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A STUDY OF PRECIPITATION AND SEGREGATION ON AN ATOMIC SCALE OF 11at.%Cr-1at.%Mo HEAT RESISTING STEEL BY ATOM-PROBE AND TEM


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Classical chemical analysis of metals and silicate and carbonate rocks; X-ray crystallography; electron microscopy and diffraction; electron microprobe analysis; atomic absorption analysis; spectrochemical analysis.
An 11at.%.Cr-1at.%.Mo commercial steel which contains C, Si, Mn, Nb and V as minor elements was investigated by atom-probe (AP) and transmission electron microscopy (TEM). This steel has an excellent heat resisting property at 600 - 650°C but undergoes the ductile - brittle transition in this temperature range. The following results were obtained: (1) After solution treatment the FIM image was homogeneous on an atomic scale. (2) After tempering at 650°C for 1 hr. a precipitate was detected AP analysis showed that the precipitate was M(C+N) where M is Nb, Cr, V, Mo and Fe. (3) After tempering at 700°C for 1 hr., a
precipitate was a Fe/Cr ratio of 46/42 (sigma phase) was detected.
(4) After tempering at 700°C for 1 hr. a precipitate Fe/Cr ratio of 60/40
(sigma phase) was also observed at the lath boundary, and adjacent to this
region the chromium concentration decreased to 1%.
A STUDY OF PRECIPITATION AND SEGREGATION ON AN ATOMIC SCALE OF 11at.%Cr-lat.%Mo HEAT RESISTING STEEL BY ATOM-PROBE AND TEM


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Abstract - An 11at.%Cr-lat.%Mo commercial steel which contains C, Si, Mn, Nb and V as minor elements was investigated by atom-probe (AP) and transmission electron microscopy (TEM). This steel has an excellent heat resisting property at 600 - 650°C but undergoes the ductile-brittle transition in this temperature range. The following results were obtained: (1) After solution treatment the FIM image was homogeneous on an atomic scale. (2) After tempering at 650°C for 1 hr a precipitate was detected. AP analysis showed that the precipitate was M(C+N) where M is Nb, Cr, V, Mo and Fe. (3) After tempering at 700°C for 1 hr, a precipitate with a Fe/Cr ratio of 46/42 (sigma phase) was detected. (4) After tempering at 700°C for 1 hr a precipitate Fe/Cr ratio of 60/40 (sigma phase) was also observed at the lath boundary, and adjacent to this region the chromium concentration decreased to 1%.

I - INTRODUCTION

In the research and development of alloy steels, the problems of micro-precipitation and microsegregation are becoming more important for control of the properties of steels. Hitherto, these studies have been carried out by auger electron spectroscopy /1,2/. However this method is not good enough to know the microstructure on an atomic scale. Therefore, it is meaningful to use a field ion microscope (FIM) and AP to solve these problems. There have been many reports on steel /3,4,5/, but in this study, a 11at.%Cr-lat.%Mo commercial steel, which includes C, Si, Mn, Nb and V as minor elements, was observed. This steel has an excellent heat resisting property at 600 - 650°C but there is the problem of the ductile-brittle transition in this temperature range /6/. Because of this phenomenon it is very important to study and clarify the microstructures of this steel. This steel is conventionally used after quenching and tempering and is known to have microstructures of dual phase with tempered martensite and sigma ferrite.
II - EXPERIMENTAL PROCEDURE

The bulk chemical composition of the heat resisting steel used in this investigation is given in Table 1. This material was melted in air, and after rolling and annealing, finished with wire drawing into 0.2 mm wire. The solution treatment was carried out at 1050°C for 30 min in a vacuum of 2x10^-3 Pa. Then, tempering was performed at 650°C and 750°C for 1 hr, respectively. As for FIM imaging, Ne was used at 2x10^-4 Pa, and the observation was performed at 30 K. For TEM observation, a JEOL 100B was used.

Table 1 - Chemical composition.

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<tr>
<th></th>
<th>C</th>
<th>Cr</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
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<th>V</th>
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<td>wt.%</td>
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<td>1.2</td>
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III - EXPERIMENTAL RESULTS AND DISCUSSION

1 - MC type microprecipitate

Photo 1 shows the FIM microphotograph of a solution treated specimen. After solution treatment the (110) surface (in the center) was observed and the bright spots were uniformly observed. In this case, the chemical composition measured by AP was the same as that of the chemical analysis. After tempering at 650°C for 1 hr microprecipitates were observed in both the FIM image and the TEM image, which are shown in Photo 2(a) and (b), respectively.

Photo 1 - Field ion microphotograph of the heat resisting steel solution annealed at 1050°C for 30 min.

