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SECONDARY HARDENING IN HIGH SPEED STEELS

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Abstract – Secondary hardening precipitates in six high speed tool steels have been analysed with the atom probe field ion microscope. The precipitates were of the types MC and M₂C. The precipitate size was only a few nanometers and was smaller in the cobalt containing steels than in the cobalt free grades. All precipitates were of a very mixed composition and contained molybdenum, chromium, vanadium, tungsten and some iron. The role of the different carbide forming elements is described in the paper.

I – INTRODUCTION

High speed steels are used for cutting and cold forming operations, particularly when more complicated shapes are to be manufactured so that a standard cemented carbide tool cannot be used. The requirements on high speed steels are hot hardness, wear resistance, and sufficient toughness. These properties are brought about by alloying with high amounts of strong carbide forming elements such as tungsten, molybdenum, vanadium and chromium. High speed steel tools are shaped in the annealed condition and subsequently heat treated by hardening from about 1200 °C and tempering at 550–560 °C, usually three times one hour. After this heat treatment the steels consist of about 6-15 vol.% of micron size hard carbides of type MC and M₆C (primary carbides), dispersed in a matrix of tempered martensite.

The matrix contains a fine and dense dispersion of nanometer size precipitates (secondary carbides), which contribute to the high hot hardness of the steels. Whereas the composition of the primary carbides is well known from e.g. analytical electron microscopy studies [1,2,3,4], the structure and composition of the very small secondary precipitates have been difficult to determine with more conventional methods. We have therefore used atom probe microanalysis to study the influence of steel composition on the secondary precipitate size, structure and composition [1,5,6].

The first high speed steels designed at the beginning of the century were tungsten rich steels such as T₁ (18 wt.% W - 0% Mo - 1% V; small amounts of molybdenum may be present as an impurity.) The chromium content of this steel, as well as of all high speed steels developed later, is about 4%. Later on molybdenum rich steels were developed, mainly for economical reasons. A classical example is M₂ (6W-5Mo-2V), where some of the tungsten was substituted by an equal atomic fraction of molybdenum. One step further in substitution of tungsten by molybdenum is M₇ (2W-9Mo-2V). M₂ is the most widely used
high speed steel today. With M2 as a base, another line of development can be followed, where more vanadium is added in order to increase the volume fraction of primary MC precipitates, e.g. in M3:2 (6W-5Mo-3V). Also cobalt has been added to provide a higher hot hardness. One example is the grade ASP 30 (6W-5Mo-3V+8Co). The introduction of powder metallurgical production now also enables the addition of much larger amounts of strong carbide formers, e.g. in the steel ASP 60 (7W-7Mo-6V+10Co). The development of high speed steels is further illustrated in Figure 1.

All steels mentioned above have been studied with atom probe field ion microscopy. In this paper the methods of analysis are discussed, and some results are presented. The metallurgical implications of our results are given elsewhere [7].

II – EXPERIMENTAL

Six high speed steels have been investigated, and their compositions are given in Table I. In this paper the results from analysis of the six steels in the commercially used fully hardened and tempered condition are described. The following hardening temperatures were used: 1270 °C (T1), 1220 °C (M2), 1190 °C (M7) and 1180 °C (M3:2, ASP 30, ASP 60). The steels were tempered at 550-560 °C for 3 times 1 hour. Specimens were prepared by cutting thin rods from the heat treated material using spark cutting or a low speed diamond wafer saw. The rods were then electropolished at room temperature in two steps: first a neck was formed by etching at 25 V in an electrolyte of 10% perchloric acid, 15% glycerol and 75% ethanol, floating on trichloroethylene. Then a tip was formed by polishing in 2% perchloric acid and 98% 2-butoxyethanol at 18 V, using an automatic circuit breaker which terminates the polishing when the lower part of the specimen drops off. The atom probe instrument used for the investigation has been described before [8,9]. Field ion imaging and atom probe analysis were performed at a temperature of 90 K.

The brightly imaging secondary precipitates were easily located in the neon field ion image. The precipitates were usually very small and their field ion image often appeared as a row of bright atoms. This made it impossible to analyse the precipitates without collecting atoms from the surrounding matrix. Atom probe analysis was performed at a pressure in the 10⁻¹⁰ torr range. Comparisons between atom probe and STEM/EDS analysis of the same primary carbides showed that at 90 K, correct atom probe analyses were obtained when using a pulse fraction of 15% of the standing voltage [10]. Typically only 50 ions could be collected from each precipitate. Between 9 and 28 precipitates were analysed from each steel.

