Abstract: Sinter-hardening is a cost-effective process, as it combines sintering and hardening operation in one step. Utilisation of the sinter-hardening process in combination with tailor made alloying system gives a unique combination of strength, toughness and hardness. A variety of microstructures are obtained by changing the post-sintering cooling rate, type and amount of alloying elements. Carbon, molybdenum, copper, nickel and chromium prealloyed and/or admixed with iron promote its hardenability. By using tailor made alloying system different amount of martensite and as a consequence different mechanical properties are obtained after sintering. This paper gives a general overview of the properties and microstructures that are obtained for sinter-hardening materials. Focus is paid on PM materials prealloyed with chromium, molybdenum and nickel with and without additions of copper.

Introduction
Sinter hardening can be defined as a process where the cooling rate experienced in the cooling zone of a sintering furnace can be accelerated to achieve more than 50% martensite. The major advantages with sinter hardening are cost savings and the possibility to control the microstructure in the produced parts. Many P/M parts are heat treated, in a secondary operation to achieve a martensitic structure. By accelerating the post sintering cooling rate the desired amount of martensite, and as a consequence the desired hardness and mechanical properties, can be obtained directly after sintering. 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. Allying 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 influences 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 are investigated.
Experimental procedure

Materials

Six materials based on Distaloy DH-1, Astaloy CrM and Astaloy A were investigated. The chemical composition of the base powders used is reported in table 1.

<table>
<thead>
<tr>
<th>Grade</th>
<th>Ni %</th>
<th>Mo %</th>
<th>Cr %</th>
<th>Mn %</th>
<th>Cu %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distaloy DH-1</td>
<td>1.5</td>
<td></td>
<td></td>
<td></td>
<td>2*</td>
</tr>
<tr>
<td>Astaloy A</td>
<td>1.90</td>
<td>0.5</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Astaloy CrM</td>
<td>0.5</td>
<td>1.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Diffusion bonded

All powder grades were admixed with two different contents of Kropfmülf graphite UF4% (96-97 % C). For the materials based on Astaloy A 2% copper was added. The chemical composition of the materials studied is summarised in table 2.

<table>
<thead>
<tr>
<th>Grade</th>
<th>Cu %</th>
<th>C%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distaloy DH-1</td>
<td>0.65/0.8</td>
<td></td>
</tr>
<tr>
<td>Astaloy A</td>
<td>2</td>
<td>0.65/0.8</td>
</tr>
<tr>
<td>Astaloy CrM</td>
<td>0.45/0.55</td>
<td></td>
</tr>
</tbody>
</table>

Experimental procedure

The influence of variations in cooling rate, density and carbon content on the dimensional change apparent hardness HV10, tensile and yield strength of the materials in table 2 were evaluated. For the evaluation of hardness and mechanical properties 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 cold compacted to achieve two different density levels, 6.9 and 7.0 g/cm³, after sintering. The compacting pressure was different for the different powder grades tested due to their different compressibility. Distaloy DH-1 has higher compressibility (7.13 g/cm³ at 600 MPa when admixed with 0.6% Kenolube) than Astaloy A and Astaloy CrM (6.98 g/cm³ at 600 MPa when admixed with 0.6% Kenolube). 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 and were cooled at three different rates: 1-1.5° C/s, 2-3° C/s, 5-6° C/s. As a scatter in cooling rate was observed an interval is given (2). After sintering tempering was carried out at 200° C in air for 60 minutes.

CCT diagrams were prepared for the investigated materials and phase analysis was carried out, by help of an image on the samples cooled at different rates in the dilatometer.
Results

Dimensional change

The influence of variations in carbon content and cooling rate on the dimensional change was examined. The results obtained at the density level of 7.0 g/cm$^3$ are summarised in fig. 1.

The materials containing copper (Distaloy DH-1 and Astaloy A) swell during sintering while the Astaloy CrM based materials, not containing copper, shrink during sintering.

Hardness and mechanical properties

Figure 2 shows the influence of carbon content, density and cooling rate on the apparent hardness HV10, yield and tensile strength of the investigated materials.

Fig 2a: Hardness HV10, density 6.9 g/cm$^3$

Fig 2b: Hardness HV10, density 7.0 g/cm$^3$

Fig 2c: Yield strength, density 6.9 g/cm$^3$

Fig 2d: Yield strength, density 7.0 g/cm$^3$
The apparent hardness, HV10, increases with increased density. At one and same density it increases with increased carbon content. 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 material 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, d=7.0 g/cm³), when the lowest cooling rate is chosen. Highest hardness (HV10=450, d=7.0 g/cm³) is obtained when cooling the Distaloy DH-1 with 0.8% carbon at the rate of 5-6° C/s.

