INTERDIFFUSION BEHAVIOR IN SIGMA-PHASE USING Ni₃Al/Mo DIFFUSION COUPLES

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Abstract

The sigma-NiMo(Al) phase was formed using Ni₃Al/Mo diffusion couples at 1423, 1473 and 1523 K. The growth of formed phase and the concentration–distance profiles for each component in the diffusion couples were examined by electron probe microanalysis (EPMA). The activation energy for the parabolic growth of σ phase is found to be 525.3 kJ/mol. The concentration dependence and average ternary interdiffusion coefficients in single σ-NiMo(Al) phase were calculated, and the Arrhenius equations of the for the σ-NiMo(Al) phase are calculated, the diffusional interaction between Ni, Mo and Al in σ-NiMo(Al) phase was studied by the cross-interdiffusion coefficients. Moreover, these results were utilized to explain the σ phase formation and growth in γ’ phase.

Key words: Diffusion; TCP phase; Kinetics; Electron probe microanalysis.

1. Introduction

Current generation nickel - base superalloys enhanced by the refractory elements, such as Mo, W, Re and Ru, have remarkable creep resistance at elevated temperature [1-3]. However, the addition of these elements makes the microstructure more susceptible to the formation of the topological close packed (TCP) phases during long-term service [4, 5]. The formation of TCP phases removes important strengthening elements from alloy matrix and the phases themselves are brittle in
nature [6-7]. Therefore, a thorough understanding of the TCP phase formation and growth is critically needed. The formation and growth processes are closely related to diffusion, hence, it is essential to understand the diffusion behavior in TCP phase in detail.

Sigma (σ) phase which can be produced in Ni-Mo-based system is one of the most important phases in TCP race. However, there are few studies focused on the diffusion behavior of this phase. Lanam and Heckel [8] calculated the average interdiffusion coefficient of the σ-NiMo phase at 1473 K, whereas Chou and Link [9] also studied interdiffusion in Ni-Mo system and calculated the parabolic growth constants of the phases with diffusion couples in cylindrical geometry. In the most recent study, Divya and Balam [10] evaluated the integrated diffusion coefficient, average interdiffusion coefficient and activation energies for diffusion in σ-NiMo phase through Ni/Mo diffusion couples with planar interfaces. However, the detailed information such as the main interdiffusion coefficient for each element and the interaction among them in σ phase is still unclear now. The information is difficult to obtain because the change in composition is too small in σ phase in Ni-Mo binary system. In this study, σ phase was formed through the Ni$_3$Al/Mo diffusion couples, in which the composition change in the σ phase is large enough to evaluate the detailed interdiffusion behavior through proper analysis.

2. Experimental procedure

In the present work, Mo pieces (99.5 wt.%) and Ni$_3$Al polycrystalline samples were used as the starting materials, and cut into blocks with approximate dimensions of 4×4×1.5 mm$^3$ and 4×4×3 mm$^3$, respectively. A 4×4 mm$^2$ plane of each piece was grounded down to 2000 grit, polished with 0.3μm alumina powders. Each Ni$_3$Al/Mo diffusion couple was mounted together and spliced under a constant load of 5 MPa in a vacuum furnace at 1523 K for 1 h, then sealed in a quartz tube under an argon atmosphere. Subsequently, the couples were annealed at stabilized temperatures 1423, 1473 and 1523 K (± 1 K), and each temperature for 30 h, 60 h and 90 h.

The standard metallographic preparation was carried out perpendicularly to the diffusion interfaces of annealing couples for electron probe microanalysis (EPMA, JXA-8100, JEOL, Japan) measurement. Then the concentration–distance profiles for each component were determined by quantitative analysis on points at regular intervals of 1. The smooth function was adopted to the data points to ensure that the scatter in the concentration profiles were minimum and the gradient of elements were smooth enough for further calculation [11].

3. Results and discussion

Figure 1(a) shows a typical micrograph of the interdiffusion zone measured by scanning electron microscopy (SEM). The profiles for couple annealed at 1523 K for 30 h are presented as examples in Figure 1(b-d). It can be seen that only one intermetallic phase σ-NiMo(Al) grows in the interdiffusion zone. The observation of σ-NiMo(Al) phase confirms the previous work
by Lu et al. [12], which performed respective preliminary CALPHAD thermodynamic descriptions of the Ni-Al-Mo system. The composition analysis shows that the changes in composition of each component are observable in the σ phase.

