Multicomponent Interdiffusion In Austenitic Ni-, Fe-ni-base Alloys And L12-ni3al Intermetallic For High-temperature Applications

2009

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MULTICOMPONENT INTERDIFFUSION IN AUSTENITIC NI-, FE-NI-BASE
ALLOYS AND L1₂-NI₃AL INTERMETALLIC FOR HIGH-TEMPERATURE
APPLICATIONS

by

NARAYANA GARIMELLA
M.Tech., Banaras Hindu University, Varanasi, India. 2003
M.S., University of Central Florida, Orlando, USA, 2007

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Major Professor: Yong-Ho Sohn
ABSTRACT

Interdiffusion in multicomponent-multiphase alloys is commonly encountered in many materials systems. The developments of multicomponent-multiphase alloys require control of microstructure through appropriate heat treatment, involving solid-state transformations, precipitation processes, and surface modification, where the interdiffusion processes play a major role. In addition, interdiffusion processes often control degradation and failure of these materials systems. Enhanced performance and reliable durability always requires a detailed understanding of interdiffusion.

In this study, ternary and quaternary interdiffusion in Ni-Cr-X (X = Al, Si, Ge, Pd) at 900°C and 700°C, Fe-Ni-Cr-X (X = Si, Ge) at 900°C, and Ni₃Al alloyed with Ir, Ta and Re at 1200°C were examined using solid-to-solid diffusion couples. Interdiffusion fluxes of individual components were calculated directly from experimental concentration profiles determined by electron probe microanalysis. Moments of interdiffusion fluxes were examined to calculate main and cross interdiffusion coefficients averaged over selected composition ranges from single diffusion couple experiments. Consistency in the magnitude and sign of ternary and quaternary interdiffusion coefficient were verified with interdiffusion coefficients determined by Boltzmann-Matano analysis that requires multiple diffusion couples with intersecting compositions. Effects of alloying additions, Al, Si, Ge and Pd, on the interdiffusion in Ni-Cr-X and Fe-Ni-Cr-X alloys were examined with respect to Cr₂O₃-forming ability at high temperature. Effects of Ir, Ta and Re additions on interdiffusion in Ni₃Al were examined with respect to phase stability and site-preference.

In addition, a numerically refined approach to determine average ternary interdiffusion
coefficients were developed. Concentrations and moments of interdiffusion fluxes are employed to generate multiple combinations of multicomponent interdiffusion coefficient as a function of moments. The matrix of multicomponent interdiffusion coefficients corresponds to the lowest order of the moment. It yields real and positive eigen values which provides reliable average interdiffusion coefficients for the selected composition range.
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CHAPTER 1: INTRODUCTION

Commercially important materials for sustaining applications consist of multicomponent systems, and it is important to understand the interactions among all components with diffusional and thermodynamic considerations. Atomic transport process’s in multicomponent systems are commonly observed phenomena in various materials applications including solid-state phase transformations, oxidation, bonding, coatings, electronic packaging, etc. Multicomponent diffusion is defined [1] as the transport process, which occurs when the interdiffusion flux of a component is influenced by the concentration gradient of all independent components.

The phenomenological description of multicomponent diffusion can be expressed by Onsager’s formalism [2-4], and is the important basis for experimental investigation of multicomponent systems. Experimental diffusion studies for isothermal conditions may enable the determination of interdiffusion coefficients, intrinsic diffusion coefficients, atomic mobilities and vacancy wind parameters. The Boltzmann-Matano analysis [5,6] employs independent interdiffusion couple experiments for a multicomponent system to determine interdiffusion coefficients at the intersecting composition of compositional diffusion paths. Dayananda and coworkers [7-12] developed a direct method to determine interdiffusion flux of individual components from experimental concentration profiles without the need of interdiffusion coefficients. This method paved way for a new analysis [13] to determine average interdiffusion coefficients for selected composition ranges from the single diffusion couple experiments. Numerous interdiffusion studies made use of these methods to analyze experimental concentration profiles. The experimental and numerical studies of current work mainly rely on these two techniques for the determination of ternary and quaternary interdiffusion coefficients.
Austenitic Ni-Cr and Fe-Ni-Cr based alloys are widely used in a variety of high-temperature applications because of their ability to form a protective Cr$_2$O$_3$ scale [14-21]. Alloying additions not only are intended for improving mechanical properties of these alloys, but also for their high-temperature corrosion resistance. Low amounts of alloying additions (< 6 at.%) to both Ni-Cr and Fe-Ni-Cr alloys are found to have beneficial affect in forming and retaining chromia scale [20-22]. Diffusional effects of minor alloy additions may play a significant role in formation and growth of Cr$_2$O$_3$ scale. Intermetallics have been a subject of numerous investigations [23-25]. L1$_2$ Ni$_3$Al is one of the well-known intermetallic phases that maintains its strength up to its melting point. Various studies on these materials mainly focus on improving its high temperature stability. This long-range ordered solution accepts a very low amount of solutes. Understanding of multicomponent diffusional interactions can provide insight to site preference of solute elements in this intermetallic.

An extended analytical method of the new analysis [13] has been developed, in which average main and cross interdiffusion coefficients are determined over selected regions in the single diffusion couple experiment from the moments (series of higher-order integrands) of interdiffusion flux and associated concentration profiles. This involves a mathematical treatment of simultaneous solutions of the zero moment interdiffusion flux flow equation with that of the higher-moment equations for the same component. Implementing this treatment for two independent components in ternary diffusion yields a series of four interdiffusion coefficients as a function of moment of the equation. These individual moments of interdiffusion quantities are treated as coefficients of linear equations in order to solve average ternary interdiffusion coefficients as variables using matrix algebra methods.
The work presented herein is in essence an analysis of diffusional interactions for high-temperature alloys for oxidation and hot-corrosion resistance. Alloys employed in this work are produced by arc-melting and drop-casting techniques. Solid-solid diffusion couples were made by diffusion annealing the polished disks together at 1200°C, 900°C and 700°C. After the isothermal treatments for designed length of time, the couple assemblies were quenched, and polished cross sections were analyzed for concentration profiles. Experimental concentration profiles were analyzed to determine interdiffusion coefficients. These interdiffusion coefficients were examined with respect to an ability to form protective oxide scales and preferential site occupation.

This dissertation is divided into several chapters starting with Chapter 2 that surveys the literature on (1) diffusion and high temperature oxidation resistance of Ni-Cr, Fe-Ni-Cr systems with the addition of active alloying elements, (2) phenomenology of isothermal interdiffusion and (3) properties and application to the Ni3Al system. Chapter 3 presents an experimental isothermal interdiffusion investigation in Ni-Cr-X (X=Al, Si, Ge, Pd) alloys at 900°C and 700°C. Chapter 4 reports a similar work carried out for Fe-Ni-Cr-X (X=Si, Ge) alloys at 900°C. Chapter 5 presents an experimental isothermal interdiffusion study in Ni3Al-X (X=Ir, Ta, Re) at 1200°C. Chapter 6 describes a refined analytical method to determine average ternary interdiffusion coefficients using moments of interdiffusion fluxes. Finally, Chapter 7 summarizes the findings from this work.
1.1 References


CHAPTER 2: LITERATURE REVIEW

2.1 Austenitic Ni- and Fe-Ni-base alloys and their applications

Austenitic Ni- and Fe-Ni-base alloys find a wide range of applications due to their remarkable abilities to withstand oxidative and corrosive environments and also because of their versatile mechanical enduring abilities [1]. Nickel has extensive solid-solubility within the fcc $\gamma$-phase, and it readily accepts several alloying additions to form either a homogeneous solid-solution strengthened further with precipitates dispersed within the matrix [2]. It can dissolve 35 wt.% of Cr, 20 wt.% Mo, 20 wt.% W and 5 to 10 wt.% Al, Ti, Mn and V[3]. The dissolution of extensive elements within the ductile matrix of the $\gamma$-phase enables these alloys to possess excellent solid solution strengthening and corrosion and oxidation resistance characteristics [4].

Al addition together with other alloying additions provides a strong solution-hardening effect, whereas Fe and Cr additions remain weaker in this effect [2]. Unique intermetallic compounds are observed in Ni-base alloying systems. Ni$_3$(Al,Ti), commonly known as $\gamma'$-phase, is a very significant precipitate as it provides key-strengthening effect through precipitation hardening in Ni-base superalloys [1].

Ni-Cr-base alloys are known for their corrosion and oxidation resistance during severe exposure of temperature and atmosphere [4-6]. Heating-element interconnects and high-temperature alloy applications are quite common applications for these alloys. Together, both Ni and Cr form an eutectic system with approximately 45% of Cr dissolved in the austenitic solid solution of Ni and 35% of Ni dissolved in $\alpha$-solid solution of Cr at 1395°C [7]. Peritectoid reaction at 590°C temperature is responsible for the formation of the $\gamma'$ phase.
Ni dissolves 11 wt.% Al in its austenitic phase at the maximum temperature of approximately 1400°C[7]. This limit drastically reduces at room temperature. Because of the great difference in the melting points of Ni (1455°C) and Al (660°C), the Ni-Al binary system incorporates several peritectic invariant reactions. NiAl, Ni₃Al and Ni₅Al are widely-known intermetallics formed in this system. Ni dissolves up to 8 wt.% Si in austenite solution at a temperature of 1143°C. The combination of eutectic, peritectic and peritectoid reactions associated with this system explains the complexity of this system to attain an extended solid solubility based on the Hume-Rothery rule. Ni-Ge system [7] has great similarity in comparison to the Ni-Si system [7] because of the similar properties of Si and Ge belonging IVA group. Nickel dissolves Ge up to 20 wt.% at the maximum temperature of 1124°C. The combination of several invariant reactions such as eutectic, eutectoid and peritectic explains the great dissimilarities in Ni and Ge. Several intermetallics can be observed in this binary system. In accordance with Hume-Rothery rules, Ni and Pd a noble metal exhibit complete solubility in both solid and liquid states.

Fe-Ni-base alloys are very common and can be considered are economical substitution to Ni-base alloys in several aspects [7]. Most of the versatility factors of Ni base alloys are reflected in these alloys provided 25 wt.% minimum of Ni is dissolved in. Complete solubility of Fe and Ni can be observed in between 900 to 1400°C as fcc austenitic phase. This system provides the basis for stainless steels and other ferrous alloys to combat mainly corrosion related problems. The evolution of various Fe-Ni-base alloys is shown in Figure 2.1[8], with reference to 304 stainless steel.
The Fe-Cr system has been a basis for many engineering alloys for high-strength, corrosion-resistant applications. Cr is an bcc α-stabilizer, and it suppresses the fcc γ-phase (e.g., γ-loop). Oxidation of Fe-Cr alloys has been widely studied under different atmospheres [4-6]. Fe-Ni-Cr alloys offer excellent corrosion resistance properties in severe environments due to the well maintained impervious Cr$_2$O$_3$ scale formation. With a proper amount of Ni content, these alloys can operate at a maximum temperature of 1200°C. The application of Fe-Ni-Cr alloys
ranges from petrochemical environments to sulphurous atmospheres accompanied by high temperature.

2.2 Oxidation and Hot-Corrosion Resistance of Ni and Fe-Ni-base Alloys

Different types of corrosion or degradation of these alloys are mainly due to operation environments that include oxidation, carburization, nitridation, sulfidation and halogenation[3]. Addition of alloying elements has different influence on each of the corrosive environment. Most heat resistant alloys have sufficient amounts of Cr (with or without Al or Si) to form Cr$_2$O$_3$, Al$_2$O$_3$ or SiO$_2$ protective oxide scales which provide resistance to environmental degradation.

Cr-addition improves oxidation, carburization and sulfidation resistance of Ni- and Fe-Ni-base alloys below 950°C. Ni- and Fe-Ni-base alloys with Cr addition can serve well against degradation by oil ash corrosion and molten glass. However, the addition of Cr does not provide any protection against fluorine and nitriding environment. Si-addition to Ni- and Fe-Ni-base improves resistance against oxidation, nitridation, sulfidation and carburization, and synergistically improves the scale resilience with Cr addition. However, Ni- and Fe-Ni-base alloys with Si addition degrades under chlorination environment. Al-addition to Ni- and Fe-Ni-base alloys independently and synergistically (e.g., with Cr) improves the oxidation resistance, and helps against sulfidizing and carburization, but does not improve nitridation resistance.
2.3 Ni$_3$Al Intermetallic and Its Properties

Ni$_3$Al is known as $\gamma'$ phase, and finds a wide range of high-temperature applications including precipitation strengthening constituents in Ni-base superalloys [4]. These Ni$_3$Al precipitates can be spherical or cuboidal. Alloying additions can further enhance its high-temperature strength, environmental stability and room-temperature toughness [9]. The compatibility of Ni$_3$Al phase in terms of crystal structure and lattice parameter with an fcc Ni allows homogeneous nucleation of precipitates with low surface energy and extraordinary stability. Ni$_3$Al precipitates contribute to remarkable strengthening in Ni-base superalloys by interaction with dislocations. In addition, the strength of Ni$_3$Al increases as temperature increases [4].

Figure 2.2(a) illustrates the crystal structure of Ni$_3$Al[10]. Elemental additions to Ni$_3$Al with high electronegativity tend to occupy Ni sites, whereas electropositive ones occupy the Al sites [4]. The coordination number of this L1$_2$ structure in terms of atoms surrounding Ni and Al are illustrated in Figure 2.2(b) and Figure 2.2(c) respectively. Ni has eight number of nearest neighboring sites to facilitate the substitutional exchange mechanism. On the other hand, Al is surrounded by 12 Ni atoms. For this reason, Ni and Ni-replacing alloying additions tend to have higher magnitude of interdiffusion coefficients than for Al and Al-replacing alloying elements.
Figure 2.2: Unit cell of Ni$_3$Al and nearest neighboring atoms surrounding Ni and Al sites.
2.4 Multicomponent Interdiffusion

The phenomenology of multicomponent interdiffusion can be understood from Fick’s law [11]. The interdiffusion flux ($\tilde{J}_i$) of component (i) is directly proportional to its concentration gradient, $\partial C_i / \partial x$:

$$\tilde{J}_i = -\tilde{D}_i \frac{\partial C_i (x,t)}{\partial x} \quad (2.1)$$

where $D_i$ is called interdiffusion coefficient of component i. The negative sign indicates the nature of diffusion to occur down the concentration gradient.

The phenomenological description of interdiffusion in multicomponent systems expressed on the basis of Onsager’s Formalism [12-14]. This requires (n-1) number of independent components to obtain (n-1)$^2$ interdiffusion coefficients. Accordingly, interdiffusion flux for an independent components ‘i’ can be expressed as:

$$\tilde{J}_i = -\sum_{j=1}^{n-1} \tilde{D}_{ij} \frac{\partial C_j (x,t)}{\partial x} \quad (i = 1,2,\ldots,n-1) \quad (2.2)$$

The above equation requires (n-1) number of concentration gradients in the form of $\partial C_i / \partial x$, to relate (n-1)$^2$ numbers of interdiffusion coefficients in the form of $\tilde{D}_{ij}$. Concentration dependent interdiffusion coefficients can be determined in ternary systems using the Boltzmann-Matano analysis [15, 16].
Eq. (2.2) can be used to express interdiffusion flux in a ternary system:

\[
\widetilde{J}_i = -\overline{D}_{i1} \frac{\partial C_i}{\partial x} - \overline{D}_{i2} \frac{\partial C_2}{\partial x} \quad (i=1,2)
\]

(2.3)

where \( \overline{D}_{i1} \) and \( \overline{D}_{i2} \) refer to the average main and cross-interdiffusion coefficients (for the component \( i \)), respectively. Component 3 serves as dependent concentration variable.

Implementing Eq. (2.3) for the interdiffusion fluxes of both independent components will yield two equations. Finding another such set of ternary interdiffusion flux equations for another independent diffusion couple experiment of the same ternary system, provided the diffusion paths of both these separate experiments have a common intersecting composition will enable determination of all the four interdiffusion coefficients. This analysis is known as Boltzmann-Matano analysis. Figure (2.3) illustrates series of such independent intersecting diffusion paths with one common path of AB. This illustrates one way of Boltzmann-Matano analysis to determine interdiffusion coefficients along one direction of composition points.
A method of direct determination of interdiffusion fluxes for all components of the concentration profiles without invoking the interdiffusion coefficients has been developed [17-19] on the basis of an integration of the continuity equation:

$$\left( \frac{\partial \bar{C}_i}{\partial t} \right)_x = -\left( \frac{\partial \bar{J}_i}{\partial x} \right)_t$$

(2.4)

where $t$ is the time of diffusion annealing, $\bar{J}_i$ is the interdiffusion flux and $x$ is the diffusion distance that is perpendicular to the bonding interface of two solid materials. Figure 2.2 (a) represents a schematic concentration profile for a component ‘$i$’ that develops in a solid-solid diffusion couple in an n-component system. The interdiffusion flux at any section $x$ of this concentration profile can be calculated directly using the relation [20-25]:
\[ \tilde{J}_i = \frac{1}{2t} \int_{C_{i-\infty}}^{C_{i+\infty}} (x - x_0) dC_i \quad (i = 1, 2, \ldots, n) \]  

(2.5)

where \( C_{i-\infty} \) and \( C_{i+\infty} \) are the terminal concentrations and \( x_0 \) refers to the location of the Matano plane. The determination of \( x_0 \) is based on the mass balance of individual behavior of the concentration profiles, using [11,25,26]:

\[ \int_{C_i^{-\infty}}^{C_i^{+\infty}} (x - x_0) dC_i = 0 \quad (i=1, 2, 3) \]  

[2.6]

The integral in Eq. (2.6) for a selected value of \( x \) is given by the hatched area \( S_1 \) as shown in Figure 2.4(a). The interdiffusion flux \( \tilde{J}_i \) of component ‘i’ determined as a function of \( x \) from Eq. (2.5) is shown schematically in Figure 2.4(b). The direct determination of interdiffusion fluxes enables assessing of diffusional behavior of the components to understand the concepts such as zero-flux-planes and flux-reversals [28-32].
Figure 2.4: A schematic concentration profile (a) for component i in a solid-solid diffusion couple and (b) the corresponding interdiffusion flux profile. \( C_i^o \) and \( \tilde{J}_i \) refer to the concentration and the interdiffusion flux, respectively, at the Matano plane. The hatched area \( S \) in (a) corresponds to the term \( \int_{C_i^o}^{C(x)} (x - x_o) dC_i \) and the cross-hatched area in (b) corresponds to the term \( \int_{x_o}^{x_1} \tilde{J}_i dx \) for a component i.

### 2.5 High-temperature oxidation

High temperature oxidation of metals and alloys is very common phenomena where the combination of elevated temperature, oxygen, air and any oxide prevailing atmospheres are unavoidable. Oxidation between metal (M) and oxygen (O\(_2\)) in its gaseous form can be expressed as:

\[
M(s) + O_2 (g) = MO_2(s)
\]  

\[ (2.7) \]
The equilibrium partial pressure of oxygen that associates with the metal system can be related to the standard free energy of oxidation reaction as below.

\[
\Delta G^\circ = -RT \ln \left( \frac{a_{MO_2}}{a_{M_{p(O_2)}}} \right)
\]  

(2.8)

where \(a_{MO_2}\) and \(a_{M}\) are the activities of the oxide and the metal respectively and \(p(O_2)\) is the partial pressure of the oxygen gas.

As metal and metal oxide are solid phases in the Eq. (2.7), the activities of these phases can be assumed as unities, then, Eq. (2.8) can be expressed as:

\[
\Delta G^\circ = RT \ln(p_{O_2})
\]  

(2.9)

\[
p_{O_2} = \exp(\Delta G^\circ / RT)
\]  

(2.10)

Therefore, standard free energy of formation is required to use Eq. (2.10) to in order to determine partial pressure of oxygen.

The change in this work function can be expressed using second law of thermodynamics as:

\[
\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ
\]  

(2.11)

where \(\Delta H^\circ\) and \(\Delta S^\circ\) are changes in standard enthalpy and entropy respectively.
The Ellingham diagram[33] makes use of Eq. (2.11) to express standard free energies of oxide formation to predict the predominant influence of oxides over each other. For the current oxidation work in Ni-Cr-X and Fe-Ni-Cr-X alloys, this information of standard oxide formation is expressed in Figure 2.5. From this figure it is evident that oxides of Al and Si are more stable than Cr, Ni and Fe. For this reason Ni and Fe-Ni are considered as solvents of these alloys expecting less tendency of formation of these oxides. The medium tendency of chromia formation is compensated by considering higher amount of Cr to expect predominance of this oxide on the alloy system.

![Ellingham Diagram](image)

Figure 2.5 : Ellingham diagram of oxides pertaining to current studies.
The Ellingham diagram is of only thermodynamic help in assessing the stability of oxides, kinetics of oxide formation are also very important to find out the extent of the reaction required to form the required oxide and also to estimate thickness and hierarchy of oxides
forming on the alloy system. The kinetics of oxidation follow either a logarithmic law or a parabolic law or a linear law or the combination of any of them in deciding the rate of oxide growth depending on the composition (partial pressure) and temperature combinations. However, the parabolic law is considered more relevant for high temperature oxidation. Figure 2.6 [21], illustrates the parabolic growth rate constant values of few oxides[4]. The lower the position of oxide, the more it will be beneficial in terms of providing slow-growth rate.

Figure 2.6 : Kinetics of metal oxides at high temperatures.
According to the parabolic rate law of oxidation, the oxide growth proceeds with the
continuos decrease in oxidation rate. Therefore, the rate of oxidation is inversely proportional to
the scale thickness or weight of the oxide formed.

\[
\frac{dx}{dt} = \frac{K_p}{x} \quad (2.12)
\]

\[
\Rightarrow x^2 = 2K_p t + C \quad (2.13)
\]

Most of the alloys obey the parabolic law of oxidation at elevated temperatures. The diffusion of
ions or electrons through the initially formed oxide scale is the characteristic feature of this
oxidation.

According to Wagner [34], when a metal is exposed to high temperature, oxidation
proceeds in two steps. Figure 2.7 illustrates Wagner’s application of metal oxidation [35]. The
first is to form a monolayer of oxide and second is its growth. Both these steps require transfer of
metals ions from the substrate or oxygen ions from the atmospheric gaseous phase. Metal-oxide
and Gas-oxide interfaces move relatively opposite to each other. Diffusion is the rate controlling
step and is mainly due to the defect structure of the oxide. For thick scale formation ions have to
move a larger distance whereas for thinner scales this distance decreases. The kinetics of oxide
formation is parabolic in nature. Wagner’s model of parabolic oxidation rate obeys the following
assumptions [4].

1. The oxide scale is dense and impervious.
2. Transport of ions, charged species or electrons is the rate controlling step.

3. Thermodynamic equilibrium is established at metal-oxide and oxide-metal interfaces.

4. Thermodynamic equilibrium is established thought the scale.

5. The oxide follows negligible deviation from stoichiometry.

6. The metal contains only negligible amount of oxide dissolved in it.

7. The scale size is thicker than the distances required for space charges.

![Figure 2.7: Wagner’s illustration of metal oxidation [36].](image)

As a thermodynamic equilibrium prevails at interfaces of metal-oxide and oxide-oxygen phases, activity depletion of the metal from the metal-oxide interface to oxygen-oxide interface and a reduction in partial pressure of oxygen from the oxide-oxygen interface to the metal-oxide interface complement each other. This consequently leads to ion migration. Thereby, both chemical and electrical potential gradients develop to provide a driving force for the oxidation. The result of this whole phenomenology can be expressed as a parabolic rate constant [4]:

\[
\text{Rate} = k \left( \frac{a_m^{M^{\text{II}}} \cdot \text{p(O}_2\text{)}^0_m}{a_m^0} \right)^n
\]
where $D_M$ and $D_O$ are diffusivities of metal and oxygen respectively, in the oxide, and $Z_M$ is the metal volume, and $u$ and $u'$ are the chemical potentials of oxygen at the metal-oxide and oxide-oxygen interfaces, respectively.

Oxidation of alloys is more complex than the oxidation of metals, and Wagner classified alloys into following groups: (1) base solute alloying additions in noble solvent, and (2) base solute with base solvent alloy. As shown in Figure 2.8, in this case element B is more reactive than element A. Depending on the amount of B, two sub-cases exist as shown in figure. In first sub-case, B is dilute in amount and tends to form dispersions of internal oxide within the matrix of selected A rich region. But, in the second sub-case when the B content is sufficient enough to form its own oxide, no discontinuous regions are observed. The critical amount of B to form continuous oxide can be expressed, according to [4] as:

$$B_{Critical} \geq [0.3N_O(D_O / D_B)(V_m / V_{mO})]^{1/2}$$  \hspace{1cm} (2.15)$$

Where, $D_O, D_B$ are the diffusivities of O and B respectively in the alloy. $V_m$ and $V_{mO}$ are molar volumes of metal and oxide formed, and $N_O$ is the solubility of oxygen in the alloy. But, it is possible to form continuous oxide of B at its lower concentration, provided $N_O, D_O$ and $V_m$ are low and $D_B$ and $V_{mO}$ are high.
As shown in Figure 2.9, in this second case, though both elements A and B are reactive, BO is more stable than AO. When B content is not sufficient enough, it leads to the first sub-case, where AO forms externally with BO remaining as internal oxide. On the other hand, with the availability of sufficient B, external BO only forms on the alloy surface. This second sub-case is commonly used in designing alloys to withstand high temperature oxidation resistance. Also, this manifests parabolic oxide growth rate.

In 1937, Griffiths and Pfeil [37] showed that rare earth addition to Ni-20Cr alloys had
beneficial effects in enhancing the life time of these alloys under cycling conditions for the application of heating elements. The presence of minor amount of an elemental constituent can induce changes in properties: physical, mechanical, chemical and quite out of proportion to the amount added. The beneficial effect of active elements on the oxidation behavior of high temperature NiCr and FeNiCr alloys has been observed for the last 5 decades and minor additions of active elements are now used with various MCrAl alloys (M= Fe and/or Ni), which include Cr₂O₃-as well as Al₂O₃ forming alloys. Active elements can be incorporated in one or the other forms with the substrate alloys.

1. Dissolving minor element and form an alloy by melting.
2. As an oxide dispersion on substrate surface.
3. Ion implantation.

The active elements promote the formation of a protective scale reduce the rate of continuing scale growth or inhibit the scale failure process. The major effect of alloying is to improve scale adherence. Different theories [38-44] have been proposed to explain the effects of minor alloying elements. These theories mainly incorporate:

1. Active element oxides act as nucleation sites and promote selective oxidation of the protective-scale forming element, thereby curtailing the transient stage of oxidation.
2. Modify growth mechanism of the oxide, especially applicable to Cr₂O₃ forming alloys.
3. Modification of scale morphology and structure.
4. Improvement of the scale plasticity by refining grain size.
5. Formation of an secondary or intermediate scale.
6. Forming oxide pegs internally to key the surface oxide along with the substrate.
7. Act as vacancy sinks.

8. Establish chemical bonding.


Some of the important parameters those can greatly help in designing alloys for high temperature protective oxide scales are:

- Free energy of oxides of the alloying elements.
- Crystallographic structure of oxides.
- Pilling and Bedworth ratio of oxide compounds.
- Solubility of elements in both substrate and coating systems.
- Diffusivity of active elements in oxide scale and alloy.
- Valencies of active elements and their atomic or ion radii.
- Thermal conductivities of oxides.

Active element addition can promote selective oxidation of Cr in alloy [43], and thereby initially protective \( \text{Cr}_2\text{O}_3 \) forms and prevents forming the other base metal oxides. The most possible mechanism [44] is shown Figure [2.8]. In this, the dispersed active element oxide particles form at the alloy surface and act as heterogeneous nucleation sites for the initially-forming oxides, thereby reducing the spacing between nuclei. It minimizes time required for subsequent lateral growth processes to connect nuclei to form a protective \( \text{Cr}_2\text{O}_3 \) scale. This mechanism is proven to be reasonable and consistent with further similar studies of oxidation.
Figure 2.10: Schematic representation of role of active element oxide particles in providing heterogeneous nucleation sites and in favoring further oxidation.

2.6 References


CHAPTER 3: INTERDIFFUSION IN NI-CR-X ALLOYS AT
900°C AND 700°C

3.1 Introduction

Nickel-chromium base alloys are widely used in a variety of high-temperature applications due to their combination of good oxidation resistance and excellent high-temperature strength, and are the basis for a number of commercial superalloy families [1-3]. Oxidation resistance in these alloys is derived from a continuous, slow-growing, adherent $\text{Cr}_2\text{O}_3$-base oxide scale [1-3]. In particular, composition in the range of Ni alloyed with 20–30 wt.% Cr have been extensively studied as a model material for $\text{Cr}_2\text{O}_3$ scale formation [4-13].

Minor alloying additions (< 5wt.%) can significantly improve the oxidation resistance of Ni-base $\text{Cr}_2\text{O}_3$-forming alloys [14-16]. Effects include: (1) establishment of continuous $\text{Cr}_2\text{O}_3$ scale formation at reduced Cr concentrations; (2) a decrease in the growth rate of $\text{Cr}_2\text{O}_3$; and (3) enhanced scale adherence [1,14,17]. For example, the addition of Si in Ni-28wt.%Cr promoted formation of both $\text{Cr}_2\text{O}_3$ and $\text{SiO}_2$ [13], in which a continuous inner $\text{SiO}_2$ layer acted as a diffusion barrier, and reduced the isothermal oxidation rate by suppressing cation transport through the $\text{Cr}_2\text{O}_3$ scale [6,13,17-20]. However, the same inner $\text{SiO}_2$ layer can also reduce the spallation resistance, dependent on the level of Si and the continuity and thickness of the inner $\text{SiO}_2$ layer formed [21].

Diffusional effects of minor alloy additions may play a significant role in the initial establishment of a continuous protective oxide scale [2,14,16,22,23]. It can also play a significant role in maintaining protective scale growth. For example, the growth of $\text{Cr}_2\text{O}_3$ can locally deplete Cr from the alloy in the subsurface region [24]. If the scale is locally damaged or
spalled, such a depletion can prevent the reformation of the Cr$_2$O$_3$ scale, and result in a transition to less-protective or non-protective oxidation behavior. Understanding of diffusional interactions in Ni-Cr-X alloys where X represents minor alloying additions can help design Ni base Cr$_2$O$_3$-forming alloys with improved resistance against environmental degradation [25].

In this work, interdiffusion in Ni-22at.%Cr-X (fcc $\gamma$ phase) alloys with small additions of X ($X = \text{Al, Si, Ge, or Pd}$) is investigated using solid-to-solid diffusion couples annealed at 900°C for 168 hours and 700°C for 720 hours. This information can be used as a part of a larger study whose goal is to better elucidate the effects of minor alloying additions on oxidation of Cr$_2$O$_3$-forming alloys. Addition of Si was selected because it has long been known to be beneficial to Cr$_2$O$_3$ scale formation [17] via both establishment of an inner layer of SiO$_2$ and possibility enhanced diffusivity of Cr. To help probe these effects, additions of Ge were also selected. Germanium is thermochemically similar to Si in many regards, but does not form a protective oxide scale as does Si. Additions of Al at levels $> 3$–$4$wt.$\%$ can improve the oxidation via the formation of a protective Al$_2$O$_3$ scale [2,14,16,26]. At subcritical levels (2–3wt.$\%$), Al may also be beneficial to the oxidation resistance of Ni-Cr alloys, in part via the formation of semi-continuous inner region of Al$_2$O$_3$ particles [26,27]. Palladium was chosen for the study because it is a noble alloying addition, and would be expected to accumulate at the alloy/scale interface during oxidation and may improve the oxide/metal adhesion [28,29].

In this ternary interdiffusion study at 900°C and 700°C, the experimental concentration profiles were used to calculate interdiffusion fluxes of individual components, and to determine average effective interdiffusion coefficients $\tilde{D}_i^{\text{eff}}$ and average ternary interdiffusion coefficients
$D_{ij}^{\text{Ni}}$ (i,j=Cr,X). Values of $\tilde{D}_{\text{Cr}}^{\text{eff}}$ and $\tilde{D}_{\text{CrX}}^{\text{Ni}}$ are examined to assess the effects of alloying additions on the interdiffusion behavior of Cr, and the Cr$_2$O$_3$-forming ability in Ni-Cr-X alloys.