Previous transmission electron microscopy has shown that two types of secondary carbides are present in the matrix of M2-based high speed steels: MC and $M_2C$ [11]. All precipitates analysed in the atom probe

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>W</th>
<th>Mo</th>
<th>Cr</th>
<th>V</th>
<th>Co</th>
<th>Si</th>
<th>Mn</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>0.76</td>
<td>17.6</td>
<td>0.3</td>
<td>4.1</td>
<td>1.1</td>
<td>-</td>
<td>0.24</td>
<td>0.28</td>
<td>bal.</td>
</tr>
<tr>
<td>M2</td>
<td>0.94</td>
<td>6.8</td>
<td>4.7</td>
<td>4.4</td>
<td>1.8</td>
<td>-</td>
<td>0.25</td>
<td>0.29</td>
<td>bal.</td>
</tr>
<tr>
<td>M7</td>
<td>1.06</td>
<td>2.0</td>
<td>8.6</td>
<td>3.7</td>
<td>1.9</td>
<td>-</td>
<td>0.28</td>
<td>0.31</td>
<td>bal.</td>
</tr>
<tr>
<td>M3:2 (ASP 23)</td>
<td>1.30</td>
<td>6.3</td>
<td>4.8</td>
<td>4.0</td>
<td>3.1</td>
<td>0.41</td>
<td>0.62</td>
<td>0.28</td>
<td>bal.</td>
</tr>
<tr>
<td>ASP 30</td>
<td>1.26</td>
<td>6.1</td>
<td>4.9</td>
<td>4.0</td>
<td>3.0</td>
<td>8.0</td>
<td>0.60</td>
<td>0.32</td>
<td>bal.</td>
</tr>
<tr>
<td>ASP 60</td>
<td>2.26</td>
<td>6.7</td>
<td>7.0</td>
<td>4.2</td>
<td>6.4</td>
<td>10.3</td>
<td>0.41</td>
<td>0.30</td>
<td>bal.</td>
</tr>
</tbody>
</table>

Table I - Composition of the six steels studied.
were identified from their morphology and their carbon content. For each steel an average composition was calculated for both the MC and $M_2C$ precipitates. It was necessary to subtract from the recorded atom probe spectra those ions which originated from the surrounding matrix. Silicon, manganese and (in the cobalt containing steels) cobalt were used for this subtraction, and it was found that the iron content was typically around 5% of the metal content of the $M_2C$ precipitates and less for MC. Since it proved very difficult to make this subtraction accurately, all the iron is omitted in the presentation of the data below. Note that this will slightly increase the apparent carbon content.

Alloying elements were subtracted from precipitate analysis in proportion to iron, using measured matrix compositions (Figure 2). The matrix between the precipitates was analysed with $5 \times 10^{-8}$ torr of image gas present. The phosphor screen of the chevron channel plate ion detector was observed during analysis, and the brightly imaging precipitates were avoided by tilting the specimen as soon as the ion current increased.

### III – RESULTS

Two kinds of precipitate morphology were found: platelets (Figure 3) and rods (Figure 4). Analyses showed that the platelets were of the MC type, whereas the rod-shaped precipitates were of the $M_2C$ structure. The size of the precipitates was smaller in the cobalt containing grades (Figure 5). Table II contains estimates from field ion micrographs of typical precipitate sizes in M3:2 (=ASP 23) and ASP 30. These two steels differ only in their cobalt contents.

Atom probe analysis showed that in all steels the secondary precipitates were of a very mixed composition. Both types of precipitates contain substantial amounts of chromium, typically 30% of the metal content, and also large amounts of molybdenum. Atom probe analyses were made of both types of precipitates in all six steels. Typical results from three of these steels are given in table III; the full set of data will be reported elsewhere [7]. Replacing tungsten with molybdenum in the steel composition (T1 to M2 to M7) leads to a higher molybdenum content in both MC and $M_2C$. However, an increase in the vanadium content (M2 to M3:2 to ASP 30 to ASP 60) mainly leads to higher amounts of primary MC carbides without affecting the secondary carbide composition. By contrast, the small size of the precipitates in the cobalt containing steels leads to a higher chromium and a slightly lower vanadium content. It is interesting to note that the main characteristics of the secondary precipitates, i.e. a mixed composition and a high chromium content, does not change even for these large changes in alloy composition.