Photo 2 - TEM image and FIM image of the heat resisting steel tempered at 650°C for 1 hr. (a) TEM image and (b) FIM image of the same specimen.
As shown in Photo 2(b) the shape of the precipitate was elliptical and the size was about $20 \times 10 \text{nm}^2$. Fig. 1 shows the results of an AP analysis of this precipitate. A total of 3200 atoms were analysed. Since the probe-hole limits the number of atoms per atomic plane to about 25 substitutional atoms, the thickness of the precipitate was found to be 14 substitutional atomic layers with 5 substitutional atomic transient layers including the phase boundary. The AP analysis showed that the precipitate consisted of $64\text{Nb}$, $18\text{Cr}$, $18\text{V}$, $6\text{Mo}$ and $3\text{Fe}$ substitutional atoms with $30\text{C}$ and $70\text{N}$ interstitial atoms. Therefore, this precipitate was revealed to be M(C+N) mainly consisting of NbN, because the total metal atoms was 109 and the total C or N atoms was 100. In the case of the matrix, the AP analysis showed uniformity with $2270\text{Fe}$, $297\text{Cr}$, $29\text{Mo}$, $18\text{Mn}$, $3\text{V}$ and $23\text{N}$ atoms. In the transition layers there were no significant anomalies. Table 2 shows the concentrations of each element in the precipitate, matrix and transient layer including the phase boundary.

![Fig. 1 - Depth profile of the chemical composition in the precipitate, matrix and transient region. The thickness of the precipitate was revealed to be 14 atomic layers with 5 atomic transient layers.](image)

**Table 2 - Concentration of the precipitate, matrix and transient region.**

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Cr</th>
<th>Nb</th>
<th>Mo</th>
<th>Mn</th>
<th>V</th>
<th>C</th>
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<td>1.4</td>
<td>8.6</td>
<td>30.6</td>
<td>2.9</td>
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<td>8.6</td>
<td>14.4</td>
<td>33.5</td>
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<td>Transient region</td>
<td>42.1</td>
<td>12.9</td>
<td>15.7</td>
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<td>0</td>
<td>3.6</td>
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<tr>
<td>Matrix</td>
<td>86.4</td>
<td>11.3</td>
<td>1.1</td>
<td>0.7</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
<td>0.9</td>
</tr>
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</table>
2 - Sigma phase microprecipitate 
2 - 1 Precipitate along grain boundary
Photo 3 shows the microprecipitate along the grain boundary. The AP analyses are
shown in Fig. 2 and Fig. 3. Fig. 2 shows that the precipitate is mainly Fe and Cr
atoms with a ratio of 46/42 (sigma phase) Fig. 3 shows that minor metallic elements
were also detected. Usually the sigma phase can be observed only when the Cr
concentration is above 17 at.% in iron chromium alloy. But in this study the average
concentration of chromium was 11 at.%. It is, however, considered that near the grain
boundary, the free energy increases with strain energy and there is the possibility
to find the sigma phase as the "local equilibrium state" even thought the chromium
concentration is lower than 17 at.%. In this case the concentration of Cr of the
surrounding matrix showed some deficiency at about 6.9 at.%, and Fe was 91.8%. At
the interface of the precipitate, the concentration of Cr was found to be the
averaged value between the precipitate and surrounding matrix.

Photo 3 - Sigma phase microprecipitate along the grain boundary.

![Graph showing concentration of Fe and Cr atoms per atomic layer](image)

**Fig. 2** - Concentration of Fe and Cr atoms per atomic layer for the heat resisting
steel tempered at 700°C for 1hr.

![Graph showing concentration of Si, O, C, Mo, V and Mn atoms per atomic layer](image)

**Fig. 3** - Concentration of Si, O, C, Mo, V and Mn atoms per atomic layer for heat
resisting steel tempered at 700°C for 1hr.
2 - 2 Precipitate along the lath boundary

Photo 4 shows a TEM image of the tip specimen tempered at 700°C for 1 hr. Photo 5 shows the FIM image after evaporation of the surface layer of the tip shown in Photo 4. By evaporating the tip, the AP analysis was performed across the lath boundary. From FIM and AP analysis the lath boundary in tempered state seems to be a small angle boundary including both tilt and twist. Fig. 4 shows the depth profile of chemical composition. In the precipitate the ratio of Fe/Cr was 60/40 (sigma phase). This figure shows that there is enrichment of chromium along the grain boundary and depletion of chromium outside this region.

Photo 4 - TEM image of the tip specimen tempered at 700°C for 1 hr.

Photo 5 - FIM image after evaporation of the surface layer of the tip shown in Photo 4.

Fig. 4 - Concentration of Fe, Cr and Mn atoms per atomic layer for the heat resisting steel tempered at 700°C for 1 hr.
IV - SUMMARY

In this study the microprecipitate and microsegregation in an 11at.%Cr-lat.%Mo heat resisting steel were revealed.

(1) After solution treatment the FIM image showed homogeneity and no precipitate was observed.

(2) After tempering at 650°C for 1 hr precipitates of about 20x10nm² were detected by both TEM and FIM. From the results of the AP measurements, the precipitate was revealed to be M(C+N) where M is 64Nb, 18Cr, 18V, 6Mo and 3Fe atoms (total 109 atoms), and C is 30 and N is 70 atoms (total 100 atoms). There was no segregation to the transient region of the phase boundary.

(3) After tempering at 700°C for 1 hr, the precipitate, which has the high chromium concentration, was detected along the grain boundary. In the precipitate the ratio of Fe/Cr was 46/42 (sigma phase) with additional minor elements. There was no significant segregation at the interface between the precipitate and matrix.

(4) After tempering at 700°C for 1 hr, a high chromium concentration was observed at the lath boundary. Outside this layer the chromium concentration decreased to 1%. In the precipitate the ratio of Fe/Cr was 60/40 (sigma phase).

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