SEGREGATION ANALYSIS OF MELT-GROWN CRYSTALS OF Fe-Ni ALLOYS WITH THE USE OF ELECTRON MICROPROBE

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The segregation behavior of solute elements is of importance in the preparation of materials by zone refining and the Czochralski process. We have carried out the present study to understand the segregation behavior of S, P, Ge, Ir, and C in melt-grown crystals of Fe-Ni alloys.

Experimental

Alloy crystals were grown from the melt by the Bridgman technique in which the liquid alloy, contained within an alumina crucible, was withdrawn from a gradient heating furnace at a slow rate. This procedure promotes the growth of solid crystals with a planar solid-liquid interface. The details of this procedure and the master alloy preparation methods have been given previously. The compositions of the alloys used in this study are listed in Table 1. Figure 1 illustrates the general microstructural features of alloy 1, melt-grown with a planar interface. The microstructure consists of a proeutectic phase, γ (f.c.c.), and two eutectics. Small amounts of sulfide inclusions form within the proeutectic phase. The phosphide eutectic consists of \( \gamma \), \((FeNi)_3P\), and FeS. The sulfide eutectic consists of \( \gamma \) and FeS.

A JEOL 733 microprobe with an automated stage was used. X-ray intensities were measured by wavelength-dispersive spectrometers (WDS). An accelerating voltage of 15 kV was used to obtain optimum peak-to-background (P/B) intensities for elements with high (Fe and Ni) and low (P and S) characteristic x-ray energies. For Ge and Ir, 30 kV was used to obtain a high P/B ratio. To obtain a large number of x-ray counts, a high beam current (100-200 nA) was used. The x-ray counting times used for P, Ge, and Ir were between 60 and 200 s. Pure elements were used as standards for Fe, Ni, Ge, and Ir; FeS and \((FeNi)_3P\) were used as standards for S and P, respectively. By linear interpolation, the value of the background intensity at the peak position was determined from the values of x-ray intensities measured at slightly above and below the characteristic wavelength.

X-ray intensities for Fe, Ni, S, and P were measured with an operating voltage of 15 kV and a 50 x 50μm raster scan at intervals of about 1 mm along the crystal. Smaller intervals were used near the end of the proeutectic region. Since the sample is about 15 mm long (Fig. 1), it was possible to use broad-beam analysis without sacrificing spatial resolution. The x-ray data were converted to compositions by a ZAF matrix correction program. If the alloy contained either Ir or Ge, the data were retaken at 30 kV. The computer-controlled specimen stage in the microprobe was used for relocating the sample during the second run. In the eutectic region, 20 to 40 measurements were made to obtain an average composition of the eutectic.

Meteoritic cohenite \((FeNi)_3C\), which contains 6.67% C, was used for the C standard. The background intensity was measured on a C-free Fe-Ni ferrite sample. A liquid-nitrogen cold finger was used to minimize C contamination of the sample. X-ray data were obtained for 60 s with a defocused beam of 20 μm in diameter, a beam current of 100 nA, and an operating voltage of 5 kV. The use of a low voltage reduced the x-ray absorption effect for C. Two methods for data reduction were employed. In the first method, the x-ray data were converted to composition by a ZAF calculation. In the second method, a calibration curve of x-ray intensity for C, less its background, measured in Fe-Ni-C alloys of known compositions vs wt% C was constructed. The background-corrected x-ray data for C obtained from the melt-grown alloys were converted by interpolation to composition with the use of the calibration curve.

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The values obtained from these methods agree with each other.

The analytical sensitivity $\Delta C$ was determined by the Ziebold expression given as

$$\Delta C = 2.33\sigma/(N - NB)v,$$

where $C$ is the measured composition, $\sigma$ is the standard deviation, $N$ is the total counts at the peak position, $NB$ is the total background counts, and $n$ is the number of measurements. The analytical sensitivity was: 0.004 wt\% for P, 0.005 wt\% for Ge, 0.012 wt\% for Ir, 0.17 wt\% for Ni, and 0.06 wt\% for C. The detectability limit $CDL$ was determined by the Ziebold expression

$$CDL \geq 3.2\sigma/(n\tau\sqrt{P/B}),$$

where $\alpha$ is an empirical constant, $\tau$ is the counting time, $P$ is the pure element counting rate, and $P/B$ is the peak-to-background ratio of the pure element. The detectability limit for trace elements was 0.015 wt\% for P, 0.009 wt\% for Ge, 0.02 wt\% for Ir, and 0.2 wt\% for C.

