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Study on Diffusion in the Multicomponent $\beta$-NiAl Phase

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Abstract. Diffusion data at $950^\circ$C are estimated as function of concentration in the multicomponent $\beta$-NiAl phase grown in a nickel-base superalloy by the pack-aluminizing technique. The calculated interdiffusion coefficients are observed to be concentration dependent within the examined composition range. Interdiffusion coefficient of Al and Ni in the multicomponent $\beta$-NiAl phase is obviously less than the reported data. It is speculated that variation in the thermodynamic properties and the structural factor due to the solid solution of the alloying elements may be responsible principally for the decrease in interdiffusion coefficient of Al and Ni in the multicomponent $\beta$-NiAl phase.

1. Introduction
Most of the metallurgical systems involve more than two components and hence it is essential to understand the interactions among various components both from diffusional and thermodynamic consideration. Experimental studies of diffusion in binary and ternary systems are several in literatures [1,2]. Diffusion phenomena in binary NiAl have been thoroughly investigated [3,4]. It is known that NiAl as coating is in fact composed of more than two components resulting from the solid solution of elements from superalloy. Its diffusion behavior is more complicated than in binary system owing to the interaction among the components. It is difficult to extrapolate the experimental data acquired by the binary diffusion couples to an engineering application. Most importantly, interdiffusion of elements of the protective coatings into the alloy can occur and cause degradation of both physical and mechanical properties of coated superalloys [5]. Unfortunately, the thermodynamic model for multicomponent NiAl phase has been not until now set up. It is impossible to estimate the diffusion data in the multicomponent NiAl phase where diffusion data are known to correlate with the thermodynamic interaction parameters of the components. There is no available data on diffusion in multicomponent $\beta$-NiAl phase, which are very critical fundamental system of high temperature coatings. Therefore, the object of this paper is to investigate interdiffusion...
coefficients in the multicomponent \( \beta \)-NiAl phase at 950\(^\circ\)C by means of analyzing interdiffusion fluxes from concentration profiles of the pack-aluminizing nickel-base superalloy.

2. Experimental

The pack-aluminizing technique is used in this study for examining the interdiffusion behavior of multicomponent \( \beta \)-NiAl phase. Diffusion data are determined by analyzing the interdiffusion fluxes from concentration profiles. The chemical compositions of superalloy as substrate are Cr 0.081, Co 0.096, Al 0.13, Ti 0.03 (at%). In the pack aluminizing process, the specimens with the size of 12mm\( \times \)10mm\( \times \)5mm are embedded into the semi-permeable pipe filled with a powder consisting of 96 wt pct FeAl powder as supplier of Al and 4 wt pct NH\(_4\)Cl as activator that is decomposed during heating. Concentration profiles over the diffusion zone are measured using electron probe microanalysis (EPMA) on a JSM-6301F microprobe.

3. Modeling of diffusivity

The average diffusion velocities \( v_i \) of component \( i \) in an arbitrary coordinate system are related to the molar flux of \( j \) by \( v_i = v_j x_j \), where \( x_j \) and \( v_j \) are the mole fraction and mole volume of component \( i \), respectively. If the velocity difference constitutes an invariant regardless of the choice of a special coordinate system, it is possible to use it as a basis for defining the interdiffusivity. It is known that the \( \beta \)-NiAl formation can be regarded as a one dimensional semi-infinite diffusion process. All elements participating in \( \beta \)-NiAl formation are divided into two kinds according to the diffusion direction, one of which is inward diffusion elements defined as A, such as Al. Another is outward diffusion elements defined B, such as Cr, Co, Ti and Ni. The velocity difference, \( v_A - v_B \), is defined as a basis for defining the interdiffusivity where \( v_b = \sum v_j (j = Cr, Co, Ti, Ni) \). Combining with Wagner’s work [6] gives the definition of interdiffusivity, \( D_{ij} = (\sum_j x_j v_j - x_j v_j \sum_j J_j)/(\partial x_j/\partial z) \). Since vacancy is one of the factors influencing the diffusion property of \( \beta \)-NiAl, the parameter \( S \) is introduced to account for the net flux of the vacancy compensating the unequal diffusion fluxes in a substitutional solution. Interdiffusivity can be defined as

\[
\tilde{D}_{ij} = S \sum_{j=1}^{n} x_j \frac{\partial \ln a_j}{\partial x_j} \left[ \sum_{j=1}^{n} x_j \frac{M_k \cdot RT}{x_k} + x_j \sum_{j=1}^{n} RT \sum_{j=1}^{n} \frac{L_{ij}}{x_j} \right]
\]  

