Communications

Surface Oxide on fcc Iron-Nickel Alloys

K. B. REUTER, D. B. WILLIAMS, J. I. GOLDSTEIN, and E. P. BUTLER

A transformation of interest in the Fe-Ni system is the disorder-to-order transformation whereby disordered Fe-Ni with the fcc structure transforms to ordered FeNi with an L1₃ superstructure. This transformation can be studied with the transmission electron microscope (TEM) because the superstructure gives rise to superlattice reflections in the selected area diffraction patterns (SADPs). A problem arises, however, because an oxide surface layer forms on thin-foil Fe-Ni specimens giving rise to extra reflections that may be confused with those arising from internal precipitation reactions.

Through the work of Chen and Morris this confusion has been alleviated for bcc Fe-Ni alloys. This study extends the work of Chen and Morris to include Fe-Ni alloys with the fcc structure with the aim of discriminating oxide and superlattice reflections in SADPs.

Fe-35 wt pct Ni and Fe-50 wt pct Ni alloys were prepared from high purity (99.998 pct) Fe and Ni, homogenized, and rolled to 10 to 12 mils. Discs, 3 mm in diameter, were punched from the sheet and austenitized. The discs were thinned to 3 to 4 mils by grinding on fine SiC papers. Thin-foil specimens were then prepared in one of three ways: jet-polishing, ion-beam thinning, or jet-polishing followed by ion cleaning. The jet-polishing was carried out using a Fischione twin-jet electropolisher operated at 105 V using a 2 pct perchloric/98 pct ethanol solution at −40 °C.

Ion-beam thinning was performed on a Technics ion-beam milling machine with the specimen at a 15 deg angle to the ion beam and cleaned for 20 minutes. The Fe-35 wt pct Ni specimens were examined in a Philips EM400T operating at 120 kV. The Fe-50 wt pct Ni specimens were observed in an AEI-EM7 high voltage electron microscope (HVEM) operating at 1 MeV.

TEM examination of all of the specimens revealed extra reflections in the SADPs. By assuming that a surface layer of NiFe₂O₄ or Fe₃O₄ had formed, all of the extra reflections could be accounted for. The lattice parameters of Fe₃O₄ (8.396 A) and NiFe₂O₄ (8.339 A) are too similar to determine which of the oxides was present using conventional electron diffraction. Chen and Morris found that the same oxides form on bcc Fe-Ni thin-foil specimens.

Specimen preparation had an effect on the oxide layer formed. Specimens that were ion-beam thinned or jet-polished followed by ion cleaning had many oxide reflections in their SADPs (Figure 1(a)). The jet-polished specimens, however, had fewer, less intense reflections (Figure 2(a)). Thus, although oxide reflections were observed in SADPs from all specimens regardless of preparation technique, jet-polishing minimized the problem.

Three low-index zone axis diffraction patterns were analyzed: two [011] variants previously mentioned along with a [001], pattern obtained from an Fe-50 wt pct Ni specimen examined in the AEI-EM7 HVEM. Throughout the discussion the ‘γ’ subscript will refer to the fcc metal orientation and the ‘OX’ subscript will refer to the oxide orientation. In the figures, the indexed oxide reflections are underlined.

The diffraction pattern in Figure 1 was taken from an ion-beam thinned Fe-35 wt pct Ni specimen close to a [011] orientation. From the analysis in Figures 1(b), (c), and (d), three variants of the [112]ox oxide exist, as shown in Table I.

Table I. Variants of [112]ox Present on [011]γ; Ion-Beam Thinned Fe-35 Wt Pct Ni Specimen

| Variant | Laue Orientation | Laue Orientation
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<td>Variant #1</td>
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<td>(220)ox</td>
</tr>
<tr>
<td>Variant #2</td>
<td>(111)γ</td>
<td>7 deg</td>
</tr>
<tr>
<td>Variant #3</td>
<td>(111)γ</td>
<td>4 deg</td>
</tr>
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The analysis in Figures 3(c) through (g) shows that the remaining reflections can be accounted for by one oxide [112]ox variant plus triple diffraction. The orientation relationships are listed in Table III. Chen and Morris also indexed a [001]ax pattern. Their analysis showed a much simpler orientation relationship:

\[
[100]_a \parallel [100]_{ox} \\
(011)_a \parallel (010)_{ox}
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Table II. Variant of [112]ox Present on [011]γ; Jet-Polished Fe-35 Wt Pct Ni Specimen

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Fig. 1—Ion-beam thinned Fe-35Ni specimen (fcc). (a) SADP from specimen oriented close to [011], zone with 3 variants of \([\overline{1}12]_m\) oxide present. •—fcc matrix; X—oxide. (b) Index of [001] zone. (c) Index of one \([\overline{1}12]_m\) oxide variant. (d) Orientation of the 3\([\overline{1}12]_m\) oxide variants present. Note: all oxide indexing is underlined as in (c).