### 3.2 Determination of Interdiffusion Fluxes and Coefficients

Onsager’s formalism for the interdiffusion flux $\tilde{J}_i$ of component i in a ternary system can be written as [30]:

$$\tilde{J}_i = -\tilde{D}_i \frac{\partial C_1}{\partial x} - \tilde{D}_i \frac{\partial C_2}{\partial x}$$  \hspace{0.5cm} (i, j = 1, 2) \hspace{0.5cm} (3.1)

where $\partial C_1/\partial x$ and $\partial C_2/\partial x$ are the two independent concentration gradients, and $\tilde{D}_i$ and $\tilde{D}_j$ refer to the ternary interdiffusion coefficients. An experimental determination of the four concentration-dependent interdiffusion coefficients requires the use of the Boltzmann-Matano analysis with two independent diffusion couples that develop a common composition in the diffusion zone. Instead, the interdiffusion fluxes $\tilde{J}_i$ of all components can be determined directly from their concentration profiles of an infinite diffusion couple without the need of the interdiffusion coefficients on the basis of the relation [31]:

$$\tilde{J}_i = \frac{1}{2t} \int_{-C_i}^{+C_i} (x - x_o) dC_i \hspace{0.5cm} (i = 1, 2, ..., n) \hspace{0.5cm} (3.2)$$

where t is the time, $C_i^-$ and $C_i^+$ are the terminal concentrations of the alloys employed for the
couple and \( x_0 \) refers to the location of the Matano plane.

The interdiffusion flux \( \tilde{J}_i \), determined from Eq. (3.2) can be integrated with respect to position \( x \) to define average effective interdiffusion coefficient \( \tilde{D}_i^{\text{eff}} \) [32]:

\[
\tilde{D}_i^{\text{eff}} = \frac{x_1}{C_i^{x_2} - C_i^{x_1}} \int_{x_1}^{x_2} \tilde{J}_i \, dx \quad (i = 1, 2, 3)
\]  

(3.3)

This effective interdiffusion coefficient incorporates all multicomponent diffusional interactions for the system to provide an effective value for the interdiffusion of a component species as defined by:

\[
\tilde{D}_i^{\text{eff}} = \tilde{D}_i^n + \sum_{j \neq i} \frac{\tilde{D}_{ij}^n \partial C_j / \partial x}{\partial C_i / \partial x} \quad (i \neq j)
\]  

(3.4)

The interdiffusion flux \( \tilde{J}_i \), determined from Eq. (3.2) as a function of \( x \), can be multiplied by \((x-x_0)^n\) and integrated over a selected region, \( x_1 \) to \( x_2 \); in the light of Eq. (3.1), one gets [33]:

\[
\int_{x_1}^{x_2} \tilde{J}_i (x-x_0)^n \, dx = -\tilde{D}_{ij}^{c_i^{(x_1)}} \int_{C_i^{(x_1)}}^{c_i^{(x_2)}} (x-x_0)^n \, dC_i - \tilde{D}_{ij}^{c_j^{(x_2)}} \int_{C_j^{(x_1)}}^{c_j^{(x_2)}} (x-x_0)^n \, dC_j \quad (i, j = 1, 2)
\]  

(3.5)

where \( \tilde{D}_{ij}^{(i,j=1,2)} \) coefficients are the average values of main and cross-interdiffusion coefficients treated as constants over the selected composition range. Eq. (3.5) can provide four
equations involving the $\overline{D}_{ij}^n$ interdiffusion coefficients (n = 0, 1 or 2) and can be set up from interdiffusion fluxes calculated on the basis of Eq. (3.2) from the concentration profiles of a single diffusion couple. The $\overline{D}_{ij}^n$ coefficients, characteristic of the diffusion path, can be determined over selected composition ranges that include nonlinear segment of the profiles [33]. Determination of ternary interdiffusion coefficients by using Eq. (3.5) do not require the use of concentration gradients (i.e., $\partial C_i / \partial x$), and significantly reduces the uncertainty involved on the determination of interdiffusion coefficients arising from microprobe measurement and concentration smoothening procedure [33].

### 3.3 Experimental Procedure

Binary and ternary alloys with compositions reported in Table 3.1 were prepared with 99.9% pure Ni, Cr, Al, Si, Ge and Pd by arc melting under an argon atmosphere. The alloys were chill-cast by water-cooled copper mold into rods with approximately vacuum 12 mm in diameter. The alloy rods were placed in a quartz tube, evacuated to a pressure less than $10^{-6}$ torr, and flushed with hydrogen. This hydrogen-flushing procedure was repeated several times and Ar was filled into a quartz capsule before the final seal. They were homogenized at 900°C for 168 hours in a horizontal Lindberg™ 3-zone tube furnace and water-quenched to preserve the high temperature microstructure. The microstructures and compositions of the alloys were examined by optical microscopy, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and electron microprobe analysis (EMPA). No measurable variation in the alloy compositions was observed and all alloys consisted of fcc Ni solid solution ($\gamma$-phase).
Table 3.1: Compositions of Ni-Cr-X alloys employed for solid-to-solid diffusion couples.

<table>
<thead>
<tr>
<th>Alloy Identification</th>
<th>Composition (atom fraction)</th>
<th>Composition (weight fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>100.0</td>
<td>100</td>
</tr>
<tr>
<td>NiCr (X = None)</td>
<td>78.0 22.0</td>
<td>80 20</td>
</tr>
<tr>
<td>NiCrAl (X = Al)</td>
<td>72.5 21.3 6.2</td>
<td>77 20 3</td>
</tr>
<tr>
<td>NiCrSi (X = Si)</td>
<td>74.0 22.0 4.0</td>
<td>78 20 2</td>
</tr>
<tr>
<td>NiCrGe (X = Ge)</td>
<td>76.3 22.1 1.6</td>
<td>78 20 2</td>
</tr>
<tr>
<td>NiCrPd (X = Pd)</td>
<td>76.1 22.3 1.6</td>
<td>77 20 3</td>
</tr>
</tbody>
</table>

Diffusion disks with approximate thickness of 2 mm were cut from the rods of alloys and prepared metallographically by polishing through 0.25 µm diamond paste. Table 3.2 presented ternary diffusion coupes that were assembled with the disks held together in Invar™ steel jig consisting of two end plates and three threaded rods. The couples were placed in quartz capsules, which were sealed at one end, and evacuated to a pressure less than 10^{-6} torr and flushed with hydrogen several times. Ar was filled into a capsule before the final sealing. The capsules containing the couples were annealed in a horizontal Lindberg 3-zone furnace at 900°C for 168 hours and at 700°C for 720 hours. After the anneal, the couples were quenched in water to preserve the high temperature microstructures.
Table 3.2: List of Ni vs. Ni-Cr-X and NiCr vs. Ni-Cr-X solid-to-solid diffusion couples annealed at 900°C for 168 hours and at 700°C for 720 hours.

<table>
<thead>
<tr>
<th>Series</th>
<th>Diffusion Couples</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Ni vs. Ni-Cr</td>
</tr>
<tr>
<td>II</td>
<td>Ni vs. Ni-Cr-Al</td>
</tr>
<tr>
<td></td>
<td>Ni vs. Ni-Cr-Si</td>
</tr>
<tr>
<td></td>
<td>Ni vs. Ni-Cr-Ge</td>
</tr>
<tr>
<td></td>
<td>Ni vs. Ni-Cr-Pd</td>
</tr>
<tr>
<td>III</td>
<td>Ni-Cr vs. Ni-Cr-Al</td>
</tr>
<tr>
<td></td>
<td>Ni-Cr vs. Ni-Cr-Si</td>
</tr>
<tr>
<td></td>
<td>Ni-Cr vs. Ni-Cr-Ge</td>
</tr>
<tr>
<td></td>
<td>Ni-Cr vs. Ni-Cr-Pd</td>
</tr>
</tbody>
</table>

The diffusion assembly was then mounted, sectioned, metallographically prepared for microstructural observations. Excellent bonding within all diffusion couples was observed. Then, cross-section surface was repolished with 1µm diamond paste for electron microprobe analysis. The concentration profiles of Ni, Cr, Al, Si, Ge, and Pd for the diffusion couples were determined with a JEOL™ 733 microprobe by point-to-point counting techniques using pure Ni, Cr, Al, Si, Ge, and Pd as standards. Intensities of K$_\alpha$ x-radiations were measured and converted to concentrations of Ni, Cr, Al, Si, Ge, and L$_\alpha$ x-radiations for that of Pd with appropriate ZAF corrections. Concentration profiles obtained from microprobe was smoothened by weighted-spline-tool using MatLab™. It should be noted that the analytical method employed in this study to determine interdiffusion coefficients by integration of interdiffusion fluxes, *vis. Eq. (3.5)*, do not require the use of concentration gradients. This method significantly reduces the influence of smoothening procedure on the determination of interdiffusion coefficients.
3.4. Interdiffusion in Ni-Cr-X Alloys at 900°C

Figure 3.1 presents optical micrographs obtained from the diffusion couples Ni vs. Ni-Cr-Al and Ni vs. Ni-Cr-Si that was annealed at 900°C for 168 hours. Excellent bonding was achieved during the diffusion anneal for all diffusion couples. Figure 3.2 presents an example of experimental and smoothened concentration profiles that were used for the determination of interdiffusion coefficients. Scatters in the concentration profiles for all diffusion couples were minimum and within the experimental uncertainty associated with EPMA. Experimental concentration profiles were smoothened with weighted-spline routine by using MatLab™.

Figure 3.1. Typical optical micrographs of solid-to-solid diffusion couples etched with Kallings reagent: (a) Ni-Cr vs. Ni-Cr-Al, (b) Ni vs. Ni-Cr-Si annealed at 900°C for 168 hours. Specimens were slightly over-etched to clearly distinguish the experimental contact plane, $x_m$. 
Figure 3.2: Typical experimental and smoothened concentration profiles measured from solid-to-solid diffusion couples (a,b) Ni vs. Ni-Cr-Al and (c,d) Ni-Cr vs. Ni-Cr-Si, annealed at 900°C for 168 hours.

From concentration profiles obtained from series I and II diffusion couples (i.e., Ni vs. Ni-Cr, and Ni vs. Ni-Cr-X), average effective interdiffusion coefficients $\tilde{D}_{i}^{\text{eff}}$'s on either side of the Matano plane were determined using Eq. (3.3). They are reported in Table 3.3. In general, $\tilde{D}_{i}^{\text{eff}}$ was higher on the $(C_i^o \sim C_i^{+\infty})$ composition range with higher Cr concentration relative to the other side of the Matano plane. Table 3.3 also reports that Al addition to NiCr alloy can increase or decrease the $\tilde{D}_{Cr}^{\text{eff}}$ as a function of composition. This indicates appreciable variation in interdiffusion coefficients as a function of composition: specifically, Al increased $\tilde{D}_{Cr}^{\text{eff}}$ on the $(C_i^o \sim C_i^{+\infty})$ composition range with higher Cr concentration. $\tilde{D}_{Cr}^{\text{eff}}$ was observed to increase with
Si addition to NiCr alloy especially on the \((C_i^0 \sim C_i^{+\infty})\) side with higher Cr concentration.

According to Table 3.3, Ge does not change \(\tilde{D}_{Cr}^{eff}\) significantly, while Pd addition to Ni-Cr alloy increased \(\tilde{D}_{Cr}^{eff}\), quite significant on the \((C_i^0 \sim C_i^{+\infty})\) range with higher Cr concentration.

### Table 3.3: Average effective interdiffusion coefficients determined from Ni vs. Ni-Cr-X diffusion couples annealed at 900°C for 168 hours.

<table>
<thead>
<tr>
<th>Diffusion Couple</th>
<th>Composition Range</th>
<th>(\tilde{D}_{Cr}^{eff}) ((10^{-16} \text{ m}^2/\text{s}))</th>
<th>(\tilde{D}_{X}^{eff}) ((10^{-16} \text{ m}^2/\text{s}))</th>
<th>(\tilde{D}_{Ni}^{eff}) ((10^{-16} \text{ m}^2/\text{s}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni vs. Ni-Cr (X = None)</td>
<td>(C_i^- \sim C_i^0)</td>
<td>1.40</td>
<td>-</td>
<td>1.40</td>
</tr>
<tr>
<td></td>
<td>(C_i^0 \sim C_i^{+\infty})</td>
<td>1.53</td>
<td>-</td>
<td>1.53</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Al (X = Al)</td>
<td>(C_i^- \sim C_i^0)</td>
<td>0.91</td>
<td>3.31</td>
<td>1.83</td>
</tr>
<tr>
<td></td>
<td>(C_i^0 \sim C_i^{+\infty})</td>
<td>1.58</td>
<td>4.68</td>
<td>2.19</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Si (X = Si)</td>
<td>(C_i^- \sim C_i^0)</td>
<td>1.68</td>
<td>5.74</td>
<td>2.26</td>
</tr>
<tr>
<td></td>
<td>(C_i^0 \sim C_i^{+\infty})</td>
<td>3.00</td>
<td>6.91</td>
<td>3.57</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Ge (X = Ge)</td>
<td>(C_i^- \sim C_i^0)</td>
<td>1.30</td>
<td>3.09</td>
<td>1.40</td>
</tr>
<tr>
<td></td>
<td>(C_i^0 \sim C_i^{+\infty})</td>
<td>1.44</td>
<td>3.47</td>
<td>1.61</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Pd (X = Pd)</td>
<td>(C_i^- \sim C_i^0)</td>
<td>1.77</td>
<td>1.19</td>
<td>1.74</td>
</tr>
<tr>
<td></td>
<td>(C_i^0 \sim C_i^{+\infty})</td>
<td>4.09</td>
<td>2.07</td>
<td>3.92</td>
</tr>
</tbody>
</table>

From concentration profiles obtained from diffusion couple series II (i.e., Ni vs. Ni-Cr-X), average ternary interdiffusion coefficients \(\overline{D}_{ij}^{Ni}(i,j=Cr,X)\) were determined on either side of the Matano plane using Eq. (3.5). These are reported in Table 3.4. It should be noted that these diffusion couples were designed to yield the same sign of \(\partial C_{Cr}/\partial x\) and \(\partial C_{X}/\partial x\). Thus, positive and negative \(\overline{D}_{CrX}^{Ni}\) indicates an increase and a decrease in \(J_{Cr}\), respectively. In general, larger magnitudes of \(\overline{D}_{CrCr}^{Ni}\) and \(\overline{D}_{XX}^{Ni}\) were observed on the \((C_i^0 \sim C_i^{+\infty})\) composition range with higher Cr concentration. Al addition in the Ni-Cr alloy yielded positive \(\overline{D}_{CrAl}^{Ni}\), and increased \(J_{Cr}\) in
accordance with previous work by Nesbitt [25] and Morral [34]. The magnitude of $D_{\text{CrAl}}^{\text{Ni}}$ was quite large as reported in Table 3.4 on the $(C_i^\alpha \sim C_i^{-\alpha})$ with higher Cr concentration. Similarly, Si, Ge and Pd additions to Ni-Cr alloy increased $\tilde{J}_{\text{Cr}}$ with positive $D_{\text{CrX}}^{\text{Ni}}$. This effect was, again, stronger when Cr concentration is high on the $(C_i^\alpha \sim C_i^{-\alpha})$ particularly for Si and Pd.

Table 3.4: Average ternary interdiffusion coefficients determined from Ni vs. Ni-Cr-X diffusion couples (series II) annealed at 900°C for 168 hours.

<table>
<thead>
<tr>
<th>Diffusion Couple</th>
<th>Composition Range</th>
<th>$D_{\text{CrCr}}^{\text{Ni}}$ $(10^{-16} \text{ m}^2/\text{s})$</th>
<th>$D_{\text{CrX}}^{\text{Ni}}$ $(10^{-16} \text{ m}^2/\text{s})$</th>
<th>$D_{\text{XCr}}^{\text{Ni}}$ $(10^{-16} \text{ m}^2/\text{s})$</th>
<th>$D_{\text{XX}}^{\text{Ni}}$ $(10^{-16} \text{ m}^2/\text{s})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni vs. Ni-Cr-Al (X = Al)</td>
<td>$(C_i^{-\alpha} \sim C_i^\alpha)$</td>
<td>0.78</td>
<td>0.31</td>
<td>0.40</td>
<td>1.99</td>
</tr>
<tr>
<td></td>
<td>$(C_i^\alpha \sim C_i^{\alpha-\alpha})$</td>
<td>1.11</td>
<td>1.72</td>
<td>0.43</td>
<td>2.84</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Si (X = Si)</td>
<td>$(C_i^{-\alpha} \sim C_i^\alpha)$</td>
<td>1.23</td>
<td>0.15</td>
<td>0.44</td>
<td>2.92</td>
</tr>
<tr>
<td></td>
<td>$(C_i^\alpha \sim C_i^{\alpha-\alpha})$</td>
<td>2.05</td>
<td>4.88</td>
<td>0.57</td>
<td>3.35</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Ge (X = Ge)</td>
<td>$(C_i^{-\alpha} \sim C_i^\alpha)$</td>
<td>1.08</td>
<td>0.36</td>
<td>0.07</td>
<td>1.73</td>
</tr>
<tr>
<td></td>
<td>$(C_i^\alpha \sim C_i^{\alpha-\alpha})$</td>
<td>1.24</td>
<td>0.89</td>
<td>0.10</td>
<td>1.99</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Pd (X = Pd)</td>
<td>$(C_i^{-\alpha} \sim C_i^\alpha)$</td>
<td>1.43</td>
<td>4.06</td>
<td>0.01</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>$(C_i^\alpha \sim C_i^{\alpha-\alpha})$</td>
<td>3.49</td>
<td>4.86</td>
<td>0.01</td>
<td>1.76</td>
</tr>
</tbody>
</table>

Diffusion couple series III was designed with initial $\partial C_{\text{Cr}} / \partial x = 0$, so that $\tilde{J}_{\text{Cr}}$ is largely due to $\partial C_X / \partial x$, and depends on the magnitude and sign of $D_{\text{CrX}}^{\text{Ni}}$. $\tilde{J}_X$ has caused an uphill-diffusion of Cr in the direction of $\tilde{J}_X$ with positive $D_{\text{CrX}}^{\text{Ni}}$ for Al and Si. This suggests that Al and Si increase the thermodynamic activity of Cr in Ni-Cr alloys. On the other hand, $\tilde{J}_{\text{Ge}}$ and $\tilde{J}_{\text{Pd}}$ did not caused any measurable redistribution of Cr ($\tilde{J}_{\text{Cr}} \approx 0$). Average ternary interdiffusion coefficients determined from diffusion couples series III are reported in Table 3.5. It should be
noted that Ge and Pd have lower contents in the Ni-Cr-X alloys than Al and Si, as reported in Table 3.1.

<table>
<thead>
<tr>
<th>Diffusion Couple</th>
<th>Composition Range</th>
<th>$\bar{D}_{\text{Ni}}^{\text{Cr}}$ ($10^{-16}$ m$^2$/s)</th>
<th>$\bar{D}_{\text{Ni}}^{\text{CrX}}$ ($10^{-16}$ m$^2$/s)</th>
<th>$\bar{D}_{\text{Ni}}^{\text{XX}}$ ($10^{-16}$ m$^2$/s)</th>
<th>$\bar{D}_{\text{Ni}}^{\text{XX}}$ ($10^{-16}$ m$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Cr vs. Ni-Cr-Al (X = Al)</td>
<td>($C_i^{-\infty} \sim C_i^{0}$)</td>
<td>0.23</td>
<td>0.12</td>
<td>0.01</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td>($C_i^{0} \sim C_i^{+\infty}$)</td>
<td>1.20</td>
<td>0.44</td>
<td>0.13</td>
<td>1.17</td>
</tr>
<tr>
<td>Ni-Cr vs. Ni-Cr-Si (X = Si)</td>
<td>($C_i^{-\infty} \sim C_i^{0}$)</td>
<td>2.58</td>
<td>1.73</td>
<td>0.01</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td>($C_i^{0} \sim C_i^{+\infty}$)</td>
<td>1.39</td>
<td>0.63</td>
<td>1.78</td>
<td>1.97</td>
</tr>
<tr>
<td>Ni-Cr vs. Ni-Cr-Ge (X = Ge)</td>
<td>($C_i^{-\infty} \sim C_i^{0}$)</td>
<td></td>
<td></td>
<td>Δ$C_i^{0}$ / Δx = 0 and cannot be determined.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>($C_i^{0} \sim C_i^{+\infty}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-Cr vs. Ni-Cr-Pd (X = Pd)</td>
<td>($C_i^{-\infty} \sim C_i^{0}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Based on average effective interdiffusion coefficients and average ternary interdiffusion coefficients determined in this study, alloying additions of Al, Si, Ge and Pd have all increased $\bar{D}_{\text{Ni}}^{\text{eff}}$ and yielded positive $\bar{D}_{\text{Ni}}^{\text{CrX}}$ particularly at high Cr content (~22at.%). Therefore, the Cr$_2$O$_3$-forming ability of Ni-20at.%Cr-base alloy should improve with these alloying additions by establishing Cr$_2$O$_3$ scale, maintaining protective Cr$_2$O$_3$ scale formation, and in reformation of Cr$_2$O$_3$ on spallation. It should be noted that positive $\bar{D}_{\text{Ni}}^{\text{CrX}}$ reported in Tables 3.4 and 3.5 should also promote the formation of other scales (Al$_2$O$_3$, SiO$_2$) in the γ (fcc) Ni-Cr alloy, which may reduce the rate of scale growth and/or change the thermo-mechanical properties of the scale.
3.5. Interdiffusion in Ni-Cr-X Alloys at 700°C

Excellent diffusion bonding was achieved in all diffusion couples as shown by Figure 3.3 that presents a typical optical micrograph obtained by etching (Kalling’s reagent) the polished surface of the diffusion couple.

![Figure 3.3 Typical optical micrograph of solid-to-solid diffusion couple Ni vs. Ni-Cr-Ge annealed at 700°C for 720 hours.](image)

Figure 3.4 presents an example of experimental and smoothened concentration profiles that were used for the determination of interdiffusion fluxes and interdiffusion coefficients. The scatters in the concentration profiles for all diffusion couples were within the experimental uncertainty associated with EPMA. Experimental concentration profiles were smoothened with a smoothing-spline approximation by using MatLab. Consistency in experimental and smoothened concentration profiles of Cr in series III (see for example Figure 3.4), owing to similar terminal concentration was examined by multiple EPMA acquisitions (e.g., independent Cr concentration) and by close examination of concentration profiles for Ni and X ternary alloying additions (e.g.,
Consistency in terms of repeatable assessment of all concentration profiles was obtained for determination of interdiffusion fluxes and interdiffusion coefficients.

Using Eq. (3.5), average effective interdiffusion coefficients, $\tilde{D}_i^{\text{eff}}$, s on either side of the Matano plane were determined from the concentration profiles obtained from series I and II diffusion couples (i.e., Ni vs. Ni-Cr and Ni vs. Ni-Cr-X). They are reported in Tables 3.6. These average effective interdiffusion coefficients are two orders of magnitude lower than those
determined at 900°C. $\tilde{D}_i^{\text{eff}}$ was generally higher on the $(C_i^o \sim C_i^{+\infty})$ composition range with higher Cr concentration relative to the other side.

Table 3.6: Average effective interdiffusion coefficients determined from Ni vs. Ni-Cr-X diffusion couples annealed at 700°C for 720 hours.

<table>
<thead>
<tr>
<th>Diffusion Couple</th>
<th>Composition Range</th>
<th>$\tilde{D}_c^{\text{eff}}$ [10^{-18} m²/s]</th>
<th>$\tilde{D}_x^{\text{eff}}$ [10^{-18} m²/s]</th>
<th>$\tilde{D}_n^{\text{eff}}$ [10^{-18} m²/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni vs. Ni-Cr (X = None)</td>
<td>$(C_i^{-\infty} \sim C_i^o)$</td>
<td>1.98</td>
<td>-</td>
<td>1.98</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr (X = None)</td>
<td>$(C_i^o \sim C_i^{+\infty})$</td>
<td>2.34</td>
<td>-</td>
<td>2.34</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Al (X = Al)</td>
<td>$(C_i^{-\infty} \sim C_i^o)$</td>
<td>0.50</td>
<td>0.40</td>
<td>0.47</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Al (X = Al)</td>
<td>$(C_i^o \sim C_i^{+\infty})$</td>
<td>0.61</td>
<td>0.86</td>
<td>0.68</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Si (X = Si)</td>
<td>$(C_i^{-\infty} \sim C_i^o)$</td>
<td>1.22</td>
<td>2.08</td>
<td>1.27</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Si (X = Si)</td>
<td>$(C_i^o \sim C_i^{+\infty})$</td>
<td>1.95</td>
<td>2.26</td>
<td>1.99</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Ge (X = Ge)</td>
<td>$(C_i^{-\infty} \sim C_i^o)$</td>
<td>1.39</td>
<td>2.38</td>
<td>1.43</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Ge (X = Ge)</td>
<td>$(C_i^o \sim C_i^{+\infty})$</td>
<td>2.74</td>
<td>5.17</td>
<td>2.97</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Pd (X = Pd)</td>
<td>$(C_i^{-\infty} \sim C_i^o)$</td>
<td>6.91</td>
<td>6.06</td>
<td>6.85</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Pd (X = Pd)</td>
<td>$(C_i^o \sim C_i^{+\infty})$</td>
<td>9.86</td>
<td>5.41</td>
<td>9.57</td>
</tr>
</tbody>
</table>

Table 3.6 also reports that Al, Si and Ge diffuse faster than Ni in $\gamma$-phase Ni-Cr-X alloys.

In the case of Ni vs. Ni-Cr-Pd, $\tilde{D}_i^{\text{eff}}$’s for Ni, Cr and Pd are similar. These results are in general, analogues observations made at 900°C. At 700°C, Table 3.6 shows that Al and Si additions to Ni-Cr alloy reduced $\tilde{D}_c^{\text{eff}}$, but Pd additions to Ni-Cr alloy increased $\tilde{D}_c^{\text{eff}}$ significantly, especially in the composition range of $(C_i^o \sim C_i^{+\infty})$.

Concentration profiles obtained from diffusion couple series II and III (i.e., Ni vs. Ni-Cr-X and NiCr vs. Ni-Cr-X) were employed to determine average ternary interdiffusion coefficients, $\overline{D}_{ij}^{\text{Ni}}$ on either side of the Matano plane using Eq. (3.5). These are reported in Tables 3.7 and 3.8. The magnitude of these interdiffusion coefficients is approximately two orders lower than those
determined at 900°C. The sign of the cross interdiffusion coefficients remained the same with those determined at 900°C.

Series II diffusion couples were designed to yield the same sign of $\partial C_r / \partial x$ and $\partial C_x / \partial x$ where a positive and negative $\overline{D}^{Ni}_{CrX}$ indicates an increase and a decrease in $\overline{J}_r$, respectively. In general, higher magnitude of $\overline{D}^{Ni}_{CrCr}$ and $\overline{D}^{Ni}_{XX}$ was observed on the $(C_i^0 \sim C_i^{+\infty})$ composition range with higher Cr concentration. The Al addition in the Ni-Cr alloy yielded positive $\overline{D}^{Ni}_{CrAl}$, and increased $\overline{J}_r$ in agreement with the previous work by Nesbitt [14], Thomson [15] and observation made at 900°C in this study.

Table 3.7. Average ternary interdiffusion coefficients determined from Ni-Cr vs. Ni-Cr-X diffusion couples annealed at 700°C for 720 hours.

<table>
<thead>
<tr>
<th>Diffusion Couple</th>
<th>Composition Range</th>
<th>$\overline{D}^{Ni}_{CrCr}$ [10^{-18} m^2/s]</th>
<th>$\overline{D}^{Ni}_{CrX}$ [10^{-18} m^2/s]</th>
<th>$\overline{D}^{Ni}_{XX}$ [10^{-18} m^2/s]</th>
<th>$\overline{D}^{Ni}_{XX}$ [10^{-18} m^2/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni vs. Ni-Cr-Al (X = Al)</td>
<td>$(C^-\infty \sim C_i^0)$</td>
<td>0.48</td>
<td>0.53</td>
<td>0.06</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>$(C_i^0 \sim C_i^{+\infty})$</td>
<td>0.54</td>
<td>0.02</td>
<td>0.10</td>
<td>0.35</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Si (X = Si)</td>
<td>$(C^-\infty \sim C_i^0)$</td>
<td>0.96</td>
<td>0.58</td>
<td>0.03</td>
<td>1.20</td>
</tr>
<tr>
<td></td>
<td>$(C_i^0 \sim C_i^{+\infty})$</td>
<td>1.42</td>
<td>0.05</td>
<td>0.05</td>
<td>1.30</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Ge (X = Ge)</td>
<td>$(C^-\infty \sim C_i^0)$</td>
<td>0.67</td>
<td>5.44</td>
<td>Negligible</td>
<td>2.51</td>
</tr>
<tr>
<td></td>
<td>$(C_i^0 \sim C_i^{+\infty})$</td>
<td>0.93</td>
<td>5.84</td>
<td>Negligible</td>
<td>2.88</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Pd (X = Pd)</td>
<td>$(C^-\infty \sim C_i^0)$</td>
<td>6.49</td>
<td>4.92</td>
<td>Negligible</td>
<td>5.84</td>
</tr>
<tr>
<td></td>
<td>$(C_i^0 \sim C_i^{+\infty})$</td>
<td>7.59</td>
<td>5.83</td>
<td>Negligible</td>
<td>5.58</td>
</tr>
</tbody>
</table>
The Si, Ge and Pd additions to Ni-Cr alloy also increased \( \mathbf{\bar{J}}_{\text{Cr}} \) with positive \( \mathbf{\bar{D}}_{\text{CrX}}^{\text{Ni}} \). This effect was stronger when Cr concentration was high on the \( (C_i^\circ \sim C_i^{+\infty}) \) side, particularly for Ge and Pd. At 900°C, \( \mathbf{\bar{D}}_{\text{CrGe}}^{\text{Ni}} \) was not significant to this extent. The Si, Ge and Pd additions to Ni-Cr alloy also increased \( \mathbf{\bar{J}}_{\text{Cr}} \) with positive \( \mathbf{\bar{D}}_{\text{CrX}}^{\text{Ni}} \). This effect was stronger when Cr concentration is high on the \( (C_i^\circ \sim C_i^{+\infty}) \) side, particularly for Ge and Pd. Also at 900°C [9], \( \mathbf{\bar{D}}_{\text{CrGe}}^{\text{Ni}} \) was not significant while \( \mathbf{\bar{D}}_{\text{CrSi}}^{\text{Ni}} \) and \( \mathbf{\bar{D}}_{\text{CrPd}}^{\text{Ni}} \) were significantly large. This study at 700°C finds that \( \mathbf{\bar{D}}_{\text{CrGe}}^{\text{Ni}} \) and \( \mathbf{\bar{D}}_{\text{CrPd}}^{\text{Ni}} \) are large positive values while \( \mathbf{\bar{D}}_{\text{CrSi}}^{\text{Ni}} \) is not so significant.

### Table 3.8. Average ternary interdiffusion coefficients determined from NiCr vs. Ni-Cr-X diffusion couples annealed at 700°C for 720 hours.