Results and Discussion

Figure 2 shows the variation of Ni and P compositions with fraction solidified $f_S$ in alloy 1. The Ni content varies from 7.0 wt\% to 10.5 wt\% in the proeutectic and shows a large composition gradient when $f_S > 0.7$. The P content varies from 0.06 wt\% to 1.25 wt\% in the proeutectic with a large composition gradient when $f_S > 0.7$. Since we have used a very high current and a longer counting time for P analysis, we were able to measure a low composition of 0.06 wt\% with an error of ±0.004 wt\%. The minimum composition of 0.06 wt\% is well above the detectability limit of 0.015 wt\%. P is highly enriched in the phosphide eutectic and Ni is enriched in both eutectics.

Figure 3 shows the Ge composition profile in alloy 1. The Ge content varies from 0.07 wt\% to 2.10 wt\% in the proeutectic and shows a large gradient when $f_S > 0.75$. The Ge content in the eutectics is about 0.10 wt\%. By employing appropriate operating conditions, we were able to detect and measure the minimum composition of 0.07 wt\% with an error of ±0.005 wt\%. Figure 4 shows the Ir and P composition profiles in alloy 2. The Ir content decreases with $f_S$ in the proeutectic from 1.0 wt\% to an undetectable level, i.e., below 0.02 wt\%. The lowest measured Ir composition is 0.05 wt\% with an error of ±0.01 wt\%. The P content in alloy 2 also increases with $f_S$ in the proeutectic. The phosphide eutectic does not form in alloy 2.

Figure 5 shows the C composition profile in alloy 3. The C content increases from 0.5 wt\% to about 1.5 wt\% in the proeutectic and shows a considerable gradient. In the eutectic, the C content is close to the detectability limit of 0.2 wt\%. The analysis could be improved by a higher beam current and/or a longer counting time.

We infer from the composition profiles that Ni moderately segregates to the eutectic. In high-P alloy 1 with a S to P ratio of 7.5, P predominantly segregates to the eutectic. In low-P alloy 2 with a S to P ratio of 18.5, P segregates to proeutectic $\gamma$. This change in the behavior of P is attributed to the value of the S-to-P ratio in the initial melt. Ir and C completely segregate to the proeutectic. Ge segregates to the liquid up to $f_S = 0.65$ and changes its behavior for $f_S > 0.65$ by segregating to the solid phase $\gamma$. In the experimental alloys, S predominantly segregates to the eutectic since S solubility in $\gamma$ is negligible.

Summary

In this study, we have solidified Fe-Ni alloys with P, S, Ir, Ge, and C by the Bridgman crystal growth technique. We have used the electron microprobe to analyze the chemical compositions. By using appropriate operating conditions, we have shown that elements present in trace amounts can be detected and measured with a high certainty. We were also able to understand that Ni, P, Ge, Ir, and C severely segregate in melt-grown crystals of Fe-Ni alloys.

References

FIG. 1.—Illustration of microstructure of plane front alloy 1 showing proeutectic γ at three locations (1, 2, 3) and phosphide (A) and sulfide (B) eutectics. Small amounts of sulfide (label S) inclusions form within proeutectic phase. Growth direction is indicated by white arrow. γ-phosphide eutectic interface is denoted by 1. Interface between sulfide and phosphide eutectics is not shown.

FIG. 2.—Composition profiles of Ni and P in alloy 1.

FIG. 3.—Composition profile of Ge in alloy 1.

FIG. 4.—Composition profiles of Ir and P in alloy 2.

FIG. 5.—Composition profile of C in alloy 3.

### TABLE 1.—Experimental alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition, wt%</th>
<th>S/P Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>S</td>
</tr>
<tr>
<td>1</td>
<td>7.7</td>
<td>2.25</td>
</tr>
<tr>
<td>2</td>
<td>7.1</td>
<td>1.67</td>
</tr>
<tr>
<td>3</td>
<td>10.5</td>
<td>1.64</td>
</tr>
</tbody>
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Initial Composition of Melt:
- Fe-7.7% Ni-2.25% S-0.30% P-0.09% Ge
  SE Sulphide Eutectic
  PE Phosphide Eutectic

Initial Composition of Metal:
- Fe-7.7% Ni-1.67% S-0.09% P-0.66% Ir
  SE Sulphide Eutectic
  PE Phosphide Eutectic

Initial Composition of Metal:
- Fe-10.5% Ni-1.64% S-1.0% C
  SE Sulphide Eutectic
  PE Phosphide Eutectic