Fig. 2—Jet-polished Fe-35Ni specimen (fcc). (a) SADP from specimen oriented close to [011], zone with one variant of \([\overline{1}12]_m\) oxide present. •—fcc matrix; X—oxide. (b) Index of [011] zone. (c) Index of the \([\overline{1}12]_m\) oxide variant.
Fig. 3—Jet-polished HVEM irradiated Fe-50Ni specimen (fcc). (a) SADP and schematic drawing of SADP from specimen oriented close to [001]. Superlattice reflections are present along with oxide and multiple diffraction effects. •—fcc matrix; ©—superlattice reflections; X—oxide. (b) Index of [001] zone including superlattice reflections. (c) Index of one [112] oxide variant. (d) Reflections due to multiple diffraction of [112] oxide variant. (e) Reflections not yet accounted for shown as ©. (f) Index of one [111] oxide variant, •—fcc matrix and superlattice reflections; X—oxide; ▲—multiple diffraction. (e) Reflections not yet accounted for shown as ©. (g) Index of one [111] oxide variant, •—fcc matrix plus superlattice reflections; ©—[111] oxide variant; ▲—multiple diffraction from [111] variant; X—oxide (accounted for in (d)).
The most important aspect of the above analyses is that the oxide and superlattice reflections can be distinguished. In the [011] orientation shown in Figure 1(a), the {001}, superlattice reflections are clearly separate from any oxide reflections. The {011}, superlattice reflections, however, are very close to the {113}$\alpha$ reflections and should not be used for CDF imaging if any oxide is present. In the [011], orientation shown in Figure 2(a), the {001}, superlattice reflections are again distinct. On the other hand, the {011}, superlattice reflections are close to the {022}$\alpha$, but with careful measurement, the oxide reflections can be distinguished.

In the [001] orientation shown in Figure 3(a), the {001}, and the {011}, superlattice reflections are close to oxide reflections, but they are distinguishable when the oxide variants are indexed and any multiple diffraction effects are taken into account.

To alleviate confusion, if any oxide is present in a (001), or (011), orientation, the {011}, superlattice reflections should not be used for CDF imaging. Instead, the {001}, superlattice reflections should be used because the {001}, superlattice reflections are clearly separate from any oxide reflections.

Finally, the oxide morphology on the fcc iron-nickel alloys was studied. Figure 4(a) shows a SADP from a typical

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**Table III.** Variant of [112]$\alpha$ and [111]$\alpha$ Present on [001]$\alpha$; Jet-Polished Fe-50 Wt Pct Ni Specimen

<table>
<thead>
<tr>
<th>Metal/Oxide Variant #1</th>
<th>[001]$\gamma$</th>
<th>[112]$\alpha$</th>
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Fig. 4—Fe-35 Ni jet-polished ion-beam cleaned. (a) SADP showing oxide reflections. (b) Centered dark field (CDF) of reflection indicated in (a) showing oxide morphology; marker = 0.2 $\mu$m.

Fig. 5—Fe-65Ni irradiated at 300 °C. (a) SADP with superlattice reflections. (b) CDF of superlattice reflection indicated. Bright regions are superlattice domains; marker = 0.1 $\mu$m.
area examined in the TEM. The extra reflections in the SADP reveal that oxide is present. The oxide reflection indicated was imaged and gave rise to tiny oxide islands (<30 nm) as shown in Figure 4(b). Chen and Morris found a similar oxide morphology on bcc iron-nickel specimens. The similarity between this oxide morphology and CDF images of small ordered regions in Fe-Ni alloys can be seen by comparing Figures 4 and 5. It is obvious that the oxide and ordered phase are indistinguishable by their morphology alone.

This study shows that an oxide layer of Fe$_3$O$_4$ or NiFe$_2$O$_4$ forms on fcc Fe-Ni thin-foil specimens, independent of the specimen preparation technique. This oxide can be minimized, however, by using the jet-polishing technique followed by immediate examination of the foil. The oxide forms as small (<30 nm), discrete, oriented particles on the fcc specimens. The orientation between the fcc Fe-Ni and the oxide was determined for the metal orientations of [001], and [011]. For these orientations, the oxide formed only with [112]$_{oa}$ or [111]$_{oa}$ orientations. From the analyses, the superlattice reflections arising from ordered FeNi can be distinguished from oxide reflections under the specific conditions.

The support of NASA grant #NAG 9-45 is gratefully acknowledged.

REFERENCES