<table>
<thead>
<tr>
<th>Diffusion Couple</th>
<th>Composition Range</th>
<th>( \mathbf{\bar{D}}_{\text{CrCr}}^{\text{Ni}} ) [10^{-18} m²/s]</th>
<th>( \mathbf{\bar{D}}_{\text{CrX}}^{\text{Ni}} ) [10^{-18} m²/s]</th>
<th>( \mathbf{\bar{D}}_{\text{XCr}}^{\text{Ni}} ) [10^{-18} m²/s]</th>
<th>( \mathbf{\bar{D}}_{\text{XX}}^{\text{Ni}} ) [10^{-18} m²/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Cr vs. Ni-Cr-Al</td>
<td>( C_i^{\circ} \sim C_i^{\circ} )</td>
<td>1.98</td>
<td>0.73</td>
<td>1.97</td>
<td>0.78</td>
</tr>
<tr>
<td>(X = Al)</td>
<td>( C_i^{\circ} \sim C_i^{+\infty} )</td>
<td>2.65</td>
<td>1.00</td>
<td>1.01</td>
<td>0.76</td>
</tr>
<tr>
<td>Ni-Cr vs. Ni-Cr-Si</td>
<td>( C_i^{\circ} \sim C_i^{\circ} )</td>
<td>6.91</td>
<td>5.87</td>
<td>0.11</td>
<td>0.62</td>
</tr>
<tr>
<td>(X = Si)</td>
<td>( C_i^{\circ} \sim C_i^{+\infty} )</td>
<td>2.59</td>
<td>2.22</td>
<td>0.16</td>
<td>1.35</td>
</tr>
<tr>
<td>Ni-Cr vs. Ni-Cr-Ge</td>
<td>( \Delta C_{\text{Cr}} \approx 0 ) and cannot be determined</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(X = Ge)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-Cr vs. Ni-Cr-Ge</td>
<td>( \Delta C_{\text{Cr}} \approx 0 ) and cannot be determined</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(X = Ge)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Diffusion couple series III was designed so that the initial \( \partial C_{\text{Cr}} / \partial x \approx 0 \). Therefore, \( \mathbf{\bar{J}}_{\text{Cr}} \) is mainly due to \( \partial C_X / \partial x \), and the magnitude and sign of \( \mathbf{\bar{D}}_{\text{CrX}}^{\text{Ni}} \). \( \mathbf{\bar{J}}_{\text{Al}} \) and \( \mathbf{\bar{J}}_{\text{Si}} \) have caused an uphill-diffusion of Cr owing to positive \( \mathbf{\bar{D}}_{\text{CrAl}}^{\text{Ni}} \) and \( \mathbf{\bar{D}}_{\text{CrSi}}^{\text{Ni}} \), respectively. On the other hand, \( \mathbf{\bar{J}}_{\text{Ge}} \) and \( \mathbf{\bar{J}}_{\text{Pd}} \) did not cause any measurable redistribution of Cr (\( \mathbf{\bar{J}}_{\text{Cr}} \approx 0 \)). However, Ge and Pd are lower in
concentration than those of Al and Si, in the Ni-Cr-X alloys, as reported in Table 3.1. Based on average effective interdiffusion coefficients and average ternary interdiffusion coefficients determined at 700°C, alloying additions of Al, Si, Ge and Pd have yielded positive $\bar{D}_{\text{CrX}}^{\text{Ni}}$. Therefore, Cr₂O₃-forming ability of Ni-22at.%Cr alloy should improve with these alloying additions.
3.6 Summary

From experimental solid-to-solid diffusion couples, small addition of Al, Si, Ge, or Pd was observed to increase the overall interdiffusion flux of Cr in Ni-22at.%Cr-X (fcc γ phase) alloys. Experimental concentration profiles, measured after annealing at 900°C and 700°C in a three-zone tube furnace for 168 and 720 hours, respectively, were employed to determine interdiffusion fluxes, average effective interdiffusion coefficients and average ternary interdiffusion coefficients. In general, $\bar{D}_{\text{eff}}$ was observed to increase with higher Cr concentration. Also, $\bar{D}_{\text{NiCrX}}$ coefficients were determined to be positive with alloying additions of Al, Si, Ge, or Pd. These results suggest that these alloying additions can help the formation of Cr$_2$O$_3$-scale for initial scale formation, maintaining scale homogeneity during prolonged high-temperature exposure, and reformation after scale-spallation.

3.7 References


CHAPTER 4: TERNARY AND QUATERNARY INTERDIFFUSION IN Fe-Ni-Cr-X ALLOYS AT 900°C

4.1 Introduction

Austenitic (fcc-γ) Cr₂O₃ forming Fe-Ni-Cr alloys are of potential interest for many applications due to their combination of good oxidation/corrosion resistance and high temperature strength [1-7]. Minor alloying additions (< 5 wt.%) on these alloys are found to increase the oxidation resistance by forming a slowly growing, adherent, continuous and impervious layer of Cr₂O₃ [4,8,9]. In this work, effects of Si and Ge alloying additions on the interdiffusion behavior of quaternary Fe-Ni-Cr-X (X = Si, Ge) alloys (fcc γ-phase) were studied by using solid-to-solid diffusion couples with due respect for the formation and growth kinetics of protective Cr₂O₃ scale of these alloys.

Ternary and quaternary interdiffusion coefficients are important tools to explain the effects of minor alloying additions on the oxidation of Cr₂O₃-forming alloys. In this work, interdiffusion in Fe-24at.%Ni-22at.%Cr-X (fcc γ phase) alloys (X = Si, Ge) was examined using solid-to-solid diffusion couples annealed at 900°C for 168 hours. The selection criteria of minor alloying additions (e.g., Si, Ge) for the case of Ni-Cr alloys has been described in earlier interdiffusion studies carried out at 900°C and 700°C [10,11]. Experimental concentration profiles are employed to calculate interdiffusion fluxes of individual components, and determine average effective interdiffusion coefficients and average ternary and quaternary interdiffusion coefficients. Interdiffusion coefficients are examined to assess effects of alloying additions on the interdiffusion behavior of Cr in promoting Cr₂O₃-formation in Fe-24at.%Ni-22at.%Cr-X alloys.
4.2 Determination of Interdiffusion Coefficients

In this study, the interdiffusion fluxes $\tilde{J}_i$ of all components were determined directly from their concentration profiles using Eq. (3.2). Based on the integration of interdiffusion fluxes described in section 3.2, average effective interdiffusion coefficients, $\tilde{D}^\text{eff}_i$ were calculated using Eq. (3.3) for individual components. Average ternary interdiffusion coefficients, as defined and described in section 3.2 were determined using Eq. (3.5) for ternary Fe-Cr-X alloys while those for quaternary Fe-Ni-Cr-X alloys were determined using the expression:

$$\int_{x_1}^{x_2} \tilde{J}_i (x - x_o)^n dx = -\tilde{D}^4_{i1} \int_{c_1(x_1)}^{c_1(x_2)} (x - x_o)^n dC_1$$
$$- \tilde{D}^4_{i2} \int_{c_2(x_1)}^{c_2(x_2)} (x - x_o)^n dC_2 - \tilde{D}^4_{i3} \int_{c_3(x_1)}^{c_3(x_2)} (x - x_o)^n dC_3 \quad (i = 1, 2, 3)$$

Eq. (3.5) provides four equations involving the $\tilde{D}^3_{ij}$ interdiffusion coefficients ($n = 0, 1$) and can be set up from interdiffusion fluxes calculated using Eq. (3.2) from the concentration profiles of a single diffusion couple of the ternary system. Similarly, Eq. (4.1) provides nine equations involving nine $\tilde{D}^4_{ij}$ interdiffusion coefficients ($n = 0, 1$ and 2) from the single diffusion couple in a quaternary system. The $\tilde{D}^k_{ij}$ coefficients, characteristic of the diffusion path, can be determined over selected composition ranges that include nonlinear segment of the profiles [15].
4.3 Experimental Procedure

Ternary and quaternary alloys of Fe-Ni-Cr-X (fcc $\gamma$ phase) system with compositions reported in Table 4.1 were prepared with 99.9% pure Fe, Ni, Cr, Si and Ge by arc melting under an argon atmosphere. These alloys were chill-cast by water-cooled copper molds into rods with approximately 12 mm in diameter. The alloy rods were placed in a quartz capsule, evacuated to pressure below $10^{-6}$ torr, and flushed with hydrogen. The hydrogen-flush procedure was repeated several times, and Ar was finally filled into the capsule before the final encapsulation. They were homogenized at 900°C for 168 hours in a horizontal Lindberg™ 3-zone tube furnace, and water-quenched to retain the high temperature microstructure. The microstructures and compositions of the alloys were examined by optical microscopy, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and electron microprobe analysis (EMPA). No measurable variation in the alloy compositions was found, and all alloys consisted single-phase fcc solid solution ($\gamma$-phase).

Table 4.1 Nominal compositions of Fe-Ni-Cr-X alloys employed for solid-to-solid diffusion couple studies. Values in parenthesis are standard deviation.

<table>
<thead>
<tr>
<th>Alloy Identification</th>
<th>Composition (atom percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>Fe-Ni</td>
<td>76.3 (0.7)</td>
</tr>
<tr>
<td>Fe-Ni-Cr</td>
<td>55.5 (0.7)</td>
</tr>
<tr>
<td>Fe-Ni-Cr-Si (X = Si)</td>
<td>52.2 (0.7)</td>
</tr>
<tr>
<td>Fe-Ni-Cr-Ge (X = Ge)</td>
<td>53.4 (0.3)</td>
</tr>
</tbody>
</table>
Alloy disks of approximately 2 mm in thickness were sliced from the rods of alloys, and prepared metallographically by polishing through 0.25 µm diamond paste. Table 4.2 presents ternary and quaternary diffusion couples that were assembled with the disks held together in Invar™ steel jig consisting of two end plates and three threaded rods. The couples were placed in quartz capsules, which were sealed at one end, and evacuated to a pressure less than 10⁻⁶ torr and flushed with hydrogen several times. Ar was filled into a capsule before the final sealing. The capsules containing the couples were annealed at 900°C in a horizontal Lindberg 3-zone furnace for 168 hours. After the diffusion anneal, the couples were quenched in water to preserve the high temperature composition and/or microstructure.

<table>
<thead>
<tr>
<th>Series</th>
<th>Diffusion Couples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Ni</td>
<td>Fe-Ni vs. Fe-Ni-Cr</td>
</tr>
<tr>
<td>vs. Fe-Ni-Cr-X (Si,Ge)</td>
<td>Fe-Ni vs. Fe-Ni-Cr-Si</td>
</tr>
<tr>
<td></td>
<td>Fe-Ni vs. Fe-Ni-Cr-Ge</td>
</tr>
</tbody>
</table>

The diffusion couple assembly was then mounted, sectioned and metallographically prepared for microstructural observations. Excellent diffusion bonding in all couples was observed. Then, cross-section surface was polished with 1µm diamond paste for electron microprobe analysis (EPMA). The concentration profiles of Fe, Ni, Cr, Si and Ge for the diffusion couples were determined with a JEOL 733 (Tokyo, Japan) microprobe by point-to-point counting techniques using pure standards of all the constituent alloying elements. Intensities of Kα X-radiations were measured and converted to concentrations of Fe, Ni, Cr, Si and Ge with appropriate ZAF (atomic number, Z; absorption, A; fluorescence, F) corrections.
Concentration profiles obtained from EPMA were smoothened by a smoothening-spline-tool using MatLab (The Math Works, Natick, MA). The analytical method used in this study to determine interdiffusion coefficients is by the integration of interdiffusion fluxes (e.g. Eqs. 3.5 and 4.1) only. It does not require the determination of concentration gradients that significantly reduces the influence of a smoothening procedure on the determination of interdiffusion coefficients.

**4.4. Results and Discussions**

Figures 4.1 and 4.2 present examples of experimental and smoothened concentration profiles that were used for the determination of interdiffusion fluxes and interdiffusion coefficients. The scatters in the concentration profiles for all diffusion couples were minimal and within the experimental uncertainty associated with EPMA. Consistency in experimental and smoothened concentration profiles of Ni, owing to similar terminal concentration was examined by multiple EPMA acquisitions (e.g., independent Ni concentration) and by close examination of concentration profiles for Cr and X ternary alloying additions (e.g., dependent Ni concentrations).
Figure 4.1: Typical experimental and smoothened concentration profiles from solid-to-solid diffusion couple, Fe-Ni vs. Fe-Ni-Cr-Si annealed at 900°C for 168 hours.

From concentration profiles obtained from diffusion couples, average effective interdiffusion coefficients $\tilde{D}_i$'s on either side of the Matano plane were determined using Eq. 3.2, and are reported in Table 4.3. Fe-Ni vs. Fe-Ni-Cr is considered as a reference to compare and contrast the diffusional interactions of alloying elements Si and Ge. Average effective interdiffusion coefficients reported in Table 4.3 are comparable in magnitude to those determined for Ni-Cr-X (Si, Ge) alloys at 900°C [12]. Allying additions have increased the
magnitude of average effective interdiffusion coefficients of Cr and Fe on the \( (C_i^0 \sim C_i^{\infty}) \) side with \( X (X = \text{Si or Ge}) \) alloying additions.

Figure 4.2: Typical experimental and smoothened concentration profiles from solid-to-solid diffusion couple, Fe-Ni vs. Fe-Ni-Cr-Ge annealed at 900°C for 168 hours.
Table 4.3: Average effective interdiffusion coefficients determined from Fe-Ni vs. Fe-Ni-Cr-X (Si, Ge) diffusion couples annealed at 900°C for 168 hours. (Units: 10^{-16} m^2/s)

<table>
<thead>
<tr>
<th>Diffusion Couple</th>
<th>Composition Range</th>
<th>( \tilde{D}^e_{Cr} )</th>
<th>( \tilde{D}^e_X )</th>
<th>( \tilde{D}^e_{Ni} )</th>
<th>( \tilde{D}^e_{Fe} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Ni vs. Fe-Ni-Cr</td>
<td>( C_i^{\infty} \sim C_i^0 )</td>
<td>0.6</td>
<td>N/A</td>
<td>N/A</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>( C_i^0 \sim C_i^{\infty} )</td>
<td>0.3</td>
<td>N/A</td>
<td>N/A</td>
<td>0.3</td>
</tr>
<tr>
<td>Fe-Ni vs. Fe-Ni-Cr-Si (X = Si)</td>
<td>( C_i^{\infty} \sim C_i^0 )</td>
<td>0.7</td>
<td>1.3</td>
<td>-2.8</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>( C_i^0 \sim C_i^{\infty} )</td>
<td>0.8</td>
<td>1.2</td>
<td>-2.3</td>
<td>1.0</td>
</tr>
<tr>
<td>Fe-Ni vs. Fe-Ni-Cr-Ge (X = Ge)</td>
<td>( C_i^{\infty} \sim C_i^0 )</td>
<td>0.7</td>
<td>2.8</td>
<td>3.9</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>( C_i^0 \sim C_i^{\infty} )</td>
<td>1.8</td>
<td>2.7</td>
<td>2.9</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Note: \( \tilde{D}^e_{Ni} \) could not be determined since there was no observable development of concentration gradient (i.e., pseudo-binary).

Duh’s [16] study for interdiffusion in Fe-Ni-Cr alloys at 1100°C reported a decrease in \( \tilde{D}^e_{Cr} \) values with an increase in Cr at constant Ni concentration. Similar observation was made in this study from Fe-Ni vs. Fe-Ni-Cr diffusion couple where \( \tilde{D}^e_{Cr} \) was observed to decrease on the \( C_i^0 \sim C_i^{\infty} \) region with higher Cr content. However, the influence of Si and Ge alloying additions on quaternary diffusion couples altered this trend by increasing the \( \tilde{D}^e_{Cr} \) on the \( C_i^0 \sim C_i^{\infty} \) side where the contents of both Cr and X (X = Si or Ge) are higher. \( \tilde{J}_{Si} \) caused an uphill-diffusion of Ni as shown in Figure 4.1, which yielded a negative average effective interdiffusion coefficients of Ni, \( \tilde{D}^e_{Ni} \), reported in Table 4.3. This indicates a significant diffusional interaction between Ni and Si in austenitic Fe-based alloys where \( \tilde{J}_{Ni} \) would be significantly influence by the concentration gradient of Si, \( \partial C_{Si}/\partial \xi \). There was no “noticeably-unusual” redistribution of Ni in Fe-Ni vs. Fe-Ni-Cr-Ge diffusion couple as shown in Figure 4.2. However, a higher magnitude of \( \tilde{D}^e_{Ni} \) in Table 4.3 is noted for all concentration ranges within this diffusion couple.
Concentration profiles obtained from diffusion couples were employed to determine the average quaternary interdiffusion coefficients $\overline{D}^{Fe}_{ij}(i,j=Cr,Ni,X)$ on either side of the Matano plane using Eq. (4.1). They are reported in Table 4.4. Table 4.4 reports that the magnitude of these interdiffusion coefficients are comparable to those obtained for Ni-Cr-X alloys at 900°C [11]. These diffusion couples were designed with initial $\partial C_{Ni}/\partial x \approx 0$, and to yield the same sign of $\partial C_{Cr}/\partial x$ and $\partial C_{X}/\partial x$, so that a positive and negative $\overline{D}^{Fe}_{CrX}$ indicates an increase and a decrease in $\overline{j}_{Cr}$, respectively. Also, the initial $\partial C_{Ni}/\partial x \approx 0$ implies that, $\overline{J}_{Ni}$ is mainly due to $\partial C_{Cr}/\partial x$ and/or $\partial C_{X}/\partial x$, and the magnitude and sign of $\overline{D}^{Fe}_{NiCr}$ and/or $\overline{D}^{Fe}_{NiX}$.

Table 4.4: Average quaternary interdiffusion coefficients determined from Fe-Ni vs. Fe-Ni-Cr-X (X = Si or Ge) diffusion couples annealed at 900°C for 168 hours. (Units: $10^{-16}$ m$^2$/s)

<table>
<thead>
<tr>
<th>Couple</th>
<th>Composition Range</th>
<th>$\overline{D}^{Fe}_{CrCr}$</th>
<th>$\overline{D}^{Fe}_{CrNi}$</th>
<th>$\overline{D}^{Fe}_{CrX}$</th>
<th>$\overline{D}^{Fe}_{NiCr}$</th>
<th>$\overline{D}^{Fe}_{NiNi}$</th>
<th>$\overline{D}^{Fe}_{NiX}$</th>
<th>$\overline{D}^{Fe}_{XCr}$</th>
<th>$\overline{D}^{Fe}_{XNi}$</th>
<th>$\overline{D}^{Fe}_{XX}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Ni vs. Fe-Ni-Cr-Si (X=Si)</td>
<td>$(C_{i}^{-\infty} \sim C_{i}^{0})$</td>
<td>1.1</td>
<td>0.3</td>
<td>-2.1</td>
<td>-0.1</td>
<td>2.7</td>
<td>2.7</td>
<td>0.2</td>
<td>Neg.</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>$(C_{i}^{0} \sim C_{i}^{+\infty})$</td>
<td>1.0</td>
<td>0.3</td>
<td>-1.1</td>
<td>-0.3</td>
<td>1.6</td>
<td>4.2</td>
<td>0.1</td>
<td>Neg.</td>
<td>0.3</td>
</tr>
<tr>
<td>Fe-Ni vs. Fe-Ni-Cr-Ge (X=Ge)</td>
<td>$(C_{i}^{-\infty} \sim C_{i}^{0})$</td>
<td>0.8</td>
<td>-0.1</td>
<td>0.4</td>
<td>-0.3</td>
<td>4.3</td>
<td>4.3</td>
<td>0.1</td>
<td>-0.6</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>$(C_{i}^{0} \sim C_{i}^{+\infty})$</td>
<td>1.6</td>
<td>-0.4</td>
<td>2.9</td>
<td>-0.3</td>
<td>3.2</td>
<td>3.3</td>
<td>Neg.</td>
<td>-0.3</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Note: “Neg.” refers to magnitude less than 0.1 $\times 10^{-16}$ m$^2$/s.

The $\overline{D}^{Fe}_{CrNi}$ and $\overline{D}^{Fe}_{NiCr}$ cross coefficients have been reported small in magnitude and both positive and negative signs in literature [16-18] for Fe-Ni-Cr alloys. This holds true for quaternary cross coefficients, $\overline{D}^{Fe}_{CrNi}$ and $\overline{D}^{Fe}_{NiCr}$ reported in Table 4.4. This implies that there is no
significant influence of Ni and Cr on each other in austenitic Fe alloys. The magnitude of $\overline{D}_{\text{NiSi}}^\text{Fe}$ is lower than that of both $\overline{D}_{\text{NiNi}}^\text{Fe}$ and $\overline{D}_{\text{CrCr}}^\text{Fe}$ coefficients for Fe-Ni-Cr-Si alloys. However, the magnitude of $\overline{D}_{\text{CrSi}}^\text{Fe}$ and $\overline{D}_{\text{NiSi}}^\text{Fe}$ coefficients is comparable to that of $\overline{D}_{\text{CrCr}}^\text{Fe}$ and $\overline{D}_{\text{NiNi}}^\text{Fe}$ coefficients. The large magnitude of $\overline{D}_{\text{NiSi}}^\text{Fe}$ would have caused an uphill-diffusion of Ni. The magnitude of $\overline{D}_{\text{GeGe}}^\text{Fe}$ coefficient is comparable with that of $\overline{D}_{\text{CrCr}}^\text{Fe}$, and slightly lower than that of $\overline{D}_{\text{NiNi}}^\text{Fe}$ coefficient. Even though the magnitude of $\overline{D}_{\text{NiGe}}^\text{Fe}$ is large, an apparent uphill-diffusion of Ni is absent due to a large $\overline{D}_{\text{NiNi}}^\text{Fe}$ despite a very small $\partial C_{\text{Ni}} / \partial x$.

### 4.5. Summary

Interdiffusion in Fe-Ni-Cr (fcc $\gamma$ phase) alloys with small additions of Si and Ge was studied using solid-to-solid diffusion couples annealed at 900°C for 168 hours. Alloaying addition of Si or Ge altered diffusional behavior of Ni and Cr in austenitic Fe-Ni-Cr alloys. Large magnitude of cross coefficients, $\overline{D}_{\text{CrSi}}^\text{Fe}$, $\overline{D}_{\text{CrGe}}^\text{Fe}$, $\overline{D}_{\text{NiSi}}^\text{Fe}$ and $\overline{D}_{\text{NiGe}}^\text{Fe}$ were observed in Fe-Ni-Cr-X (X=Si or Ge) alloys. The Si addition has caused on uphill-diffusion of Ni while there was no measurable uphill diffusion of Ni due to an increase in $\overline{D}_{\text{NiNi}}^\text{Fe}$ in Fe-Ni-Cr-Ge alloy, despite the large positive $\overline{D}_{\text{NiGe}}^\text{Fe}$.

### 4.6 References


CHAPTER 5: EFFECTS OF IR, TA AND RE ALLOYING ON INTERDIFFUSION OF L12-Ni3Al AT 1200°C

5.1. Introduction

Nickel-base superalloys are extensively used in both aviation and land-based gas turbines, and many studies have been devoted to improve their mechanical properties and microstructural stability [1]. Ni-base superalloys are typically composed of L1₂ γ'-phase (Ni₃Al) coherently precipitated in an fcc γ-phase matrix. The diffusion mobility database for Ni-base superalloys is available for fcc phase [2]. Although γ’ is the strengthening phase of Ni-base superalloys, a limited number of studies exists on interdiffusion of the γ'-phase [3-9], particularly when alloyed with other constituents in superalloys. An understanding of multicomponent diffusion processes in these alloys is very important because it is essential to achieve a durable microstructure for strength and oxidation resistance at high temperature. This study is also fueled by recent conceptual development of refractory based superalloys with L1₂ precipitates and refractory-modified aluminide coatings [10-15] for optimized oxidation resistance along with reduced interdiffusion between oxidation resistant coatings and structural superalloy substrate (e.g. to mitigate the formation of deleterious phases due to interdiffusion at the interface).

The crystal structure of Ni₃Al is derived from an fcc based Cu₃Au prototype lattice with face centered sublattice sites (α-sites) occupied by Ni-atoms and corner sublattice sites (β-sites) by Al-atoms. In general, highly electronegative substitutional elements (e.g. Pt, Cu and Co) occupy the α sites, where as highly electropositive ones (e.g. Ti, Ta and Nb) occupy the β sites in Ni₃Al [1]. The relative site-preference for ternary alloying elements can be best illustrated
from the direction of the solubility lobes for the $\gamma'$ phase within the ternary isotherm of Ni-Al-X (X = alloying addition) system at 1273K as shown by Figure 1 [16]. Site preference of ternary alloying additions to Ni$_3$Al has attracted significant interest, as this true solid solution accepts considerable amount of third elements into solution [17-19].

Figure 5.1: Solubility ranges of selected ternary alloying additions in Ni$_3$Al (adopted from Ochiai [16]) at 1273K.
The alloying phenomenon plays an important role in enhancing the mechanical properties and high temperature oxidation resistance of this intermetallic [18-25]. The behavior of ternary substitutional alloying additions to Ni₃Al was first reported by Guard and Westbrook [17] as Ni-occupiers, Al-occupiers or Ni-and-Al-occupiers. Several studies [26-28] have predicted the change in site preference of alloying elements as a function of temperature and chemical composition of Ni₃Al.

Diffusional interactions of a ternary alloying addition to Ni₃Al can be a tool to examine the site preference. The diffusion mechanism in ordered alloys is recognized to be more complex than for disordered solid solutions [29]. In the case of L₁₂ structure, the diffusion mechanism is even more complex than that for B₂ structure. Diffusion can occur through α or β site where Ni or Al atoms mainly occupy, respectively, and the diffusion coefficient largely depends on the alloy composition, namely the degrees of order [30-32]. While tracer diffusion studies in γ’ Ni₃Al are difficult since ⁶⁶Al is not readily available, self-diffusion of Ni and chemical/impurity diffusion in Ni₃Al binary and Ni₃Al-X ternary alloys (X= Co, Cu, Pt, Ti, Si, W, Ge, In, V, Mb, Cr, Fe, Mn) have been studied [3-5]. The temperature dependency of the diffusion for a ternary alloying addition is evident from Arrhenius rate law [5, 33-35]. The β-site occupiers have been observed to diffuse slower than the α-site occupiers [29,36]. This is attributed to the fact that, in L₁₂-ordered structure, each Ni atom is surrounded by 4 Al atoms and 8 Ni atoms, where as an Al atom is surrounded by 12 Ni atoms. Therefore, the activation enthalpy of alloying element increases mainly due to the antisite-defect formation [36].

For an additional insight to understand the diffusion process in L₁₂ structure, to enhance microstructural stability of Ni-base superalloys, and to develop refractory-modified aluminide
oxidation resistant coatings, we examined the ternary diffusional interaction of Ir, Ta and Re additions to the L1₂ Ni₃Al phase. Solid-to-solid diffusion couples were assembled and annealed at 1473K for 5 hours. Based on concentration profiles obtained by electron probe microanalysis, average ternary interdiffusion coefficients from an integration of interdiffusion fluxes, and ternary interdiffusion coefficients via Boltzmann-Matano analysis were determined to assess how Ir, Ta and Re additions influence interdiffusion behavior of Ni and Al in L1₂ Ni₃Al phase. Additional estimates of binary interdiffusion coefficients in Ni₃Al, and tracer diffusion coefficients of Ir, Ta and Re in Ni₃Al were made.

5.2. Determination of ternary interdiffusion coefficients

From Onsager’s formalism [37,38] and Fick’s law [39], the interdiffusion flux \( \tilde{J}_i \) of component i in a ternary system can be expressed in terms of two independent concentration gradients \( \frac{\partial C_j}{\partial x} \) by:

\[
\tilde{J}_i = -\tilde{D}_{i1} \frac{\partial C_1}{\partial x} - \tilde{D}_{i2} \frac{\partial C_2}{\partial x} \quad (i = 1, 2)
\]  

(5.1)

where \( \tilde{D}_{ij} \)'s refer to the ternary interdiffusion coefficients. An experimental determination of the four concentration-dependent interdiffusion coefficients is generally carried out by the use of Boltzmann-Matano analysis with two independent diffusion couples that develop a common composition in the diffusion zone where the interdiffusion coefficients can be evaluated [40,41].
Alternatively, the interdiffusion fluxes of individual components can be determined directly from their concentration profiles without the need or use of the interdiffusion coefficients. The interdiffusion flux at any section \( x \) can be calculated directly from the concentration profile from the relation [42,43]:

\[
\tilde{J}_i = \frac{1}{2t} \int_{C_i^- \text{ or } C_i^+}^{C_i(x)} (x - x_o) \, dC_i \quad (i = 1, 2, \ldots, n)
\]  

(5.2)

where \( t \) is the time, \( C_i^- \) and \( C_i^+ \) are the terminal concentrations, and \( x_o \) refers to the location of the Matano plane. Based on the direct determination of interdiffusion fluxes, diffusional behavior of components can be examined, and observations of zero-flux-planes (ZFPs) and flux-reversals have been reported for individual components in isothermal ternary interdiffusion studies [42-45]. Furthermore, the calculated interdiffusion fluxes can be related to interdiffusion parameters which can be employed to generate and characterize concentration profiles developed in ternary diffusion couples [46-49].

The interdiffusion flux \( \tilde{J}_i \) determined from Eq. (5.2) as a function of \( x \) can be integrated over a selected region, \( x_1 \) to \( x_2 \), to yield an expression based on Eq. (5.1) [49]:

\[
\int_{x_1}^{x_2} \tilde{J}_i \, dx = -\int_{C_i(x_1)}^{C_i(x_2)} \tilde{D}_i \, dC_i - \int_{C_i(x_1)}^{C_i(x_2)} \tilde{D}_2 \, dC_2 \quad (i = 1, 2)
\]

(5.3)

\[
= \tilde{D}_i \left[ C_1(x_1) - C_1(x_2) \right] + \tilde{D}_2 \left[ C_2(x_1) - C_2(x_2) \right] \quad (i = 1, 2)
\]
where $\overline{D}_{ij}^3$'s correspond to the average values of main and cross interdiffusion coefficients.

With $\overline{D}_{ij}^3$'s taken as constants, Eq. (5.1) is re-written as:

$$\bar{J}_i = -\overline{D}_{i1}^3 \frac{\partial C_1}{\partial x} - \overline{D}_{i2}^3 \frac{\partial C_2}{\partial x} \quad (i = 1, 2) \quad (5.4)$$

If both sides of Eq. (5.4) are multiplied by $(x - x_o)^m$ and integrated over the diffusion zone between $x_1$ and $x_2$, one obtains in general [49]:

$$\int_{x_1}^{x_2} \bar{J}_i (x - x_o)^m \, dx = -\overline{D}_{i1}^3 \int_{C_{i(x_1)}}^{C_{i(x_2)}} (x - x_o)^m \, dC_1 - \overline{D}_{i2}^3 \int_{C_{i(x_1)}}^{C_{i(x_2)}} (x - x_o)^m \, dC_2 \quad (i = 1, 2) \quad (5.5)$$

If the exponent $m$ is chosen to be zero, Eq. (5.5) becomes identical to Eq. (5.3). For $m=1$, Eq. (5.5) yields [49]:

$$\int_{x_1}^{x_2} \bar{J}_i (x - x_o) \, dx = -\overline{D}_{i1}^3 \int_{C_{i(x_1)}}^{C_{i(x_2)}} (x - x_o) \, dC_1 - \overline{D}_{i2}^3 \int_{C_{i(x_1)}}^{C_{i(x_2)}} (x - x_o) \, dC_2$$

$$= 2t \left\{ \overline{D}_{i1}^3 [\bar{J}_1(x_1) - \bar{J}_1(x_2)] + \overline{D}_{i2}^3 [\bar{J}_2(x_1) - \bar{J}_2(x_2)] \right\} \quad (i = 1, 2) \quad (5.6)$$

Eqs. (5.3) and (5.6) provide four equations involving the $\overline{D}_{11}^3$, $\overline{D}_{12}^3$, $\overline{D}_{21}^3$ and $\overline{D}_{22}^3$ interdiffusion coefficients and can be easily set up from experimental concentrations and the
corresponding interdiffusion fluxes. Hence, from the concentration profiles of a single diffusion couple, $\overline{D}_{ij}^{3}$ ($i,j = 1,2$) coefficients, characteristic of the diffusion path, can be determined by using Eqs. (5.3) and (5.6) over selected composition ranges in the diffusion zone [49]. Eqs. (5.3) and (5.6) provide independent relations when the composition ranges are selected to include non-linear segments of the profiles. This analysis method to determine average ternary interdiffusion coefficients has been directly employed in various studies [3, 50-59]. In addition, the independence of Eq. (5.3) and (5.5) in solving the average ternary interdiffusion coefficients for the concentration profiles obtained in this study is demonstrated in section 5.4.2. In this paper, the analysis applied to the concentration profiles of experimental ternary diffusion couples in L12 Ni-Al-X (X = Ir or Ta) intermetallics is carried out for 2 segments, one on either side of the Matano plane; the two chosen composition ranges are $\left(C_i^o - C_i^o\right)$ and $\left(C_i^o - C_i^o\right)$, where $C_i^o$ refers to the concentration at the Matano plane. The average ternary interdiffusion coefficients, $\overline{D}_{ij}^{3}$, determined on either side of the Matano plane are employed to simulate experimental concentration profiles using error-function solution for infinite ternary systems from Fujita and Gosting [60]. For Ni-Al vs. Ni-Al-Ir diffusion couples, the average ternary interdiffusion coefficients, $\overline{D}_{ij}^{3}$, are found to be consistent with ternary interdiffusion coefficients, $\hat{D}_{ij}^{3}$, determined by Boltzmann-Matano analysis [40,41].

