Tie-Line Compositions of the σ and (γ , δ) Phases in the Re-Cr-Ni System at 1573 K^{*1}

Shigeru Saito¹, Toshiyuki Takashima¹, Katsumi Miyama¹,
Kazuya Kurokawa² and Toshio Narita^{2,*2}

¹Hokkaido Institute of Technology, Sapporo 006-8585, Japan

²Center for Advanced Research of Energy and Materials, Faculty of Engineering,
Hokkaido University, Sapporo 060-0808, Japan

Compositions with tie lines between the σ and (γ , δ) phases in a ternary Re-Cr-Ni system were investigated by heat treating various ternary Re-Cr-Ni alloys at 1573 K in vacuum for up to 2000 h. The microstructures of the Re-containing alloys that had been water quenched after various heat treatment for times were observed and their concentration profiles for Re, Cr, and Ni were measured using an electron probe microanalyzer. The Re-Cr-Ni alloys consisted of the σ phase with either the γ or δ phase. The concentration profiles of the γ phase became flat after short heat treatment, whereas longer times of up to 2000 h were required to achieve the same effect for the σ and δ phases.

The tie-line composition (at%) of each phase at 1573 K was experimentally determined as follows. The σ phase tie-line with the γ phase (17.3 Re, 20.6 Cr, and 62.1 Ni) consists of 53.1 Re, 25.5 Cr, and 21.4 Ni. The σ phase tie-lined with the γ phase (16.9 Re, 19.2 Cr, and 63.9 Ni) consists of 53.0 Re, 24.6 Cr, and 22.4 Ni. The σ phase tie-line with the γ phase (12.7 Re, 24.8 Cr, and 62.5 Ni) consists of 48.4 Re, 30.9 Cr, and 20.7 Ni. The σ phase tie-line with the γ phase (6.1 Re, 46.2 Cr, and 47.7 Ni) consists of 28.1 Re, 52.3 Cr, and 19.6 Ni. The σ phase tie-line with the δ phase (85.6 Re, 5.2 Cr, and 9.2 Ni) consists of 61.1 Re, 27.7 Cr, and 11.2 Ni. [doi:10.2320/matertrans.M2011206]

(Received July 6, 2011; Accepted September 30, 2011; Published November 25, 2011)

Keywords: rhenium-chromium-nickel, phase diagrams, sigma phase, diffusion barrier layer, tie-line

1. Introduction

To enhance the thermal efficiencies of gas turbines and jet engines, the temperature of the combustion gas has been continuously increased. Next-generation gas turbines^{1,2)} employ a turbine inlet temperature of 1973 K. Thermal barrier coating (TBCs) are used to protect the Ni-based superalloy in the turbine 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.^{3,4)} However, even when TBCs and cooling systems are employed,⁵⁾ Ni-based single-crystal superalloy with high-temperature strength still needs to be developed because the temperature of the base material is expected to exceed 1273 K. One problem is the inward diffusion of Al, placed in the bond coating layer for the purpose of forming protective scales of Al₂O₃, which reduces the concentration of Al and lowers the oxidation resistance of the coating. It has also been reported that diffusion of alloying elements in the substrate could lead to decrease in the mechanical properties of the Ni-based superalloy.⁶⁾ To prevent diffusion of Al into the substrate, a number of diffusion barrier coatings have been proposed;^{7–10)} however, after a relatively short oxidation time the barrier layer loses the layer structure, resulting in rapid, catastrophic oxidation behavior. Narita *et al.* proposed a diffusion barrier coating with a duplex layer structure, containing the σ -phase of Re-Cr-Ni as the diffusion barrier layer. In the coating, the σ -layer was sandwiched between a Ni-based superalloy and Ni-aluminides in the Al-reservoir layer.^{11,12)}

To elucidate the properties of the Re-Cr-Ni alloy, information regarding the phase diagrams and diffusivity

is required.^{13,14)} It is essential to determine the structural stability of the sandwiched Re-Cr-Ni alloy layer. Narita *et al.* proposed for a formation process of the diffusion barrier layer at high-temperature such as 1573 K.¹⁵⁾

In this study, we discuss experimental results with respect to the tie-line compositions of the σ and (γ , δ) phases in the Re-Cr-Ni phase diagram for a formation process of the diffusion barrier layer at 1573 K.

2. Experimental Procedure

We used Re-Cr-Ni alloys with the compositions (at the time of mixing) shown in Table 1. Alloy samples #1, #2, #3, and #4 are in the γ - σ two-phase region and sample #5 is in the δ - σ two-phase region.

