Tie-Line Compositions of the $\gamma$ and $\delta$ Phases in the Binary Re–Ni System*1

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Compositions with tie lines between the $\gamma$ and $\delta$ phases in a binary Re–Cr–Ni system were investigated at 1423, 1573, and 1773 K by heat treating of Ar-arc-melted Re–40 at%Ni alloy. The microstructures of the Re–40 at%Ni alloy which had been water quenched after various heat treatment were observed and their concentration profiles for Re and Ni were measured using an electron probe microanalyzer. The Re–40 at%Ni alloy consisted of the $\gamma$ and $\delta$ phases. The tie lined compositions of the $\gamma$ and $\delta$ phases are summarized as follows (in at%): $\gamma$: 13.4 Re–86.6 Ni, $\delta$: 71.7 Re–28.3 Ni at 1423 K, $\gamma$: 16.4 Re–83.6 Ni, $\delta$: 69.3 Re–30.7 Ni at 1573 K, $\gamma$: 20.2 Re–79.8 Ni, $\delta$: 65.3 Re–34.7 Ni at 1773 K. The Re–Ni alloy powder sintered using the Spark Plasma Sintering (SPS) method were investigated. Solubility limit of Ni in the $\delta$ phase in the binary alloy system at 1423 K was found to be 28.3 at%Ni.

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1. Introduction

To enhance the thermal efficiencies of gas turbines and jet engines, the temperature of the combustion gas has been continuously increasing.¹ To provide protective coatings for turbines and rotor blades from such extremely hot combustion gases and internal air or steam cooling is employed to reduce the temperature rise of the base material.² However, even when TBCs and cooling systems are employed,³ Ni-based single-crystal superalloys with high-temperature strength still need to be developed because the temperature of the base material is expected to exceed 1273 K. One problem is inward diffusion of Al, which is placed in the bond coating layer for the purpose of forming protective scales of $\text{Al}_2\text{O}_3$. Such diffusion reduces the concentration of Al and lowers the oxidation resistance of the coating.⁴⁻⁵ To prevent diffusion of Al into the substrate, a number of diffusion barrier coatings have been proposed;⁶⁻⁹ however, after a relatively short oxidation time the barrier layer loses its layer structure, resulting in rapid, catastrophic oxidation. Narita et al. proposed a diffusion barrier coating with a duplex layer structure, containing the $\sigma$-phase of Re–Cr–Ni as the diffusion barrier layer. In this coating, the $\sigma$-layer was sandwiched between a Ni-based superalloy and Ni-aluminides in the Al-reservoir layer.¹⁰⁻¹¹

To elucidate the properties of the Re–Cr–Ni alloy, information regarding its phase diagram and diffusivity is required.¹²⁻¹³ It is essential to determine the structural stability of the sandwiched Re–Cr–Ni alloy layer. Narita et al. proposed that the diffusion barrier layer should be formed at high-temperature such as 1573 K.¹⁴

Both experimental and calculated Re–Cr–Ni phase diagrams have been reported,¹⁵⁻¹⁷ and a comparison shows a distinctive difference in the Ni solid solubility limit in the $\delta$ phase of the Re–Ni binary system. Two-phase diagrams for the Re–Ni binary system have been reported by Okamoto¹⁸ and Nash et al.¹⁹

In this present study, we discuss experimental results with respect to the tie-line compositions of the $\gamma$ and $\delta$ phases in the binary phase diagram for a formation process of the diffusion barrier layer.

2. Experimental Procedure

2.1. Re–40 at%Ni alloy by arc melting

Re–40 at%Ni alloy in the $\gamma$–$\delta$ two-phase region was used in the present study. The starting materials were Re powder (purity: 99.9 mass%) and Ni powder (purity: 99.95 mass%). After weighing the powders, metal foams ($\varphi$15 mm × 13 mm pellets weighing about 4 g) were fabricated by pressurization (load: 502 MPa). The metal foams were produced by dissolution and solidification using an argon-arc-melting furnace with a titanium getter. The resulting ingot was cut perpendicularly to obtain alloy test samples.

The segmented arc-melted samples for the heat-treatment experiment were enclosed in transparent quartz tubes ($\varphi$13 mm) with a reduced pressure of approximately $5 \times 10^{-4}$ Pa. After maintaining them at 1423 K for 2400 h, 1573 K for 2100 h, and 1773 K for 24 h, the tubes were crushed under water to quench the samples.