5.3. Experimental Details

Ni-Al, Ni-Al-Ir, Ni-Al-Ta and Ni-Al-Re alloys were prepared by the vacuum arc melting of 99.97 wt.% Ni, 99.9 wt.% Al, 99.2 wt.% Ir, 99.2 wt.% Ta, and 99.2 wt. Re according to the
compositions presented in Table 5.1. The alloys were cast into a semi-cylindrical mold with the diameter of 8 mm in an arc furnace. The alloy rods were homogenized at 1473K for 137 hours in the vacuum furnace evacuated to a pressure less than $10^{-2}$ Pa. The homogenized alloys were then sectioned into discs with the height of 1.5 mm. The surfaces of alloy discs were polished metallographically up to 1200-grit and cleaned thoroughly prior to diffusion couple assembly.

<table>
<thead>
<tr>
<th>Alloy Identification</th>
<th>Composition (atom percent)</th>
<th>Composition (weight percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-24.5Al</td>
<td>76.0 24.0 0</td>
<td>59.3 40.7 0</td>
</tr>
<tr>
<td>Ni-25Al</td>
<td>75.0 25.0 0</td>
<td>58.0 42.0 0</td>
</tr>
<tr>
<td>Ni-26Al</td>
<td>74.5 25.5 0</td>
<td>57.3 42.7 0</td>
</tr>
<tr>
<td>Ni-23.5Al-1Ir</td>
<td>75.5 23.5 1.0</td>
<td>59.5 40.3 0.2</td>
</tr>
<tr>
<td>Ni-24.5Al-1Ir</td>
<td>74.5 24.5 1.0</td>
<td>58.2 41.6 0.2</td>
</tr>
<tr>
<td>Ni-23Al-2Ir</td>
<td>74.5 23.5 2.0</td>
<td>59.0 40.5 0.5</td>
</tr>
<tr>
<td>Ni-23Al-3Ir</td>
<td>74.0 23.0 3.0</td>
<td>59.2 40.0 0.7</td>
</tr>
<tr>
<td>Ni-23Al-1.5Ta</td>
<td>75.5 23.0 1.5</td>
<td>59.9 39.7 0.4</td>
</tr>
<tr>
<td>Ni-23.5Al-0.5Re</td>
<td>76.0 23.5 0.5</td>
<td>59.7 40.2 0.1</td>
</tr>
<tr>
<td>Ni-23.5Al-0.7Re</td>
<td>75.8 23.5 0.7</td>
<td>59.6 40.2 0.2</td>
</tr>
</tbody>
</table>
Table 5.2 presents diffusion couples that were assembled and analyzed in this study. Coupled alloys were put into a Si$_3$N$_4$ jig and annealed at 1473K for 0.5 hour in a vacuum furnace to promote initial bonding. Since the metal discs have larger thermal expansion coefficients than the Si$_3$N$_4$ jig, the discs can adhere to each other due to the compression during the annealing treatment. Each diffusion couple fabricated in this manner was then sealed in an evacuated transparent quartz capsule, and annealed at 1473K for 4.5 hours in an atmosphere furnace. All diffusion couples were water quenched after the high-temperature anneal to preserve high temperature microstructure and concentrations. In this study, the time required for the diffusion bonding treatment (0.5 hour) was added to the total annealing time. Thus, concentration profiles from all diffusion couples were analyzed with diffusion anneal time of 5 hours.

Table 5.2: Diffusion couples assembled and analyzed after anneal at 1473K for 5 hours.

<table>
<thead>
<tr>
<th>Series</th>
<th>Diffusion Couples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Al vs. Ni-Al-Ir</td>
<td>Ni-25Al vs. Ni-23.5Al-1Ir</td>
</tr>
<tr>
<td></td>
<td>Ni-24.5Al vs. Ni-24.5Al-1Ir</td>
</tr>
<tr>
<td></td>
<td>Ni-26Al vs. Ni-23Al-2Ir</td>
</tr>
<tr>
<td></td>
<td>Ni-24Al vs. Ni-24Al-2Ir</td>
</tr>
<tr>
<td></td>
<td>Ni-25Al vs. Ni-23Al-3Ir</td>
</tr>
<tr>
<td></td>
<td>Ni-25Al vs. Ni-23Al-2Ir</td>
</tr>
<tr>
<td>Ni-Al vs. Ni-Al-Ta</td>
<td>Ni-24Al vs. Ni-23Al-1.5Ta</td>
</tr>
<tr>
<td></td>
<td>Ni-25Al vs. Ni-23Al-1.5Ta</td>
</tr>
<tr>
<td></td>
<td>Ni-26Al vs. Ni-23Al-1.5Ta</td>
</tr>
<tr>
<td>Ni-Al vs. Ni-Al-Re</td>
<td>Ni-24.5Al vs. Ni-23.5Al-0.5Re</td>
</tr>
<tr>
<td></td>
<td>Ni-24.5Al vs. Ni-23.5Al-0.7Re</td>
</tr>
<tr>
<td></td>
<td>Ni-25Al vs. Ni-23.5Al-0.5Re</td>
</tr>
<tr>
<td></td>
<td>Ni-26Al vs. Ni-23.5Al-0.7Re</td>
</tr>
</tbody>
</table>
Microstructures and concentration profiles of the annealed diffusion couples were analyzed by JEOL-JXA-8900 electron probe microanalyzer (EPMA). An accelerating voltage of 20 kV, a beam current of 50 nA, and a probe diameter of 1 μm were employed for data acquisition of Ni K\textsubscript{α} x-radiation peak using LIF crystal, Al K\textsubscript{α} x-radiation peak using TAP crystal, Ir L\textsubscript{α} x-radiation using LIFH crystal, and Ta L\textsubscript{α} x-radiation using LI FH crystal. Pure element standards of Ni, Al, Ir, Ta, along with ZAF correction [61], were used for quantification of concentrations via point-to-point count technique.

5.4. Results and Analysis

5.4.1 Profiles of concentrations and interdiffusion fluxes

Figures 5.2, 5.3 and 5.4 present typical concentration profiles obtained by EPMA measurements from diffusion couples, Ni-26Al vs. Ni-23Al-2Ir, Ni-24.5Al vs. Ni-23Al-1.5Ta, and Ni-25Al vs. Ni-23.5Al-0.5Re, respectively, annealed at 1473K for 5 hours. The x-axis represents the distance from the Matano plane and the open circles are EPMA measurement. Scatter in the concentration profiles for all diffusion couples were minimum and within the experimental uncertainty associated with EPMA. The interdiffusion fluxes of individual components were then determined using Eq. (5.2) from experimental concentration profiles that were smoothend with a series of weighted splines.

While no zero-flux plane was observed, a significant diffusional interactions between Ni and Ir, Al and Ta, and Al and Re were observed when Ni\textsubscript{3}Al was diffusion annealed against Ni\textsubscript{3}Al alloyed with Ir, Ta, and Re respectively, as shown in Figures 5.2, 5.3, and 5.4. Clearly, the interdiffusion of Ni was greatly enhanced by the interdiffusion of Ir down the Ir gradient, while
Al exhibited an uphill diffusion against its own gradient due to the interdiffusion of Ta. In addition, interdiffusion of Al was reduced by the interdiffusion of Re against the gradient of Al. However, diffusional influences of Ir on Al, Ta on Ni, and Re on Ni are difficult to ascertain from the profiles presented in Figures 5.2, 5.3, and 5.4. Determination of ternary interdiffusion coefficients can quantify the extent and magnitude of these diffusional interactions, and provide competent approaches to compositional design, modification of alloys and protective coatings.
Figure 5.2: Concentration profiles of (a) Ni, (b) Al and (c) Ir obtained from diffusion couple Ni-26Al vs. Ni-23Al-2Ir annealed at 1473K for 5 hours. Open circles and solid lines represent EPMA measurement and calculated concentration profiles, respectively.
Figure 5.3 : Concentration profiles of (a) Ni, (b) Al and (c) Ta obtained from diffusion couple Ni-24.5Al vs. Ni-23Al-1.5Ta annealed at 1473K for 5 hours. Open circles and solid lines represent EPMA measurement and calculated concentration profiles, respectively.
Figure 5.4: Concentration profiles of (a) Ni, (b) Al and (c) Re obtained from diffusion couple Ni-25Al vs. Ni-23.5Al-0.5Re annealed at 1473K for 5 hours. Open circles and solid lines represent EPMA measurement and calculated concentration profiles, respectively.
5.4.2 Average ternary interdiffusion coefficients

From profiles of concentration and interdiffusion fluxes in Ni-Al vs Ni-Al-Ir diffusion couples, average ternary interdiffusion coefficients, $\overline{D}_{ij}^{Ni}(i,j=Al,Ir)$ and $\overline{D}_{ij}^{Al}(i,j=Ni,Ir)$, were determined on either side of the Matano plane using Eqs. (5.3) and (5.6). Use of Eqs. (5.3) and (5.6) provides independent relations for the determination of average ternary interdiffusion coefficients as presented in Figure 5.5. In this Figure, for diffusion couple Ni-26Al vs. Ni-23Al-2Ir whose concentration profiles are presented in Figure 5.2, the variation of $\overline{D}_{ij}^{Al}(i,j=Ni,Ir)$ in Eq. (5.5) where $m = 0$, equivalent to Eq. (5.3), and $m = 1$, equivalent to Eq. (5.6), is presented. The two lines generated by Eqs. (5.3) and (5.6) are sufficiently independent to obtain an unique solution of $\overline{D}_{ij}^{Al}(i,j=Ni,Ir)$ coefficients that are reported in Table 5.3.
Figure 5.5: Variation of $\overline{D}_{ij}^{\text{Al}} (i,j = \text{Ni}, \text{Ir})$ coefficients in Eq. (5.3), equivalent to Eq. (5.5) when $m = 0$, and (5.6) equivalent to Eq. (5.5) when $m = 1$. The two lines generated by Eqs. (5.3) and (5.6) are sufficiently independent to obtain an unique solution of $\overline{D}_{ij}^{\text{Al}} (i,j = \text{Ni}, \text{Ir})$ coefficients that are reported for the composition ranges of $(C_i - C_i^o)$ and $(C_i^o - C_i^+)$ in Table 5.3.
Table 5.3: Average ternary interdiffusion coefficients ($10^{-16}$ m$^2$/s) determined from Ni-Al vs. Ni-Al-Ir diffusion couples annealed at 1473K for 5 hours.

<table>
<thead>
<tr>
<th>Diffusion Couple</th>
<th>Composition Range</th>
<th>$\bar{D}_{NiAl}$</th>
<th>$\bar{D}_{NiIr}$</th>
<th>$\bar{D}_{IrAl}$</th>
<th>$\bar{D}_{IrIr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-25Al vs. Ni-23.5Al-1Ir</td>
<td>$C_i^{\infty} \sim C_i^{0}$</td>
<td>623.7</td>
<td>-117.2</td>
<td>Ngl.</td>
<td>13.6</td>
</tr>
<tr>
<td></td>
<td>$C_i^{0} \sim C_i^{\infty}$</td>
<td>511.6</td>
<td>-166.6</td>
<td>Ngl.</td>
<td>11.2</td>
</tr>
<tr>
<td>Ni-24.5Al vs. Ni-24.5Al-1Ir</td>
<td>$C_i^{\infty} \sim C_i^{0}$</td>
<td>541.0</td>
<td>-84.7</td>
<td>Ngl.</td>
<td>10.5</td>
</tr>
<tr>
<td></td>
<td>$C_i^{0} \sim C_i^{\infty}$</td>
<td>816.9</td>
<td>-75.7</td>
<td>Ngl.</td>
<td>19.1</td>
</tr>
<tr>
<td>Ni-26Al vs. Ni-23Al-2Ir</td>
<td>$C_i^{\infty} \sim C_i^{0}$</td>
<td>871.4</td>
<td>-52</td>
<td>Ngl.</td>
<td>15.4</td>
</tr>
<tr>
<td></td>
<td>$C_i^{0} \sim C_i^{\infty}$</td>
<td>591.5</td>
<td>-117.3</td>
<td>Ngl.</td>
<td>13.0</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23Al-2Ir</td>
<td>$C_i^{\infty} \sim C_i^{0}$</td>
<td>522</td>
<td>-107.3</td>
<td>Ngl.</td>
<td>16.4</td>
</tr>
<tr>
<td></td>
<td>$C_i^{0} \sim C_i^{\infty}$</td>
<td>494</td>
<td>-116.6</td>
<td>Ngl.</td>
<td>15.9</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23Al-3Ir</td>
<td>$C_i^{\infty} \sim C_i^{0}$</td>
<td>440.9</td>
<td>-92.8</td>
<td>Ngl.</td>
<td>15.1</td>
</tr>
<tr>
<td></td>
<td>$C_i^{0} \sim C_i^{\infty}$</td>
<td>441.2</td>
<td>-135.5</td>
<td>Ngl.</td>
<td>19.3</td>
</tr>
<tr>
<td>Ni-24Al vs. Ni-24Al-2Ir</td>
<td>$C_i^{\infty} \sim C_i^{0}$</td>
<td>267.2</td>
<td>14.1</td>
<td>Ngl.</td>
<td>11.8</td>
</tr>
<tr>
<td></td>
<td>$C_i^{0} \sim C_i^{\infty}$</td>
<td>318.0</td>
<td>9.8</td>
<td>Ngl.</td>
<td>14.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Diffusion Couple</th>
<th>Composition Range</th>
<th>$\bar{D}_{NiNi}$</th>
<th>$\bar{D}_{NiIr}$</th>
<th>$\bar{D}_{IrNi}$</th>
<th>$\bar{D}_{IrIr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-25Al vs. Ni-23.5Al-1Ir</td>
<td>$C_i^{\infty} \sim C_i^{0}$</td>
<td>623.7</td>
<td>727.3</td>
<td>Ngl.</td>
<td>13.6</td>
</tr>
<tr>
<td></td>
<td>$C_i^{0} \sim C_i^{\infty}$</td>
<td>511.6</td>
<td>667.0</td>
<td>Ngl.</td>
<td>11.2</td>
</tr>
<tr>
<td>Ni-24.5Al vs. Ni-24.5Al-1Ir</td>
<td>$C_i^{\infty} \sim C_i^{0}$</td>
<td>541.0</td>
<td>615.2</td>
<td>Ngl.</td>
<td>10.5</td>
</tr>
<tr>
<td></td>
<td>$C_i^{0} \sim C_i^{\infty}$</td>
<td>816.9</td>
<td>873.5</td>
<td>Ngl.</td>
<td>19.1</td>
</tr>
<tr>
<td>Ni-26Al vs. Ni-23Al-2Ir</td>
<td>$C_i^{\infty} \sim C_i^{0}$</td>
<td>871.4</td>
<td>908.0</td>
<td>Ngl.</td>
<td>15.4</td>
</tr>
<tr>
<td></td>
<td>$C_i^{0} \sim C_i^{\infty}$</td>
<td>591.5</td>
<td>695.8</td>
<td>Ngl.</td>
<td>13.0</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23Al-2Ir</td>
<td>$C_i^{\infty} \sim C_i^{0}$</td>
<td>522</td>
<td>612.9</td>
<td>Ngl.</td>
<td>16.4</td>
</tr>
<tr>
<td></td>
<td>$C_i^{0} \sim C_i^{\infty}$</td>
<td>494</td>
<td>594.7</td>
<td>Ngl.</td>
<td>15.9</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23Al-3Ir</td>
<td>$C_i^{\infty} \sim C_i^{0}$</td>
<td>440.9</td>
<td>518.6</td>
<td>Ngl.</td>
<td>15.1</td>
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<tr>
<td></td>
<td>$C_i^{0} \sim C_i^{\infty}$</td>
<td>441.2</td>
<td>557.4</td>
<td>Ngl.</td>
<td>19.3</td>
</tr>
<tr>
<td>Ni-24Al vs. Ni-24Al-2Ir</td>
<td>$C_i^{\infty} \sim C_i^{0}$</td>
<td>267.2</td>
<td>241.3</td>
<td>Ngl.</td>
<td>11.8</td>
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<tr>
<td></td>
<td>$C_i^{0} \sim C_i^{\infty}$</td>
<td>318.0</td>
<td>293.4</td>
<td>Ngl.</td>
<td>14.8</td>
</tr>
</tbody>
</table>

Note: Ngl refers to magnitude less than $0.1 \times 10^{-16}$ m$^2$/sec.
The main diffusion coefficients, $\overline{D}_{\text{NiAl}}$ and $\overline{D}_{\text{AlNi}}$, correspond well to the interdiffusion coefficients of Al and Ni reported in literature for binary Ni$_3$Al at 1473K [3-9]. Estimation of binary interdiffusion coefficients from the ternary diffusion couples and the comparison to the interdiffusion coefficients of Al and Ni reported in literature for binary Ni$_3$Al are presented in detail in section 5.4.4. The magnitude of these main coefficients for Al and Ni are observed to be larger with higher Al content as well. The main interdiffusion coefficient of Ir, $\overline{D}_{\text{IrNi}}$, is 20 to 40 times lower in magnitude than the main coefficients of Ni and Al. Table 5.3 reports that $\overline{D}_{\text{AlNi}}$ coefficients are negative, and smaller in magnitude than $\overline{D}_{\text{NiAl}}$ coefficients, and $\overline{D}_{\text{IrAl}}$ coefficients are negligibly small (< 0.1 x 10$^{-16}$ m$^2$/sec). Thus the interdiffusion flux of Al can be influenced only slightly by the interdiffusion of Ir. However, $\overline{D}_{\text{NiIr}}$ coefficients are positive and large (e.g., larger than the $\overline{D}_{\text{AlNi}}$ coefficients in some cases), while $\overline{D}_{\text{IrNi}}$ coefficients are negligibly small (< 0.1 x 10$^{-16}$ m$^2$/sec). The large positive $\overline{D}_{\text{NiIr}}$ coefficient corresponds well with an enhanced interdiffusion of Ni (e.g., down the gradient of Ir). Against the concentration gradient of Ir, the large positive $\overline{D}_{\text{NiIr}}$ coefficient can therefore reduce the interdiffusion of Ni. The average ternary interdiffusion coefficients reported in Table 5.3 indicate a strong diffusional interaction between Ni and Ir, both occupying the $\alpha$-site in L1$_2$ lattice structure.

The average ternary interdiffusion coefficients, $\overline{D}_{i,j}^\text{Ni}(i,j = \text{Al,Ta})$ and $\overline{D}_{i,j}^\text{Al}(i,j = \text{Ni,Ta})$, determined on either side of the Matano plane for Ni-Al vs. Ni-Al-Ta couples are reported in Table 5.4. For diffusion couple Ni-24.5Al vs. Ni-23Al-1.5Ta whose concentration profiles are presented in Figure 5.3, the variation of $\overline{D}_{i,j}^\text{Ni}(i,j = \text{Al,Ta})$ in Eq. (5.3), equivalent to Eq. (5.5) where $m = 0$, and Eq. (5.6), equivalent to Eq. (5.5) where $m = 1$ is presented in Figure 5.6. The
two lines generated by Eqs. (5.3) and (5.6) are again sufficiently independent to obtain an unique solution of $\overline{D}_{ij}^{Ni} (i,j = Al,Ta)$ coefficients that are reported in Table 5.4.

Figure 5.6: Variation of $\overline{D}_{AlAl}^{Ni}$ coefficients in Eq. (5.3), equivalent to Eq. (5.5) when $m = 0$, and (5.6) equivalent to Eq. (5.5) when $m = 1$. The two lines generated by Eqs. (5.3) and (5.6) are sufficiently independent to obtain an unique solution of $\overline{D}_{ij}^{Ni} (i,j = Al,Ta)$ coefficients that are reported for the composition ranges of $(C_i^o - C_i^o)$ and $(C_i^o - C_i^o)$ in Table 5.4.
Table 5.4: Average ternary interdiffusion coefficients (10^{-16} m^2/s) determined from Ni-Al vs. Ni-Al-Ta diffusion couples annealed at 1473K for 5 hours.

<table>
<thead>
<tr>
<th>Diffusion Couple</th>
<th>Composition Range</th>
<th>$\overline{D}_{\text{AlAl}}^{\text{Ni}}$</th>
<th>$\overline{D}_{\text{AlTa}}^{\text{Ni}}$</th>
<th>$\overline{D}_{\text{TaAl}}^{\text{Ni}}$</th>
<th>$\overline{D}_{\text{TaTa}}^{\text{Ni}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-24.5Al vs. Ni-23Al-1.5Ta</td>
<td>$C_i^{-\infty} \sim C_i^{o}$</td>
<td>561</td>
<td>501.3</td>
<td>Ngl.</td>
<td>3.2</td>
</tr>
<tr>
<td>Ni-24.5Al vs. Ni-23Al-1.5Ta</td>
<td>$C_i^{o} \sim C_i^{+\infty}$</td>
<td>482.6</td>
<td>451.8</td>
<td>Ngl.</td>
<td>1.8</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23Al-1.5Ta</td>
<td>$C_i^{-\infty} \sim C_i^{o}$</td>
<td>810.4</td>
<td>807.1</td>
<td>Ngl.</td>
<td>3.4</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23Al-1.5Ta</td>
<td>$C_i^{o} \sim C_i^{+\infty}$</td>
<td>652.7</td>
<td>580.5</td>
<td>Ngl.</td>
<td>1.9</td>
</tr>
<tr>
<td>Ni-26Al vs. Ni-23Al-1.5Ta</td>
<td>$C_i^{-\infty} \sim C_i^{o}$</td>
<td>313.2</td>
<td>333.6</td>
<td>Ngl.</td>
<td>3.7</td>
</tr>
<tr>
<td>Ni-26Al vs. Ni-23Al-1.5Ta</td>
<td>$C_i^{o} \sim C_i^{+\infty}$</td>
<td>445</td>
<td>391.9</td>
<td>Ngl.</td>
<td>5.6</td>
</tr>
</tbody>
</table>

Note: Ngl refers to magnitude less than 0.1 x 10^{-16} m^2/sec.

The main diffusion coefficients, $\overline{D}_{\text{AlAl}}^{\text{Ni}}$ and $\overline{D}_{\text{AlNi}}^{\text{Ni}}$, again correspond well to the interdiffusion coefficients of Al and Ni reported in literature [3-9] for Ni$_3$Al at 1473K. Aforementioned, estimation of binary interdiffusion coefficients from the ternary diffusion couples along with the comparison to the interdiffusion coefficients of Al and Ni reported in literature for binary Ni$_3$Al are presented in detail in section 5.4.4. The main interdiffusion coefficient of Ta, $\overline{D}_{\text{TaTa}}$, is 10 to 40 times lower in magnitude than the main coefficients of Ni and Al. Table 5.4 reports that $\overline{D}_{\text{AlTa}}^{\text{Ni}}$ coefficients are positive, and comparable in magnitude to
$D_{NiAl}$ coefficients, while $D_{TaAl}$ coefficients are negligibly small ($< 0.1 \times 10^{-16}$ m$^2$/sec). Thus, the large positive $D_{NiTa}$ coefficient corresponds well with an interdiffusion flux of Al (e.g., uphill diffusion) against the gradient of Ta. The $D_{AlNi}$ coefficients are positive, but much smaller than the $D_{NiNi}$ coefficients, and $D_{TaNi}$ coefficients are negligibly small ($< 0.1 \times 10^{-16}$ m$^2$/sec). Thus the interdiffusion flux of Ni can be influenced only slightly by the interdiffusion flux of Ta. The average ternary interdiffusion coefficients reported in Table 5.4 indicate a strong diffusional interaction between Al and Ta, both occupying the $\beta$-site in L1$_2$ lattice structure.

From profiles of concentration and interdiffusion fluxes in Ni-Al vs. Ni-Al-Re diffusion couples, average ternary interdiffusion coefficients, $\overline{D}_{Ni}(i, j = Al, Re)$ and $\overline{D}_{Al}(i, j = Ni, Re)$, were determined on either side of the Matano plane using Eqs. (5.3) and (5.6). They are reported in Table 5.5. The magnitudes of main diffusion coefficients, $D_{NiNi}$ and $D_{AlAl}$ are similar to the interdiffusion coefficients of Al and Ni reported in literature for binary Ni$_3$Al at 1473K [3-10]. Estimation of binary interdiffusion coefficients from the ternary diffusion couples and the comparison to the interdiffusion coefficients of Al and Ni reported in literature for binary Ni$_3$Al are presented in detail in section 5.4.4. The main interdiffusion coefficient, $D_{ReRe}$ is approximately 100 times smaller in magnitude than $D_{NiNi}$ and $D_{AlAl}$. Table 5.5 reports that $D_{AlRe}$’s are positive and comparable to the magnitude of $D_{NiNi}$, while $D_{ReAl}$ coefficients are negligibly small ($< 0.1 \times 10^{-16}$ m$^2$/sec). Thus the interdiffusion of Al can be strongly influenced by the interdiffusion of Re. The $D_{AlNi}$ coefficients are also positive, but only 2 to 13 times smaller in magnitude than the $D_{NiNi}$’s.
Table 5.5: Average ternary interdiffusion coefficients ($10^{-16}$ m$^2$/s) determined from Ni-Al vs. Ni-Al-Re diffusion couples annealed at 1473K for 5 hours.

<table>
<thead>
<tr>
<th>Diffusion Couple</th>
<th>Composition Range</th>
<th>$\bar{D}_{\text{NiAl}}$</th>
<th>$\bar{D}_{\text{NiRe}}$</th>
<th>$\bar{D}_{\text{ReAl}}$</th>
<th>$\bar{D}_{\text{ReRe}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-24.5Al vs. Ni-23.5Al-0.5Re</td>
<td>$C_i^0$ to $C_i^\alpha$</td>
<td>417.7</td>
<td>380.2</td>
<td>Ngl. 3.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$C_i^\alpha$ to $C_i^{\alpha\alpha}$</td>
<td>265.1</td>
<td>191.0</td>
<td>Ngl. 4.0</td>
<td></td>
</tr>
<tr>
<td>Ni-24.5Al vs. Ni-23.5Al-0.7Re</td>
<td>$C_i^0$ to $C_i^\alpha$</td>
<td>509.9</td>
<td>463.4</td>
<td>Ngl. 4.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$C_i^\alpha$ to $C_i^{\alpha\alpha}$</td>
<td>362.8</td>
<td>304.1</td>
<td>Ngl. 3.4</td>
<td></td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23.5Al-0.5Re</td>
<td>$C_i^0$ to $C_i^\alpha$</td>
<td>463.2</td>
<td>294.6</td>
<td>Ngl. 3.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$C_i^\alpha$ to $C_i^{\alpha\alpha}$</td>
<td>668.3</td>
<td>477.4</td>
<td>Ngl. 2.4</td>
<td></td>
</tr>
<tr>
<td>Ni-26Al vs. Ni-23.5Al-0.7Re</td>
<td>$C_i^0$ to $C_i^\alpha$</td>
<td>449.9</td>
<td>336.6</td>
<td>Ngl. 5.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$C_i^\alpha$ to $C_i^{\alpha\alpha}$</td>
<td>298.9</td>
<td>123</td>
<td>Ngl. 4.7</td>
<td></td>
</tr>
</tbody>
</table>

Note: Ngl refers to magnitude less than $0.1 \times 10^{-16}$ m$^2$/sec.
The average ternary interdiffusion coefficients reported in Tables 5.3, 5.4 and 5.5 were employed to generate concentration profiles using error-function solution provided by Fujita and Gosting [60]. Excellent agreement between EPMA measurement and calculated concentration profiles were found for all couples. Typical examples are presented in Figures 5.2, 5.3 and 5.4 where open circles are the EPMA measurements and solid lines are the calculated concentration profile.

5.4.3 Ternary interdiffusion coefficients determined by Boltzmann-Matno analysis

For the diffusion couples Ni-Al vs. Ni-Al-Ir and Ni-Al vs. Ni-Al-Re, several intersecting compositions were found among the diffusion paths. Intersecting diffusion paths shown in Figures 5.7 and 5.8 represent typical challenges in determining the interdiffusion coefficients by Boltzmann-Matano analysis for ordered intermetallics with ternary alloying addition. Two diffusion paths can intersect at a shallow angle or with negligible Ir and Re concentration gradient. In order to determine the ternary interdiffusion coefficients at these compositions, Boltzmann-Matano analysis was employed using a range of concentrations and distance that are certain with respect to EPMA measurement. The values of ternary interdiffusion coefficients estimated in this study are reported in Tables 5.6 and 5.7, and correspond well to the average ternary interdiffusion coefficients for either side of the Matano plane reported in Tables 5.3 and 5.5, respectively. Slight deviation in values and change in signs of the $D_{\text{NiRe}}^{\text{Al}}$ coefficients are attributed to the uncertainty in concentration gradient of Re.
Figure 5.7: Typical intersecting diffusion paths of Ni-Al vs. Ni-Al-Ir diffusion couples annealed at 1473K for 5 hours. Compositions at these intersections were employed for the determination of ternary interdiffusion coefficients based on Boltzmann-Matano analysis.
Figure 5.8: Typical intersecting diffusion paths of Ni-Al vs. Ni-Al-Re diffusion couples annealed at 1473K for 5 hours. Compositions at these intersections were employed for the determination of ternary interdiffusion coefficients based on Boltzmann-Matano analysis.
Table 5.6: Ternary interdiffusion coefficients ($10^{-16}$ m$^2$/s) determined by Boltzmann-Matano analysis from Ni-Al vs. Ni-Al-Ir diffusion couples annealed at 1473K for 5 hours.

<table>
<thead>
<tr>
<th>Diffusion Couples with Intersecting Diffusion Paths</th>
<th>Intersecting Composition (atom fraction)</th>
<th>$\tilde{D}_{\text{AlNi}}$</th>
<th>$\tilde{D}_{\text{NiIr}}$</th>
<th>$\tilde{D}_{\text{IrAl}}$</th>
<th>$\tilde{D}_{\text{IrIr}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-25Al vs. Ni-23Al-3Ir</td>
<td>Al: 0.24</td>
<td>1021.3</td>
<td>-15.0</td>
<td>-39.9</td>
<td>12.5</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-24Al-2Ir</td>
<td>Ir: 0.005</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23Al-2Ir</td>
<td>Al: 0.239</td>
<td>494.7</td>
<td>-36.3</td>
<td>Ngl.</td>
<td>17.2</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23Al-3Ir</td>
<td>Ir: 0.019</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-26Al vs. Ni-23Al-2Ir</td>
<td>Al: 0.239</td>
<td>563.9</td>
<td>-33.0</td>
<td>Ngl.</td>
<td>17.3</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23Al-3Ir</td>
<td>Ir: 0.020</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-24Al vs. Ni-24Al-2Ir</td>
<td>Al: 0.240</td>
<td>634.5</td>
<td>-3.4</td>
<td>Ngl.</td>
<td>11.5</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23.5Al-1Ir</td>
<td>Ir: 0.001</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-24Al vs. Ni-24Al-2Ir</td>
<td>Al: 0.241</td>
<td>419.3</td>
<td>-117.6</td>
<td>Ngl.</td>
<td>25.9</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23Al-2Ir</td>
<td>Ir: 0.019</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23Al-3Ir</td>
<td>Al: 0.243</td>
<td>594.0</td>
<td>-38.5</td>
<td>-15.0</td>
<td>11.0</td>
</tr>
<tr>
<td>Ni-26Al vs. Ni-23Al-2Ir</td>
<td>Ir: 0.001</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23Al-3Ir</td>
<td>Al: 0.245</td>
<td>827.3</td>
<td>28.1</td>
<td>Ngl.</td>
<td>15.2</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23Al-2Ir</td>
<td>Ir: 0.017</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-24.5Al vs. Ni-24.5Al-1Ir</td>
<td>Al: 0.240</td>
<td>623.0</td>
<td>-26.9</td>
<td>Ngl.</td>
<td>13.7</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23.5Al-1Ir</td>
<td>Ir: 0.010</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-24.5Al vs. Ni-24.5Al-1Ir</td>
<td>Al: 0.245</td>
<td>644.4</td>
<td>-73.2</td>
<td>Ngl.</td>
<td>12.0</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23Al-3Ir</td>
<td>Ir: 0.0002</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23.5Al-1Ir</td>
<td>Al: 0.240</td>
<td>623.0</td>
<td>-26.9</td>
<td>Ngl.</td>
<td>13.7</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23.5Al-1Ir</td>
<td>Ir: 0.0002</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: Ngl refers to magnitude less than $0.1 \times 10^{-16}$ m$^2$/sec.
Table 5.7: Ternary interdiffusion coefficients (10^{-16} \text{m}^2/\text{s}) determined by Boltzmann-Matano analysis from Ni-Al vs. Ni-Al-Re diffusion couples annealed at 1473K for 5 hours.