(1)

By comparing Eq.(1) with Darken’s equation [7], it is apparent that the terms \( S \), \( \sum_{j=1}^{n} x_j \frac{\partial \ln a_j}{\partial x_j} \), \( \frac{M_k \cdot RT}{x_k} \) and \( \sum_{j=1}^{n} RT \sum_{j=1}^{n} \frac{L_{ij}}{x_j} \) are, respectively, referred as structural factor, thermodynamic factor, tracer diffusion coefficient and integrated tracer diffusion coefficient. According to the work of Wagner [6] and of Whittle et al [8], for a binary single phase system, If let \( d\lambda = dz / \sqrt{t} \) in accord with Boltzmann variable \( \lambda = z / \sqrt{t} \), interdiffusion coefficient \( \tilde{D}_{ij} \) can be estimated from the concentration profile of component \( j \) by:

\[
D_{ij}(\lambda) = \frac{1}{2(\frac{d\lambda}{dz})_{x=\lambda}} \left[ (1-Y_j) \int_{-\lambda}^{\lambda} Y_j \frac{d\lambda}{dz} + Y_j \int_{-\lambda}^{\lambda} (1-Y_j) \frac{d\lambda}{dz} \right]
\]

(2)
where \( Y_j = \frac{(x_j^* - x_j^*)}{(x_j^* - x_j^*)} \), the subscript * in the \( \lambda \) and \( x_j^* \) indicates particular values of the distance and the composition, respectively, for which \( \tilde{D}_j(x_j^*) \) is being calculated. The values of the \( Y \) in brackets vary from \( x_j^* \) to \( x_j^* \) in the first integral and from \( x_j^* \) to \( x_j^* \) in the second integral.

For multicomponent substitutional solid solution of \( \beta \)-NiAl in this study, it is known according to the above description that the component is in fact the combination of Co, Cr, Ti and Ni. According to the characteristics of the formation of the multicomponent \( \beta \)-NiAl, if contribution of concentration gradients of Cr, Co and Ti to interdiffusion fluxes of Ni and Al is ignored, \( \tilde{D}_j(x_j^*) \) can be directly estimated from the concentration profile of component \( j \). The thermodynamic factor in the Ni-Al-Cr-Co-Ti system is taken by Thermo-Calc software and TTNi7 Ni-base Superalloy Database [9].

![Fig.1: Concentration profiles against Boltzmann variable along the cross-section of the diffusion zone of the couple at 950°C](image)

4. Results and discussion
Concentration profiles determined by EPMA for the selected couples are shown in Fig.1. It is clear that all elements present in the substrate asymmetrically distribute throughout the diffusion zone where the profiles of just Ni, Al and Cr can be observed to abruptly fluctuate. This phenomenon is possibly caused by the steep concentration gradient developed in the diffusion-controlled reaction. The physical meaning of the existence of this gradient is the slow diffusion in the region of \( \beta \)-NiAl, which reflects its degree of ordering in this compositional interval. It can be predictable that the solutes as substitutional have a profound influence on interdiffusion in \( \beta \)-NiAl.

From the concentration profiles of each component, the corresponding profiles of interdiffusion flux as function of \( \lambda \) can be calculated, if the variation in molar volume is considered to be negligible in the outerdiffusion zone, on the basis of the relation given [10,11] by

\[ \lambda = \frac{x}{t^{1/2}}, \quad 10^7/m s^{1/2} \]
where $x_i^-$ and $x_i^+$ refer to the concentration of the terminal alloys and $\lambda_o$ identifies the location of the Matano plane. Since the interdiffusion zone is the multiphase region of $\gamma, \gamma'$ and $\beta$, the flux profiles only in the outerdiffusion zone, that is, in the single-phase region of $\beta$-NiAl are estimated by Eq.(3) and the variation of the calculated fluxes with $\lambda$ are shown in Fig.2. It is easily found that the location of the $\beta/\beta+\gamma'$ interface can not in an agreement with that of Matano plane. There are two possible reasons, one of which is that the slopes of concentration profiles of Ni, Al and Cr in addition to Ti and Co near the $\beta/\beta+\gamma'$ interface change abruptly, possibly leading to the big error when locating Matano plane through performing integral operation. Another is that the solubility limits of the refractory elements into $\beta$-NiAl are so low that they slightly take part in the diffusion process.