The yield strength has not been reported for the materials having an elongation at break lower than 0.2%. The yield strength values of the materials with lowest carbon content increases with increased cooling rate. The yield strength improves with 30% both for the Distaloy DH-1 and Astaloy CrM based materials at the density of 7.0 g/cm³ when going from the lowest to the highest cooling rate. The material based on Astaloy CrM (density 7.0 g/cm³) has highest yield strength when cooled at the rate of 2-3 and 5-6° C/s (950 MPa and 1000 MPa respectively). For the Astaloy A and Distaloy DH-1 materials with 0.8%C the yield strength is constant or lower if compared to the materials with lower carbon content. 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 lowest carbon content the tensile strength increases with increased cooling rate. However, the increase in tensile strength is larger for the Distaloy DH-1 material (20%) if compared to the Astaloy A and Astaloy CrM materials (5 and 2% respectively). The Distaloy DH-1 and the Astaloy CrM based materials achieve a tensile strength over 1000 MPa at the density of 7.0. However, for the Astaloy CrM material such strength is obtained at the cooling rate of 1-1.5° C/s, while for the Distaloy DH-1 material a cooling rate of 5-6° C/s is needed. 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 Distaloy DH-1 based material (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 0.6% for all investigated materials.
CCT diagrams and phase amount versus cooling rate

Figure 3 shows the CCT diagrams and phase amount (bainite, indicated with B and martensite indicated with M) as a function of the cooling rate for Astaloy CrM with 0.4 and 0.5% C, for Astaloy A with 2% Cu and 0.6 respectively 0.7% C and finally for Distaloy DH-1 with 0.6 respectively 0.8% C.

*Fig 3a:* CCT diagram for Astaloy CrM with 0.4 and 0.5% C

*Fig 3b:* Phase amount vs cooling rate for Astaloy CrM with 0.4 and 0.5% C

*Fig 3c:* CCT diagram for Astaloy A with 2% Cu and 0.6 and 0.7% C

*Fig 3d:* Phase amount vs cooling rate for Astaloy A with 2% Cu and 0.6 and 0.7% C

*Fig 3e:* CCT diagram for Distaloy DH-1 with 0.6 and 0.8% C

*Fig 3f:* Phase amount vs cooling rate for Distaloy DH-1 with 0.6 and 0.8% C
The microstructure of both Astaloy CrM with 0.5% C and Astaloy A with 2% Cu and 0.7% C consists of more than 90% martensite for cooling rates ≥ 1° C/s. For Distaloy DH-1 with 0.8% C the amount of martensite varies between 50% and 90% for cooling rates in the range 1-2.5° C/s. Retained austenite is present between the martensite needles in the Astaloy A material with 0.7% C and in the Distaloy DH-1 material with 0.8% C.

Discussion

The Astaloy CrM material with 0.5% carbon and the Astaloy A material with 2% Cu and 0.7% C have highest hardenability, as shown in figure 3. For both materials more than 90% martensite is obtained at the cooling rate of 1° C/s. For the Astaloy CrM material no copper additions are needed and 0.5% carbon is sufficient to get >90% martensite. A larger amount of martensite can be expected for the Astaloy A material with 0.8% C when cooled at 1° C/s which was confirmed by the metallographic investigation carried out on the sinter-hardened samples showing >95% martensite. For Distaloy DH-1 with 0.8% carbon a cooling rate ≥ 2.5°C/s is needed to obtain >90% martensite. The different hardenability of the investigated materials is related to the type and amount of alloying elements present in the base powders used. Alloying elements such as Ni, Mo, Cr, Mn and Cu increase the hardenability as follows Mn>Cr>Mo>Cu>Ni.

Large variations in martensite and bainite content are observed for the Distaloy DH-1 materials both with 0.65%C and 0.8%C for cooling rates in the range 1 to 2.5° C/s. This is in agreement with the increase in apparent hardness (40%), yield strength (35% for 0.65%C and 25% for 0.8%) and tensile strength (20% for 0.65%C and 11% for 0.8%) obtained when increasing the post-sintering cooling rate from 1-1.5 to 5-6 ° C/s.

The microstructure of the Astaloy A and Astaloy CrM materials, with highest carbon content, is less sensitive to variations in cooling rate, if compared to Distaloy DH-1 with 0.8%C. More than 90% martensite forms at the cooling rates of 1° C/s. An increase in hardness with 7% is observed for the Astaloy CrM material when increasing the cooling rate from 1-1.5 to 2-3° C/s. No increase in hardness is obtained when further increasing the cooling rate, as the microstructure is fully martensitic. For the Astaloy A material with 0.8% C the hardness is almost independent of the cooling rate. The tensile strength of both materials decreases (3% for the Astaloy CrM material and 8% for the Astaloy A material) with increased cooling rate.

For all investigated materials the hardness increases with increased carbon content. However, small amounts of retained austenite are present in the Distaloy DH-1 with 0.8% C and in the Astaloy A materials with more than 0.7% carbon. This indicates that a further increase in carbon content does 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 further increased by increasing the carbon content up to 0.6-0.7%.

Hardness and tensile strength reach their maximum for different carbon contents. The Astaloy A, Astaloy CrM and Distaloy DH-1 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.

Regarding the dimensional change swelling is observed for the copper containing materials, while shrinkage is observed for the Astaloy CrM materials. This indicates that if all materials were pressed at one and same green density the materials containing copper would have had a lower sintered density, if compared to the Astaloy CrM materials.
Conclusions

- The microstructure of Astaloy CrM+0.5%C and Astaloy A+2%Cu+0.7%C consists of >90% when cooling at the rate of 1°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 and cooling rate of 1-1.5°C/s. The highest hardness, 450 HV10, is achieved by the Distaloy DH-1 material with 0.8% carbon, cooled at 5-6°C/s.

- The hardness of the Astaloy CrM material can be increased by 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 Distaloy DH-1 material with 0.65% carbon cooled at the rate of 5-6°C/s. This at the density of 7.0 g/cm³.

- 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 Distaloy DH-1 material with 0.6% C, cooled at the rate of 5-6°C/s. This at the density of 7.0 g/cm³.

References