Interdiffusion in Co-Based Co–Al–W Ternary Alloys at Elevated Temperatures

Satoshi OBATA, Md. MONIRUZZAMAN* and Yoshinori MURATA

Department of Materials, Physics and Energy Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8603 Japan.

(Received on February 21, 2014; accepted on June 4, 2014)

L12-type Co3(Al,W) compound is a very important phase in Co-based high temperature materials. This study investigated the interdiffusions of Co-based Co–Al–W ternary alloys at 1423, 1473 and 1523 K. Two types of diffusion couples were employed to estimate four diffusivity matrix coefficients (\(D_{\text{CoW}}\), \(D_{\text{CoAl}}\), \(D_{\text{AlW}}\) and \(D_{\text{AlAl}}\)). A modified ternary Boltzmann-Matano method was employed for the evaluation of interdiffusion coefficients. The estimated cross-interdiffusion coefficients \(D_{\text{CoAl}}\) and \(D_{\text{AlCo}}\) had opposite signs at 1523 K which is not contradictory to but rather consistent with the Onsager’s reciprocity theorem. The second derivative of the Gibbs free energy with respect to the Al concentration, \(\partial^2 G_i / \partial C_i^2\)), may have a sign opposite to that of W concentration, \((\partial^2 G_j / \partial C_j^2))\). Experimental results revealed that the effect of W on the Al diffusion flux is greater than that of Al on the diffusion flux of W by about one order of magnitude.

KEY WORDS: interdiffusion coefficient; Co-based alloy; ternary alloy; Onsager’s reciprocity theorem; Gibbs free energy.

1. Introduction

The mechanical properties of the of L12-type intermetallic compound, Ni3Al, have attracted considerable research attention for over 50 years owing to its stress anomaly, i.e., the positive temperature dependence of its strength. Further, among various L12 compounds, Ni3Al has been investigated extensively because it is the most important strengthening phase of Ni-based superalloys. Recently, a new Co-based L12 compound Co3(Al,W) was found by Sato et al. Co-based two-phase alloys composed of a face-centered cubic Co matrix and the compound as precipitates show good high temperature properties. The mechanical properties of materials, such as yield stress and temperature dependence, are their primary characteristics and are the governing factors for their practical applicability. These properties depend on the microstructure and its temperature stability. Microstructural evolution proceeds by atomic diffusion of alloying elements. Hence, diffusion coefficients are parameters that enable prediction and/or interpretation of the mechanical behavior of a material. Apart from mechanical properties, diffusion phenomena are also rate controlling in processes such as phase transformation, oxidation, grain growth etc. The increasing use of superalloys at high temperatures necessitates a clear understanding of their diffusion behavior because diffusion phenomena play a major role in high temperature processes including homogenization and precipitation of \(\gamma\) in the \(\gamma\) matrix. Thus, information on the interdiffusion coefficient as well as on the interaction and thermodynamic relation among the alloying elements is important for effective design of alloys in the future.

The phenomenological description of multicomponent diffusion formulated originally by Onsager has served as an adequate basis for the analysis of diffusion in ternary systems. Two main interdiffusion coefficients, \(D_{ij}\) and \(D_{ji}\), as well as two cross-interdiffusion coefficients, \(D_{ij}\) and \(D_{ji}\), are necessary for describing the atomic diffusion in a ternary system. \(D_{ij}\) and \(D_{ji}\) represent the influence of the concentration gradients of elements i and j, respectively, on their own fluxes. \(D_{ii}\) and \(D_{jj}\) represent the influence of the concentration gradients of elements j and i on the fluxes of elements i and j, respectively. The cross-interdiffusion coefficient is a measure of interaction between elements i and j in the host element k. Despite the importance of the Co3(Al,W) compound, the diffusion in Co-based alloys has not yet been studied. Therefore, this study aims to analyze the interdiffusion coefficients in Co-based ternary alloys and to elucidate the physical meaning of the two cross-interdiffusion coefficients considering the relation between these cross-interdiffusion coefficients and thermodynamic functions.