Following heat treatment at 1423, 1573, and 1773 K for various times, the surfaces of the quenched samples were mirror-polished using poly crystalline diamond abrasives. Microstructural observations and quantitative elemental analysis were then conducted using an electron probe microanalyzer (EPMA; JEOL, JXA8200). Point analysis was then conducted using an electron probe microanalyzer (EPMA; JEOL, JXA8200). Point analysis

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2.2 Re–Ni alloys by spark plasma sintering

The Re melting point (3459 K) is about 2000 K higher than that of Ni, the sample fabricated by arc melting was not possible to obtain an alloy sample in the δ single-phase region. Therefore, to smelt alloy samples possessing a δ single-phase structure, Re and Ni powders were uniformly mixed in a planetary ball mill, and were sintered using spark plasma sintering.

The Re–Ni alloys had the compositions (at the time of mixing) shown in Table 1. Alloy samples #1 and #2 are in the δ single-phase region and samples #3, #4, and #5 are in the γ–δ two-phase region.

The mixed Re and Ni powders were compressed in a graphite die at 32 MPa using a cylindrical graphite punch in a vacuum of 4 Pa at 1313 K for 10 min in order to prepare sintered samples (φ9 mm × 13 mm pellets). The samples were then segmented for the heat-treatment experiment and enclosed in transparent quartz tubes (φ13 mm) with a reduced pressure of approximately 5 × 10⁻⁴ Pa. After maintaining them at 1423 K for 169 h and 1903 K for 5 min, the tubes were crushed under water to quench the samples.

Microstructural observations and quantitative elemental analysis were then conducted using EPMA.

3. Results and Discussions

Figure 1 shows the macrostructure (a) and microstructure (b) of the lower part of the cross section of the arc-melted sample. Gray and dark gray forms are visible in the lower part of the sample, which possess a structure that surrounds the grain structures or dendrite structures clearly visible in the images.

Figure 2 shows the cross-sectional microstructure and profiles measured along a line for the Re–40 at% Ni alloy that was quenched in water following heat treatment at 1573 K for 240 h. There are bright and dark gray microstructures in the cross-sectional microstructure and concentration distribution data, which correspond respectively to the γ and δ phases. In addition, there are reverse concentration gradients between Re and Ni in the δ phase near the γ/δ interface.

Figure 3 shows the cross-sectional microstructure and Re and Ni concentration profiles measured along lines for the Re–40 at% Ni alloy that had been quenched in water following a heat treatment of (a) 2400 h at 1423 K, (b) 2100 h at 1573 K and (c) 24 h at 1773 K. In all samples, the cross-sectional microstructure exhibits bright and dark gray contrast, indicating the presence of a γ–δ two-phase composition. In addition, within each phase, the concentration of each element is uniform except near the phase interface.

Based on the data shown in Fig. 3, the tie-line compositions for the γ and δ phases were determined. The results are summarized in Table 2, where the values in parentheses show the average with maximum and minimum deviation of the concentrations. The tie-line compositions from Table 2 are shown superimposed on the phase diagram for the binary Re–Ni system.
Ni system reported by Okamoto in Fig. 4, and that reported by Nash et al. in Fig. 5. A line indicating the solid solubility limit of the \(\delta\) phase is shown in Fig. 4 (solid) and Fig. 5 (dotted), but it is unclear what this line truly represents. From the results of the present study, the Ni solubilities of the \(\gamma\) phase and the tie-line compositions of the \(\delta\) phase are 28.3 at\% for 1423 K, 30.7 at\% for 1573 K, and 34.7 at\% for 1773 K. Moreover, Narita et al.\(^{20}\) reported values of 28–30 at\% for 1373–1573 K. These results are shown along with those of Neubauer et al.\(^{21}\) in Figs. 4 and 5. In other words, it is clear that the results of the present study are in agreement.

Fig. 3 Cross-sectional microstructure and concentration profiles of Re and Ni measured along lines for Re–40 at\%Ni alloy following heat treatment. (a) 2400 h at 1423 K, (b) 2100 h at 1573 K and (c) 24 h at 1773 K.

Fig. 4 Compositions of the \(\gamma\) and \(\delta\) phases of a binary Re–Ni system in contrast to those reported by Okamoto,\(^{18}\) Narita,\(^{20}\) and Neubauer et al.\(^{21}\)

Table 2 Terminal compositions (at\%) of \(\gamma\) and \(\delta\) phases in Re–40 at\%Ni alloy obtained by heat treatment at 1423, 1573 and 1773 K.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>(\gamma) phase</th>
<th>(\delta) phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Re</td>
<td>Ni</td>
</tr>
<tr>
<td>1423</td>
<td>13.4 (0.3)</td>
<td>86.6 (0.3)</td>
</tr>
<tr>
<td>1573</td>
<td>16.4 (0.3)</td>
<td>83.6 (0.3)</td>
</tr>
<tr>
<td>1773</td>
<td>20.2 (0.3)</td>
<td>79.8 (0.3)</td>
</tr>
</tbody>
</table>
with those of previously reported dispersion experiments. In addition, the phase diagrams reported by Okamoto and Nash et al. essentially agree regarding the Ni solubility limit of the $\gamma$ phase for alloys fabricated by both arc melting and spark plasma sintering.