The kinetic growth of the σ phase can be investigated immediately as a series of isothermal diffusion experiments have been conducted in this study. The layer thicknesses of σ phase after different annealing time at different temperatures are shown in Figure 2 (a). It can be seen that the curves present parabolic nature to a good approximation. The parabolic growth constant, \( k_p \), is calculated according to the equation \( k_p = \frac{(\Delta x_p)^2}{2t} \), where \( \Delta x_p \) is the thickness of the σ phase and \( t \) is the annealing time. The parabolic rate constants (m²s⁻¹) calculated at 1423, 1473 and 1523 K are equal to \( k_{p1} = 7.79 \times 10^{-17} \), \( k_{p2} = 5.29 \times 10^{-16} \), \( k_{p3} = 1.42 \times 10^{-15} \), respectively. The constants are close to the results measured in [9] but somewhat smaller than that of [10]. The probable reason is the diffusion experiments conducted in [10] were with bonding fixture, and the formation and growth kinetics of σ phase may be susceptible to stress. Further more, the activation energy, \( Q \) (J mol⁻¹), could be determined from the Arrhenius equation of the parabolic growth,

\[
k_p = k^* \exp\left(-\frac{Q}{RT}\right)
\]

where \( k^* \) (m²s⁻¹) is the pre-exponential factor, R (J mol⁻¹K⁻¹) is the gas constant and T (K) is the temperature [13]. The Arrhenius...
plot of the parabolic growth constants is shown in Figure 2b, which yields a value of 525.3 KJ mol⁻¹ for Q, the result is much bigger than that of [10], the reason is mainly because the different end member of diffusion couples were used, the Ni₃Al/Mo diffusion couples were used in this article, while Ni/Mo diffusion couples were used in that of [10].

In order to identify the detailed diffusion behavior in the σ phase, the interdiffusion coefficients were determined in this study. For an isothermal solid–solid diffusion couple, the interdiffusion flux \( \tilde{J}_i \) for each component can be determined at any section \( x \) directly from the smoothed concentration profiles by using the method developed by Dayananda [14]:

\[
\tilde{J}_i(x^*) = \frac{(C_i^e - C_i^o)}{2t} Y_i
\]

\[
\int_{x^*}^{x} (1 - Y_i) dx + (1 - Y_i^*)
\]

\[
\int_{x^*}^{x} Y_i dx (i = 1, 2, ..., n)
\]

where \( C_i^e, C_i^o \) are the terminal concentrations of diffusion couple, and \( Y_i \) is relative concentration variable denoted by \( Y_i = \frac{C_i^e - C_i^o}{C_i^e - C_i^o} \).

According to Dayananda and Cermak’s analysis [15, 16] the concentration dependent interdiffusion coefficients \( \tilde{D}_i^c \) can be calculated from experimental concentrations and the corresponding interdiffusion fluxes by following equation sets:

\[
\int_{x^*}^{x} \tilde{J}_i dx = \tilde{D}_i^c [C_i(x_i) - C_i(x_o)] + \tilde{D}_i^c [C_j(x_i) - C_j(x_o)]
\]

\[
\int_{x^*}^{x} \tilde{J}_i (x - x_o) dx = 2t \left[ \tilde{D}_i^c [J_i (x_i) - J_i (x_o)] + \tilde{D}_j^c [J_j (x_i) - J_j (x_o)] \right]
\]

where \( t \) is the annealing time, \( x_o \) is determined as the average position of Matano plane of component 1 and 2, and \( \tilde{D}_i^c \) refers to the main interdiffusion coefficient \( (i = j) \) or cross interdiffusion coefficient \( (i \neq j) \).

Accordingly, the concentration dependent interdiffusion coefficients in the σ-NiMo(Al) phase were evaluated. The obtained results, \( \tilde{D}_i^c \), and \( \tilde{D}_j^c \), are indicated in Fig. 3. Common features in Fig. 3 can be summarized as follows: (1) The main interdiffusion coefficients of Mo, \( \tilde{D}_i^c \), in the σ -NiMo(Al)

**Figure 2.** (a) The thicknesses of σ phase layer after different annealing time at different temperatures. (b) The Arrhenius plot of the parabolic growth constant \( k_p \) for σ phase.
phase, are larger in magnitude than those of Ni; (2) $D_{\text{MoNi}}^{\text{Ni}}$ tends to increase with the increasing concentration of Mo in $\sigma$ phase; (3) $D_{\text{MoNi}}^{\text{Mo}}$ shows little dependence on Mo concentration and even can be approximated by a straight line in plots of log $D$ vs. $C(\text{Mo})$.

Since the influence of variation in concentration on the interdiffusion coefficients was not significant in this phase, the average ternary interdiffusion coefficients,

$$\tilde{D}_y = \frac{\int_{C(x)}^{} D_y dC_i}{\int_{C(x)}^{} dC_i} \quad ... (5)$$

were determined and listed in Table 1. It is obvious that the influence between Mo and Ni, $\tilde{D}_{\text{MoMo}}^{\text{Ni}}$ and $\tilde{D}_{\text{MoNi}}^{\text{Mo}}$, are comparable in magnitude with each other.