2. Determination of Interdiffusion Coefficients in Ternary Systems

In a ternary alloy system, the interdiffusion flux, \(\mathbf{J}_i\), \((i = 1, 2)\) can be expressed in terms of coefficients of the diffusivity matrix and the concentration gradients by the following equations:
The four interdiffusion coefficients ($D_{ij}^k$, $D_{ji}^k$, $D_{ii}^k$ and $D_{jj}^k$) represent the diffusivity of the solute elements, $i$ and $j$, in the host element $k$. The superscript $k$ represents Co in this case, $C_i$ denotes the concentration of an element, and $x$ is the diffusion distance.

In this study the Boltzmann-Matano method, which was later extended by Whittle and Green\textsuperscript{9)} for application to multicomponent systems, was adopted for calculating the interdiffusion coefficients. Schematic of the method is shown in Fig. 1. This method enables calculation of the interdiffusion coefficients accurately without determination of the Matano interface.\textsuperscript{10) According to Whittle and Green\textsuperscript{9)} interdiffusion coefficients of a ternary system are obtained from the concentration profiles using the following equations:

$$J_1 = -\frac{\partial C_i}{\partial x} + \frac{\partial C_j}{\partial x} = \frac{1}{2r} \left[ \frac{dx}{dY} \right] \left[ (1-Y_i)\int_{-\infty}^{\infty} \sum_{j} Y_j dx + \sum_{j} (1-Y_j) dx \right],$$

$$J_2 = -\frac{\partial C_j}{\partial x} + \frac{\partial C_i}{\partial x} = \frac{1}{2r} \left[ \frac{dx}{dY} \right] \left[ (1-Y_j)\int_{-\infty}^{\infty} \sum_{i} Y_i dx + \sum_{i} (1-Y_i) dx \right],$$

$$D_{ii}^k = \frac{\partial C_i}{\partial x} = \frac{1}{2r} \left[ \frac{dx}{dY} \right] \left[ (1-Y_i)\int_{-\infty}^{\infty} \sum_{j} Y_j dx + \sum_{j} (1-Y_j) dx \right],$$

$$D_{jj}^k = \frac{\partial C_j}{\partial x} = \frac{1}{2r} \left[ \frac{dx}{dY} \right] \left[ (1-Y_j)\int_{-\infty}^{\infty} \sum_{i} Y_i dx + \sum_{i} (1-Y_i) dx \right].$$

The mole fraction of element $i$ at a distance $x$, $C_i^+$ and $C_i^-$ are the terminal mole fractions at the positions, $x = +\infty$ and $x = -\infty$ (corresponding to the two terminal alloys), respectively, and $t$ is the diffusion time. For a specific ternary system, two types of diffusion couples are employed so that the resulting two diffusion paths intersect at a common composition. The diffusion paths are obtained by re-plotting the concentration profiles of each set of diffusion couples into the Gibbs free energy triangle of Co-rich isothermal section. The diffusivity matrix coefficients ($D_{ii}^k$, $D_{ii}^k$, $D_{jj}^k$ and $D_{jj}^k$) are determined at the cross point composition of the diffusion paths using Eqs. (3)–(5). Data obtained from a set of diffusion couples solve these simultaneous equations and give the four diffusivity matrix coefficients. The detailed procedure using this method has been described elsewhere.\textsuperscript{11)"

3. Experimental

Four types of button ingots of Co alloys (Co-3Al, Co-9Al, Co-3Al-3W and Co-9Al-3W: at%) were prepared by arc melting under high purity argon (Ar) gas atmosphere using high purity Co (99.9 mass%), Al (99.999 mass%) and W (99.96 mass%). The homogenization and grain growth of each specimen were accomplished by 10% cold rolling followed by annealing at 1473 K for 100 h. In all four alloys, grain sizes large enough for diffusion experiments were obtained after the annealing. A representative optical microstructure after homogenization is shown in Fig. 2. The homogenized samples were ground flat into plate samples (7 × 7 × 2 mm), which were then polished with a 0.05 μm alumina powder finish. The plate specimens were subsequently cleaned with acetone in an ultrasonic cleaner. Each diffusion couple listed in Table 1 was assembled with inert markers of alumina fibers 0.3 μm in diameter, placed between the polished surfaces of the two plate specimens.
and clamped using a molybdenum holder. Schematic of the diffusion couple is shown in Fig. 3. Before this arrangement was established, the surfaces of the holder were coated with 1 μm diameter alumina powders to prevent direct contact with the alloys. Two types of diffusion couples were prepared, as shown in Table 1. They were encapsulated in quartz ampoules under Ar gas for diffusion annealing, which was performed at three different temperatures for different durations, as presented in Table 1. The ampoules were evacuated under the pressure of 10⁻⁵ Torr and then filled with high purity (grade A) Ar gas. Moreover, the interface of two specimens in the diffusion couple was covered by surface area of both the samples and they were compressed tightly pressurized by the Mo holder. Possibility of the interface oxidation of samples was thus prevented. The capsules were then quenched in water by breaking the ampoules and subsequently sectioned perpendicular to the diffusion interface. The exposed surface was polished using a 0.05 μm alumina powder finish and cleaned with acetone in an ultrasonic cleaner. The concentration profiles of the elements along the diffusion zone were measured by scanning electron microscopy (SEM) /energy dispersive X-ray spectroscopy (EDX) with the position of the inert alumina marker fixed as the origin of the diffusion distance.