Figures 6(a), 6(b) and 6(c) respectively show the cross-sectional microstructure of sintered alloy samples #1 (Re–5 at%Ni), #2 (Re–11 at%Ni) and #3 (Re–22 at%Ni) that were quenched in water following heat treatment for 169 h at 1423 K. The uniform bright contrast indicates that these samples all consist of a single phase. Voids in the samples appear as dark gray regions. Moreover, based on the concentration of Re and Ni, the samples have a $\delta$-phase composition with a Ni content of (a) 5.9 to 6.4 at%, (b) 11.2 to 12.0 at%, and (c) 22.0 to 22.1 at%.

Although the peritectic temperature is 1893 K based on the phase diagrams reported by Okamoto and Nash et al., differences between the Ni solid solubility limit in the $\delta$ phase were observed. Therefore, heat treatment experiments were conducted at 1423 and 1903 K in order to clarify the Ni solid solubility limit of the $\delta$ phase.

Figures 7(a) and 7(b) show photographs of sintered alloy samples #4 (Re–30 at%Ni) that was quenched in water following heat treatment at 1423 K for 169 h. The bright $\delta$ phase is seen to consist of 71.7 at%Re and 28.3 at%Ni, whereas the gray $\gamma$ phase consists of 15.3 at%Re and 84.7 at%Ni. Moreover, the Re and Ni concentrations in the $\gamma$ and $\delta$ phases are seen to be fairly uniform. From these results, the Ni solid solubility in the $\delta$ phase is similar to that for the alloy sample prepared by arc melting and rapidly cooled after heat treatment at 1423 K for 2400 h.
Figures 9(a) and 9(b) show the cross-sectional macrostructure and microstructure, respectively, of sintered alloy samples #5 (Re–70 at% Ni) that was quenched in water following heat treatment at 1903 K for 5 min. Figure 9(b) shows the profiles measured along a line indicated in the cross-sectional microstructure. It can be seen that the bright γ-phase grains are completely enclosed in the Ni-rich δ-phase.

In contrast to the Re–30 at% Ni alloy shown in Fig. 8, the γ-phase possesses a fine-grained structure, whereas the δ-phase forms the basic matrix.

At 1903 K, as shown by the phase diagrams reported by Okamoto and Nash et al., because the liquid and δ-phases can coexist, it is believed that the γ-phase melted during the heat treatment. Moreover, from the Re and Ni distributions obtained in the present study, the Ni concentration in the δ-phase is 35 at%.

Although locally uniform regions were produced in the alloy samples fabricated by arc melting, it was not possible to obtain a uniform structure across the entire sample even when heat treatment was performed for long time periods. On the other hand, it was possible to produce samples with a δ single-phase structure by the spark plasma method; however, large differences (the precise values are not reported) occurred at the melting points of the δ and γ-phases, and numerous voids were formed in the sample. The results obtained in the present study concerning the Ni solid solubility limits in the δ-phase using both sample preparation methods do not agree with results obtained from previously reported phase diagrams.

4. Conclusions

Re–Ni alloys were fabricated by arc melting and spark plasma sintering, followed by heat treatment for a prescribed period of time and subsequent quenching in water. Using these samples, the tie-line compositions of the δ and γ-phases in the binary Re–Ni system were experimentally determined by cross-sectional microstructural observations and compositional analysis using EPMA. The following results were obtained:

1. For the Re–40 at% Ni alloy fabricated by arc melting, the tie-line compositions of the δ and γ-phases were experimentally determined at 1423, 1573, and 1773 K.

2. The solid solubility of Re in the γ-phase was 13.4 at% at 1423 K, 16.4 at% at 1573 K, and 20.2 at% at 1773 K, which was in accordance with the results of the calculated phase diagrams and previously reported diffusion-couple experiments.

3. The solid solubility of Ni in the δ-phase was 28.3 at% at 1423 K, 30.7 at% at 1573 K, and 34.7 at% at 1773 K, which agreed with the results of the previously reported diffusion-couple experiments.

4. In the Re–30 at% Ni alloy fabricated by spark plasma sintering, the solid solubility of Ni in the δ-phase at 1423 K was 28.3 at%.

5. The solid solubility of Ni in the δ-phase was in agreement for alloy samples prepared by both arc melting and spark plasma sintering, but did not agree with values obtained from the previously reported phase diagrams.
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