The orientation relationships of Table I are shown in a stereographic projection in Figure 9, in which one can better see that the relationship of hcp needle and bcc matrix is

\[(0\overline{1}\overline{1})_{\text{bcc}}/\langle 0001 \rangle_{\text{hcp}}\]

\[[\overline{1}\overline{1}1]_{\text{bcc}}/\langle 1\overline{1}20 \rangle_{\text{hcp}}\]

These are the Burgers relationships.\,[7,8,9] These relationships evidently arose as part of the transformation mechanism from bcc-to-hcp martensite.\,[10]

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REFERENCES


High-Resolution Auger Electron Spectroscopy of Grain Boundary Phosphorus Segregation in NiCrMoV and NiCr Steels

J.E. WITTIG and A. JOSHI

A number of previous Auger electron spectroscopy (AES) studies of interface segregation in steels have predominantly measured the average grain boundary enrichment of impurity elements.\,[11-15] This communication presents some AES data which compare average measurements of grain boundary phosphorus segregation to those from specific microstructural features such as the prior austenite grain boundary carbide/ferrite interface.

Two steel alloys doped with phosphorus were obtained from the University of Pennsylvania, Philadelphia, PA.\,[16] Both steels had similar compositions, with the exception of molybdenum and vanadium additions (Table I). Air cooling from an austenitizing temperature of 985 °C had produced a bainitic microstructure. The air-cooled materials had been subsequently tempered to two hardness levels on the Rockwell C scale of Rc30 and 20. After tempering, the four initial conditions, NiCrMoV Rc30, NiCrMoV Rc20, NiCr Rc30, and NiCr Rc20, were aged at 480 °C for 2400 hours to induce grain boundary segregation. During aging at 480 °C, the NiCrMoV materials maintained a constant hardness while the NiCr alloy softened considerably, from NiCr Rc30 to Rc18 and NiCr Rc20 to Rc15.

Samples for AES analysis had a 2 × 2 mm cross section with a thin nickel strip spot welded to the side behind the notch. This configuration enabled the fractured samples to be bent back upon themselves in order to investigate segregation at mating fracture features. The AES analysis was performed using a PERKIN-ELMER* 595 scanning Auger microprobe with vacuum levels between 2 and 5 × 10⁻¹⁰ torr. Using a 10 keV incident beam energy, both survey spectra from 0 to 1000 eV and multiplex scans over energy windows were collected. The high-resolution AES measurements utilized probe sizes of approximately 400 nm, which restricted the data acquisition to multiplex owing to the reduced counting rates.

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Table I. Compositions of the NiCrMoV and NiCr Steels (Weight Percent)

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>C</th>
<th>P</th>
<th>Si</th>
<th>Mn</th>
<th>Sn</th>
<th>S</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCrMoV</td>
<td>3.43</td>
<td>1.70</td>
<td>0.61</td>
<td>0.10</td>
<td>0.25</td>
<td>0.02</td>
<td>0.02</td>
<td>0.32</td>
<td>0.02</td>
<td>0.005</td>
<td>bal.</td>
</tr>
<tr>
<td>NiCr</td>
<td>3.50</td>
<td>1.71</td>
<td>0.01</td>
<td>0.01</td>
<td>0.24</td>
<td>0.02</td>
<td>0.02</td>
<td>0.31</td>
<td>0.02</td>
<td>0.004</td>
<td>bal.</td>
</tr>
</tbody>
</table>

Peak height ratios (PHR) of the phosphorus 120 eV peak to the iron 703 eV peak were used as a measure of phosphorus segregation at the intergranular features. For the molybdenum-containing alloys, the molybdenum 120 eV contribution to the phosphorus 120 eV peak was determined by the size of the molybdenum 186 eV peak and then subtracted from the phosphorus signal.

The fracture surfaces of the embrittled materials were virtually 100 pct intergranular along prior austenite grain boundaries. The AES survey spectrum in Figure 1, from the area which contains over 100 intergranular fracture facets in Figure 2, accurately measured a statistically significant average grain boundary phosphorus segregation. Comparing data produced by this method from different regions on this sample revealed less than a 5 pct variation in the P_{120}/Fe_{703} PHR's. Also, comparison of the survey spectra with multiplex data revealed reproducible P_{120}/Fe_{703} PHR's. Table II summarizes the average P_{120}/Fe_{703} PHR's from the intergranular fractures of the four materials after aging for 2400 hours at 480 °C.

After equivalent aging treatments of 2400 hours at 480 °C, the two NiCr materials both exhibited approximately the same amount of intergranular segregation of phosphorus, while the NiCrMoV R_20 and R_30 had 15 pct and 30 pct less grain boundary phosphorus segregation, respectively. These results are consistent with a number of other reports where nickel-chromium steels containing vanadium and/or molybdenum additions exhibit lower levels of phosphorus grain boundary segregation.[6-10] A scavenging mechanism based on a strong molybdenum phosphorus interaction has been previously proposed to account for these observations.[6-9] However, recent studies have shown that molybdenum additions have no effect on grain boundary phosphorus segregation for binary and ternary Fe-P and Fe-Mo-P alloys.[11] In contrast to the phosphorus segregation behavior in these binary and ternary model alloys, the results presented here provide additional evidence that alloying elements like molybdenum and vanadium can affect phosphorus segregation at prior austenite boundaries in complex steels.

Site competition of phosphorus with carbon at the grain boundaries is believed to reduce phosphorus grain boundary segregation.[11,12,13] This mechanism is complicated in alloys with strong carbide-forming elements, such as chromium, molybdenum, and vanadium, since grain boundary carbon segregation can be rapidly removed by grain boundary carbide precipitation. Also, strong carbide-forming elements, which are dissolved in the ferrite matrix, influence the carbon activity and the kinetics of carbide precipitation during tempering and aging. Although identification of the actual mechanism responsible for the variation in the phosphorus segregation behavior of these NiCr and NiCrMoV steels is beyond the scope of this communication, any of these interrelated factors could be involved.

Auger electron spectroscopy (AES) data from mating fracture areas provide a measure of the total interfacial segregation.[14,15] Figure 3 shows a pair of mating fracture surfaces from the embrittled NiCrMoV R_30 material where AES measurements of phosphorus grain boundary enrichment were obtained from individual grain facets. The P_{120}/Fe_{703} PHR's from these grain boundaries and a similar set from the NiCr R_20 sample are

Fig. 1 — The Auger survey spectrum from the region in Fig. 2 reveals the intergranular composition of the NiCrMoV R_20 material after aging at 480 °C for 2400 h.

Fig. 2 — The fracture surfaces from the embrittled materials were virtually 100 pct intergranular along prior austenite grain boundaries. AES measurements from areas such as the one depicted by this secondary electron image from the NiCrMoV R_20 sample provided a statistically accurate determination of the average grain boundary phosphorus segregation.