The starting materials used to prepare these alloy samples were Re powder (purity: 99.9 mass%), Cr powder (purity: 99.99 mass%), and Ni powder (purity: 99.95 mass%). After weighing them, metal foams (ϕ 13 mm $\times$ t2.5 mm pellets weighing about 2.2 g) were produced by pressurization (load: 502 MPa). The metal foams were obtained 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

Table 1 Nominal alloy compositions (at%).

Alloy	Re	Cr	Ni
#1 (Re-28Cr-60Ni)	12	28	60
#2 (Re-25Cr-30Ni)	45	25	30
#3 (Re-30Cr-35Ni)	35	30	35
#4 (Re-50Cr-30Ni)	20	50	30
#5 (Re-20Cr-10Ni)	70	20	10

^{*1}This Paper was Originally Published in Japanese in J. Japan Inst. Metals
75 (2011) 361–365.

^{*2}Emeritus Professor, Hokkaido University

Fig. 1 Cross-sectional microstructure and Re, Cr, and Ni concentration profiles measured along a line on sample #1 (Re-28 at%Cr-60 at%Ni) after heat treatments at 1573 K for 700 h.

Fig. 2 Cross-sectional microstructure and Re, Cr, and Ni concentration profiles measured along a line on sample #1 (Re-28 at%Cr-60 at%Ni) after heat treatments at 1573 K for 1500 h.

(ϕ 12 mm) with a reduced pressure of approximately 5×10^{-4} Pa. After maintaining them at 1573 K for up to 2000 h (approximately 83 days), the tubes containing the samples were crushed underwater to quench the samples.

After being heat treated at 1573 K for various times, the surface of the quenched samples were mirror-polished using polycrystalline diamond abrasives. Microstructure observations and quantitative elemental analysis were then conducted using an electron probe microanalyzer (EPMA; JEOL, JXA8200). Point analysis was performed at 1 μ m intervals for EPMA analysis conditions of an acceleration voltage of 15 kV and a probe current 3.5×10^{-8} A. After confirming that the Re, Cr, and Ni concentrations were uniform (i.e., within ± 1 at%) over the entire phase, the tie-line composition was determined from the average of the measurement points within the area from 2 to 7 μ m depth from the interface. Data from the region closer to the interface were not used because of uncertainties due to the beam size (ϕ 1 μ m) of the EPMA.

3. Results and Discussions

Figure 1 shows the cross-sectional microstructure and profiles measured along a line on the alloy sample #1 (Re-28 at% Cr-60 at% Ni) quenched in water after heat treatment at 1573 K for 700 h. There are bright and dark gray microstructures in the cross-sectional microstructure and concentration distribution data, which correspond respectively to the σ and γ phases. In addition, there are reverse concentration gradients between Re and Ni in the σ phase near the σ/γ interface.

Figure 2 shows the cross-sectional microstructure and Re, Cr, and Ni concentration profiles measured along a line on alloy sample #1 (Re-28 at% Cr-60 at% Ni) that has been

quenched in water after heat treatment at 1573 K for 1500 h. In the cross-sectional microstructure, the dark gray microstructure is surrounded by the bright microstructure. The concentration distribution reveals that the concentration of each element is approximately uniform except near the phase interface. The bright microstructure has the σ phase with a composition of 53.1 at% Re-25.5 at% Cr-21.4 at% Ni and the dark gray microstructure has the γ phase with a composition of 17.3 at% Re-20.6 at% Cr-62.1 at% Ni.

In this study, the Re-Cr-Ni alloy was fabricated by arc melting and heat treated at 1573 K for a long period (2000 h) to determine the tie-line composition of the σ phase and the γ and δ phases. However, segregation due to solidification varies greatly across the sample and we were unable to achieve homogeneity over the entire sample. Consequently, we discuss the results obtained in the upper part of the samples where local equilibrium was achieved in all phases.

Figures 3(a), 3(b), and 3(c) respectively show the cross-sectional microstructure and Re, Cr, and Ni concentration profiles measured along lines on the alloy samples #2 (Re-25 at% Cr-30 at% Ni), #3 (Re-30 at% Cr-35 at% Ni), and #4 (Re-50 at% Cr-30 at% Ni) that had been quenched in water after heat treatment for 2000 h at 1573 K. In all samples, the cross-sectional microstructure has bright and dark gray areas. The concentration distribution shows γ - σ two-phase structures in Figs. 3(a), 3(b), and 3(c). In addition, in each phase the concentration of each element is uniform except near the phase interface.