<table>
<thead>
<tr>
<th>Diffusion Couples with Intersecting Diffusion Paths</th>
<th>Intersecting Composition (atom fraction)</th>
<th>$\tilde{D}_{\text{NiAl}}$</th>
<th>$\tilde{D}_{\text{NiRe}}$</th>
<th>$\tilde{D}_{\text{ReAl}}$</th>
<th>$\tilde{D}_{\text{ReRe}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-24.5Al vs. Ni-23.5Al-0.5Re Ni-25Al vs. Ni-23.5Al-0.5Re</td>
<td>Al: 0.239 Re: 0.005</td>
<td>832.5</td>
<td>926.5</td>
<td>Ngl.</td>
<td>2.8</td>
</tr>
<tr>
<td>Ni-24.5Al vs. Ni-23.5Al-0.5Re Ni-24.5Al vs. Ni-23.5Al-0.7Re</td>
<td>Al: 0.2382 Re: 0.005</td>
<td>244.2</td>
<td>216.0</td>
<td>Ngl.</td>
<td>3.1</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23.5Al-0.5Re Ni-24.5Al vs. Ni-23.5Al-0.7Re</td>
<td>Al: 0.2393 Re: 0.005</td>
<td>726.1</td>
<td>734.9</td>
<td>Ngl.</td>
<td>3.1</td>
</tr>
<tr>
<td>Diffusion Couples with Intersecting Diffusion Paths</td>
<td>Intersecting Composition (atom fraction)</td>
<td>$\tilde{D}_{\text{NiNi}}$</td>
<td>$\tilde{D}_{\text{NiRe}}$</td>
<td>$\tilde{D}_{\text{ReNi}}$</td>
<td>$\tilde{D}_{\text{ReRe}}$</td>
</tr>
<tr>
<td>Ni-24.5Al vs. Ni-23.5Al-0.5Re Ni-25Al vs. Ni-23.5Al-0.5Re</td>
<td>Al: 0.239 Re: 0.005</td>
<td>832.5</td>
<td>-96.8</td>
<td>Ngl.</td>
<td>2.8</td>
</tr>
<tr>
<td>Ni-24.5Al vs. Ni-23.5Al-0.5Re Ni-24.5Al vs. Ni-23.5Al-0.7Re</td>
<td>Al: 0.2382 Re: 0.005</td>
<td>244.2</td>
<td>25.0</td>
<td>Ngl.</td>
<td>3.1</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23.5Al-0.5Re Ni-24.5Al vs. Ni-23.5Al-0.7Re</td>
<td>Al: 0.2393 Re: 0.005</td>
<td>726.1</td>
<td>-11.9</td>
<td>Ngl.</td>
<td>3.1</td>
</tr>
</tbody>
</table>

Note: Ngl refers to magnitude less than 0.1 x 10^{-16} \text{m}^2/\text{sec}.

Several relative maxima and minima in concentration profiles (e.g., $\partial C_i/\partial x = 0$) were also observed for Ni in Ni-Al vs. Ni-Al-Ir couples and for Al in Ni-Al vs. Ni-Al-Ta couples as shown in Figures 5.2 and 5.3. Ternary interdiffusion coefficients at these compositions were also determined since one of the terms in Eq. (5.1) becomes zero. These values are reported in Table 5.8 for Ni-Al vs. Ni-Al-Ir couples, and correspond well to the average ternary interdiffusion coefficients on either side of the Matano plane reported in Table 5.3, and ternary interdiffusion coefficients determined by Boltzmann-Matano analysis reported in Table 5.6. Unfortunately, for Ni-Al vs. Ni-Al-Ta couples, the concentration and its gradient for Ta, where the concentration gradient of Al became zero (e.g., relative maxima and minima of Al), were uncertain (e.g., $C_{\text{Ta}} \approx 0$ and $\partial C_{\text{Ta}}/\partial x \approx 0$) to determine any ternary interdiffusion coefficients. The relative maxima and minima in concentration profiles were not observed in any Ni-Al vs. Ni-Al-Re diffusion couples.
Table 5.8: Ternary interdiffusion coefficients \( (10^{-16} \text{ m}^2/\text{s}) \) determined at relative maxima and minima of concentration profiles in Ni-Al vs. Ni-Al-Ir diffusion couples annealed at 1473K for 5 hours.

<table>
<thead>
<tr>
<th>Couple</th>
<th>Extrema Composition (atom fraction)</th>
<th>Ternary Interdiffusion Coefficients at Extrema</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-25Al vs. Ni-23.5Al-1Ir</td>
<td>Al: 0.2452, Ir: 0.00037</td>
<td>( \tilde{D}^{\text{Al}}<em>{\text{NiIr}} ) 737.4, ( \tilde{D}^{\text{Ir}}</em>{\text{NiIr}} ) 12.5</td>
</tr>
<tr>
<td></td>
<td>Al: 0.2420, Ir: 0.0091</td>
<td></td>
</tr>
<tr>
<td>Ni-24.5Al vs. Ni-24.5Al-1Ir</td>
<td>Al: 0.2451, Ir: 0.00005</td>
<td>( \tilde{D}^{\text{Al}}<em>{\text{NiIr}} ) 1190.4, ( \tilde{D}^{\text{Ir}}</em>{\text{NiIr}} ) 12.0</td>
</tr>
<tr>
<td></td>
<td>Al: 0.2443, Ir: 0.0102</td>
<td></td>
</tr>
<tr>
<td>Ni-26Al vs. Ni-23Al-2Ir</td>
<td>Al: 0.2501, Ir: 0.001</td>
<td>( \tilde{D}^{\text{Al}}<em>{\text{NiIr}} ) 656.5, ( \tilde{D}^{\text{Ir}}</em>{\text{NiIr}} ) 18.9</td>
</tr>
<tr>
<td></td>
<td>Al: 0.245, Ir: 0.0186</td>
<td></td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23Al-2Ir</td>
<td>Al: 0.2453, Ir: 0.00045</td>
<td>( \tilde{D}^{\text{Al}}<em>{\text{NiIr}} ) 552.2, ( \tilde{D}^{\text{Ir}}</em>{\text{NiIr}} ) 12.4</td>
</tr>
<tr>
<td></td>
<td>Al: 0.2408, Ir: 0.0187</td>
<td></td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23Al-3Ir</td>
<td>Al: 0.2409, Ir: 0.00011</td>
<td>( \tilde{D}^{\text{Al}}<em>{\text{NiIr}} ) 1195.6, ( \tilde{D}^{\text{Ir}}</em>{\text{NiIr}} ) 8.8</td>
</tr>
<tr>
<td></td>
<td>Al: 0.2374, Ir: 0.0296</td>
<td></td>
</tr>
</tbody>
</table>

5.4.4 Estimation of binary interdiffusion coefficients in Ni₃Al

The ternary interdiffusion coefficients \( \tilde{D}^{\text{Al}}_{\text{NiIr}} \) and \( \tilde{D}^{\text{Al}}_{\text{NiNi}} \) approach the binary \( \tilde{D}_i \) for Ni₃Al as the concentration of Ir, Ta or Re decreases to zero. Hence, values of \( \tilde{D}_i \) (i = Ni or Al) were estimated from ternary diffusion couples where Ir, Ta or Re concentration was negligibly small in segments of the diffusion zone (e.g., Fick’s law for substitutional binary alloys). Such regions were found in all couples since \( \tilde{D}^{\text{IrIr}} \), \( \tilde{D}^{\text{TaTa}} \), and \( \tilde{D}^{\text{ReRe}} \) coefficients are much smaller than \( \tilde{D}^{\text{Al}}_{\text{NiIr}} \) and \( \tilde{D}^{\text{Al}}_{\text{NiNi}} \). The \( \tilde{D}_i \) values extrapolated from the ternary couples with large enough concentration
difference (e.g., $\Delta C_{Al}$ or $\Delta C_{Ni} > 2 \text{ at.\%}$) in terminal alloys are presented in Figures 5.9 and 5.10. The magnitude of $\bar{D}_i$ appears consistent with the available binary diffusion data [3-9] for Ni$_3$Al. However, the composition-dependence could not be evaluated correctly since this estimation is carried out near the terminal end of the concentration profiles with high uncertainty in the magnitude of concentration gradient for Al, and assumes that the Ir, Ta and Re concentration, less than 2 at.\%, do not influence the value of $\bar{D}_i$.

Figure 5.9 : Interdiffusion coefficients of Ni or Al in Ni$_3$Al at 1473K compiled from this investigation and literature review.
Figure 5.10: Interdiffusion coefficients of Ni or Al in Ni$_3$Al at 1473K compiled from this investigation and literature review.
5.4.5 Estimation of tracer diffusion coefficient of Ir and Ta in Ni₃Al

For component i diffusing into a binary alloy j-k, the cross interdiffusion coefficient
\( \tilde{D}_{ij}^k \) (\( i \neq j \)) becomes negligible at infinite dilution of component i in a j-k alloy [62]. Then the
value of the main coefficient \( \tilde{D}_{ii} \) approaches that of the tracer diffusion coefficient \( D_i^* \) for
component i:

\[
\frac{C_i}{\partial} \rightarrow 0 \quad \tilde{J}_i = -\tilde{D}_{ii} \frac{\partial C_i}{\partial x} \approx -D_i^* \frac{\partial C_i}{\partial x} \quad (5.7)
\]

Thus, the tracer diffusion coefficients of Ir, Ta and Re in Ni₃Al alloy can be estimated from the
main interdiffusion coefficient of Ir, \( \tilde{D}_{IrIr}^N_i \) or \( \tilde{D}_{IrIr}^N_i \), Ta, \( \tilde{D}_{TaTa}^N_i \) or \( \tilde{D}_{TaTa}^N_i \), and Re, \( \tilde{D}_{ReRe}^N_i \) or \( \tilde{D}_{ReRe}^N_i \)
using Eq. (5.7), provided that the concentration of Ir or Ta or Re approaches zero within the
diffusion zone so that the cross interdiffusion coefficients, \( \tilde{D}_{IrAl}^N_i \) or \( \tilde{D}_{IrNi}^N_i \), \( \tilde{D}_{TaAl}^N_i \) or \( \tilde{D}_{TaNi}^N_i \), and
\( \tilde{D}_{ReAl}^N_i \) or \( \tilde{D}_{ReNi}^N_i \) become negligible. Such regions were found in all couples since \( \tilde{D}_{IrIr} \), \( \tilde{D}_{TaTa} \) and
\( \tilde{D}_{ReRe} \) coefficients are much smaller than \( \tilde{D}_{AlAl}^N_i \) and \( \tilde{D}_{NiNi}^N_i \). Values of tracer diffusion coefficients
of Ir, \( D_{Ir}^* \), Ta, \( D_{Ta}^* \), and Re, \( D_{Re}^* \) were extrapolated from the main interdiffusion coefficients, \( \tilde{D}_{IrIr}^N_i \)
or \( \tilde{D}_{IrIr}^N_i \) or \( \tilde{D}_{TaTa}^N_i \), and \( \tilde{D}_{ReRe}^N_i \) or \( \tilde{D}_{ReRe}^N_i \) as the concentration of Ir, Ta, and Re, respectively,
becomes zero. The extrapolations for \( D_{Ir}^* \), \( D_{Ta}^* \) and \( D_{Re}^* \) from the ternary interdiffusion
coefficients on the basis of Eq. (5.7) are presented in Figures 5.11, 5.12, and 5.13, respectively.
The estimated values of \( D_{Ir}^* \) and \( D_{Ta}^* \) are reported in Table 5.9.
Figure 5.11: Extrapolation of $D_{\text{Ir}}$ coefficient for the estimation of tracer diffusion coefficient of Ir in Ni$_3$Al at 1473K.
Figure 5.12: Extrapolation of $\tilde{D}_{\text{TaTa}}$ coefficient for the estimation of tracer diffusion coefficient of Ta in Ni$_3$Al at 1473K.
Figure 5.13: Extrapolation of $\tilde{D}_{\text{ReRe}}$ coefficient for the estimation of tracer diffusion coefficient of Re in Ni$_3$Al at 1473K.
Table 5.9: Tracer diffusion coefficients (10^{-16} m^2/s) of Ir, Ta and Re in Ni_3Al extrapolated from concentration profiles of ternary diffusion couples at 1473K.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Tracer Component</th>
<th>$D_t$ (10^{-16} m^2/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75.4Ni-24.6Al</td>
<td>Ir</td>
<td>15.1</td>
</tr>
<tr>
<td>75.3Ni-24.7Al</td>
<td>Ir</td>
<td>14.6</td>
</tr>
<tr>
<td>75.5Ni-24.5Al</td>
<td>Ir</td>
<td>13.3</td>
</tr>
<tr>
<td>76.1Ni-24.1Al</td>
<td>Ir</td>
<td>13.6</td>
</tr>
<tr>
<td>76.2Ni-23.8Al</td>
<td>Ir</td>
<td>16.9</td>
</tr>
<tr>
<td><strong>Average Value for Ir</strong></td>
<td></td>
<td><strong>14.7 ± 1.4</strong></td>
</tr>
<tr>
<td>75.6Ni-24.3Al</td>
<td>Ta</td>
<td>0.6</td>
</tr>
<tr>
<td>75.1Ni-24.8Al</td>
<td>Ta</td>
<td>5.3</td>
</tr>
<tr>
<td>74.2Ni-25.8Al</td>
<td>Ta</td>
<td>2.0</td>
</tr>
<tr>
<td><strong>Average Value for Ta</strong></td>
<td></td>
<td><strong>2.6 ± 2.4</strong></td>
</tr>
<tr>
<td>75.2Ni-24.8Al</td>
<td>Re</td>
<td>4.0</td>
</tr>
<tr>
<td>75.6Ni-24.4Al</td>
<td>Re</td>
<td>8.1</td>
</tr>
<tr>
<td>75.5Ni-24.5Al</td>
<td>Re</td>
<td>4.1</td>
</tr>
<tr>
<td><strong>Average Value for Re</strong></td>
<td></td>
<td><strong>5.4 ± 2.3</strong></td>
</tr>
</tbody>
</table>

At these dilute concentration of Ir, Ta, Re the magnitude of tracer diffusion coefficients of Ir, Ta and Re are very similar to their respective main ternary interdiffusion coefficients. The estimated tracer diffusion coefficient for the $\beta$-site-occupying Ta (2.6 x 10^{-16} ± 2.4 x 10^{-16} m^2/sec) is lower than that for the $\alpha$-site-occupying Ir (14.7 x 10^{-16} ± 1.4 x 10^{-16} m^2/sec). The tracer diffusion coefficient of Re (5.4 x 10^{-16} ± 2.3 x 10^{-16} m^2/sec) falls between the two tracer diffusion coefficients for Ir and Ta.

### 5.5. Summary

Ternary interdiffusion interactions of Ir and Ta addition on the L1_2 Ni_3Al phase were examined using solid-to-solid diffusion couples annealed at 1473K for 5 hours. Average ternary interdiffusion coefficients were determined from an integration of interdiffusion fluxes for
individual components. The magnitude of $\tilde{D}_\text{NiNi}^{\text{Al}}$ and $\tilde{D}_\text{AlAl}^{\text{Ni}}$ coefficients was determined to be much larger than that of $\tilde{D}_\text{IrIr}^{\text{Al}}$, $\tilde{D}_\text{TaTa}^{\text{Ni}}$, and $\tilde{D}_\text{ReRe}^{\text{Al}}$ coefficients. The $\tilde{D}_\text{NiIr}^{\text{Al}}$ coefficient was determined to be positive and large in magnitude; Ir substitutes in Ni-site and influences the interdiffusion of Ni significantly. The $\tilde{D}_\text{AlTa}^{\text{Ni}}$ coefficient was positive and large in magnitude; Ta substitutes in Al-site and influences the interdiffusion of Al significantly. The $\tilde{D}_\text{NiAlRe}^{\text{D}}$ coefficient was determined to be positive and large in magnitude; Re substitutes in Al-site and influences the interdiffusion of Al significantly. Ternary interdiffusion coefficients were also determined at compositions of intersecting diffusion paths, and at relative maxima and minima in concentration profiles for Ir-alloyed Ni$_3$Al. Consistency among ternary interdiffusion coefficients was observed. Profiles of concentrations were also examined to estimate binary interdiffusion coefficients in Ni$_3$Al. The results agreed well with published values. Tracer diffusion coefficients of Ir, Ta and Re in Ni$_3$Al were also estimated as $D_{\text{Ir}}^*=14.7 \times 10^{-16} \pm 1.4 \times 10^{-16}$ m$^2$/sec, $D_{\text{Ta}}^*=2.6 \times 10^{-16} \pm 2.4 \times 10^{-16}$ m$^2$/sec, and $D_{\text{Re}}^*=5.4 \times 10^{-16} \pm 2.3 \times 10^{-16}$ m$^2$/sec at 1473K.

The experiment and analysis reported herein demonstrates the practical use of analytical technique for multicomponent interdiffusion based on the determination and an integration of interdiffusion fluxes. The large magnitude of $\tilde{D}_\text{NiIr}^{\text{Al}}$, $\tilde{D}_\text{AlTa}^{\text{Ni}}$, and $\tilde{D}_\text{NiAlRe}^{\text{D}}$ coefficients also signifies a correlation in ternary diffusional interactions and site-preference of ordered ternary intermetallic alloys. In practical applications such as $\gamma$'-Ni$_3$Al containing oxidation resistant coatings, Ir can substitute for Ni to reduce the interdiffusion fluxes of Ni from the Ni-rich superalloy substrate into the Al-rich oxidation resistant coatings [10-15]. Presence of Ta and Re in Ni-base superalloy
substrate can also reduce the interdiffusion fluxes of Al from the Al-rich coatings into the superalloy substrate. Microstructural stability of Ni-base superalloy can also improve by appropriate partitioning of Ir, Ta and Re in \( \gamma' \)-Ni\(_3\)Al precipitates and fcc-Ni matrix.

5.6 References


28. M. Enomoto, H. Harada, Analysis of γ'/γ equilibrium in Ni–Al–X alloys by the Cluster


CHAPTER 6: DETERMINATION OF AVERAGE TERNARY INTERDIFFUSION COEFFICIENTS USING MOMENTS OF INTERDIFFUSION FLUX AND CONCENTRATION PROFILES

6.1 Introduction

The analysis of multicomponent diffusion often requires nonlinear fitting procedures with careful attention required even for the near-linear segments. Determination of composition dependent interdiffusion coefficients from concentration profiles obtained from diffusion couples can become a highly complex process. Consequently, reporting unquestionable values even within a single-phase region of the diffusion couple experiment can pose challenges. The objective of this work is to present an extended analytical method of a analytical approach [1], wherein average main and cross interdiffusion coefficients are determined over selected regions from a single diffusion couple experiment using moments (series of higher order integrands) of interdiffusion flux. For a ternary system, implementing this analytical technique yields the four interdiffusion coefficients as a function of interdiffusion-flux-moments for two independent components. The analysis is applied to selected single-phase isothermal diffusion couples including hypothetical A vs. B, and experimental ones in Ni₃Al-Ir [2] and Fe-Ni-Al [3] systems.

6.2 Description of a Refined Approach

From phenomenological description of ternary diffusion based on Onsager’s formalism of Fick’s law [4-6], an average ternary interdiffusion coefficients [1] can be employed to express
the interdiffusion flux $\dot{J}_i$ of a component $i$ in terms of two independent concentration gradients $\partial C_j / \partial x (j=1,2)$ by:

$$\dot{J}_i = -\overline{D}_{ii} \frac{\partial C_1}{\partial x} - \overline{D}_{i2} \frac{\partial C_2}{\partial x} \quad (i=1,2)$$

(6.1)

where $\overline{D}_{ii}$ and $\overline{D}_{i2}$ refer to the average main and cross-interdiffusion coefficients, respectively. The interdiffusion flux at any section $x$ can be calculated directly from the experimental concentration profile using the relation [7]:

$$\dot{J}_i = -\frac{1}{2t} \int_{C_i^-}^{C_i^+} (x - x_o) dC_i \quad (i=1,2)$$

(6.2)

where $t$ is the time, $C_i^-$ and $C_i^+$ are the terminal concentrations, and $x_o$ refers to the location of the Matano plane. Figure 6.1(a) illustrates a typical concentration profile, and Figure 6.1(b) shows the corresponding interdiffusion flux profile determined using Eq. (6.2).
Figure 6.1: Schematic profiles of (a) concentration $C_i$, (b) interdiffusion flux $\tilde{J}_i$, (c) $\tilde{J}_i(x-x_0)$, (d) $\tilde{J}_i(x-x_0)^2$, (e) $\tilde{J}_i(x-x_0)^3$, and (f) $\tilde{J}_i(x-x_0)^{50}$ for a solid-solid diffusion couple. Area $S_1$, $S_2$, $S_3$, $S_4$, $S_5$ and $S_{50}$ correspond to

$$\int_{C_1}^{C_2}(x-x_0)\,dC_i \quad \int_{x_1}^{x_2} \tilde{J}_i\,dx \quad \int_{x_1}^{x_2} \tilde{J}_i(x-x_0)\,dx \quad \int_{x_1}^{x_2} \tilde{J}_i(x-x_0)^2\,dx \quad \int_{x_1}^{x_2} \tilde{J}_i(x-x_0)^3\,dx \quad \int_{x_1}^{x_2} \tilde{J}_i(x-x_0)^{50}\,dx$$

respectively. $C_1$, $C_2$ and $x_1$, $x_2$ are arbitrarily chosen limits of concentration and distance, respectively.
The interdiffusion flux \( \tilde{J} \) for ‘m’ number of moments can be determined from Eq. (6.2) as a function of x, by multiplying both sides of Eq. (6.1) with \((x-x_o)^m\). An integration over a selected region, \(x_1\) to \(x_2\), yields [1]:

\[
M(m) = \int_{x_1}^{x_2} \tilde{J}_i(x-x_o)^m dx = -\overline{D}_{i1}^{3} \int_{C_i(s_i)}^{C_i(s_2)} (x-x_o)^m dC_1 - \overline{D}_{i2}^{3} \int_{C_2(s_i)}^{C_2(s_2)} (x-x_o)^m dC_2 \quad (i = 1,2) \quad (6.3)
\]

Eq. (6.3) is the recursion equation [8], and also can be referred as “Modified Onsager’s Flow Equation” that involves moments of interdiffusion fluxes. By varying the m values from \(m = 0\) to \(m = \infty\) for the two independent components (e.g., 1 and 2), Eq. (6.3) can be written to provide infinite number for set of four equations to solve for the four \(\overline{D}_{ij}^{3}\) interdiffusion coefficients. Solving each combination of these equations provides values of individual series for all the four average ternary interdiffusion coefficients.

Variation of \(\int_{x_1}^{x_2} \tilde{J}_i(x-x_o)^m dx\) integral is presented in Figures 1(b) through 1(f). For the moments \(m = 0, 1\) and 2 Eq. (6.3) can be written as:

\[
M(0) = \int_{x_1}^{x_2} \tilde{J}_i dx = -\overline{D}_{i1}^{3} \int_{C_i(s_i)}^{C_i(s_2)} dC_1 - \overline{D}_{i2}^{3} \int_{C_2(s_i)}^{C_2(s_2)} dC_2 \quad (i = 1,2) \quad (6.4)
\]

\[
M(1) = \int_{x_1}^{x_2} \tilde{J}_i (x-x_o) dx = -\overline{D}_{i1}^{3} \int_{C_i(s_i)}^{C_i(s_2)} (x-x_o) dC_1 - \overline{D}_{i2}^{3} \int_{C_2(s_i)}^{C_2(s_2)} (x-x_o) dC_2 \quad (i = 1,2) \quad (6.5)
\]

\[
M(2) = \int_{x_1}^{x_2} \tilde{J}_i (x-x_o)^2 dx = -\overline{D}_{i1}^{3} \int_{C_i(s_i)}^{C_i(s_2)} (x-x_o)^2 dC_1 - \overline{D}_{i2}^{3} \int_{C_2(s_i)}^{C_2(s_2)} (x-x_o)^2 dC_2 \quad (i = 1,2) \quad (6.6)
\]
Eq. (6.4) is a statement of mass conservation, Eq. (6.5) is proportional to the centroid or the mean of the distribution in terms of concentration integral of the diffusion distance, and Eq. (6.6) is proportional to moment of inertia or dispersion [8]. Eqs. (6.4), (6.5) and (6.6) and all higher order equations can provide linearly independent equations that can yield unique solution at the intersection of any two equations.

6.3 Thermodynamic Criteria of Interdiffusion Coefficients

Numerical requirement of ternary interdiffusion coefficients based on Fickian behavior and thermodynamic stability of the solid solutions are presented by Eq. (6.7) and Eqs. (6.8) through (6.10), respectively [9]. These can be used as selection criteria to identify the representing values of the average ternary interdiffusion coefficients in a single-phase region. Use of these selection criteria will ensure real positive eigen-values of the diffusivity matrix, which then can be employed for the generation of concentration profiles based on analytical error function solution given by Fujita and Gosting [10].

\[
\begin{align*}
\bar{D}_{11}^3 &> 0 \quad \bar{D}_{22}^3 > 0 \\
\bar{D}_{11}^3 + \bar{D}_{22}^3 &> 0 \\
(\bar{D}_{11}^3 \bar{D}_{22}^3 \bar{D}_{12}^3 \bar{D}_{21}^3) &\geq 0 \\
(\bar{D}_{11}^3 + \bar{D}_{22}^3)^2 - 4(\bar{D}_{11}^3 \bar{D}_{22}^3 - \bar{D}_{12}^3 \bar{D}_{21}^3) &\geq 0
\end{align*}
\]
6.4. Application of the Method

The interdiffusion coefficients determined at the lowest possible m-value that satisfy all the above requirements and constraints represent the average interdiffusion coefficients of a particular composition range within the diffusion couple. In most cases, solving Eq. (6.4) where \( m = 0 \) and Eq. (6.5) where \( m = 1 \) yields reliable ternary interdiffusion coefficients. Aforementioned, extrapolating polynomial curves of all 4 interdiffusion coefficients determined as a function of \( m \), to the \( m = 0 \) will further improve the accuracy of the interdiffusion coefficients. But for cases where Eqs. (6.4) and (6.5) do not satisfy the above mentioned requirements and constraints, \textit{vis.} Eqs. (6.7) through (6.10), higher order combinations (e.g., \( m = 0 \) and \( m > 1 \)) may provide values of average ternary interdiffusion coefficients.

In Table 6.1 are listed solid-to-solid isothermal diffusion couples in the A-B, (Ni,Ir)\textsubscript{2}Al and Fe-Ni-Al systems selected from literature [2,3]. Hypothetical A vs. B couple has been chosen to verify the accuracy in obtaining parent interdiffusion coefficient to regenerate the concentration profiles. These initial values are chosen such that they obey all requirements and constraints given in Eqs. (6.7) through (6.10). Concentration profiles from Ni-26.0Al vs. Ni-23.0Al-2Ir diffusion couple exhibits an relative maximum and minimum for Ni with a strong diffusional interaction with Ir. The \( \beta_8 \) vs. \( \beta_9 \) couple from the Fe-Ni-Al system presents “near-linear” segments in Ni and Al concentration profiles.
Table 6.1: Selected hypothetical and experimental ternary diffusion couples investigated in various systems.

<table>
<thead>
<tr>
<th>Diffusion Couples and Terminal Compositions (At. Pct)</th>
<th>Diffusion Annealing Parameters</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (0C1-0C2-100C3) vs. B (60C1-40C2-0C3)</td>
<td>Temperature (°C)</td>
<td>Time (hours)</td>
</tr>
<tr>
<td>Ni-26.0Al vs. Ni-23.0Al-2Ir</td>
<td>1200</td>
<td>5</td>
</tr>
<tr>
<td>β8 (18.0Fe-51.0Ni-20.9Al) vs. β9 (37.9Fe-39.0Ni-23.1Al)</td>
<td>1000</td>
<td>96</td>
</tr>
</tbody>
</table>

The hypothetical and experimental concentration profiles of selected ternary diffusion couples listed in Table 6.1 are presented in Figures 6.2(a), 6.3(a) and 6.4(a). Thick lines represent parent or experimental concentration profiles where as thin lines correspond to calculated profiles. Interdiffusion fluxes of individual components were calculated using Eq. (6.2). Average ternary interdiffusion coefficients $\overline{D}_{ij}$ were determined by solving two equations of Eq. (6.3) with $m = 0$ and Eq. (6.2) with $m = 1, 2, 3, ..., 50$ on either side of the Matano plane. Variation in $\overline{D}_{ij}$’s as a function of $m$ values in second equation was examined as presented in Figure 6.2(b), 6.3(b) and 6.4(b). The variation was extrapolated to $m = 0$ using polynomial extrapolation. Requirement given by Eq. (6.7) can then be addressed from Figures 6.2(b), 6.3(b) and 6.4(b). The average ternary interdiffusion coefficients determined were also examined by utilizing thermodynamic constraints given by Eq. (6.8) denoted as constraint 1, Eq. (6.9) denoted as constraint 2, and Eq. (6.10) denoted as constraint 3. Figures 6.2(c), 6.3(c) and 6.4(c) presents left-hand-side of Eq. (6.8), Eq. (6.9) and Eq. (6.10) plotted against non-zero “m” value used for the determination of average ternary interdiffusion coefficients.
Figure 6.2: (a) Hypothetical and calculated concentration profiles in diffusion couple A vs. B with chosen annealing time of 100 hours. (b) Variation in $D_{ij}$’s as a function of m on either side of the Matano plane $x_o$. (c) Thermodynamic constraints of interdiffusion coefficients as a function of m on either side of the Matano plane $x_o$. 

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Figure 6.3: (a) Experimental and calculated concentration profiles for Ni-Al-Ir (L12) diffusion couple Ni$_3$Al vs. Ni$_3$Al-Ir annealed at 1200°C for 5 hours. (b) Variation in $D_{ij}$'s as a function of $m$ on either side of the Matano plane $x_0$. (c) Thermodynamic constraints of interdiffusion coefficients as a function of $m$ on either side of the Matano plane $x_0$. 
Figure 6.4: (a) Experimental and calculated concentration profiles for Fe-Ni-Al (B2) diffusion couple $\beta_8$ vs. $\beta_9$ annealed at 1000ºC for 96 hours. (b) Variation in $\bar{D}_i$’s as a function of m on either side of the Matano plane $x_0$. (c) Thermodynamic constraints of interdiffusion coefficients as a function of m on either side of the Matano plane $x_0$. 

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Values of average ternary interdiffusion coefficients determined by extrapolation to m = 0 was the most accurate for couples A vs. B and Ni-26.0Al vs. Ni-23.0Al-2Ir. Table I shows the excellent agreement between the “input” $D_{ij}^{3}$'s with calculated $D_{ij}^{3}$'s for the hypothetical diffusion couple A vs. B. This comparison proves that extrapolation to m = 0 for the determination of $D_{ij}^{3}$ coefficients removes the uncertainty (i.e., ± 5%) observed in backcalculated values by Dayananda and Sohn [1]. For the case of $\beta_8$ vs. $\beta_9$ couple, use of Eqs. (6.4) where m = 0 and (6.5) where m = 1 does not provide $D_{ij}^{3}$ coefficients that satisfy Eqs. (6.7) through (6.10). This is due to the fact that the concentration profiles seen in Figure 6.4 consist mostly of “linear” segments. For $\beta_8$ vs. $\beta_9$ couple, use of Eq. (6.4) where m = 0 and Eq. (6.3) where m=9 yielded $D_{ij}^{3}$ coefficients that satisfy Eqs. (6.7) through (6.10) on the concentration range of $(C^{-}\infty-C^0)$. Similarly use of Eq. (6.4) where m = 0 and Eq. (6.3) where m = 11 yielded $D_{ij}^{3}$ coefficients that satisfy Eqs. (6.7) through (6.10) on the concentration range of side $(C^0-C^{+\infty})$. The average ternary interdiffusion coefficients determined for $\beta_8$ vs. $\beta_9$ couple can be utilized for generation of concentration profiles as well. It should be noted that $D_{ij}^{3}$ coefficients determined in this study correspond well to those determined by Boltzmann-Matano analysis [2,3].
Table 6.2: A comparison between the “input” \( \bar{D}^3_{ij} \)'s with calculated \( \bar{D}^3_{ij} \)'s on either side of the Matano plane for the hypothetical ternary diffusion couple A vs. B, and experimental diffusion couples Ni-26.0Al vs. Ni-23.0Al-2Ir and \( \beta_8 \) vs. \( \beta_9 \).

