7,19</td>
</tr>
<tr>
<td>Astaloy B</td>
<td>7,06</td>
<td>7,26</td>
</tr>
<tr>
<td>Astaloy CrM</td>
<td>6,98</td>
<td>7,19</td>
</tr>
</tbody>
</table>

Astaloy Mo has highest compressibility while Astaloy A and Astaloy CrM have lowest compressibility among the investigated materials.

Sintering was carried out in a laboratory-sintering furnace from ABBOT. The furnace was equipped with a system, VARICOOL, for increasing the cooling rate. The parts were sintered at 1120 °C for 30 minutes in a mixture of 80/20 nitrogen/hydrogen. In order to achieve different cooling rates the VARICOOL unit was set to 0, 15 and 60 Hz. After sintering tempering was carried out at 200 °C in air for 60 minutes.

Testing
Hardness was tested with the Vickers method (HV10). Tensile testing was performed in a MTS Sintech 20D tensile testing machine. The elongation was measured over a gauge length of 25 mm by extensometer. The amount of phases present after sintering was evaluated by help of an image analyser.

RESULTS
Evaluation of cooling rate by metallography
In order to find out what is the cooling rate corresponding to the settings 0, 15 and 60 Hz of the Varicoool unit a material made of Distaloy DC-1+ 0,5% C was sintered together with the materials summarised in table 1. Distaloy DC-1 is alloyed with 2% nickel and 1,5% molybdenum and is manufactured by diffusion annealing Astaloy Mo with 2% nickel.

Figure 1 shows the CCT diagram and phase amount diagram derived from samples cooled at different rates in a dilatometer, for Distaloy DC-1 with 0,5% carbon. The phase amount reported in
Figure 1b is corrected for the porosity present in the material. The microstructure of Distaloy DC-1+0.5%C consists of a mixture of bainite and martensite for cooling rates in the range 0.1-8 °C/s. For cooling rates higher than 8 °C/s the material consists of 98% martensite. Due to the presence of nickel 2% austenite is present in the microstructure, independently on the cooling rate. As the amount of martensite continuously increases for a wide interval of cooling rates this material was judged to be suitable for estimating the cooling rate corresponding to different settings of the Varicool unit.

**Fig 1a:** CCT diagram for Distaloy DC-1+0.5%C. Cooling from 1120 °C

**Fig 1b:** Phase amount vs cooling rate for Distaloy DC-1+0.5%C. Cooling from 1120 °C/s
The microstructures of Distaloy DC-1 with 0.5% carbon representative for the different settings of the Varicool unit are illustrated in figure 2.

By comparing the amount of phases obtained when setting the Varicool unit at 0, 15 and 60 Hz with figure 1b information regarding the cooling rate at which the investigated samples were cooled can be obtained. The setting 0 Hz corresponds to a cooling rate of 1°C/s, the setting 15 Hz corresponds to a cooling rate of 2.5°C/s, and finally the setting 60 Hz corresponds to a cooling rate of 6°C/s. A slight scatter in phase amount was found between samples cooled with the same setting of the Varicool unit. Therefore, it has been estimated that 0 Hz corresponds to a cooling rate of 1-1.5°C/s, 15 Hz corresponds to a cooling rate of 2-3°C/s and 60 Hz corresponds to a cooling rate of 5-6°C/s.

**Influence of carbon content, cooling rate and density on mechanical properties**

The apparent hardness and mechanical properties for the investigated materials are compared at three density levels, for two carbon contents, at the cooling rates of 1-1.5, 2-3 and 5-6°C/s.

To start with the influence of variations in carbon content and cooling rate on the mechanical properties of the investigated materials are compared at the density of 7.0 g/cm³. The carbon content chosen are 0.65% and 0.8% for the Astaloy A, Astaloy B and Astaloy Mo based material, 0.45% and 0.55% for the Astaloy CrM based material. Finally the apparent hardness and mechanical properties of the Astaloy A, Astaloy Mo and Astaloy B based materials with 0.8% carbon and of the Astaloy CrM based material with 0.55% carbon are compared at the density levels of 6.9 and 7.2 g/cm³.

The carbon content always refers to the combined carbon, analysed after sintering.

