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Interdiffusion in fcc Ni–X (X = Rh, Ta, W, Re and Ir) alloys

Juan Chen [a], Jinkun Xiao [b], Lijun Zhang [a, *], Yong Du [a]

[a] State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, China
[b] College of Mechanical Engineering, Yangzhou University, Yangzhou, 225127, China

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ABSTRACT

The interdiffusion coefficients in binary face-centered cubic (fcc) Ni–X (X = Rh, Ta, W, Re and Ir) alloys at 1473, 1523, 1573 and 1623 K were measured by using semi-infinite diffusion couples together with the Sauer–Freise method. A scientific method was employed to evaluate the errors of the determined interdiffusivities by considering the error propagation. The measured interdiffusion coefficients agree in general with the literature data. In order to find out the possible substitutional element for Re in Ni-based superalloys, a comprehensive comparison among the interdiffusion coefficients in fcc Ni–X (X = Nb, Mo, Ru, Rh, Pd, Ta, W, Re, Os, Ir and Pt) alloys with 6 wt% X at 1473–1623 K was conducted. The comparison results indicate that fcc Ni-6 wt% Os alloys exhibit the lowest diffusion coefficient, followed by Ni-6 wt% Re and Ni-6 wt% Ir alloys. The further analysis on the variation of interdiffusion coefficient with its influence factors including alloying concentration, temperature, atomic number, activation energy, atomic radius and compressibility was also performed.

1. Introduction

The crystal structure of nickel (Ni) is a stable face centered cubic (fcc) crystal structure at temperatures ranging from room temperature to its melting point [1]. This structure allows it to resist mechanical and chemical degradation at elevated temperatures, and for this reason nickel-based superalloys are widely used in both aviation and land-based gas turbine environments [2–5]. The nickel-based superalloys exhibit a typical microstructure consisting of a high volume fraction of coherently precipitated γ' (ordered fcc-$L1_2$ structure) cubes separated by thin channels of γ-matrix (disordered fcc-A1 structure). To meet the extreme requirements for function at high temperatures, nickel-based superalloys require high resistance to creep deformation. Resistance to creep deformation depends largely on diffusion coefficients, and thus the refractory alloying elements are usually added into γ-matrix phase of nickel-based superalloys [6,7]. For instance, rhenium (Re), which exhibits fairly low diffusion coefficients, is often added to nickel-based superalloys to improve creep resistance [8]. The amount of Re used in these superalloys has increased from 3 wt% in the second generation to 6 wt% in the third generation [9]. Though the addition of higher amounts of Re can improve creep resistance, this method has some drawbacks [8], including, *i*) the formation of topologically packed phases (TCPs), and *ii*) increased costs due to the high price of Re. Therefore, in recent years, efforts [8,10–19] have been made to evaluate alloy elements with comparable diffusion coefficients for use in next generation superalloys.

First, it is necessary to obtain reliable measurements of interdiffusion coefficients in Ni-rich binary alloys (in the fcc structure) consisting of Ni and the potential elements. One pragmatic method for selecting potential substitutional elements is to start with the elements adjacent in the periodic table to Re, including Nb, Mo, Ru, Rh, Pd, Ta, W, Os, Ir and Pt. There have been some reports on interdiffusivities in all the related binary systems, i.e., Ni–Nb [14,20], Ni–Mo [14,21–25], Ni–Ru [12,13,15], Ni–Rh [15], Ni–Pd [11,15], Ni–Ta [16], Ni–W [12,16,21,26–28], Ni–Os [29,30], Ni–Ir [15] and Ni–Pt [10,15,25]. However, there is only one report for Ni–Rh, Ni–Ta and Ni–Ir systems, by Karunaratne et al. [15,16]. Our recently measured interdiffusion coefficients in fcc Ni–Os alloys [29] was inconsistent with previous data in the literature [30]. Therefore, new experimental data are needed to validate the interdiffusion coefficients for Ni–Rh, Ni–Ta and Ni–Ir systems. For fcc Ni–Re alloys, the data measured by Mabruri et al. [12] and Karunaratne et al. [16] was limited to temperatures $\leq$ 1573 K, and thus new experiments at higher temperatures need to be conducted. For the fcc Ni–W alloys, although there is a range of reported interdiffusivities in the literature [12,16,21,26–28], certain deviation exists among them, so new experimental

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* Corresponding author.
E-mail addresses: xueyun168@gmail.com, lijun.zhang@csu.edu.cn (L. Zhang).