<table>
<thead>
<tr>
<th>Couple</th>
<th>Composition Range</th>
<th>Average ternary interdiffusion coefficients (calculated)</th>
<th>Average ternary interdiffusion coefficients [1]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( \bar{D}^3_{ij} ) (X10^{-15} m^2/s)</td>
<td>( \bar{D}^3_{ij} ) (X10^{-15} m^2/s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \bar{D}_{11}^3 )</td>
<td>( \bar{D}_{12}^3 )</td>
</tr>
<tr>
<td>A vs. B</td>
<td>( (C^-C^0) )</td>
<td>0</td>
<td>23.7</td>
</tr>
<tr>
<td></td>
<td>( (C^0-C^{+z}) )</td>
<td>0</td>
<td>23.7</td>
</tr>
<tr>
<td>Ni-26Al vs. Ni-23Al-2Ir</td>
<td>( (C^-C^0) )</td>
<td>0</td>
<td>94.5</td>
</tr>
<tr>
<td></td>
<td>( (C^0-C^{+z}) )</td>
<td>0</td>
<td>60.6</td>
</tr>
<tr>
<td>( \beta_8 ) vs. ( \beta_9 )</td>
<td>( (C^-C^0) )</td>
<td>9</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>( (C^0-C^{+z}) )</td>
<td>12</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Note: For Ni-26Al vs. Ni-23Al-2Ir, \( 1=Ni, 2=Ir, 3=Al \); For \( \beta_8 \) vs. \( \beta_9 \), \( 1=Al, 2=Ni, 3=Fe \); * Ng. refers to magnitudes less than \( 0.1 \times 10^{-15} \) m^2/sec.

6.5. Summary

A refined analysis is developed to determine average ternary interdiffusion coefficients in single-phase diffusion couples and successfully implemented to selected hypothetical and experimental data. This technique allows determination of interdiffusion coefficients in ternary alloys even from concentration profiles with linear segments, and are comparable to those measured by Boltzmann-Matano Analysis. This approach can be applied to near-linear segment of the concentration profiles and higher order alloy systems within the single-phase regions.

6.6 References


CHAPTER 7: SUMMARY

Interdiffusion in Ni-Cr (fcc $\gamma$ phase) alloys with small additions of Al, Si, Ge, or Pd was investigated using solid-to-solid diffusion couples annealed at 900°C and 700°C for 168 and 720 hours, respectively. Ni-Cr-X alloys having compositions of Ni-22at.%Cr, Ni-21at.%Cr-6.2at.%Al, Ni-22at.%Cr-4.0at.%Si, Ni-22at.%Cr-1.6at.%Ge and Ni-22at.%Cr-1.6at.%Pd were cast using arc-melting and homogenized at 900°C for 168 hours. The diffusion couples were assembled in an Invar™ steel jig, encapsulated in Ar after several hydrogen purges, and annealed at 900°C and 700°C in a three-zone tube furnace for 168 and 720 hours, respectively. Experimental concentration profiles were determined from polished cross-section of these couples by using electron probe microanalysis with pure element standards. Interdiffusion fluxes of individual components were calculated directly from the experimental concentration profiles, and the moments of interdiffusion fluxes were examined to determine average ternary interdiffusion coefficients. In general, $\tilde{D}_{i}^{\text{eff}}$ was observed to increase with higher Cr concentration. Also, $\overline{D}_{\text{CrX}}^{\text{Ni}}$ coefficients were determined to be positive with alloying additions of Al, Si, Ge, or Pd. The results suggest that these alloying additions can help the formation of Cr$_2$O$_3$-scale for initial scale formation, maintaining scale homogeneity during prolonged high-temperature exposure, and reformation after scale-spallation.

A similar experimental investigation for interdiffusion in Fe-Ni-Cr (fcc $\gamma$ phase) alloys with small additions of Si and Ge at 900°C was also studied using solid-to-solid diffusion couples. Alloy rods, Fe-24 at.%Ni, Fe-24 at.%Ni-22at.%Cr, Fe-24 at.%Ni-22at.%Cr-4at.%Si and Fe-24 at.%Ni-22at.%Cr-1.7at.%Ge were cast using arc-melt, and homogenized at 900°C for 168
hours and diffusion couples from these alloys were annealed at 900°C for 168 hours. Large magnitudes of cross coefficients, $\overline{D}_{\text{CrSi}}^\text{Fe}$, $\overline{D}_{\text{CrGe}}^\text{Fe}$, $\overline{D}_{\text{NiSi}}^\text{Fe}$ and $\overline{D}_{\text{NiGe}}^\text{Fe}$ were observed in Fe-Ni-Cr-X (X=Si or Ge) alloys. The Si addition has caused on uphill-diffusion of Ni while there was no measurable uphill diffusion of Ni due to an increase in $\overline{D}_{\text{NiNi}}^\text{Fe}$ in Fe-Ni-Cr-Ge alloy, despite the large positive $\overline{D}_{\text{NiGe}}^\text{Fe}$.

Ternary interdiffusion in L12-Ni3Al with ternary alloying additions of Ir, Ta and Re was investigated at 1473K using solid-to-solid diffusion couples. Average ternary interdiffusion coefficients were determined from an integration of interdiffusion fluxes calculated directly from experimental concentration profiles. The magnitude of $\overline{D}_{\text{NiNi}}$ and $\overline{D}_{\text{AlAl}}$ coefficients was determined to be much larger than that of $\overline{D}_{\text{IrIr}}$, $\overline{D}_{\text{TaTa}}$, and $\overline{D}_{\text{ReRe}}$ coefficients. Ir substituting in Ni-site influenced the interdiffusion of Ni significantly, and $\overline{D}_{\text{NiIr}}^\text{Al}$ coefficients were determined to be large and positive. Similar observations was made for Re with large positive $\overline{D}_{\text{NiRe}}^\text{Al}$ coefficients. On the other hand Ta substituting for Al influenced the interdiffusion of Al significantly, and $\overline{D}_{\text{NiTa}}^\text{Al}$ coefficients were determined to be large and positive. An excellent agreement was found with ternary interdiffusion coefficients determined by Boltzmann-Matano analysis. Profiles of concentrations and interdiffusion fluxes were also examined to estimate binary interdiffusion coefficients in Ni3Al, and tracer diffusion coefficients of Ir (14.7 x 10^{-16} ± 1.4 x 10^{-16} m^2/sec), Ta (2.6 x 10^{-16} ± 2.4 x 10^{-16} m^2/sec) and Re (5.4 x 10^{-16} ± 2.3 x 10^{-16} m^2/sec) in Ni3Al.

Finally, a refined approach to determine average ternary interdiffusion coefficients was developed using Onsager’s flow equations with moments of the interdiffusion-parameter
integrands. The new analysis [1] developed by Dayananda and Sohn is the basis for this refined approach. The interdiffusion coefficients determined by this method are more accurate and can be applied to concentration profiles that contains linear segments.
APPENDIX A : LIST OF PUBLICATIONS AND REPRINTS
During the course of study for Ph.D. in materials science and engineering, the following papers were published.


Interdiffusion in (Face-Centered Cubic) Ni-Cr-X (X = Al, Si, Ge, or Pd) Alloys at 900 °C

Narayana Garimella, and M.P. Brady, and Yongho Sohn

(Submitted April 3, 2006; in revised form July 19, 2006)

Interdiffusion in nickel (Ni)-chromium (Cr) (face-centered cubic phase) alloys with small additions of aluminum (Al), silicon (Si), germanium (Ge), or palladium (Pd) was investigated using solid-to-solid diffusion couples, Ni-Cr-X alloys having compositions of Ni-22wt. % Cr, Ni-21wt. % Cr-6.2at. % Al, Ni-22wt. % Cr-4.0at. % Si, Ni-22wt. % Cr-1.6at. % Ge, and Ni-22wt. % Cr-1.6at. % Pd were manufactured by arc casting. The diffusion couples were assembled in an Invar steel jig encapsulated in Ar after several hydrogen purges and annealed at 900 °C in a three-zone tube furnace for 168 h. Experimental concentration profiles were determined from polished cross sections of these couples by using electron probe microanalysis with pure element standards. Interdiffusion fluxes of individual components were calculated directly from the experimental concentration profiles, and the moments of interdiffusion fluxes were used to determine the average ternary interdiffusion coefficients. The effects of ternary alloying additions on the diffusion behavior of Ni-Cr-X alloys are presented in the light of the diffusional interactions and the formation of a protective Cr₂O₃ scale.

Keywords: Boltzmann/Maxwell analysis, diffusion coefficient, diffusivity coefficient, experimental study, interdiffusion, multi-component diffusion, ternary system

1. Introduction

Nickel (Ni)-chromium (Cr)-base alloys are widely used in a variety of high-temperature applications due to their combination of good oxidation resistance and excellent high-temperature strength, and are the basis for a number of commercial superalloy families. Oxidation resistance in these alloys is derived from a continuous, slow-growing, adherent Cr₂O₃-base oxide scale. In particular, compositions in the range of Ni alloys with 20-30 wt. % Cr have been extensively studied as a model material for Cr₂O₃ scale formation.

Minor alloying additions (<5 wt. %) can significantly improve the oxidation resistance of Ni-base Cr₂O₃-forming alloys. Effects include: the establishment of continuous Cr₂O₃ scale formation at reduced Cr concentrations; a decrease in the growth rate of Cr₂O₃; and enhanced scale adherence.

For example, the addition of silicon (Si) in Ni-28wt. % Cr promoted the formation of both Cr₂O₃ and SiO₂ in which a continuous inner SiO₂ layer acted as a diffusion barrier, and reduced the isothermal oxidation rate by suppressing cation transport through the Cr₂O₃ scale. However, the same inner SiO₂ layer can also reduce the spallation resistance, which is dependent on the level of Si and on the continuity and thickness of the inner SiO₂ layer formed.

Diffusional effects of minor alloy additions may play a significant role in the initial establishment of a continuous protective oxide scale. It can also play a significant role in maintaining protective scale growth. For example, the growth of Cr₂O₃ can locally deplete Cr from the alloy in the subsurface region. If the scale is locally damaged or spalled, such depletion can prevent the reformation of the Cr₂O₃ scale and result in a transition to less protective or nonprotective oxidation behavior. An understanding of diffusional interactions in Ni-Cr-X alloys, where X represents minor alloying additions, can help to design Ni-base Cr₂O₃-forming alloys with improved resistance against environmental degradation.

In this work, interdiffusion in Ni-22wt. % Cr-X (face-centered cubic (fcc) phase) alloys with small additions of X [Al, Si, germanium (Ge), or palladium (Pd)] is investigated using solid-to-solid diffusion couples at 900 °C for 168 h. This information will be used as a part of a larger study, the goal of which is to better elucidate the effects of minor alloying additions on the oxidation of Cr₂O₃-forming alloys. Additions of Si were selected because it has long been known to be beneficial to Cr₂O₃ scale formation via both the establishment of an inner layer of SiO₂ and the possibility of enhanced diffusion of Cr. To help probe these effects, additions of Ge were also selected. Ge is thermochemically similar to Si in many regards.

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Narayana Garimella and Yongho Sohn, Advanced Materials Processing and Analytical Center and Department of Mechanical, Materials and Aerospace Engineering, University of Central Florida, Orlando, FL; and M.P. Brady, Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN. Contact e-mail: ysohn@ufl.edu.
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but does not form a protective oxide scale as does Si. Additions of Al at levels > 34 wt.% can improve the oxidation via the formation of a protective Al2O3 scale.14,15,28,29 At subcritical levels (2-3 wt.%), Al may also be beneficial to the oxidation resistance of Ni-Cr alloys, in part via the formation of semicircular inner region of Al2O3 particles.3,27,29 Al was chosen for the study because it is a noble alloying addition and would be expected to accumulate at the alloy-oxide interface during oxidation,29 30

In this ternary interdiffusion study at 900 °C, the experimental concentration profiles were used to calculate interdiffusion fluxes of individual components, and to determine the average effective interdiffusion coefficients $D_{ij}^{eff}$ and the average ternary interdiffusion coefficients $D_{ij}^{ter} (i,j = \text{Cr}, X)$. Values of $D_{ij}^{ter}$ and $D_{ij}^{eff}$ are examined to assess the effects of alloying additions on the interdiffusion behavior of Cr, and the Cr2O3-forming ability in Ni-Cr-X alloys.

2. Determination of Interdiffusion Coefficients From Ternary Isothermal Diffusion Couples

Onsager’s formalism for the interdiffusion flux $J_i$ of component $i$ in a ternary system can be written as:

$$J_i = \frac{D_{ij}^{ter}}{x_j} \frac{C_j}{C_i} \frac{C_j}{x_j} \text{ } i,j = 1, 2$$

(Eq 1)

where $C_j / x_j$ and $C_i / x_i$ are the two independent concentration gradients, and $D_{ij}^{ter}$ and $D_{ij}^{eff}$ refer to the ternary and interdiffusion coefficients, respectively. An experimental determination of the four concentration-dependent interdiffusion coefficients requires the use of the Boltzmann-Matano analysis with two independent diffusion couples that develop a common composition in the diffusion zone. Instead, the interdiffusion fluxes $J_i$ of all components can be determined directly from their concentration profiles of an infinite diffusion couple without the need of the interdiffusion coefficients on the basis of the relation:

$$J_i = \frac{C_j}{x_j} \frac{C_j}{x_i} \int_{x_i}^{x_j} \frac{dx}{x}$$

(Eq 2)

where $t$ is the time, $C_j$ and $C_i$ are the terminal concentrations of the alloys used for the couple, and $x_i$ refers to the location of the Matano plane. The interdiffusion flux $J_i$ determined from Eq 2 can be integrated with respect to position $x$ to define the average effective interdiffusion coefficient $D_{ij}^{eff}$:

$$J_i = \frac{x_j}{C_i} \frac{C_j}{C_i} \text{ } i = 1, 2, 3$$

(Eq 3)

This effective interdiffusion coefficient incorporates all components diffusion interactions for the system to provide an effective value for the interdiffusion of a component species as defined by:

$$D_{ij}^{eff} = \frac{D_{ij}^{ter} + \frac{D_{ij}^{ter} C_i}{C_j} \frac{C_j}{x_j} \text{ } i,j = 1, 2}$$

(Eq 4)

The interdiffusion flux $J_i$ determined from Eq 2 as a function of $x$, can be multiplied by $(x - \bar{x}_i)^p$ and integrated over a selected region, $x_1$ to $x_2$, in the light of Eq 1, one gets:

$$J_i = \int_{x_1}^{x_2} \frac{C_j}{x_j} \frac{C_j}{x_i} \text{ } \frac{dx}{x}$$

$$x_i \frac{dx}{x} = \int_{x_1}^{x_2} \frac{C_j}{x_j} \frac{C_j}{x_i} \text{ } \frac{dx}{x}$$

(Eq 5)

where $D_{ij}^{ter}$ ($i,j = 1, 2$) coefficients are the average values of main and cross-interdiffusion coefficients treated as constants over the selected composition range. Equation 5 can provide four equations involving the $D_{ij}^{ter}$ interdiffusion coefficients ($i = 0, 1, 2$) and can be set up from interdiffusion fluxes calculated on the basis of Eq 2 from the concentration profiles of a single diffusion couple. The $D_{ij}^{ter}$ coefficients, characteristic of the diffusion path, can be determined over selected composition ranges that include the nonlinear segment of the profiles.33,34 The determination of ternary interdiffusion coefficients by using Eq 5 does not require the use of concentration gradients (i.e., $C_j / x$) and significantly reduces the uncertainty involved in the determination of interdiffusion coefficients arising from microprobe measurement and the concentration smoothing procedure.

3. Experimental Procedure

Binary and ternary alloys with compositions reported in Table 1 were prepared with 99.9% pure Ni, Cr, Al, Si, Ge, and Pb by arc melting under an argon (Ar) atmosphere. The alloys were chill-cast by water-cooled copper mold into
Table 2  List of Ni versus Ni-Cr-X and NiCr versus Ni-Cr-X solid-to-solid diffusion couples annealed at 900 °C for 168 h

<table>
<thead>
<tr>
<th>Series</th>
<th>Diffusion couple</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Ni vs. Ni-Cr</td>
</tr>
<tr>
<td>II</td>
<td>Ni vs. Ni-Cr-Al</td>
</tr>
<tr>
<td></td>
<td>Ni vs. Ni-Cr-Si</td>
</tr>
<tr>
<td></td>
<td>Ni vs. Ni-Cr-Ge</td>
</tr>
<tr>
<td></td>
<td>Ni vs. Ni-Cr-Pd</td>
</tr>
<tr>
<td>III</td>
<td>Ni-Cr vs. Ni-Cr-Al</td>
</tr>
<tr>
<td></td>
<td>Ni-Cr vs. Ni-Cr-Si</td>
</tr>
<tr>
<td></td>
<td>Ni-Cr vs. Ni-Cr-Ge</td>
</tr>
<tr>
<td></td>
<td>Ni-Cr vs. Ni-Cr-Pd</td>
</tr>
</tbody>
</table>

rods with a vacuum 12 mm in diameter. The alloy rods were placed in a quartz tube, evacuated to a pressure <10^{-6} torr, and flushed with hydrogen. This hydrogen-flushing procedure was repeated several times, and a quartz capsule was filled with Ar before the final seal. They were homogenized at 900 °C for 168 h in a horizontal Lindberg three-zone tube furnace and water-quenched to preserve the high-temperature microstructure. The microstructures and compositions of the alloys were examined by optical microscopy, scanning electron microscopy, energy dispersive spectroscopy, and electron microprobe analysis (EPMA). No measurable variation in the alloy compositions was observed, and all alloys consisted of face-centered cubic (fcc) Ni solid solution (γ phase).

Diffusion disks with approximate thicknesses of 2 mm were cut from the rods of alloys and were prepared metallographically by polishing with 0.25μm diamond paste. Table 2 presented ternary diffusion couples that were assembled with the disks held together in an Invar steel jig consisting of two end plates and three threaded rods. The couples were placed in quartz capsules, which were sealed at one end, evacuated to a pressure <10^{-6} torr, and flushed with hydrogen several times. A capsule was filled with Ar before the final sealing. The capsules containing the couples were annealed at 900 °C in a horizontal Lindberg three-zone furnace for 168 h. After the anneal, the couples were quenched in water to preserve the high-temperature microstructures.

The diffusion assembly was then mounted, sectioned, and metallographically prepared for microstructural observations. Excellent bonding within all diffusion couples was observed. Then, the cross section surface was polished with 1μm diamond paste for EPMA. The concentration profiles of Ni, Cr, Al, Si, Ge, and Pd for the diffusion couples were determined with a JBL 735 (Tokyo, Japan) microprobe by point-to-point counting techniques using pure Ni, Cr, Al, Si, Ge, and Pd as standards. Intensities of K X-radiation were measured and converted to concentrations of Ni, Cr, Al, Si, Ge, and L X-radiation for that of Pd with appropriate ZAF atomic number, Z; absorption, A; fluorescence, F; corrections. Concentration profiles obtained from EPMA was smoothed by a weighted spline tool using Matlab (The Math Works, Natick, MA). It should be noted that the analytical method used in this study to determine interdiffusion coefficients by the integration of interdiffusion fluxes (e.g., Eq 5) do not require the use of concentration gradients. This method significantly reduces the influence of a smoothing procedure on the determination of interdiffusion coefficients.

4. Results and Discussion

Figure 1 presents an optical micrograph obtained from the diffusion couples Ni versus Ni-Cr-Al and Ni versus Ni-Cr-Si that was annealed at 900 °C for 168 h. Excellent bonding was achieved during the diffusion anneal for all diffusion couples. Figure 2 presents an example of the experimental and smoothed concentration profiles that were used for the determination of interdiffusion coefficients. The scatter in the concentration profiles for all diffusion couples was minimal and within the experimental uncertainty associated with EPMA. Experimental concentration profiles were smoothed with a weighted-spline routine by using Matlab.

From concentration profiles obtained from series I and II diffusion couples (i.e., Ni versus Ni-Cr, and Ni versus
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Fig. 2 Typical experimental and smoothed concentration profiles measured from solid-to-solid diffusion couples (a, b) Ni vs. Ni-Cr-Al and (c, d) Ni-Cr vs. Ni-Cr-Si annealed at 900 °C for 168 h

Ni-Cr-X, respectively), the average effective interdiffusion coefficients \( D^{ef}_{AB} \) on either side of the Matano plane were determined using Eq 3. In general, \( D^{ef}_{AB} \) was higher on the \((C^+_1, C^+_2)\) composition range with a higher Cr concentration relative to the other side of the Matano plane. Table 3 also reports that an Al addition to a NiCr alloy can increase or decrease the \( D^{ef}_{AB} \) as a function of composition. This indicates an appreciable variation in interdiffusion coefficients as a function of composition: specifically, Al increased \( D^{ef}_{AB} \) on the \((C^+_1, C^+_2)\) composition range with a higher Cr concentration. \( D^{ef}_{AB} \) was observed to increase with an Si addition to a NiCr alloy, especially on the \((C^+_1, C^+_2)\) side with higher Cr concentration. According to Table 3, Ge does not change \( D^{ef}_{AB} \) significantly, while a Pd addition to an NiCr alloy increased \( D^{ef}_{AB} \), which is quite significant on the \((C^+_1, C^+_2)\) range with a higher Cr concentration.

From concentration profiles obtained from diffusion couple series I and II (i.e., Ni versus Ni-Cr, and Ni versus Ni-Cr-X, respectively), average ternary interdiffusion coefficients \( D^{ef}_{ABC}(C, \text{ Cr, } X) \) were determined on either side of the Matano plane using Eq 5. These diffusion couples are reported in Table 4. It should be noted that these diffusion couples were designed to yield the same sign of \( C_{CB} x \) and \( C_{B} y x \). Thus, positive and negative \( D^{ef}_{ABC} \) indicates an increase and a decrease in \( J_{AB} \), respectively. In general, larger magnitudes of \( D^{ef}_{ABC} \) and \( D^{ef}_{AB} \) were observed on the \((C^+_1, C^+_2)\) composition range with higher Cr concentration. The Al addition in the Ni-Cr alloy yielded positive \( D^{ef}_{ABC} \) and increased \( J_{AB} \) in accordance with previous work by Nesbitt and Heckel\(^{(21)}\) and Thompson et al.\(^{(25)}\) The magnitude of \( D^{ef}_{ABC} \) was quite large, as reported in Table 4 on the \((C^+_1, C^+_2)\) with higher Cr concentration. Similarly, Si, Ge, and Pd additions to the Ni-Cr alloy increased \( J_{AB} \), positive \( D^{ef}_{ABC} \). This effect was, again, stronger when the Cr concentration was high on the \((C^+_1, C^+_2)\), particularly for Si and Pd.

Diffusion couple series III was designed with initial \( C_{CB} x = 0 \), so that \( J_{AB} \) is largely due to \( C_{B} y x \), and depends on the magnitude and sign of \( D^{ef}_{ABC} \). \( J_{AB} \) has caused an uphill diffusion of Cr in the direction of \( J_{AB} \) with positive \( D^{ef}_{ABC} \) for Al and Si. This indicates that Al and Si should increase the thermodynamic activity of Cr in Ni-Cr alloys.

### Table 3. Average effective interdiffusion coefficients determined from Ni vs. Ni-Cr-X diffusion couples annealed at 900 °C for 168 h

| Diffusion couple | Composition range | \( \mu_{AB}^{m} \) & 10\(^{-14}\) m/s | \( \mu_{AB}^{m} \) & 10\(^{-16}\) m/s | \( \mu_{AB}^{m} \) & 10\(^{-18}\) m/s |
|------------------|--------------------|----------------|----------------|----------------|----------------|
| Ni vs. Ni-Cr     | \( C^+_1, C^+_2 \) | 1.00           | ...            | 1.00           | ...            |
| \( \text{X None} \) | \( C^+_1, C^+_2 \) | 1.53           | ...            | 1.53           | ...            |
| Ni vs. Ni-Cr-Al  | \( C^+_1, C^+_2 \) | 0.91           | 3.21           | 1.83           | ...            |
| \( \text{X Al} \) | \( C^+_1, C^+_2 \) | 1.58           | 4.68           | 2.19           | ...            |
| Ni vs. Ni-Cr-Si  | \( C^+_1, C^+_2 \) | 1.68           | 5.74           | 2.26           | ...            |
| \( \text{X Si} \) | \( C^+_1, C^+_2 \) | 3.00           | 6.91           | 3.57           | ...            |
| Ni vs. Ni-Cr-Ge  | \( C^+_1, C^+_2 \) | 1.30           | 3.69           | 1.40           | ...            |
| \( \text{X Ge} \) | \( C^+_1, C^+_2 \) | 1.44           | 3.47           | 1.64           | ...            |
| Ni vs. Ni-Cr-Pd  | \( C^+_1, C^+_2 \) | 1.77           | 1.19           | 1.74           | ...            |
| \( \text{X Pd} \) | \( C^+_1, C^+_2 \) | 4.09           | 2.67           | 3.92           | ...            |
### Table 4  Average ternary interdiffusion coefficients determined from Ni vs. Ni-Cr-X diffusion couples annealed at 900 °C for 168 h

<table>
<thead>
<tr>
<th>Diffusion couple</th>
<th>Composition range</th>
<th>$D_{Ni-Cr}$ ($10^{-18}$ m$^2$/s)</th>
<th>$D_{Ni-Ni}$ ($10^{-18}$ m$^2$/s)</th>
<th>$D_{Cr-Cr}$ ($10^{-18}$ m$^2$/s)</th>
<th>$D_{Ni-X}$ ($10^{-18}$ m$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni vs. Ni-Cr-Al (X = Al)</td>
<td>(C3, C7)</td>
<td>0.78</td>
<td>0.31</td>
<td>0.49</td>
<td>1.99</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Si (X = Si)</td>
<td>(C3, C7)</td>
<td>1.11</td>
<td>1.72</td>
<td>0.43</td>
<td>2.84</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Ge (X = Ge)</td>
<td>(C3, C7)</td>
<td>2.05</td>
<td>4.88</td>
<td>0.57</td>
<td>3.35</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Pd (X = Pd)</td>
<td>(C3, C7)</td>
<td>1.08</td>
<td>0.56</td>
<td>0.07</td>
<td>1.73</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Ge (X = Ge)</td>
<td>(C3, C7)</td>
<td>1.24</td>
<td>0.89</td>
<td>0.10</td>
<td>1.99</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Pd (X = Pd)</td>
<td>(C3, C7)</td>
<td>1.43</td>
<td>4.64</td>
<td>0.01</td>
<td>0.98</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Pd (X = Pd)</td>
<td>(C3, C7)</td>
<td>5.49</td>
<td>8.36</td>
<td>0.01</td>
<td>1.76</td>
</tr>
</tbody>
</table>

### Table 5  Average ternary interdiffusion coefficients determined from Ni-Cr vs. Ni-Cr-X diffusion couples annealed at 900 °C for 168 h

<table>
<thead>
<tr>
<th>Diffusion couple</th>
<th>Composition range</th>
<th>$D_{Ni-Cr}$ ($10^{-18}$ m$^2$/s)</th>
<th>$D_{Ni-Ni}$ ($10^{-18}$ m$^2$/s)</th>
<th>$D_{Cr-Cr}$ ($10^{-18}$ m$^2$/s)</th>
<th>$D_{Ni-X}$ ($10^{-18}$ m$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Cr vs. Ni-Cr-Al (X = Al)</td>
<td>(C3, C7)</td>
<td>0.23</td>
<td>0.12</td>
<td>0.01</td>
<td>0.67</td>
</tr>
<tr>
<td>Ni-Cr vs. Ni-Cr-Si (X = Si)</td>
<td>(C3, C7)</td>
<td>1.20</td>
<td>0.44</td>
<td>0.13</td>
<td>1.17</td>
</tr>
<tr>
<td>Ni-Cr vs. Ni-Cr-Ge (X = Ge)</td>
<td>(C3, C7)</td>
<td>2.58</td>
<td>1.73</td>
<td>0.01</td>
<td>0.68</td>
</tr>
<tr>
<td>Ni-Cr vs. Ni-Cr-Pd (X = Pd)</td>
<td>(C3, C7)</td>
<td>1.39</td>
<td>0.63</td>
<td>1.78</td>
<td>1.97</td>
</tr>
</tbody>
</table>

On the other hand, $J_{Ni}$ and $J_{Pd}$ did not cause any measurable redistribution of Cr ($\Delta Cr = 0$). It should be noted that Ge and Pd have lower contents in the Ni-Cr-X alloys than Al and Si, as reported in Table 1.

Based on the average effective interdiffusion coefficients and average ternary interdiffusion coefficient determined in this study, alloying additions of Al, Si, Ge, and Pd have all increased $D_{Ni-Cr}$ and yielded positive $D_{Ni-X}$, particularly with high Cr content (22 at % Cr). Therefore, the Cr$_2$O$_3$ forming ability of the Ni-20at.%Cr-based alloy should improve with these alloying additions by establishing Cr$_2$O$_3$ scale, by maintaining protective Cr$_2$O$_3$ scale formation, and in reforming of Cr$_2$O$_3$ on spallation. It should be noted that the positive $D_{Ni-Cr}$ reported in Tables 4 and 5 should also promote the formation of other scales (Al$_2$O$_3$, SiO$_2$) in the (f.c.c) Ni-Cr alloy, which may reduce the scale growth and/or change the thermomechanical properties of the scale.

### 5. Summary

Based on experimental solid-to-solid diffusion couples, a small addition of Al, Si, Ge, or Pd was observed to increase the overall interdiffusion flux of Cr in Ni-22at.%Cr-X (f.c.c) phase alloys. Experimental concentration profiles, measured after annealing at 900 °C in a three-zone tube furnace for 168 h, were used to determine interdiffusion fluxes, average effective interdiffusion coefficients, and average ternary interdiffusion coefficients. In general, $D_{Ni}$ was observed to increase with a higher Cr concentration. Also, $D_{Ni-Cr}$ coefficients were determined to be positive with alloying additions of Al, Si, Ge, or Pd. These results suggest that these alloying additions can help the formation of Cr$_2$O$_3$ scale for initial scale formation, maintaining scale homogeneity during prolonged high-temperature exposure, and for reformation after scale spallation.

### Acknowledgments

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Integrated, Effective and Average Interdiffusion Coefficients and Their Applications in Multicomponent Alloys for Energy Production Technologies

Y.H. Sohn\textsuperscript{1,a}, N. Garimella\textsuperscript{1,b}, E. Perez\textsuperscript{1,c}, R. Mohanty\textsuperscript{1,d}, J. Liu\textsuperscript{1,e}

\textsuperscript{1}Advanced Materials Processing and Analysis Center and Department of Mechanical, Materials and Aerospace Engineering, University of Central Florida, Orlando, FL 32816
\textsuperscript{a}ysohn@mail.ucf.edu, \textsuperscript{b}ga825540@pegasus.cc.ucf.edu, \textsuperscript{c}em168604@pegasus.cc.ucf.edu, \textsuperscript{d}rmohanty@mail.ucf.edu, \textsuperscript{e}j181643@pegasus.cc.ucf.edu

Keywords: Interdiffusion, Microstructure, Multicomponent Alloys, Interdiffusion Coefficients, Thermal Barrier Coatings, NiCoCrAlY, Nickel Aluminides, Superalloys, Metallic Nuclear Fuels

Abstract. Solid-state diffusion is a subject of great interest for many industrial applications. It also provides excellent educational studies with cross-fertilization of science and technology. This paper examines the importance of multicomponent-multiphase interdiffusion with specific examples from materials science and coatings for components in advanced energy production systems, including gas turbines and nuclear reactors. Results and analysis from laboratory experiments are presented in terms of interdiffusion fluxes, integrated interdiffusion coefficients, effective interdiffusion coefficients, and average multicomponent interdiffusion coefficients. Applications are highlighted for materials and coatings for components in advanced energy production technologies. Additional consideration is given to the refined approach to assess composition-dependent interdiffusion coefficients in multicomponent alloys.

Interdiffusion in Gas Turbine and Nuclear Reactor Components

Interdiffusion in multicomponent-multiphase alloys is commonly encountered in many materials systems employed in gas turbine and nuclear reactor environment. The developments of multicomponent-multiphase alloys require control of microstructure through appropriate heat treatment, involving solid-state transformations, precipitation processes, and surface modification, where the interdiffusion processes play a major role. In addition, interdiffusion processes often control degradation and failure of these materials systems, and enhanced performance and reliable durability always requires a detailed understanding of interdiffusion.