### Table 1. Experimental conditions of diffusion couples.

<table>
<thead>
<tr>
<th>Diffusion couple (at%)</th>
<th>Homogenization heat treatment</th>
<th>Diffusion annealing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-3Al/Co-9Al-3W</td>
<td>1 473 K, 100 h</td>
<td>1 423 K, 312 h</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 473 K, 144 h</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 523 K, 72 h</td>
</tr>
<tr>
<td>Co-9Al/Co-3Al-3W</td>
<td>1 473 K, 100 h</td>
<td>1 423 K, 312 h</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 473 K, 144 h</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 523 K, 72 h</td>
</tr>
</tbody>
</table>

### Table 2. Interdiffusion coefficients in Co–Al–W ternary system.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Co-6.7Al-1.9W</th>
<th>Co-6.3Al-2.2W</th>
<th>Co-6.5Al-2.1W</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 423 K</td>
<td>1.7x10⁻¹⁴</td>
<td>3.7x10⁻¹⁴</td>
<td>8.6x10⁻¹⁴</td>
</tr>
<tr>
<td>1 473 K</td>
<td>2.0x10⁻¹⁵</td>
<td>7.1x10⁻¹⁵</td>
<td>1.8x10⁻¹⁴</td>
</tr>
<tr>
<td>1 523 K</td>
<td>3.8x10⁻¹⁵</td>
<td>7.4x10⁻¹⁵</td>
<td>4.8x10⁻¹⁷</td>
</tr>
</tbody>
</table>

4. Results and Discussion

The concentration profiles and the corresponding diffusion paths after diffusion annealing at 1 423, 1 473 and 1 523 K are shown in Figs. 4–6, respectively. The concentration profiles exhibited sigmoidal curves without any discontinuity, indicating that atomic diffusion occurred in the solid solution region. The diffusion paths show curved shape lines. The calculated diffusivity matrix coefficients ($D_{AlAl}^{Co}$, $D_{AlW}^{Co}$, $D_{WAl}^{Co}$) and the corresponding cross-compositions for the three experimental temperatures are listed in Table...
The main interdiffusion coefficients show positive values which are larger than the cross-interdiffusion coefficients, indicating that the influence of the elements’ own concentration gradients is dominant. At 1423 K, the cross-interdiffusion coefficient, $D_{ij}$, is much smaller than the other cross-interdiffusion coefficients, indicating that the presence of Al has negligible effect on the interdiffusion of W in the Co–Al–W system. The effect of W on the diffusion flux of Al and the effect of Al on the diffusion flux of W can be evaluated with the ratio of the corresponding cross-interdiffusion coefficient to the major one, i.e., $|D_{ij}/D_{ii}|$ and $|D_{ij}/D_{jj}|$, respectively, as given in Table 3. The larger ratio of $|D_{ij}/D_{ii}|$ indicates that the effect of W on the diffusion flux of Al is stronger than that of Al on the diffusion flux of W and it is about one order of magnitude higher.