Figure 4 shows the cross-sectional microstructure and Re, Cr, and Ni concentration profiles measured along a line on alloy sample #5 (Re-20 at% Cr-10 at% Ni) that had been quenched in water after heat treatment for 2000 h at 1573 K. The data indicates that the bright δ phase consists of 85.6 at% Re-5.2 at% Cr-9.2 at% Ni and the dark gray σ phase consists

Fig. 3 Cross-sectional microstructures and Re, Cr, and Ni concentration profiles measured along lines for the alloys after heat treatment at 1573 K for 2000 h. (a) Sample #2 (Re-25 at%Cr-30 at%Ni), (b) sample #3 (Re-30 at%Cr-35 at%Ni) and (c) sample #4 (Re-50 at%Cr-30 at%Ni).

Fig. 4 Cross-sectional microstructure and Re, Cr, and Ni concentration profiles measured along a line on sample #5 (Re-20 at%Cr-10 at%Ni) after heat treatments at 1573 K for 2000 h.

of 61.1 at% Re-27.7 at% Cr-11.2 at% Ni. In both the δ and σ phases, the concentration of each element is uniform except near the phase interface.

Based on the data shown in Figs. 2, 3, and 4, we determined the tie-line compositions for the γ and σ phases and the δ and σ phases. The results are summarized in Table 2 (the values in parentheses show the average with maximum and minimum deviation of the concentrations).

Table 2 Terminal compositions (at%) of the γ , σ and δ phases in a Re-Cr-Ni system obtained from the heat treatment at 1573 K.

Sample	γ -phase			σ -phase			δ -phase		
	Re	Cr	Ni	Re	Cr	Ni	Re	Cr	Ni
#1	17.3 (0.2)	20.6 (0.5)	62.1 (0.8)	53.1 (0.6)	25.5 (0.5)	21.4 (0.8)			
#2	16.9 (0.2)	19.2 (0.2)	63.9 (0.2)	53.0 (0.6)	24.6 (0.4)	22.4 (0.3)			
#3	12.7 (0.2)	24.8 (0.4)	62.5 (0.4)	48.4 (0.4)	30.9 (0.4)	20.7 (0.4)			
#4	6.1 (0.3)	46.2 (0.5)	47.7 (0.7)	28.1 (0.2)	52.3 (0.4)	19.6 (0.5)			
#5				61.1 (0.7)	27.7 (0.3)	11.2 (0.6)	85.6 (0.8)	5.2 (0.2)	9.2 (0.4)

Figure 5 shows the phase diagram for the Re-Cr-Ni system at 1573 K constructed based on the results in Table 2. In this figure, the open circles indicate the tie-line compositions of the γ and σ phases whereas the δ and σ phases the thin solid lines connecting the open circles indicate the experimentally determined two-phase tie-lines. Thus, the solid solubility of Ni in the σ phase was found to be 19.6~22.4 at% and the Cr concentration of the σ phase tie line with the γ phase increased from 24.6 to 52.3 at% with decreasing solid solubility of Ni.

The solid solubility of Re in the γ phase tie line with the σ phase was found to be 6.1~17.3 at%. A tie line was established between the σ and the δ phase, where the Cr and Ni concentrations are respectively 27.7 and 11.2 at% in the σ phase and 5.2 and 9.2 at% in the δ phase.

Figure 6 show the phase diagram for the Re-Cr-Ni system at 1423 K. The open circles in this figure indicate the tie-line

Fig. 5 Tie lines obtained in the present investigation plotted on the phase diagram of Re-Cr-Ni ternary system at 1573 K.

Fig. 6 Tie lines obtained in the present investigation plotted on the phase diagram of Re-Cr-Ni ternary system at 1423 K reported by Saito *et al.*¹⁴⁾

compositions of the σ and (γ , δ) phases and the thin experimental curves connecting the data points show the two-phase tie lines. The compositions of the σ phase tie line with the γ and δ phases are plotted on the phase boundary line of the σ phase. The phase boundary line of the σ phase at 1573 K was found to be approximately equal to that at 1423 K. The tie lines of all compositions of the γ phase with the σ phase are plotted in the γ - σ two-phase coexistence region at 1423 K. These results imply that at 1573 K, the γ single-phase region expands and the γ - σ two-phase coexistence region contracts.