**Influence of carbon content and cooling rate on mechanical properties**

Figure 3 shows the influence of carbon content and cooling rate on the apparent hardness HV10, yield and tensile strength of the investigated materials at the density level of 7.0 g/cm³.
The apparent hardness, HV10, increases with increased carbon content and/or cooling rate. For Astaloy CrM with 0.55%C similar hardness is found when increasing the cooling rate from 2-3 to 5-6 °C/s. The hardness of Astaloy A with 0.8%C is almost independent on the cooling rate. Astaloy CrM with 0.55%C and Astaloy A with 2%Cu and 0.8%C achieve highest apparent hardness (HV10=400), when the lowest cooling rate is chosen. Highest hardness (HV10=450) is obtained when cooling the Astaloy Mo based material with 0.8% carbon at the rate of 5-6 °C/s.

The yield strength of the Astaloy B based material with 0.65 and 0.8% carbon cooled at 5-6 °C/s and that of the Astaloy CrM material with 0.55% carbon cooled at the rate of 2-3 and 5-6 °C/s are not reported as the elongation at break is lower than 0.2%.

The 0.2% offset yield strength values of the materials with lowest carbon content increases with increasing cooling rate except for the Astaloy B based material cooled at 5-6 °C/s. The yield strength improves with 30% both for the Astaloy Mo and Astaloy CrM based materials when going from the lowest to the highest cooling rate. The material based on Astaloy CrM has highest yield strength when cooling at the rate of 2-3 and 5-6 °C/s. The yield strength is 950 MPa for the cooling rate 2-3 °C/s and 1000 MPa for the cooling rate 5-6 °C/s. The Astaloy B based material has lowest yield strength at the cooling rates tested.

For the Astaloy A and Astaloy Mo based materials with 0.8%C the yield strength is constant or lower if compared to the materials with lower carbon content. For the Astaloy B based materials the yield strength increases with increased carbon content at the cooling rates of 1-1.5 °C/s and 2-3
°C/s. The yield strength of the Astaloy CrM based material increases with increased carbon content at the cooling rate 1-1,5 °C/s.

For the materials with low carbon content the tensile strength increases with increasing cooling rate. The Astaloy Mo and the Astaloy CrM based materials achieve a tensile strength over 1000 MPa. However, for the Astaloy CrM material such strength is obtained at the cooling rate of 1-1,5 °C/s while for the Astaloy Mo material a cooling rate of 5-6 °C/s is needed. The increase in cooling rate resulted in an improvement in tensile strength from 850 to 1025 MPa for the Astaloy Mo based material. The Astaloy CrM and Astaloy A based materials show a slight increase in tensile strength when going from the lowest to the highest cooling rate. Astaloy A and Astaloy Mo show a similar tensile strength when cooled at a rate of 2-3 °C/s.

When increasing the carbon content the tensile strength decreases or remains constant for all materials investigated, when the comparison is made at the same cooling rate. For the materials based on Astaloy Mo and Astaloy B with 0.8% carbon the tensile strength increases with the cooling rate. For the Astaloy A material with 0.8% carbon and the Astaloy CrM material with 0.55% carbon the tensile strength decreases with increased cooling rate.

The elongation is below 0.5% for all investigated materials. For the Astaloy B material with 0.65 and 0.8% carbon cooled at 5-6 °C/s and the Astaloy CrM material with 0.55% carbon cooled at 2-3 °C/s and 5-6 °C/s the elongation is lower than 0.2%.

**Influence of density and cooling rate on mechanical properties**

The influence of the density and cooling rate on the mechanical properties of the materials with highest carbon content (0.8% combined carbon for Astaloy A, Astaloy Mo, Astaloy B and 0.55% for Astaloy CrM) are presented in figure 4.

The apparent hardness and tensile strength increase with increasing density from 6.9 to 7.2 g/cm³ at all cooling rates investigated. The yield strength increases with increased density for the Astaloy Mo and Astaloy A based material. For the Astaloy B material the yield strength increases with increased density at the cooling rates 1-1,5 °C/s and 2-3 °C/s. The yield strength is not reported when the elongation at break is < 0.2%.