According to Onsager’s reciprocity theorem, $L_{ij} = L_{ji}$, where $L_{ij}$ and $L_{ji}$ are Onsager coefficients. The cross-interdiffusion coefficients are expressed by the following equations in the ideal solution:

\[
\tilde{D}_i^j = L_{ij} \left( \frac{\partial^2 G_i}{\partial C_j^2} \right), \quad \tilde{D}_j^i = L_{ji} \left( \frac{\partial^2 G_j}{\partial C_i^2} \right),
\]

where, $G_i$ is the Gibbs free energy of a ternary solid solution and $C_i$ and $C_j$ are the concentrations of elements $i$ and $j$ respectively. The sign of the second derivative of $G_i$ with respect to the concentration $C_i$ depends on the curvature of the free energy plane in the ternary system. If the solid solution of this system shows a trend for phase separation, then the sign of the second derivative becomes negative. Furthermore, if the free energy plane has a saddle point, there is a possibility that $(\partial^2 G_i / \partial C_j^2)$ and $(\partial^2 G_j / \partial C_i^2)$

Table 3. Ratio of cross to major interdiffusion coefficients in Co–Al–W ternary system.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>1 423 K</th>
<th>1 473 K</th>
<th>1 523 K</th>
<th>Summary</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{AlW}/D_{AlAl}$</td>
<td>0.12</td>
<td>0.20</td>
<td>0.21</td>
<td>$D_{AlW}/D_{AlAl} &gt; D_{AlW}/D_{AlAl}$</td>
</tr>
<tr>
<td>$D_{WAl}/D_{WAl}$</td>
<td>0.03</td>
<td>0.08</td>
<td>0.07</td>
<td>$D_{WAl}/D_{WAl} &gt; D_{WAl}/D_{WAl}$</td>
</tr>
</tbody>
</table>

Fig. 5. Concentration profile of Al and W in (a) Co-3Al/Co-9Al-3W, (b) Co-9Al/Co-3Al-3W couples after diffusion annealing at 1473 K and (c) the corresponding diffusion paths.

Fig. 6. Concentration profile of Al and W in (a) Co-3Al/Co-9Al-3W, (b) Co-9Al/Co-3Al-3W couples after diffusion annealing at 1523 K and (c) the corresponding diffusion paths.

2. The main interdiffusion coefficients show positive values which are larger than the cross-interdiffusion coefficients, indicating that the influence of the elements’ own concentration gradients is dominant. At 1423 K, the cross-interdiffusion coefficient, $D_{AlW}$, is much smaller than the other cross-interdiffusion coefficients, indicating that the presence of Al has negligible effect on the interdiffusion of W in the Co–Al–W system. The effect of W on the diffusion flux of Al and the effect of Al on the diffusion flux of W can be evaluated with the ratio of the corresponding cross-interdiffusion coefficient to the major one, i.e., $|D_{AlW}/D_{AlAl}|$ and $|D_{WAl}/D_{WAl}|$, respectively, as given in Table 3. The larger ratio of $|D_{AlW}/D_{AlAl}|$ indicates that the effect of W on the diffusion flux of Al is stronger than that of Al on the diffusion flux of W and it is about one order of magnitude higher.
exhibit opposite signs. In such a case, the sign of $\tilde{D}_j^k$ is opposite to that of $D_{ij}$ without any contradiction to Onsager’s theorem.

According to the above discussion, at 1523 K, the solid solution of the system is supposed to have a trend for phase separation resulting in the sign of the second derivative negative. So, $D_{ij}$ became negative at 1523 K. However, this is a qualitative explanation because $G_c$ value at all temperatures is based on the thermodynamical data base (ThermoCalc). It is hard to know the true value. In particular, sign of $D_j$ is related to $\left( \frac{\partial^2 G_c}{\partial C^2} \right)$ which is strongly affected by the concentration dependence of $G_c$. So, it is still difficult to present the quantitative relationship between $D_j$ and $\left( \frac{\partial^2 G_c}{\partial C^2} \right)$.

5. Conclusions

Interdiffusions in Co–Al–W ternary alloys were investigated at 1423, 1473 and 1523 K. Coefficients of the diffusivity matrix were estimated using the modified Boltzmann-Matano method to evaluate the diffusion interaction among the elements in the system. The following conclusions were drawn from the study:

(1) The presence of W in the Co–Al–W ternary system accelerates the interaction between Al and Co.

(2) The effect of presence of W on the diffusion flux of Al is stronger than that of Al on the diffusion flux of W and it is about one order of magnitude higher.

Acknowledgement

This work was supported partly by the Iron and Steel Institute of Japan (Tekkou Kenkyu Shinko Josei) and the Grant-in-Aid for Scientific Research of Japan Society for the Promotion of Science, Japan.

REFERENCES

1) R. Lowrie: Trans. AIME, 194 (1952), 1093.