4. Conclusions

Using the Re-Cr-Ni alloys fabricated by arc melting, heat treated for up to 2000 h, and then quenched in water, the tie-line compositions of the σ and (γ , δ) phases at 1573 K were experimentally determined from cross-sectional microstruc-

ture observations and the element concentration distribution were determined by EPMA. The following results were obtained:

- (1) The Re-Cr-Ni alloy fabricated by arc melting required long-term heat treatment (2000 h) to achieve the equilibrium composition.
- (2) The tie-line compositions of the σ phase and the γ and δ phases are as follows:
 - (a) The γ phase (17.3 at% Re-20.6 at% Cr-62.1 at% Ni) has a tie line with the σ phase (53.1 at% Re-25.5 at% Cr-21.4 at% Ni).
 - (b) The γ phase (16.9 at% Re-19.2 at% Cr-63.9 at% Ni) has a tie line with the σ phase (53.0 at% Re-24.6 at% Cr-22.4 at% Ni).
 - (c) The γ phase (12.7 at% Re-24.8 at% Cr-62.5 at% Ni) has a tie line with the σ phase (48.4 at% Re-30.9 at% Cr-20.7 at% Ni).
 - (d) The γ phase (6.1 at% Re-46.2 at% Cr-47.7 at% Ni) has a tie line with the σ phase (28.1 at% Re-52.3 at% Cr-19.6 at% Ni).
 - (e) The δ phase (85.6 at% Re-5.2 at% Cr-9.2 at% Ni) has a tie line with the σ phase (61.1 at% Re-27.7 at% Cr-11.2 at% Ni).
- (3) The solid solubility of Ni in the σ phase is in the range 19.6~22.4 at%, and the Cr concentration in the σ phase tie line with the γ phase decreases when the solid solubility of Ni increases from 24.6 to 52.3 at%.

Acknowledgment

This work was supported by a Grant-in-Aid for Scientific Research (Young Scientists (B), No. 21760591) from Japan Society for the Promotion of Science.

REFERENCES

- 1) H. Harada: J. Gas Turbine Soc. Japan **31** (2003) 94–107.
- 2) Y. Yoshioka, H. Doi, J. Takeda, K. Nanba, I. Okada, K. Take and T. Ito: J. Gas Turbine Soc. Japan **32** (2004) 130–173.
- 3) T. Hino, Y. Yoshioka, Y. Ishiwatari, A. Nagata, T. Kobayashi, Y. Koizumi and H. Harada: Report of the 123rd Committee on Heat-Resisting Materials and Alloys, (Japan Society for the Promotion of Science, **40**, 1999) pp. 141–150.
- 4) H. Arikawa and Y. Kojima: J. Surf. Finish. Soc. Japan **52** (2001) 11–15.
- 5) Y. Koizumi, J. X. Zhang, T. Kobayashi, T. Yokokawa, H. Harada, Y. Aoki and M. Arai: J. Japan Inst. Metals **67** (2003) 468–471.
- 6) P. Elliott and A. F. Hampton: Oxid. MET **14** (1979) 449–468.
- 7) H. Hosoda, T. Kingetsu and S. Hanada: Proc. Third Pacific Rim Int. Conf. on Advanced Materials and Processing (PRICM 3), (1998) pp. 2379–2384.
- 8) J. Mülle and D. Neuschütz: Vacuum **71** (2003) 247–251.
- 9) R. Cremer, M. Witthaut, K. Reichert, M. Schierling and D. Neuschütz: Surf. Coat. Technol. **108–109** (1998) 48–58.
- 10) O. Knotek, F. Löffler and W. Beele: Surf. Coat. Technol. **61** (1998) 6–13.
- 11) T. Narita: J. High Temperature Soc. **28** (2002) 135–143.
- 12) H. Matsumaru, S. Hayashi and T. Narita: Mater. Sci. Forum **522–523** (2006) 285–292.
- 13) S. Saito, K. Kurokawa, S. Hayashi, T. Takashima and T. Narita: J. Japan Inst. Metals **71** (2007) 608–614.
- 14) S. Saito, K. Kurokawa, S. Hayashi, T. Takashima and T. Narita: J. Japan Inst. Metals **72** (2008) 132–137.
- 15) T. Narita, T. Izumi, T. Nishimoto, Y. Shibata, K. Z. Tosin and S. Hayashi: Mater. Sci. Forum **522–523** (2006) 1–14.