The influence of the cooling rate on the apparent hardness and mechanical properties at the density levels of 6.9 and 7.2 g/cm³ is similar to that observed for the materials with density 7.0 g/cm³ and same carbon content. No significant improvement in elongation is observed when increasing the density from 6.9 to 7.2 g/cm³.
**Fig 4a:** Hardness at the density 6.9 and 7.2 g/cm³

**Fig 4b:** Yield strength at the density 6.9 and 7.2 g/cm³

**Fig 4c:** Tensile strength at the density 6.9 and 7.2 g/cm³
Metallographic investigation
The materials were studied in a light optical microscope. The amount of bainite, martensite and residual austenite found when cooling at 1-1.5 °C/s and 5-6 °C/s are summarised in table 3.

Table 3: Phase amount after cooling at 1-1,5 and 5-6 °C/s.

<table>
<thead>
<tr>
<th>Mtrl</th>
<th>1-1,5 °C/s</th>
<th>5-6 °C/s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B%</td>
<td>M%</td>
</tr>
<tr>
<td>AstMo+2Cu+0,6C</td>
<td>≈70</td>
<td>≈30</td>
</tr>
<tr>
<td>AstMo+2Cu+0,8C</td>
<td>≈40</td>
<td>≈60</td>
</tr>
<tr>
<td>AstA+2Cu+0,6C</td>
<td>≈10</td>
<td>≈90</td>
</tr>
<tr>
<td>AstA+2Cu+0,8C</td>
<td>≈5</td>
<td>≈95</td>
</tr>
<tr>
<td>AstB+2Cu+0,7C</td>
<td>≈35</td>
<td>≈65</td>
</tr>
<tr>
<td>AstCrM+0,45C</td>
<td>≈25</td>
<td>≈75</td>
</tr>
<tr>
<td>AstCrM+0,55C</td>
<td>≈10</td>
<td>≈90</td>
</tr>
</tbody>
</table>

The amount of bainite and martensite was evaluated for the Astaloy CrM material with 0,45%C and the Astaloy A based material with 0,6% carbon cooled at the rate of 2-3 °C/s. The Astaloy CrM based material consists of 100% martensite, while the Astaloy A based material consists of 95% martensite and 5% bainite.

The amount of martensite increases with increased carbon content and cooling rate. If one defines that a material is hardened when the amount of martensite is more than 50% all investigated materials are hardened at the cooling rate of 1-1,5 °C/s except for the Astaloy Mo material with 0,6% carbon.

For the Astaloy A and Astaloy CrM based materials a cooling rate between 2-3 °C/s is sufficient to obtain >90% martensite at the lowest carbon levels. At the highest carbon level >90% martensite can be obtained at the cooling rate of 1-1,5 °C/s. Very small amounts of residual austenite were found in the Astaloy Mo and Astaloy A based materials with 0,8% carbon and cooling rate 5-6 °C/s. For Astaloy B with 0,7% carbon and 2% Cu 10% bainite is present after cooling at the rate of 5-6 °C/s.

DISCUSSION
Hardness and tensile strength reach their maximum for different carbon contents. The Astaloy A, Astaloy CrM and Astaloy Mo materials achieve the highest hardness for the highest carbon content tested and the highest yield and tensile strength for the lowest carbon content tested. With increased carbon content the martensite becomes more fragile, which results in increased hardness and decreased mechanical properties. For each material the carbon content should be chosen depending on the applications and the cooling rate available in the sintering furnace. As an example one can obtain a similar hardness when cooling the Astaloy A material with 0,65% C at the rate of 5-6 °C/s or the Astaloy A based material with 0,8% C at the rate of 1-1,5 °C/s.

The variations in apparent hardness, yield and tensile strength observed when increasing the carbon content and/or the cooling rate can be explained through the materials microstructure.

Astaloy CrM has the highest hardenability as 90% martensite is obtained without any copper additions, a carbon content of 0,55% and a cooling rate of 1-1,5 °C/s.
The Astaloy B based material has least hardenability. The martensite content in the Astaloy B based material with 0,7% carbon cooled at 5-6 °C/s is 90%. The Astaloy Mo and Astaloy A materials with 0,6% carbon and the Astaloy CrM material with 0,45%C have >99% martensite when cooled at the same rate.