### IV – DISCUSSION

It is rather astonishing to find such a mixed composition of both types of secondary hardening precipitates in all six high speed steels investigated. Not very long ago secondary hardening was discussed in terms of

<table>
<thead>
<tr>
<th>Steel</th>
<th>Precipitate size</th>
<th>Precipitate size</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MC platelet diameter, nm</td>
<td>$M_2C$ rod length, nm</td>
</tr>
<tr>
<td>M3:2 (ASP 23)</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>ASP 30</td>
<td>3</td>
<td>5</td>
</tr>
</tbody>
</table>

Table II – Approximate sizes of secondary precipitates in a cobalt-free (M3:2) steel and an identical cobalt containing (ASP 30) steel. The platelet thickness and rod diameter were in both alloys 1-2 nm. (After Wang Rong [2].)
V$_4$C$_3$ and W$_2$C precipitation [12]. In the light of the atom probe results such a picture is obviously completely unrealistic.

Chromium seems to be more important for the secondary precipitation than was previously assumed. A high chromium content will reduce the lattice misfit between matrix and both types of carbide, reducing the activation energy for precipitate nucleation. This may be instrumental in creating a high density of nuclei at early stages in the tempering process. Molybdenum obviously plays a very important role in the formation of both MC and M$_2$C, while tungsten seems to be involved to a surprisingly small degree.

V – SUMMARY

- Six high speed steels of widely different composition were analysed in the atom probe.
- Two types of secondary precipitates, MC and M$_2$C, were found in all six steels.
- MC precipitates were plate-shaped with a typical diameter of 4 nm, and M$_2$C were rod-shaped with a typical length of 8 nm.
- The precipitate size was smaller in the cobalt containing steels.
- All precipitates had a very mixed composition. Both MC and M$_2$C contained molybdenum, vanadium, chromium, tungsten and also some iron.
- The chromium content of the precipitates was surprisingly high, between 20 and 50% of the metal content.
- Molybdenum seems to be much more important than tungsten for the secondary precipitation reaction at the temperature of maximum hardness.

<table>
<thead>
<tr>
<th>Precipitate type</th>
<th>Steel</th>
<th>Approximate precipitate formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC</td>
<td>M7</td>
<td>(W$<em>{0.03}$Mo$</em>{0.56}$V$<em>{0.25}$Cr$</em>{0.22}$)C$_{0.8}$</td>
</tr>
<tr>
<td></td>
<td>M2</td>
<td>(W$<em>{0.05}$Mo$</em>{0.42}$V$<em>{0.36}$Cr$</em>{0.17}$)C$_{1.1}$</td>
</tr>
<tr>
<td></td>
<td>ASP 60</td>
<td>(W$<em>{0.07}$Mo$</em>{0.39}$V$<em>{0.32}$Cr$</em>{0.22}$)C$_{0.9}$</td>
</tr>
<tr>
<td>M$_2$C</td>
<td>M7</td>
<td>(W$<em>{0.02}$Mo$</em>{0.47}$V$<em>{0.20}$Cr$</em>{0.31}$)C$_{0.9}$</td>
</tr>
<tr>
<td></td>
<td>M2</td>
<td>(W$<em>{0.08}$Mo$</em>{0.45}$V$<em>{0.16}$Cr$</em>{0.31}$)C$_{1.1}$</td>
</tr>
<tr>
<td></td>
<td>ASP 60</td>
<td>(W$<em>{0.09}$Mo$</em>{0.35}$V$<em>{0.06}$Cr$</em>{0.53}$)C$_{0.8}$</td>
</tr>
</tbody>
</table>

Table III – Approximate composition of secondary precipitates in three high speed steels. The iron content in all precipitates has been set to zero because of the difficulty to accurately measure the iron content. In reality all precipitates contained a small amount of iron, typically 5% of the metal content, and consequently a somewhat lower carbon content.
ACKNOWLEDGEMENTS

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REFERENCES


Figure 1. Schematic illustration of the development of high speed steels. For each steel the AISI standard designation and the composition (in the order W-Mo-V) are given. The non-standard powder metallurgical ASP steels are produced by Kloster Speedsteel, Sweden.

Figure 3. Plate-shaped MC precipitate (arrow) in the steel M2. The plate diameter is about 5 nm. Neon field ion micrograph.
Figure 2. Atom probe spectrum recorded when analysing the matrix between the precipitates in the steel M2, tempered to hardness maximum (3×1 h at 560 °C). After this standard heat treatment for tools, the matrix still contains substantial amounts of carbon and the alloying elements. The appearance of molecular carbon ions suggests that clustering occurs in the matrix.

Figure 4. Neon field ion micrograph of secondary precipitates in the steel ASP 23. Rod-shaped precipitates are of type M₂C (arrows). Diameter of micrograph corresponds to approximately 200 nm.

Figure 5. Secondary precipitates in the cobalt containing steel ASP 30. The size of these precipitates are considerably smaller than those in the cobalt free steel (Fig. 4). Neon field ion micrograph; diameter of imaged area approximately 100 nm.