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interdiffusivities are needed for this alloy as well.

The major objectives of the present work are: (*i*) to measure the interdiffusivities in fcc Ni–X (Rh, Ta, W, Re and Ir) alloys by employing solid single-phase diffusion coupled together with the Sauer–Freise method, and (ii) to comprehensively compare the interdiffusion coefficients in fcc Ni–X (X = Nb, Mo, Ru, Rh, Pd, Ta, W, Os, Ir and Pt) alloys with those in fcc Ni–Re alloys at the same concentration typically used for Re in commercial Ni-based alloys to determine the optimal elements to substitute for Re.

2. Experimental procedure

2.1. Sample preparation and microchemical analysis

Ni–9.7 wt% Rh, Ni–8.4 wt% Ta, Ni–25.0 wt% W, Ni–21.4 wt% Re and Ni–21.7 wt% Ir alloy ingots were prepared in a high purity argon atmosphere using an arc melting furnace (WKDHL-1, Opto-electronics Co., Ltd., Beijing, China), which is equipped with a non-consumable tungsten electrode and a water-cooled copper anode. Ni ingots (purity: 99.99 wt%), Rh pieces (purity: 99.99 wt%), Ta ingots (purity: 99.99 wt%), W particles (purity: 99.99 wt%), Re pieces (purity: 99.99 wt%), and Ir particles (purity: 99.99 wt%) were used as the raw materials. All the five alloy ingots were prepared in the same way as described in our recent work on fcc Ni–Os alloys [29], which can make the alloy elements, i.e., Rh, Ta, W, Re and Ir, to be completely dissolved in the Ni matrix, respectively. After that, all the prepared alloy ingots and a high-purity Ni bar were then annealed in sealed quartz tubes at 1573 ± 2 K for 288 ks for further improving their homogeneity and increasing the grain size. Subsequently, the annealed ingots and pure Ni bar were cut into blocks with a dimension of 5 × 5 × 1 mm^3. After being ground and polished, the alloys and pure Ni blocks were bound together with Mo clamps to form Ni/Ni–9.7 wt% Rh, Ni/Ni–8.4 wt% Ta, Ni/Ni–25.0 wt % W, Ni/Ni–21.4 wt% Re and Ni/Ni–21.7 wt% Ir diffusion couples. Ni/Ni–9.7 wt% Rh, Ni/Ni–8.4 wt% Ta and Ni/Ni–21.7 wt% Ir diffusion couples were then encapsulated in vacuum quartz tubes and annealed for at 1473 ± 2, 1523 ± 2, 1573 ± 2 and 1623 ± 2 K for durations of 252, 129.6, 86.4 and 28.8 ks, respectively. While Ni/Ni–25.0 wt% W and Ni/Ni–21.4 wt% Re diffusion couples were encapsulated in vacuum quartz tubes and annealed for at 1473 ± 2, 1523 ± 2, 1573 ± 2 and 1623 ± 2 K for durations of 372.6, 131.4, 158.4 and 43.2 ks, respectively. Finally, the quartz tubes were taken out from the furnace and directly quenched in water. All the diffusion couples were examined by electron probe microanalyzer (EPMA) (JXA-8100, JEOL, Japan) to determine the concentration–distance profiles. The error for concentration measurements is within 1%.