The increase in hardness, yield and tensile strength observed for the Astaloy Mo and Astaloy B materials with 0,65 and 0,8% carbon when increasing the cooling rate is due to the increased amount of martensite.

For Astaloy CrM with 0,45% carbon an increase in hardness with 12% and 23% in yield strength is observed when increasing the cooling rate from 1-1,5 °C/s to 2-3 °C/s. An increase in hardness and yield strength with 5% is achieved when further increasing the cooling rate. The reason for this is that the amount of martensite increases from 75% to 100% when increasing the cooling rate from 1-1,5 °C/s to 2-3 °C/s. No change in microstructure is observed when cooling at rates ≥ 2-3 °C/s.

For the Astaloy CrM material with 0,55% carbon 90% martensite is present at the cooling rate of 1-1,5 °C/s. As the apparent hardness increases with approx. 7%, when increasing the cooling rate from 1-1,5 to 2-3 °C/s, and does not increase any further when cooling at 5-6 °C/s a totally martensitic structure is obtained at the cooling rate 2-3 °C/s.

For the Astaloy A based material with 0,65% carbon an increase in apparent hardness and yield strength with approx. 10% and an increase in tensile strength with 5% is obtained when going from the lowest to the highest cooling rate. The increase in hardness and yield strength, with increased cooling rate, is more modest if compared to Astaloy CrM with 0,45% carbon. The reason for this is that the microstructure of the Astaloy A material with 0,65% carbon consists of 90% martensite, while that of Astaloy CrM with 0,45% carbon consists of 75% martensite, at the lowest cooling rate. As 95% martensite is obtained when cooling the Astaloy A based material with 0,8% C at 1-1,5 °C/s a similar hardness is obtained for all cooling rate tested.

For all investigated materials the hardness increases with increased carbon content. In the case of the Astaloy Mo and Astaloy A based materials with 0,8% carbon small amounts of retained austenite were found when cooling at 5-6 °C/s. This indicates that a further increase in carbon content would not lead to an increase in hardness. As no traces of retained austenite are found in Astaloy CrM with 0,55%C the hardness of this material can be increased by increasing the carbon content up to 0,6-0,7%.

When choosing the Astaloy A and Astaloy CrM based materials with highest carbon content more than 90% martensite and a hardness of 400 Vickers unit can be obtained at the cooling rate of 1-1,5 °C/s. Highest hardness, 450 Vickers units is obtained when choosing the Astaloy Mo based material with 0,8% carbon cooled at 5-6 °C/s. Highest yield and tensile strength, >1000 MPa, are obtained when choosing Astaloy CrM with 0,45% carbon. This when considering a density of 7,0 g/cm³.

CONCLUSIONS

- For the Astaloy CrM based material no copper additions are needed for obtaining 90% martensite at the cooling rate of 1-1,5 °C/s.
- A hardness of 400 HV10 is achieved by the Astaloy CrM material with 0,55% carbon and by the Astaloy A material with 0,8% carbon at the density of 7,0 g/cm³, cooled at 1-1,5 °C/s. A hardness of 450 HV10 is achieved by the Astaloy Mo based material with 0,8% carbon, cooled at 5-6 °C/s.
The Astaloy CrM material with 0.55%C has similar or higher hardness if compared to the Astaloy A material with 0.8% carbon. Higher hardness can be achieved with Astaloy CrM when increasing the carbon content to 0.6-0.7%.

A yield strength >900 MPa is achieved by the Astaloy CrM material with 0.45%C cooled at rates ≥2-3 °C/s and by the Astaloy Mo material with 0.65% carbon cooled at the rate of 5-6 °C/s.

A tensile strength >1000 MPa is obtained when choosing Astaloy CrM with 0.45%C cooled at rates ≥1-1.5 °C/s and the Astaloy Mo material with 0.6% C, cooled at the rate of 5-6 °C/s.

The Astaloy B based material has least hardenability. A bainite content of 10% is present when cooling the Astaloy B material with 0.7% carbon at the rate of 5-6 °C/s.

REFERENCES