In order to validate the presently obtained interdiffusivities, they were first examined by the following constraints on the interdiffusion coefficients, which express the stability of the solid solution [17],

$$\tilde{D}_{\text{Ni}}^{\text{Ni}} + \tilde{D}_{\text{Mo}}^{\text{Ni}} > 0 \quad ... (6)$$
$$\tilde{D}_{\text{Ni}}^{\text{Ni}} \cdot \tilde{D}_{\text{Mo}}^{\text{Ni}} - \tilde{D}_{\text{Ni}}^{\text{Mo}} \cdot \tilde{D}_{\text{Ni}}^{\text{Ni}} \geq 0 \quad ... (7)$$
$$\left(\tilde{D}_{\text{Ni}}^{\text{Ni}} - \tilde{D}_{\text{Mo}}^{\text{Ni}}\right)^2 + 4 \cdot \tilde{D}_{\text{Ni}}^{\text{Ni}} \cdot \tilde{D}_{\text{Ni}}^{\text{Mo}} \geq 0 \quad ... (8)$$

Substitute the average interdiffusivities of Table 1 in Eqs. (6)–(8), and we found that the presently measured interdiffusivities of $\sigma$-NiMo(Al) phase undoubtedly fulfill these constraints.

Fig.4 shows the Arrhenius plots of $\tilde{D}_{\text{MoMo}}^{\text{Ni}}$, $\tilde{D}_{\text{NiNi}}^{\text{Ni}}$, and $\tilde{D}_{\text{NiMo}}^{\text{Mo}}$, with Al being taken to be the solvent. The presently calculated Arrhenius equations of the $\tilde{D}(m^2/s)$ for the

### Table 1: Average ternary interdiffusion coefficient in $\sigma$-NiMo(Al) phase ($10^{-17}m^2/s$)

<table>
<thead>
<tr>
<th>Diffusion system</th>
<th>Temperature</th>
<th>$\tilde{D}_{\text{MoMo}}^{\text{Ni}}$</th>
<th>$\tilde{D}_{\text{NiNi}}^{\text{Ni}}$</th>
<th>$\tilde{D}_{\text{NiMo}}^{\text{Mo}}$</th>
<th>$\tilde{D}_{\text{NiMo}}^{\text{Ni}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma$-NiMo(Al) phase</td>
<td>1523K</td>
<td>287.1</td>
<td>4.463</td>
<td>49.84</td>
<td>39.71</td>
</tr>
<tr>
<td></td>
<td>1473K</td>
<td>146.7</td>
<td>1.968</td>
<td>24.92</td>
<td>19.85</td>
</tr>
<tr>
<td></td>
<td>1423K</td>
<td>44.35</td>
<td>0.606</td>
<td>7.476</td>
<td>5.956</td>
</tr>
</tbody>
</table>
σ-NiMo(Al) phase are respectively.

\[
\begin{align*}
\bar{D}_{\text{MoAlNi}}^{\text{Al}} &= 1.17 \times 10^{-3} \exp(-337.47 / RT), \\
\bar{D}_{\text{NiAl}}^{\text{Ni}} &= 1.07 \times 10^{-4} \exp(-360.37 / RT), \\
\bar{D}_{\text{MoAlNi}}^{\text{Mo}} &= 3.06 \times 10^{-4} \exp(-342.74 / RT), \\
\bar{D}_{\text{NiAl}}^{\text{Ni}} &= 2.44 \times 10^{-4} \exp(-342.75 / RT),
\end{align*}
\]

It is well known that σ phase is easily precipitated from γ' phase because of the limited solubility of Mo in Ni₃Al [18]. In this study, it is shown that the diffusion of Mo in σ-NiMo(Al) phase are enhanced a lot by Al, and the jump of Mo among its lattice points are much more frequent. Moreover, Mo is a sensitive element to form the TCP phase [19]. A much faster diffusion behavior for Mo combining with its sensitive characteristics increase the probability of σ phase formation. Thus, that gives another reason for easy formation and growth of σ phase from γ' phase in addition to the limited solubility of Mo in Ni₃Al. The present work contributes to thermodynamic [20, 21] and diffusion information of the Ni-Al-Mo system.

4. Conclusions

The square of the thickness of σ-NiMo(Al) layer was found to vary linearly with the annealing time, indicating that the growth of σ-NiMo(Al) phase is diffusion-controlled. The activation energy for the parabolic growth in σ-NiMo(Al) phase is high up to 525.3 kJ mol⁻¹ and the diffusion in this phase is extremely slow. The interdiffusion behavior of Mo in σ-NiMo(Al) phase is significantly enhanced by Al. That is an important reason for why σ phase is easy to form from γ' phase.

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References