For example, hot section components such as blades and vanes of turbine engines for propulsion and utilities are generally coated with oxidation resistant coatings (e.g., NiCoCrAlY or NiAl) and insulating-ceramic thermal barrier coatings (TBCs) to protect load-bearing superalloys [1-5]. For TBCs, the NiCoCrAlY or NiAl-based coatings are also known as bond coats. TBCs are in general air plasma sprayed or electron beam physical vapor deposited \text{ZrO}_2-8\text{wt.}\%\text{Y}_2\text{O}_3 (YSZ) as presented in Fig. 1. In a typical gas turbine application, TBCs degrade by many diffusion-controlled phenomena including: sintering of YSZ, phase transformation (e.g., non-equilibrium tetragonal to equilibrium cubic and equilibrium monoclinic) of YSZ, formation of thermally grown oxide (TGO) due to oxidation of bond coats, polymorphic and phase transformations within the TGO scale, phase transformations in bond coats due to oxidation and interdiffusion with superalloys substrates, coarsening of precipitates in superalloys, phase transformations (e.g., TCP) in superalloys and creep of superalloys. A typical example of microstructural degradation in a NiCoCrAlY bond coat due
to oxidation and interdiffusion with superalloy underneath is presented in Fig. 2, where 
Al-rich β-NiAl phase gets dissolved by depletion of Al via interdiffusion [6].

Fig. 1. Typical microstructure of as-processed TBCs with (a) APS YSZ and NiCoCrAlY bond 
coat; (b) EB-PVD YSZ and NiCoCrAlY bond coat; (c) EB-PVD YSZ and (Ni,Pt)Al bond 
coat.

Fig. 2. Backscatter electron micrographs of TBCs with a NiCoCrAlY bond coat and IN738 
superalloy substrate illustrating growth of TGO scale and dissolution of β-phase due to 
interdiffusion as a function of cyclic oxidation at 1121°C [6]. Each thermal cycling consists of 
10-minute heat-up, 40-minute dwell at 1121°C and 10-minute forced-air-quench.

In a nuclear reactor environment, interdiffusion process with cladding and due to 
temperature gradient becomes critical in development and application of advanced metallic 
nuclear fuels (e.g., U-Pu-Zr and U-Mo). For example, a rod of U-19wt.%Pu-10wt.%Zr alloy 
under the gradient of temperature (220°C/cm for 41 days) develops a large-scale 
compositional changes and microstructure variation as a result of multicomponent 
thermotransport [7]. Also, interdiffusion between U-8~10wt.%Mo fuel-alloy with Al-cladding 
results in formation of Al-rich intermetallic compounds with low thermal conductivity [8,9] 
that degrade the rapid heat-extraction function of Al-cladding. Optimum performance and fuel 
stability require a detailed understanding of multicomponent-multiple-phase interdiffusion.
Near Hot Surface
($T_{hot}=740^\circ C$)

Near Cold Surface
($T_{cold}=600^\circ C$)

Fig. 3. Microstructural variation in U-19wt.\%Pu-10wt.\%Zr alloy after 41 days of therмотransport experiments. White and black regions correspond to $\zeta$ and Zr-rich precipitates, while gray region represents a fine mixture of $\alpha$ and $\delta$ phases [7].

Multicomponent Interdiffusion and Determination of Interdiffusion Fluxes

Isothermal interdiffusion flux of a component $i$ in a multicomponent system can be defined as [10-12]:

$$\dot{J}_i = -\sum_{j=1}^{n-1} D_i^{ij} \frac{\partial C_j}{\partial x} \quad (i = 1, 2, ..., n - 1).$$  \hspace{1cm} (1)

where $\dot{J}_i$ is the interdiffusion flux of component $i$, $D_i^{ij}$ is the $(n-1)^2$ interdiffusion coefficient of component $i$ with respect to the concentration gradient of $j$ in an n-component system, and $\frac{\partial C_j}{\partial x}$ is the $(n-1)$ independent concentration gradients. To assess interdiffusion fluxes of individual components during isothermal interdiffusion, Eq. (1) requires knowledge of $(n-1)$ independent concentration gradients and composition-dependent $(n-1)^2$ interdiffusion coefficients that are generally determined using Boltzmann-Matano analysis. This analytical approach may require a large number of experimental diffusion couples, and becomes increasingly difficult to use for quaternary and higher order systems.

Alternatively, the interdiffusion fluxes of individual components may be determined directly from their concentration profiles without the need of the interdiffusion coefficients by [13]:

$$\dot{J}_i = \frac{1}{2t} \int_{x_s}^{x_f} (x - x_s) dC_i \quad (i = 1, 2, ..., n).$$  \hspace{1cm} (2)

where $t$ is the diffusion anneal time. Determination of interdiffusion fluxes using experimental concentration profiles via Eq. (2) can provide direct insight to magnitude and direction of interdiffusion fluxes of individual components, and has lead to noble observations such as zero-flux planes and flux reversals [13,14].

Integrated and Effective Interdiffusion Coefficients

A profile of interdiffusion flux for a component $i$ can be integrated with respect to distance, and this accumulated interdiffusion flux for a component can be defined as an integrated interdiffusion coefficient, $\bar{D}_{i,ax}$ over a selected region, $x_1$ from $x_2$, as [15]:

$$\bar{D}_{i,ax} = \int_{x_1}^{x_2} \dot{J}_i dx.$$  \hspace{1cm} (3)
An effective interdiffusion coefficient, $\tilde{D}_{i}^{\text{eff}}$ over the corresponding composition range, $C_{i}^{\text{e}}$ to $C_{i}^{\text{o}}$, can be then defined as [15]:

$$\tilde{D}_{i}^{\text{eff}} = \frac{D_{i}^{\text{L}}}{C_{i}^{\text{e}} - C_{i}^{\text{o}}}. \quad (4)$$

The $\tilde{D}_{i}^{\text{eff}}$ incorporates multicomponent diffusional interactions for the system to provide an effective value for the interdiffusion of a component as defined by [15]:

$$\tilde{D}_{i}^{\text{eff}} = \tilde{D}_{i}^{0} + \sum_{j \neq i} \frac{\tilde{D}_{j}^{0} \partial C_{j} / \partial x}{\partial C_{i} / \partial x} \quad (j \neq i). \quad (5)$$

Since $\tilde{J}_{i}$ must be continuous at any location, and the effective interdiffusion coefficient can be defined on either side of any location (e.g., $\tilde{D}_{i}^{\text{eff}}$ and $\tilde{D}_{i}^{\text{eff}}$ for the left and right-hand-side of the selected plane, $x_{0}$), the following relation can be defined [16]:

$$\tilde{J}_{i} \bigg|_{x_{0}} = \sqrt{\frac{\tilde{D}_{i}^{\text{eff}}}{\alpha_{i,x}} \left( C_{i}^{\text{e}} - C_{i}^{\text{o}} \right)} = \sqrt{\frac{\tilde{D}_{i}^{\text{eff}}}{\alpha_{i,x}} \left( C_{i}^{\text{o}} - C_{i}^{\text{e}} \right)} \quad (6)$$

where $\alpha_{i,x}$ and $\alpha_{i,x}$ are dimensionless parameters. Eq. (6) is true for any selected plane within the diffusion zone including the Matano plane. For example, based on the experimental concentration profile on one side of the Matano plane, Eq. (6) can be employed to predict the effective interdiffusion coefficient on the other side of the Matano interface provided that $\alpha_{i}$ does not deviate from $\sqrt{\pi}$ [16]. This would be a good assumption for concentration profile that can be modeled using error-function solutions, such as intrinsically fast-diffusing component (e.g., Al in superalloys). A similar equation for $\tilde{D}_{i}^{\text{eff}}$ by substituting Eq. (4) into Eq. (6) can be defined as:

$$\frac{\tilde{D}_{i}^{\text{eff}}}{\tilde{D}_{i}^{0}} = \frac{C_{i}^{\text{o}} - C_{i}^{\text{e}}}{C_{i}^{\text{e}} - C_{i}^{\text{o}}} \quad (7)$$

**Average Interdiffusion Coefficients in Multicomponent Alloys**

For ternary system, the interdiffusion flux $\tilde{J}_{i}$, determined from Eq. (7) as a function of $x$, can be multiplied by $(x-x_{0})^{p}$ and integrated over a selected region, $x_{1}$ to $x_{2}$; in the light of Eq. (1), one gets [17]:

$$\int_{x_{1}}^{x_{2}} \tilde{J}_{i} (x-x_{0})^{p} dx = -\tilde{D}_{i}^{0} \int_{C_{i}(x_{1})}^{C_{i}(x_{2})} (x-x_{0})^{p} dC_{i} - \tilde{D}_{i}^{0} \int_{C_{i}(x_{1})}^{C_{i}(x_{2})} (x-x_{0})^{p} dC_{j} \quad (i,j=1,2). \quad (8)$$

where $\tilde{D}_{i}^{0}$ $(i,j=1,2)$ coefficients are the average values of main and cross-interdiffusion coefficients treated as constants over the selected composition range. For values of $p = 0$ and 1, Eq. (8) yields [17]:

$$\int_{x_{1}}^{x_{2}} \tilde{J}_{i} dx = \tilde{D}_{i}^{0} \left[ C_{i}(x_{1}) - C_{i}(x_{2}) \right] + \tilde{D}_{i}^{0} \left[ C_{j}(x_{1}) - C_{j}(x_{2}) \right] \quad (i,j=1,2). \quad (9)$$
and

$$\int_{x_1}^{x_2} J_i (x-x_j) dx = 2 \tau \left[ \bar{D}_i \left[ \tilde{J}_i (x_1) - \tilde{J}_i (x_2) \right] + \bar{D}_j \left[ \tilde{J}_j (x_1) - \tilde{J}_j (x_2) \right] \right] \quad (i, j = 1, 2). \quad (10)$$

Eqs. (9) and (10) provide four equations involving the $\bar{D}_i$ interdiffusion coefficients and can be set up from interdiffusion fluxes calculated on the basis of Eq. (2) from the concentration profiles of a single diffusion couple in a ternary system. The $\bar{D}_i$ coefficients, characteristic of the diffusion path, can be determined over selected composition ranges that include nonlinear segment of the profiles [17,18].

**Average Interdiffusion Coefficients and Heat of Transport in Multicomponent Alloys**

Under the gradients of temperature (\(\partial T/\partial x\)) and concentrations (\(\partial C_i/\partial x\)), Onsager’s formalism for the interdiffusion flux $\tilde{J}_i$ of component $i$ in a ternary system can be written as [7]:

$$\tilde{J}_i = -C_i \beta_i \dot{Q}_i \frac{1}{T} \frac{\partial T}{\partial x} - \sum_{j=1}^{2} \bar{D}_i \frac{\partial C_j}{\partial x} \quad (i=1,2). \quad (11)$$

where $\beta_i$ and $\dot{Q}_i$ refer to the mobility and heat of transport, respectively. Eq. (11) can be integrated over a selected region, $x_1$ to $x_2$, to yield [7]:

$$\int_{x_1}^{x_2} J_i dx = -\beta_i \dot{Q}_i \frac{1}{T} \frac{\partial T}{\partial C_i} \int_{C_i(x_1)}^{C_i(x_2)} C_i \frac{dT}{T} - \bar{D}_i \left[ \frac{\partial C_j}{\partial C_i} \right] dC_i \quad (i=1,2). \quad (12)$$

and

$$\int_{x_1}^{x_2} (x-x_j) dx = -\beta_i \dot{Q}_i \frac{1}{T} \frac{\partial T}{\partial C_i} \int_{C_i(x_1)}^{C_i(x_2)} C_i \left[ (x-x_j) \frac{dT}{T} - \bar{D}_i \left[ \frac{\partial C_j}{\partial C_i} \right] (x-x_j) dC_i \right] \quad (i=1,2). \quad (13)$$

where

$$\bar{D}_i = \bar{D}_i + \bar{D}_i \frac{\Delta C_j}{\Delta C_i} \quad (i \neq j). \quad (14)$$

Eqs. (12) and (13) provide four equations to determine the average thermotransport coefficients, $\beta_i \dot{Q}_i$, and average effective interdiffusion coefficients, $\bar{D}_i$, over a selected concentration range $\Delta C_i$ in the diffusion zone from experimental concentration profiles. Substituting Eq. (14) into Eqs. (12) and (13) and utilizing the calculated values of $\beta_i \dot{Q}_i$, one can also evaluate average ternary interdiffusion coefficients $\bar{D}_i$ (i,j = 1,2).

**Selection of Ni-base Superalloys for Durable NiAl Coatings**

Commercial superalloys have been developed with compositions and heat treatments to optimize high-temperature strength, as well as resistance against creep, fatigue, oxidation and hot-corrosion [1]. Also, and somewhat in parallel, similar optimizations of the composition for Al$_2$O$_3$-forming NiCoCrAlY and NiAl-based coatings have been carried out to increase the oxidation and hot-corrosion resistance. Considering the significance of diffusional interactions in these systems, the lifetime of the coatings, defined by depletion of Al and dissolution of Al-rich B2 $\beta$-NiAl [5,6], may be enhanced by controlling the interdiffusion
fluxes of individual components, particularly for Al. A system selection/development should be optimized to control the interdiffusion fluxes of diffusing components, so that Al interdiffusion flux across the coating-superalloy interface is minimized.

Diffusion couples consisting of single-phase β-NiAl (hot-extruded with equiaxed-grain diameter of 30–50 µm) vs. various commercial superalloys, namely CM247™, GTD111™, IN738™, IN939™ and Waspalloy™ were examined. The measurement of concentration profiles (and thus interdiffusion fluxes and coefficients) by electron probe microanalysis (EPMA) is difficult for fine two-phase microstructures like that of the γ′ + γ” in Ni-base superalloys. Quantitative determination of interdiffusion fluxes and coefficients can only be carried out from concentration profiles measured in single-phase β-NiAl side of the couple. Then utilizing the general expression of average effective interdiffusion coefficient, Eq. (4), along with mass balance and local continuity of interdiffusion flux, Eq. (6), integrated interdiffusion coefficients and effective interdiffusion coefficients of individual components in superalloys can be predicted using Eqs. (2) through (7).

Backscatter electron micrographs of diffusion couples, NiAl vs. CM247™, GTD111™, IN738™, IN939™ and Waspalloy™ are shown in Fig. 4. Many small precipitates, such as TCP phases rich in refractory, were observed near the interface between NiAl and superalloys. These precipitates also prevent any meaningful determination of concentration profiles by EPMA in these zones, and subsequent analysis. The concentration profiles of the major elements obtained from the diffusion couples of NiAl vs. CM247, GTD111, IN738, IN939 and Waspalloy are shown in Fig. 5. In these profiles, as expected, concentrations determined on the single-phase β-NiAl side are consistent without any scatter, while those on the multiphase superalloy side, including the precipitates near the interface exhibit large scatter.

Integrated, \( \bar{D}_{\text{NiAl}} \) and effective, \( \bar{D}_{\text{NiAl}}^{\text{eff}} \), interdiffusion coefficients for Al in the NiAl side of the diffusion couples was calculated using Eqs. (3) and (4), and are reported in Table I. Then, Eqs. (6) and (7) were employed to predict \( D_{\text{AlSA}}^{\text{eff}} \) and \( \bar{D}_{\text{AlSA}} \) for Al in the superalloy side of the couples as reported in Table I. The \( D_{\text{AlSA}}^{\text{int}} \), provided in Table I is a measure of the integrated interdiffusion flux of Al in diffusion couples. The \( D_{\text{AlSA}}^{\text{int}} \) in Table I is an average effective interdiffusion coefficient of Al in the diffusion couples. In general, superalloys with higher concentration of Cr, Mo and Ti had higher \( D_{\text{AlSA}}^{\text{eff}} \), and higher concentrations of Ta, W and Al in the superalloys were related to lower \( D_{\text{AlSA}}^{\text{eff}} \). These values can be quantitatively employed to design and/or select appropriate compositions of coatings and/or superalloys to minimize degradation due to interdiffusion.

Table I. Integrated and effective interdiffusion coefficients of Al determined from experimental concentration profiles on the NiAl side of the diffusion couples. The integrated and interdiffusion coefficients of Al for the superalloy side of the diffusion couples were predicted based on Eqs. (6) and (7).

<table>
<thead>
<tr>
<th>Superalloy</th>
<th>Constituent Element</th>
<th>( \bar{D}_{\text{NiAl}} )</th>
<th>( \bar{D}_{\text{NiAl}}^{\text{eff}} )</th>
<th>( \bar{D}_{\text{SA}} )</th>
<th>( \bar{D}_{\text{SA}}^{\text{eff}} )</th>
<th>( \bar{D}_{\text{Tot}} )</th>
<th>( \bar{D}_{\text{Tot}}^{\text{eff}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CM-247</td>
<td>Al</td>
<td>1.51</td>
<td>13.55</td>
<td>0.66</td>
<td>2.56</td>
<td>2.17</td>
<td>5.87</td>
</tr>
<tr>
<td>GTD-111</td>
<td>Al</td>
<td>1.50</td>
<td>9.87</td>
<td>0.80</td>
<td>2.80</td>
<td>2.30</td>
<td>5.30</td>
</tr>
<tr>
<td>IN-738</td>
<td>Al</td>
<td>1.91</td>
<td>12.72</td>
<td>1.06</td>
<td>3.90</td>
<td>2.97</td>
<td>6.92</td>
</tr>
<tr>
<td>IN-939</td>
<td>Al</td>
<td>1.56</td>
<td>9.56</td>
<td>0.84</td>
<td>2.74</td>
<td>2.40</td>
<td>5.14</td>
</tr>
<tr>
<td>Waspalloy</td>
<td>Al</td>
<td>2.34</td>
<td>16.16</td>
<td>1.02</td>
<td>3.10</td>
<td>3.36</td>
<td>7.15</td>
</tr>
</tbody>
</table>

Note: All interdiffusion coefficients are reported in \( 10^{-15} \text{ m}^2/\text{sec} \).
Assessment of Diffusional Interactions in Ni-Cr-X (X = Al, Si, Ge or Pd) using Average Interdiffusion Coefficients

Nickel-chromium base alloys are widely used a variety of high-temperature applications due to their combination of good oxidation resistance and excellent high-temperature strength, and are the basis for a number of commercial superalloy families [1,19,20]. Oxidation resistance in these alloys is derived from a continuous, slow-growing, adherent Cr₂O₃-base oxide scale [1,19,20]. In particular, composition in the range of Ni alloyed with 20–30 wt.% Cr have been extensively studied as a model material for Cr₂O₃ scale formation [19,20]. Minor alloying additions (< 5wt.%) can significantly improve the oxidation resistance of Ni-base Cr₂O₃-forming alloys [1,2,22]. Effects include: (1) establishment of continuous Cr₂O₃ scale formation at reduced Cr concentrations; (2) a decrease in the growth rate of Cr₂O₃; and (3) enhanced scale adherence. For example, the addition of Si in Ni-28wt.%Cr promoted formation of both Cr₂O₃ and SiO₂, in which a continuous inner SiO₂ layer acted as a diffusion barrier, and reduced the isothermal oxidation rate by suppressing cation transport through the Cr₂O₃ scale. However, the same inner SiO₂ layer can also reduce the spallation resistance, dependent on the level of Si and the continuity and thickness of the inner SiO₂ layer formed.

Diffusional effects of minor alloy additions may play a significant role in the initial establishment of a continuous protective oxide scale [19,23]. It can also play a significant role in maintaining protective scale growth. For example, the growth of Cr₂O₃ can locally deplete Cr from the alloy in the subsurface region. If the scale is locally damaged or spalled, such depletion can prevent reformation of the Cr₂O₃ scale, and result in a transition to less-protective or non-protective oxidation behavior. Understanding of diffusional interactions in Ni-Cr-X alloys where X represents minor alloying additions can help design Ni-base Cr₂O₃-forming alloys with improved resistance against environmental degradation [23].
In this work, interdiffusion in Ni-22at.%Cr-X (fcc \(\gamma\) phase) alloys with small additions of X (X = Al, Si, Ge, or Pd) was investigated using solid-to-solid diffusion couples annealed at 900\(^\circ\)C for 168 hours. Binary and ternary alloys with compositions reported in Table II were prepared with 99.9% pure Ni, Cr, Al, Si, Ge and Pd by arc melting under an argon atmosphere. Table III presents ternary diffusion couples that were assembled and annealed at 900\(^\circ\)C in a horizontal Lindberg 3-zone furnace for 168 hours. The experimental concentration profiles measured by EPMA with pure standards were smoothened by spline-fit and used to calculate interdiffusion fluxes of individual components, and to determine average effective interdiffusion coefficients \(D_{ij}^{\text{eff}}\), and average ternary interdiffusion coefficients \(D_{ij}^{\text{NI}}\) (i, j = Cr, X). Values of \(D_{ij}^{\text{eff}}\) and \(D_{ij}^{\text{NI}}\) are examined to assess the effects of alloying additions on the interdiffusion behavior of Cr, and the \(\text{Cr}_2\text{O}_3\)-forming ability in Ni-Cr-X alloys.

Table II. Compositions of Ni-Cr-X alloys employed for solid-to-solid diffusion couples.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition (atom fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td>Ni</td>
<td>100.0</td>
</tr>
<tr>
<td>NiCr (X = None)</td>
<td>78.0</td>
</tr>
<tr>
<td>NiCrAl (X = Al)</td>
<td>72.5</td>
</tr>
<tr>
<td>NiCrSi (X = Si)</td>
<td>74.0</td>
</tr>
<tr>
<td>NiCrGe (X = Ge)</td>
<td>76.3</td>
</tr>
<tr>
<td>NiCrPd (X = Pd)</td>
<td>76.1</td>
</tr>
</tbody>
</table>

Table III. List of Ni vs. Ni-Cr-X and NiCr vs. Ni-Cr-X solid-to-solid diffusion couples annealed at 900\(^\circ\)C for 168 hours.

<table>
<thead>
<tr>
<th>Series</th>
<th>Diffusion Couples</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Ni vs. Ni-Cr</td>
</tr>
<tr>
<td>II</td>
<td>Ni vs. Ni-Cr-Al</td>
</tr>
<tr>
<td></td>
<td>Ni vs. Ni-Cr-Si</td>
</tr>
<tr>
<td></td>
<td>Ni vs. Ni-Cr-Ge</td>
</tr>
<tr>
<td></td>
<td>Ni vs. Ni-Cr-Pd</td>
</tr>
<tr>
<td>III</td>
<td>Ni-Cr vs. Ni-Cr-Al</td>
</tr>
<tr>
<td></td>
<td>Ni-Cr vs. Ni-Cr-Si</td>
</tr>
<tr>
<td></td>
<td>Ni-Cr vs. Ni-Cr-Ge</td>
</tr>
<tr>
<td></td>
<td>Ni-Cr vs. Ni-Cr-Pd</td>
</tr>
</tbody>
</table>

Fig. 6 presents examples of experimental and smoothened concentration profiles that were used for the determination of interdiffusion coefficients. Scatters in the concentration profiles for all diffusion couples were minimum and within the experimental uncertainty associated with EPMA. Table IV reports the average effective interdiffusion coefficients \(D_{ij}^{\text{eff}}\)'s determined using Eq. (4) on either side of the Matano plane. In general, \(D_{ij}^{\text{eff}}\) was higher on the \((C^{i}_{j} - C^{i}_{j})\) composition range with higher Cr concentration relative to the other side of the Matano plane. In particular, Al addition to NiCr alloy was observed to increase or decrease the \(D_{ij}^{\text{eff}}\) as a function of composition. This indicates appreciable variation in interdiffusion coefficients as a function of composition: specifically, Al increased \(D_{ij}^{\text{eff}}\) on the \((C^{i}_{j} - C^{i}_{j})\) composition range with higher Cr concentration. \(D_{ij}^{\text{eff}}\) was observed to increase with Si addition to NiCr alloy especially on the \((C^{i}_{j} - C^{i}_{j})\) side with higher Cr concentration. According to Table IV, Ge does not change \(D_{ij}^{\text{eff}}\) significantly, while Pd addition to Ni-Cr alloy increased \(D_{ij}^{\text{eff}}\) quite significant on the \((C^{i}_{j} - C^{i}_{j})\) range with higher Cr concentration.
Figure 6. Typical experimental and smoothed concentration profiles measured from solid-to-solid diffusion couples (a,b) Ni vs. Ni-Cr-Al and (c,d) Ni-Cr vs. Ni-Cr-Si, annealed at 900°C for 168 hours annealed at 900°C for 168 hours.

Table IV. Average effective interdiffusion coefficients \(10^{-16} \text{ m}^2/\text{s}\) determined from Ni vs. Ni-Cr-X diffusion couples annealed at 900°C for 168 hours.

<table>
<thead>
<tr>
<th>Diffusion Couple</th>
<th>Composition Range</th>
<th>(\tilde{D}_{\text{Cr}}^{\text{eff}})</th>
<th>(\tilde{D}_{X}^{\text{eff}})</th>
<th>(\tilde{D}_{\text{Ni}}^{\text{eff}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni vs. Ni-Cr (X = None)</td>
<td>(C_{i}^{+} \sim C_{i}^{-})</td>
<td>1.40</td>
<td>-</td>
<td>1.40</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Al (X = Al)</td>
<td>(C_{i}^{+} \sim C_{i}^{-})</td>
<td>1.53</td>
<td>-</td>
<td>1.53</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Si (X = Si)</td>
<td>(C_{i}^{+} \sim C_{i}^{-})</td>
<td>1.58</td>
<td>4.68</td>
<td>2.19</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Ge (X = Ge)</td>
<td>(C_{i}^{+} \sim C_{i}^{-})</td>
<td>1.68</td>
<td>5.74</td>
<td>2.26</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Pd (X = Pd)</td>
<td>(C_{i}^{+} \sim C_{i}^{-})</td>
<td>1.44</td>
<td>3.47</td>
<td>1.61</td>
</tr>
</tbody>
</table>

Table V presents the average ternary interdiffusion coefficients, \(\tilde{D}_{G,ij}^{\text{Ni}}(i,j = \text{Cr, X})\) determined on either side of the Matano plane using Eqs. (9) and (10). It should be noted that these diffusion couples were designed to yield the same sign of \(\partial C_{i}/\partial x\) and \(\partial C_{X}/\partial x\). Thus, positive and negative \(\tilde{D}_{G,XX}^{\text{Ni}}\) indicates an increase and a decrease in \(J_{j_{i}}\), respectively. In general, larger magnitude of \(\tilde{D}_{G,XX}^{\text{Ni}}\) and \(\tilde{D}_{G,XX}^{\text{Ni}}\) were observed on the \(C_{i}^{+} \sim C_{i}^{-}\) composition range with higher Cr concentration. The Al addition in the Ni-Cr alloy yielded positive \(\tilde{D}_{G,XX}^{\text{Ni}}\), and increased \(J_{\text{Cr}}\) in accordance with previous work [23]. The magnitude of \(\tilde{D}_{G,XX}^{\text{Ni}}\) was quite large as reported in Table V on the \(C_{i}^{+} \sim C_{i}^{-}\) with higher Cr concentration. Similarly, Si, Ge
and Pd additions to Ni-Cr alloy increased $\dot{J}_{\text{Cr}}$ with positive $\overline{D}_{\text{NiCr}}^{\text{Ni}}$. This effect was, again, stronger when Cr concentration is high on the $\left(C_i^a - C_i^e\right)$ side particularly for Si and Pd. Diffusion couple series III was designed with initial $\partial C_{\text{Cr}}/\partial x = 0$, so that $\dot{J}_{\text{Cr}}$ is largely due to $\partial C_{\text{X}}/\partial x$, and depends on the magnitude and sign of $\overline{D}_{\text{CrX}}^{\text{Ni}}$. $\dot{J}_x$ has caused an uphill-diffusion of Cr in the direction of $\dot{J}_x$ with positive $\overline{D}_{\text{CrX}}^{\text{Ni}}$ for Al and Si as presented in Table VI. On the other hand, $\dot{J}_x$ and $\dot{J}_y$ did not cause any measurable redistribution of Cr ($\dot{J}_{\text{Cr}} = 0$). It should be noted that Ge and Pd have lower contents in the Ni-Cr-X alloys than Al and Si, as reported in Table II.

Based on average effective interdiffusion coefficients and average ternary interdiffusion coefficients determined in this study, alloying additions of Al, Si, Ge and Pd have all increased $\overline{D}_{\text{Cr}}^{\text{Ni}}$ and yielded positive $\overline{D}_{\text{CrX}}^{\text{Ni}}$ particularly with high Cr content (-22 at.%). Therefore, the Cr$_2$O$_3$-forming ability of Ni-20at.%Cr-base alloy should improve with these alloying additions by establishing Cr$_2$O$_3$ scale, maintaining protective Cr$_2$O$_3$ scale formation, and in reformation of Cr$_2$O$_3$ upon spallation. It should be noted that positive $\overline{D}_{\text{CrX}}^{\text{Ni}}$ reported in Tables V and VI should also promote the formation of other scales (Al$_2$O$_3$, SiO$_2$) in the $\gamma$ (fcc) Ni-Cr alloy, which may reduce the rate of scale growth and/or change the thermo-mechanical properties of the scale.

<table>
<thead>
<tr>
<th>Diffusion Couple</th>
<th>Composition Range</th>
<th>$\overline{D}_{\text{CrCr}}^{\text{Ni}}$</th>
<th>$\overline{D}_{\text{CrX}}^{\text{Ni}}$</th>
<th>$\overline{D}_{\text{XCr}}^{\text{Ni}}$</th>
<th>$\overline{D}_{\text{XX}}^{\text{Ni}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni vs. Ni-Cr-Al (X = Al)</td>
<td>$\left(C_i^a - C_i^e\right)$</td>
<td>0.78</td>
<td>0.31</td>
<td>0.40</td>
<td>1.99</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Si (X = Si)</td>
<td>$\left(C_i^a - C_i^e\right)$</td>
<td>1.11</td>
<td>1.72</td>
<td>0.43</td>
<td>2.84</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Ge (X = Ge)</td>
<td>$\left(C_i^a - C_i^e\right)$</td>
<td>2.05</td>
<td>4.88</td>
<td>0.57</td>
<td>3.35</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Pd (X = Pd)</td>
<td>$\left(C_i^a - C_i^e\right)$</td>
<td>1.08</td>
<td>0.36</td>
<td>0.07</td>
<td>1.73</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Pd (X = Pd)</td>
<td>$\left(C_i^a - C_i^e\right)$</td>
<td>1.24</td>
<td>0.89</td>
<td>0.10</td>
<td>1.99</td>
</tr>
</tbody>
</table>

Table VI. Average ternary interdiffusion coefficients ($10^{-16} \text{ m}^2/\text{s}$) determined from Ni-Cr vs. Ni-Cr-X diffusion couples annealed at 900°C for 168 hours.

<table>
<thead>
<tr>
<th>Diffusion Couple</th>
<th>Composition Range</th>
<th>$\overline{D}_{\text{CrCr}}^{\text{Ni}}$</th>
<th>$\overline{D}_{\text{CrX}}^{\text{Ni}}$</th>
<th>$\overline{D}_{\text{XCr}}^{\text{Ni}}$</th>
<th>$\overline{D}_{\text{XX}}^{\text{Ni}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Cr vs. Ni-Cr-Al (X = Al)</td>
<td>$\left(C_i^c - C_i^e\right)$</td>
<td>0.23</td>
<td>0.12</td>
<td>0.01</td>
<td>0.67</td>
</tr>
<tr>
<td>Ni-Cr vs. Ni-Cr-Al (X = Al)</td>
<td>$\left(C_i^c - C_i^e\right)$</td>
<td>1.20</td>
<td>0.44</td>
<td>0.13</td>
<td>1.17</td>
</tr>
<tr>
<td>Ni-Cr vs. Ni-Cr-Si (X = Si)</td>
<td>$\left(C_i^c - C_i^e\right)$</td>
<td>2.58</td>
<td>1.73</td>
<td>0.01</td>
<td>0.68</td>
</tr>
<tr>
<td>Ni-Cr vs. Ni-Cr-Pd (X = Pd)</td>
<td>$\left(C_i^c - C_i^e\right)$</td>
<td>1.39</td>
<td>0.63</td>
<td>1.78</td>
<td>1.97</td>
</tr>
</tbody>
</table>

$\Delta C_{\text{Cr}}/\Delta x = 0$ and could not be determined for Ni-Cr vs. Ni-Cr-Ge and Ni-Cr-Pd couples.
Non-isothermal Thermotransport in U-Pu-Zr Alloys

An U-19wt.%Pu-10wt.%Zr alloy rod was annealed under a temperature gradient of 220°C/cm with one end maintained at 740°C and the other end at 600°C for 41 days [7]. The observed redistribution of U, Pu and Zr was analyzed with due consideration of thermotransport and ternary diffusional interactions among the components. The concentration profiles of U, Pu and Zr in the γ(bcc) phase region of the alloy are shown in Fig. 7(a), from which interdiffusion fluxes of the components were determined by using Eq. (2).