2.2. Determination of diffusion coefficients

When a diffusion couple anneals at a certain temperature, the interdiffusion occurs. The concentration profile can be obtained at a certain time by measuring the concentration of the diffusion species at depth x with EPMA, and can be then used to calculate the interdiffusivities $\tilde{D}$. There are several methods which can be used to determine interdiffusion coefficients in binary systems. In the present work, the Sauer–Freise method was used to calculate the flux $\tilde{J}$ and interdiffusivities $\tilde{D}$ in fcc Ni–X (Rh, Ta, W, Re and Ir) alloys,

$$\tilde{J} = \frac{1}{2t} \cdot \left[(1 - Y_X) \cdot \int_{-\infty}^{x} Y_X \cdot dx + Y_X \cdot \int_{x}^{\infty} (1 - Y_X) \cdot dx \right] \tag{1}$$

$$\tilde{D} = \frac{1}{2t} \cdot \frac{dx}{dY_X} \cdot \left[(1 - Y_X) \cdot \int_{-\infty}^{x} Y_X \cdot dx + Y_X \cdot \int_{x}^{\infty} (1 - Y_X) \cdot dx \right] \tag{2}$$

where t is diffusion time, and Y_X is the normalized concentration given by

$$Y_X = \frac{C_X - C_X^-}{C_X^+ - C_X^-} \tag{3}$$

where C_X^- is the concentration of X (Rh, Ta, W, Re and Ir) at one end of the diffusion couple, while C_X^+ is that at the other end of the diffusion couple. C_X is the concentration at which $\tilde{D}$ is to be evaluated.

3. Results and discussion

3.1. Concentration profiles and interdiffusion coefficients

Fig. 1(a)–(e) displays the typical concentration–distance profiles of all the diffusion couples (i.e., Ni/Ni–9.7 wt% Rh, Ni/Ni–8.4 wt% Ta, Ni/Ni–25.0 wt% W, Ni/Ni–21.4 wt% Re and Ni/Ni–21.7 wt% Ir) annealed at 1573 K in the present work. To simplify presentation, all the original experimental data for the measured concentration–distance profiles of Ni/Ni–9.7 wt% Rh, Ni/Ni–8.4 wt % Ta, Ni/Ni–25.0 wt% W, Ni/Ni–21.4 wt% Re and Ni/Ni–21.7 wt% Ir diffusion couples annealed at 1473, 1523, 1573 and 1623 K for different times are provided as Supplementary Materials. As can be seen in Fig. 1, all the profiles are asymptotic, and can fit the Boltzmann curves very well, indicating that the atomic diffusion occurs in the solid solution region of each system in a good state. The diffusion time for each diffusion couple is also indicated in each plot. Though the diffusion time of Ni/Ni–Re and Ni/Ni–W couples is longer than that of Ni/Ni–Ta and Ni/Ni–Rh couples, the diffusion distances of Ta and Rh in Ni are longer than those of Re and W in Ni, indicating that interdiffusion coefficients in Ni–Ta and Ni–Rh systems are larger than those in Ni–Re and Ni–W systems. In order to perform a comprehensive comparison, accurate interdiffusion coefficients in each binary system need to be evaluated.

Based on all the measured concentration profiles, the interdiffusion coefficients in fcc-(Ni) phase of the binary Ni–X (Rh, Ta, W, Re and Ir) systems can be calculated using the Sauer–Freise method, as described in Section 2.2. The obtained interdiffusion coefficients at 1473, 1523, 1573 and 1623 K are presented in Fig. 2(a)–(e). The experimental errors of the interdiffusivities determined by the Sauer–Freise method were evaluated according to the method proposed by Léchelle et al. [31], who considered the error propagation via the following function,

$$u(f(A, B...)) = \sqrt{\sum_{\alpha=A,B...} (u(\alpha))^2 \left(\frac{\partial f}{\partial \alpha} \right)^2} \tag{4}$$

Here, A and B... are the correlation quantities of function f, while $u(\alpha)$ $(\alpha = A, B...)$ is the uncertainty in the measurements of variable α such as concentration. During the evaluation of the experimental errors, the uncertainties from different sources including the experimental measurement and the Boltzmann function fitting were propagated first to the calculation of flux in Eq. (1) and then to the calculation of diffusivities in Eq. (2). Table 1 lists the uncertainties for each parameter contributed to the error propagation in Eq. (4) during error evaluation for interdiffusivities in fcc Ni–X (Rh, Ta, W, Re and Ir) alloys. To eliminate the effect of the absolute value, the relative error, which equals to the uncertainty divided by