The interdiffusion flux of Al at each temperature is observed to be positive in the direction from $\beta$ to $\gamma+\gamma'$, while the interdiffusion fluxes of Ni, Cr, Co and Ti is negative over the entire selected zone, as shown in Fig.2. The interdiffusion fluxes of Co, Cr and Ti are expected to be apparently smaller than those of Ni and Al. It provides the direct proof that the interdiffusion of Ni and Al dominates the formation of multicomponent $\beta$-NiAl. Compared with interdiffusion flux of Cr and Co, the interdiffusion flux of Ti among all elements examined is generally smallest, possible resulting from the flatness of its concentration profiles.

![Fig.2 Interdiffusion fluxes profiles calculated only on the single-phase region of $\beta$-NiAl of the couples at 950°C](image)

Interdiffusion coefficients in the multicomponent $\beta$-NiAl phase are studied at 950°C. The obtained values of $D^i_{\text{int}}$ $(i=\text{Ni, Cr and Co})$ are presented in Fig.3 to reflect the concentration dependence of diffusivities. Within the examined composition range, values of $D^\text{Ni}_i$ and $D^\text{Cr}_i$ obviously change with composition. Values of $D^\text{int}_{\text{AlNi}}$ are found to be equivalent to those of $D^\text{int}_{\text{AlCo}}$. In contrast, values of $D^\text{int}_{\text{AlCr}}$ slightly change with composition and are about one order of magnitude less than those of $D^\text{int}_{\text{AlNi}}$ and $D^\text{int}_{\text{AlCo}}$. 
Fig. 3 Relationship of diffusion data in β-NiAl with concentration

Fig. 4 Comparison of diffusion data in this study with those in the binary system

In order to indirectly examine whether the obtained data is credible, Values of $D_{\text{int}}$ are plotted in Fig.4 together the data available in literatures. Values of $D_{\text{int}}$ are obviously lower than the reported data [3]. In the work of Seigle et al [3], a classical Boltzmann treatment of the concentration profiles is used to derive the concentration dependence of interdiffusion coefficient of β-NiAl on the basis of the independent molar volume. At the same time, according to the calculated flux profiles as shown in Fig.2, it can speculate that contribution of
interdiffusion fluxes of other solutes, especially Cr and Co, to the interdiffusion fluxes of Ni and Al is apparent, but contribution of their concentration gradients is not taken into account when calculating $D^{\text{int}}_{\text{AINi}}$ by using Eq.(2). Furthermore, it can be predictable that the solid solution of Cr, Ti and Co has an important influence on the degree of ordering of the multicomponent $\beta$-NiAl, but unfortunately, it is very difficult to determine the degree of ordering of the multicomponent $\beta$-NiAl. It means that some reasonable assumptions should be very necessary. What is the problem is that the assumptions can cause the error since the structural factor can be concentration dependent for the ordered $\beta$-NiAl. Hence variation in thermodynamic factor and structural factor in multicomponent $\beta$-NiAl owing to the solid solution of Cr, Ti and Co is also possible responsible partially for the decrease in $D^{\text{int}}_{\text{AINi}}$.

4. Conclusions
Diffusion data in the multicomponent $\beta$-NiAl are evaluated at 950°C. The results indicate that values of $D^{\text{int}}_{\text{AINi}}$ and $D^{\text{int}}_{\text{AICr}}$ are found to be strongly concentration dependent but values of $D^{\text{int}}_{\text{AICO}}$ be slightly concentration dependent. Values of $D^{\text{int}}_{\text{AINi}}$ are obviously lower than the reported data. It is speculated that variation in thermodynamic factor and structural factor in multicomponent $\beta$-NiAl owing to the solid solution of Cr, Ti and Co is possible responsible principally for the decrease in $D^{\text{int}}_{\text{AINi}}$.

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