Eqs. (12) and (13) provides four equations to determine the average thermotransport coefficients, \( \beta_i Q_i \), and average effective interdiffusion coefficients, \( D_e^{ij} \), over a selected concentration range \( \Delta C_i \) in the diffusion zone from experimental concentration profiles. Substituting Eq. (14) into Eqs. (12) and (13) and utilizing the calculated values of \( \beta_i Q_i \), one can also evaluate average ternary interdiffusion coefficients \( D_0^{ij} (i,j = 1,2) \). From the redistribution profiles of the constituents shown in Fig. 7(a), \( \beta_i Q_i \), \( D_e^{ij} \) and \( D_0^{ij} \) coefficients were determined over three selected regions, I, II, III, and are reported in Table VII.

Values of \( \beta_i Q_i \) and \( D_0^{ij} (i,j = 1,2) \) coefficients presented in Table VII were employed for estimating the three flux contributions, \( \dot{J}_{U,T/\alpha}, \dot{J}_{U,Cu/\alpha}, \dot{J}_{U,Zr/\alpha} \), arising from the gradients of temperature, U concentration, and Zr concentration, respectively [7]. In Fig. 7(b) are presented these contributions to the flux of Zr in the region I. The magnitude of the flux contributions arising from the gradients of U and Zr are much greater than that of the flux due to the temperature gradient. However, the \( \dot{J}_{U,Cu/\alpha} \) and \( \dot{J}_{U,Zr/\alpha} \) terms are opposite in sign and their sum is quite small compared to \( \dot{J}_{U,T/\alpha} \) as seen in Fig 7(b). The net interdiffusion flux of Zr is negative and contributes to the build-up of Zr in the hot-end region of the sample during annealing of the U-Pu-Zr alloy under a temperature gradient.

---

Fig. 7. (a) Experimental concentration profiles for U, Pu and Zr in the γ phase under the gradients of temperature and concentrations. (b) Estimated contributions from the gradients of temperature and concentrations of U and Zr to the interdiffusion flux of Zr in region I.
Table VII. $\beta_i Q_i$, $D^e_{ij}$ and $D^p_{ij}(i, j = U, Zr)$ coefficients calculated from the redistribution of U, Pu and Zr under the gradients of temperature and concentrations.

<table>
<thead>
<tr>
<th>Region in the $\gamma$</th>
<th>Location (µm)</th>
<th>$\beta_i Q_i$ ($10^4$ cm$^2$/sec)</th>
<th>$D^e_{ij}$ ($10^{-10}$ cm$^2$/sec)</th>
<th>$D^p_{ij}$ ($10^{-9}$ cm$^2$/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0-1000</td>
<td>0.7</td>
<td>1.2</td>
<td>-5.5</td>
</tr>
<tr>
<td>II</td>
<td>1000-2450</td>
<td>0.7</td>
<td>1.7</td>
<td>-6.8</td>
</tr>
<tr>
<td>III</td>
<td>2450-4015</td>
<td>1.1</td>
<td>1.7</td>
<td>-8.6</td>
</tr>
</tbody>
</table>

*not calculated due to uncertainties in the concentration profiles.

Refined Assessment of Average Interdiffusion Coefficients in Multicomponent Alloys

Although the use of Eqs. (9) and (10) for ternary systems is valid over a large composition range with non-linear segment of concentration profiles, use of Eq. (8) for the determination of average interdiffusion coefficients can be extended with multiple and higher “p” values for refined assessment of average multicomponent interdiffusion coefficients. It is evident that Eq. (8) can be written to provide (n-1)$^2$ equations involving the (n-1)$^2$ $D^e_i$ interdiffusion coefficients from (n-1) independent concentration profiles. Figs. 8 and 9 presents experimental (dotted lines) and calculated (solid lines) concentration profiles of Fe-Ni-Al diffusion couples, where $D^e_i$ coefficients were calculated using Eq. (8) with p = 0 and p = 1, 2, ..., 50. Accurate $D^e_i$ coefficients that are consistent with Boltzmann-Matano analysis can be obtained using the following criteria in sequence:

1. $D^e_i$ at p = 0 (extrapolated) if $\frac{\partial D^e_i}{\partial p} \rightarrow 0$ as p → 0 (for error-function profiles).
2. $D^e_i$ at p where $\frac{\partial D^e_i}{\partial p} = 0$ (see Fig. 8).
3. $D^e_i$ at p = 0 (extrapolated) if $\frac{\partial D^e_i}{\partial p} \neq 0$ at any p (see Fig. 9).

This refined approach for the determination of average multicomponent interdiffusion coefficients can be applied to near-linear segment of the concentration profiles (e.g., Fig. 8). Applicability of this technique is currently being examined for small composition ranges and higher-order systems.

Summary

Importance of multicomponent-multiphase interdiffusion was highlighted with selected examples from materials and coatings employed in gas turbines and nuclear fuels. Alternative methods to determine interdiffusion fluxes, integrated interdiffusion coefficients, effective interdiffusion coefficients, average multicomponent interdiffusion coefficients were presented along with their applications for components in advanced energy production systems including oxidation resistance/thermal barrier coatings, Cr$_2$O$_3$-forming Ni-Cr alloys, and U-Pu-Zr alloys. Alternative approach to accurately assess composition-dependent interdiffusion coefficients is continuously being examined for multicomponent alloys.
Fig. 8. Experimental (dotted lines) and calculated (solid lines) concentration profiles, and variation in $\overline{D}_1^j$ as a function of “p” on either side of the Matano plane for Fe-Ni-Al (B2) diffusion couples $\beta_8$ vs. $\beta_9$ annealed at 1000°C for 96 hours.

Fig. 9. Experimental (dotted lines) and calculated (solid lines) concentration profiles, and variation in $\overline{D}_1^j$ as a function of “p” on either side of the Matano plane for Fe-Ni-Al (B2) diffusion couples $\beta_5$ vs. $\beta_6$ annealed at 1000°C for 96 hours.

Acknowledgement

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References

Microstructure and Residual Stress of Alumina Scale Formed on Ti$_2$AlC at High Temperature in Air

J. W. Byeon · J. Liu · M. Hopkins · W. Fischer ·
N. Garimella · K. B. Park · M. P. Brady ·
M. Radovic · T. El-Raghy · Y. H. Sohn

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Abstract Ti$_2$AlC ternary carbide is being explored for various high temperature applications due to its strength at high temperatures, excellent thermal-shock resistance, and high electrical conductivity. A potential advantage of Ti$_2$AlC over conventional Al$_2$O$_3$-forming materials is the near-identical coefficient of thermal expansion (CTE) of Ti$_2$AlC and α-Al$_2$O$_3$, which could result in superior spallation resistance and make Ti$_2$AlC a promising option for applications ranging from bondcoats for thermal barrier coatings to furnace heating elements. In this study,

J. W. Byeon · J. Liu · M. Hopkins · N. Garimella · Y. H. Sohn
Advanced Materials Processing and Analysis Center and Department of Mechanical,
Materials and Aerospace Engineering, University of Central Florida, Orlando, FL, USA
E-mail: ysohn@mail.ucf.edu

W. Fischer
University High School, Orange County Public Schools, Central Florida Space Science Institute
through National Science Foundation (NSF) Research Experience for Teachers (RET) Program,
Orlando, FL, USA

K. B. Park
Department of Materials Science and Engineering, Andong National University, Andong,
Kyungbuk, Korea

M. P. Brady
Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA

M. Radovic
Department of Mechanical Engineering, Texas A&M University, College Station, TX, USA

T. El-Raghy
3-one-2, LLC, Voorhees, NJ, USA

Present Address:
J. W. Byeon
Materials Science and Engineering, University of Ulsan, Ulsan, Kyungnam, Korea
isothermal and cyclic oxidation were performed in air to examine the oxidation behavior of Ti$_2$AlC. Isothermal oxidation was performed at 1000, 1200 and 1400 °C for up to 25 h and cyclic oxidation consisted of 1,000 1-hour cycles at 1200 °C. Characteristics of the oxide scale developed in air, including mass change, residual stress in the $\alpha$-Al$_2$O$_3$ scale, phase constituents and microstructure, were examined as functions of time and temperature by thermogravimetry, photostimulated luminescence, x-ray diffraction, scanning electron microscopy, and transmission electron microscopy via focused ion beam in situ lift-out. Above a continuous and adherent $\alpha$-Al$_2$O$_3$ layer, a discontinuous-transient rutile-TiO$_2$ scale was identified in the oxide scale developed at 1000 and 1200 °C, while a discontinuous-transient Al$_2$TiO$_5$ scale was identified at 1400 °C. The continuous $\alpha$-Al$_2$O$_3$ scale thickened to more than 15 μm after 25 h of isothermal oxidation at 1400 °C, and after 1,000 1-hour cycles at 1200 °C, yet remained adherent and protective. The compressive residual stress determined by photoluminescence for the $\alpha$-Al$_2$O$_3$ scale remained under 0.65 GPa for the specimens oxidized up to 1400 °C for 25 hours. The small magnitude of the compressive residual stress may be responsible the high spallation-resistance of the protective $\alpha$-Al$_2$O$_3$ scale developed on Ti$_2$AlC, despite the absence of reactive element additions.

**Keywords** Ti$_2$AlC · Coefficient of thermal expansion · Ternary carbide · Oxidation · Residual stress · Photoluminescence spectroscopy · Transmission electron microscopy

**Introduction**

The MAX phases are ternary compounds such as Ti$_3$SiC$_2$, Ti$_3$AlC$_2$, Ti$_2$AlC, and Ti$_2$AlN that consist of an early transition metal (M), a IIIA or IVA element (A), and nitrogen or carbon as a third element (X). MAX phases can possess a combination of metallic and ceramic behaviors: good high temperature strength, machinability, excellent thermal shock resistance, good electrical/thermal conductivity, good oxidation resistance, low density and low thermal expansion coefficient [1–11]. Thus, fabrication processes and properties of various MAX phases are being explored for various high temperature applications ranging from bondcoats for thermal barrier coatings to furnace heating elements. Of the phases in the Ti–Al–C ternary system, Ti$_2$AlC has the lowest density, about 4.11 g/cm$^3$, and is one of the most thermodynamically stable [12]. Following the successful fabrication of fully-dense polycrystalline Ti$_2$AlC [13–15], its mechanical and electrical properties have been investigated with regard to high temperature applications [14, 15].

Oxidation resistance is one of the critical properties of MAX phases for high temperature applications [16–18]. Wang et al. [8, 19] reported that the oxidation resistance of Al$_2$O$_3$-forming Ti$_3$AlC$_2$ was superior to that of SiO$_2$-forming Ti$_3$SiC$_2$. Sundberg et al. [20] have also reported the oxidation kinetics and phase constituents of the scale.

In this paper, we examined the characteristics of the oxide scale formed during isothermal and cyclic oxidation of Ti$_2$AlC at high temperatures ranging from 1000 to 1400 °C in air. The characteristics of the oxide scale analyzed include: (1) mass-
gain continuously determined by thermo-gravimetric analysis as a function of time of oxidation; (2) residual stress in the α-Al₂O₃ scale determined by non-destructive photostimulated luminescence (PL) spectroscopy, and (3) microstructural development of the phase constituents in the oxide scale by X-ray diffraction (XRD) and cross-sectional electron microscopy including scanning electron microscopy (SEM) and transmission electron microscopy (TEM) via focused ion beam in situ lift-out (FIB-INLO) specimen preparation [21]. This study focused on how the relatively low CTE of Ti₂AlC, nearly identical to α-Al₂O₃, would affect the scale residual stress and spallation resistance. This was of particular interest because conventionally available Fe- and Ni-base Al₂O₃ forming alloys have relatively high CTE’s and typically require reactive element additions to improve the spallation resistance [22].

Experimental Procedure

Rods of polycrystalline Ti₂AlC [13–15] with a diameter of 15 mm were supplied by 3-ONE-2™, LLC, USA (Vorhees, NJ, USA). Impurity content in Ti₂AlC was analyzed by glow-discharge mass spectroscopy and interstitial gas analysis (Shiva Technologies, Evans Analytical Group, Syracuse, NY 13211). Tabulated results are presented in Table 1. The Ti₂AlC rods were sectioned into 1 mm thick disks by using a low-speed diamond wafering blade. Both sides of each disk were polished with SiC paper (600 grit). Kinetics of oxidation was examined at 1000, 1200, and 1400 °C in air by thermo-gravimetric analysis (TGA) using TA Instrument™ (New Castle, DE, USA) STS1100. Specimens were placed in an alumina crucible and were heated at a rate of 20 °C per minute to desired temperature while purging Ar at a rate of 100 mL per minute to minimize any oxidation during heating. Upon reaching the specified temperature, purging Ar was replaced with air. Mass change

Table 1 Impurity content in as-received Ti₂AlC analyzed by glow-discharge mass spectroscopy and interstitial gas analysis (Shiva Technologies, Evans Analytical Group, Syracuse, NY 13211)

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Impurity Constituents</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5 wt.%</td>
<td>Sr</td>
</tr>
<tr>
<td>2.2 wt.%</td>
<td>O²⁻</td>
</tr>
<tr>
<td>1.1 wt.%</td>
<td>Fe, Mo</td>
</tr>
<tr>
<td>&lt; 1000 ppm wt.</td>
<td>N²⁺, Si, Y</td>
</tr>
<tr>
<td>&lt; 100 ppm wt.</td>
<td>P, Cl, V, Cr, Mn, Ni, Ga, Cu, Zr, Nb, Hf, Ta, W</td>
</tr>
<tr>
<td>&lt; 10 ppm wt.</td>
<td>B, S²⁺, Mg, K, Ca, Co, As, Se, Rb, Ag, Sn, Sh, Ba, Pb</td>
</tr>
<tr>
<td>&lt; 1.0 ppm wt.</td>
<td>Na, Ge, Br, Rh, Pd, Cd, La, Re, Pt, Bi</td>
</tr>
<tr>
<td>&lt; 0.1 ppm wt.</td>
<td>F, Sc, Zn, Ru, Te, Ir, Au, Hg, U</td>
</tr>
<tr>
<td>&lt; 0.01 ppm wt.</td>
<td>Li, Be, Cs, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Os, Ti, Th</td>
</tr>
</tbody>
</table>

Note: * denotes results from interstitial gas analysis
due to oxidation, normalized by the initial mass, was continuously recorded as a function of time at each temperature.

In addition, isothermal oxidation in air at 1000, 1200, and 1400 °C as a function of time, ranging from 30 s up to 25 h, was carried out using a CM™ Rapid Temperature Furnace (Bloomfield, NJ, USA) where each temperature was forced-air-quenched to room temperature. Cyclic oxidation at 1200 °C in air was also carried out using specimens suspended by Pt wire in a vertical furnace. Mass change was measured as a function of number of thermal cycles up to 1,000 cycles. The 1-hour thermal cycle consists of 10-minute heat-up, 1-hour dwell at 1200 °C, and 10-minute forced-air-quench.

The residual stress in the α-Al₂O₃ scale developed after isothermal and cyclic oxidation was determined by PL spectroscopy [23]. A Renishaw (Gloucestershire, United Kingdom) 1000B Ramanscope™ with Ar-ion laser source (wavelength of 514 nm) for the optical excitation, charge-coupled device (CCD) detectors, and a software package (GRAMS™) for spectrum analysis, was used. Luminescence spectra were collected at room temperature from over 15 randomly selected locations for each specimen. The magnitude of shift in luminescence was analyzed to determine the residual stress in the α-Al₂O₃ scale [23].

Microstructure of the oxide scale was characterized by XRD, SEM, TEM and scanning TEM (STEM). Detailed cross-sectional microstructure of the scale was observed by Philips/Tecnai (FEI Company, Hillsboro, OR, USA) F30™ 300 KeV TEM using selected-area electron diffraction (SAD), high angle annular dark field (HAADF) imaging, and X-ray energy dispersive spectroscopy (XEDS). Focused ion beam in situ lift-out technique (FIB-ILNO) was employed to prepare site-specific cross-sectional TEM specimens of thin and brittle oxide scale [21].

Results and Discussion

Overall Kinetics of Oxidation

Figure 1(a) shows normalized weight change of Ti₂AlC as a function of oxidation time at 1000, 1200°C, and 1400 °C in air. Wang et al. [14] reported cubic-rate for the oxidation of Ti₂AlC for a temperature range from 1000 to 1300 °C in air, while Sonderberg et al. [15] reported parabolic rate of oxidation at 1100, 1200, 1300 °C in air. Our study finds that although a cubic growth rate of an oxide scale may best represent the overall oxide growth kinetics of Ti₂AlC as presented in Fig. 1(b), such a simple description of growth kinetics based on simple rate constant, regardless of whether it is parabolic or cubic, may not be sufficient since three oxide-phases co-exist in the scale (see Fig. 3).

Figure 2 shows the changes in specific mass gain of Ti₂AlC with 1-hour thermal cycling at 1200 °C in air compared with benchmark Al₂O₃-forming oxidation-resistant alloys. Although the rate of mass gain is the highest for Ti₂AlC, the observed rate under these aggressive test conditions is still low (and protective). More importantly, mass loss due to scale spallation was not observed during cyclic oxidation up to 1,000 cycles indicating a high degree of spallation resistance.
Fig. 1 (a) Normalized weight change of Ti₂AlC as a function of oxidation time at 1000, 1200 and 1400 °C. (b) Cubical growth rate of the oxide scale best describes the overall growth kinetics.

superior to that of un-doped NiAl, Hf-doped Ni₃Al, Y/Hf-doped NiCrAl, as presented in Fig. 2 [24].

Phase Constituents and Microstructure of the Oxide Scale

Figure 3 presents XRD patterns from the oxide scale formed after isothermal oxidation at 1200 and 1400 °C. All specimens prior to oxidation consist of Ti₂AlC, although trace amounts of Ti₃AlC₂ were observed via electron microscopy. XRD patterns from the oxide scale formed at 1000 °C are similar to those obtained from specimens oxidized at 1200 °C with the main difference being the lower intensity from oxide phases. At 1000 and 1200 °C, both rutile-TiO₂ and α-Al₂O₃ scales formed in accordance with Wang et al. [19]. No residual meta-stable Al₂O₃ was detected even in the specimen oxidized for 30 min at 1200 °C as shown in Fig. 3(a). With an increase in time of oxidation, the intensity of XRD peaks associated with
Fig. 2 Mass changes per unit area for various $\text{Al}_2\text{O}_3$-forming alloys during thermal cyclic oxidation at 1200 °C

Fig. 3 X-ray diffraction patterns from the oxide scale formed on Ti$_2$AlC as a function of time of isothermal oxidation at (a) 1200 °C and (b) 1400 °C

$\alpha$-$\text{Al}_2\text{O}_3$ increased while that of rutile-$\text{TiO}_2$ remained the same after transient formation during the initial stage of oxidation.

The Al$_2$TiO$_5$ phase in the oxide scale was observed in the specimens oxidized at 1400 °C as shown in Fig. 3(b). XRD peaks from rutile-$\text{TiO}_2$ decreased in intensity with time of oxidation at 1400 °C and disappeared after 10 h of oxidation at 1400 °C. The Al$_2$TiO$_5$ can form by a solid-state reaction of Al$_2$O$_3$ and TiO$_2$ with a very low free energy of formation at temperatures above 1300 °C [25]. Figure 4 shows the XRD pattern of Ti$_2$AlC after 1,000 1-hour thermal cycles at 1200 °C. Similar to the isothermal oxidation at 1200 °C, formation of rutile-$\text{TiO}_2$ and $\alpha$-$\text{Al}_2\text{O}_3$
Fig. 4 X-ray diffraction pattern from the oxide scale formed on Ti$_2$AlC after 1,000 thermal cycles of oxidation at 1200 °C with the dwell time of 1 h

was observed. The diffraction peaks of $\alpha$-Al$_2$O$_3$ were very intense relative to those of rutile-TiO$_2$ after prolonged growth of thick $\alpha$-Al$_2$O$_3$ scale.

For Ti$_2$AlC, the oxide scale developed after isothermal oxidation at 1000 and 1200 °C consisted of an inner Al-rich continuous scale and an outer Ti-rich discontinuous scale as shown by backscatter electron micrographs in Fig. 5. Formation of Ti$_2$AlC$_2$ due to depletion of Al and a few localized regions of internal oxidation (presumably due to pores within Ti$_2$AlC) was observed near the surface. Based on EDS analysis of the scale, the lighter gray region below the epoxy mount is the Ti-rich discontinuous scale and the darker gray layer underneath is the Al-rich continuous scale as indicated in Fig. 5(c). The inner Al-rich scale looks dense and adherent to Ti$_2$AlC. Based on the XRD analysis presented in Fig. 3 and EDS analysis, the inner and outer scales can be identified as $\alpha$-Al$_2$O$_3$ and rutile-TiO$_2$, respectively. Two distinctive morphologies of the oxide scale were observed from

Fig. 5 Cross-sectional backscatter electron micrographs of oxide scale developed on Ti$_2$AlC after isothermal oxidation at 1200 °C for (a) 1 (b) 5 and (c) 25 h. (d) Two distinctive morphologies of the oxide scale were observed from the top surface of oxidized Ti$_2$AlC at 1200 °C for 25 h.
the top surface of the specimens oxidized at 1200 °C for 25 h as presented in Fig. 5(d). Large bright grains on top and small dark ones underneath correspond to rutile-TiO₂ and α-Al₂O₃, respectively.

Cross-sectional backscatter electron micrographs and EDS from the oxide scale formed on the specimens oxidized at 1400 °C for 30 s up to 25 h are presented in Fig. 6. Like Ti₂AlC oxidized at 1000 and 1200 °C, the inner continuous scale was rich in Al. However, the outer discontinuous scale for specimens oxidized at 1400 °C consisted of Al/Ti-rich TiAl₂O₅ scale as presented in Fig. 6(d). The protective α-Al₂O₃ scale formed at 1400 °C was adherent and grew as thick as approximately 20 μm without apparent spallation after oxidation for 25 h as shown in Fig. 6(c). A few internally oxidized particles were observed at all temperatures as presented in Figs. 5 and 6.

No spallation was observed for the α-Al₂O₃ scale as thick as 15 μm formed during 1,000 1-hour thermal cycles at 1200 °C as presented by backscatter electron micrograph in Fig. 7. This microstructural observation supports the result of a continuous increase in mass with thermal cycling presented in Fig. 2.

Detailed cross-sectional microstructure of the oxide scale developed during the initial isothermal oxidation at 1400 °C for 30 s was examined by TEM as shown in Fig. 8. In accordance with XRD and SEM results, the oxide scale consisted of a continuous α-Al₂O₃ layer near to Ti₂AlC, and a mixed oxides layer of rutile-TiO₂ and Al₂TiO₅ phases above the protective α-Al₂O₃ scale. For the Ti₃AlC₂ sample oxidized at 1400 °C, it was reported [8] that voids and Al₂TiO₅ complex oxide particles formed at the interface between α-Al₂O₃ scale and Ti₃AlC₂ substrate. However, in this study, no void was observed along the interface between Ti₂AlC

![Fig. 6 Cross-sectional backscatter electron micrographs of oxide scale developed on Ti₂AlC after isothermal oxidation at 1400 °C for (a) 30 s (b) 5 and (c) 25 h. (d) The TiO₂ external scale reacted with Al₂O₃ to form Al₂TiO₅ based on EDS](image)

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and continuous $\alpha$-$\text{Al}_2\text{O}_3$ scale, although chained-voids existed at the interface between continuous $\alpha$-$\text{Al}_2\text{O}_3$ layer and the thin-transient mixed oxide layer. This work suggests that the oxidation resistance of $\text{Ti}_2\text{AlC}$ may be better than that of $\text{Ti}_3\text{AlC}_2$ under the oxidation conditions employed in this study.

Photoluminescence and Residual Stress of the Oxide Scale

PL spectroscopy was utilized to determine the residual stress in the $\alpha$-$\text{Al}_2\text{O}_3$ scale. For all oxidized $\text{Ti}_2\text{AlC}$ specimens, ruby luminescence ($R_1$ and $R_2$) from $\alpha$-$\text{Al}_2\text{O}_3$ was observed without any observable luminescence from metastable polymorphs (i.e., $\theta$-$\text{Al}_2\text{O}_3$ and $\gamma$-$\text{Al}_2\text{O}_3$). Figure 9 shows typical PL spectra as a function of oxidation time at 1000 °C. The frequency of $R_1$ and $R_2$ shifted to lower wavenumber than those of standard ruby luminescence (i.e., 14402 and 14432 cm$^{-1}$, respectively). This indicates that the scale is under residual compression [23].

The magnitude of compressive residual stress within the $\alpha$-$\text{Al}_2\text{O}_3$ scale was examined as a function of temperature and time of isothermal oxidation as reported in Table 2 and presented in Fig. 10. The magnitude of compressive residual stress within the $\alpha$-$\text{Al}_2\text{O}_3$ scale determined after 1,000 thermal cycles at 1200 °C is also presented in Fig. 10. The method to calculate the magnitude of residual stress, based on frequency shift via piezoelectric coefficients, has been developed for the $\alpha$-$\text{Al}_2\text{O}_3$ scale without any presence of other oxides [23]. Thus, in this study, the calculation of the compressive residual stress determined for the $\alpha$-$\text{Al}_2\text{O}_3$ assumes that the presence of other oxide phases such $\text{TiO}_2$ and $\text{Al}_2\text{TiO}_4$ does not affect the assumptions employed in calculation.

Overall, the magnitude of compressive residual stress was at most 0.65 GPa for $\text{Ti}_2\text{AlC}$ specimen oxidized at 1400 °C as reported in Fig. 10. This value is much smaller than 2–5 GPa reported for other $\alpha$-$\text{Al}_2\text{O}_3$-forming high temperature materials and coatings such as FeCrAlY [26] and NiAl [27]. The standard deviation in the magnitude of the compressive residual stress, based on minimum of 15 measurements at random locations, was very small for all specimens as reported in Table 2. The small (i.e., magnitude) and homogeneous (i.e., small standard
Fig. 8 (a) Cross-sectional bright-field image of oxide scale developed on Ti$_2$AlC after isothermal oxidation at 1400 °C for 30 s. The scale consisted of α-Al$_2$O$_3$, (b) rutile-TiO$_2$ and Al$_2$TiO$_5$
Fig. 9 Typical photoluminescence spectra from the z-Al₂O₃ scale on Ti₃AlC as a function of time of isothermal oxidation at 1000 °C.

deviation) compressive residual stress of the z-Al₂O₃ scale is considered to play a significant role in the excellent adherence of the scale that has a thickness of over 15 μm after cyclic oxidation of 1,000 1-hour cycles at 1200 °C and isothermal oxidation of 25 h at 1400 °C.

The small magnitudes of compressive residual stress in the z-Al₂O₃ formed on Ti₃AlC may be explained by a simple estimation of thermal stress induced upon cooling due to thermal expansion mismatch between Al₂O₃ and Ti₃AlC substrate. Thermal stress within the oxide scale is estimated by [28]:

\[
\sigma_{\text{ox}} = \frac{E_{\text{ox}}}{(1 - \nu_{\text{ox}})} \left( \frac{\alpha_{\text{ox}} - \alpha_s}{E_s(1 - \nu_s)} \right) \Delta T
\]

where, \( \sigma \), \( E \), \( \nu \), \( \alpha \), \( \Delta T \), and \( h \) represent thermal stress, Young’s modulus, Poisson’s ratio, thermal expansion coefficient, temperature difference upon cooling, and thickness, respectively. The subscripts ox and s refer to oxide scale and substrate, respectively. Thermal expansion coefficient of Ti₃AlC was determined as 9.62 × 10⁻⁶/K from dilatometer measurement in the temperature range up to 1000 °C as shown in Fig. 11. This is significantly lower than conventional Fe- and Ni-base Al₂O₃-forming alloys, which can have CTE’s in excess of 15 × 10⁻⁶/K at high temperature [29]. Thermal expansion coefficients of z-Al₂O₃ available in the published literature range from 7 × 10⁻⁶/K to 9 × 10⁻⁶/K depending on the crystallographic direction, temperature range investigated, and investigator [30]. The temperature dependence of Young’s modulus and Poisson’s ratio and thermal expansion coefficient was not considered for this simple approximation. For the calculation, the selected values of \( E_{\text{ox}} = 400 \text{ GPa} \) [26], \( E_s = 210 \text{ GPa} \) [31], \( \nu_{\text{ox}} = 0.25 \) [26], \( \nu_s = 0.2 \) [31], \( h_{\text{ox}} = 1 \text{ mm} \), \( \alpha_{\text{ox}} = 8.5 \times 10^{-6}/\text{K} \) [30] were used. The calculated values at \( h_{\text{ox}} = 5 \text{ μm} \) as a function of temperature difference, \( \Delta T \) is presented in.
Table 2 Compressive residual stress determined based on photostimulated luminescence (PL) for $\alpha$-Al$_2$O$_3$ scale developed on TiAlC as a function of time and temperature

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (hours)</th>
<th>Compressive residual stress measured by PL (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Average</td>
</tr>
<tr>
<td>1000</td>
<td>0.5</td>
<td>0.088</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.179</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.268</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.287</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.313</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.357</td>
</tr>
<tr>
<td>1200</td>
<td>0.5</td>
<td>0.504</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.536</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.590</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.495</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.409</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.370</td>
</tr>
<tr>
<td></td>
<td>1000 (cyclic)</td>
<td>0.338</td>
</tr>
<tr>
<td>1400</td>
<td>0.008 (0.5 min)</td>
<td>0.274</td>
</tr>
<tr>
<td></td>
<td>0.033 (2 min)</td>
<td>0.608</td>
</tr>
<tr>
<td></td>
<td>0.167 (10 min)</td>
<td>0.621</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.626</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.614</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.599</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.541</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.490</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.510</td>
</tr>
</tbody>
</table>

Fig. 12. In general, the magnitude calculated by Eq. (1) is slightly greater than that measured by PL, but is still lower than 1 GPa. The magnitude of compressive residual stress determined by PL increased with temperature of oxidation as presented in Fig. 10. It should be noted that the magnitude of compressive residual stress was observed to increase abruptly during the initial oxidation as presented in Fig. 10. The changes in the magnitude of compressive residual stress may be related to the growth stress during oxidation and stress-relaxation by creep.

Since the magnitude of compressive residual stress measured by PL is always smaller than that calculated using Eq. (1), the difference in residual stress within the scale may be interpreted as tensile growth stress, assuming that the creep relaxation during the air-quench is negligible. The tensile growth stress within the oxidation scale has been related to $\theta$-to-$\alpha$ Al$_2$O$_3$ transformations [32, 33], although PL in this study did not observe any presence of metastable form of Al$_2$O$_3$ at any time, and the difference in residual stress persists throughout high temperature oxidation.
Summary

Oxide scales formed during isothermal and cyclic oxidation in air at 1000, 1200 and 1400 °C were characterized to examine the oxidation resistance of Ti₂AlC for high temperature applications. A continuous α-Al₂O₃ scale and a transient and isolated rutile-TiO₂ scale were found to form during isothermal oxidation in air at high temperature. At 1400 °C, transient Al₂TiO₅ phase was also observed. Protective α-Al₂O₃ scale exhibited excellent adherence with Ti₂AlC even after isothermal oxidation at 1400 °C for 25 h, and 1,000 1-hour thermal cycles at 1200 °C. This behavior is consistent with reports by Sundberg et al. [20] who also showed excellent spallation resistance and promise for furnace element applications.
No voids were observed at the interface between Ti2AlC/\(z\)-Al2O3. The compressive residual stress for the \(z\)-Al2O3 scale determined by PL was homogeneous and very small in magnitude (less than 0.65 GPa) for both isothermal and cyclic oxidation likely due to similar thermal expansion coefficients of Ti2AlC and \(z\)-Al2O3. These behaviors should make Ti2AlC of particular interest for applications requiring oxidaton/spallation resistance. Recent work has also shown excellent adhesive strength of Al2O3 film on Ti2AlC and Ti2AlC2 [34].

Acknowledgements The authors would like to thank Dr. B.A. Pirt for assistance with cyclic oxidation testing and comparison data. J. Liu and W. Fischer have contributed to this study as an Amelia Earhart Fellow of Zonta International and a participant of NSF-RET program at UCF (EEC-0401926), respectively. M. P. Brady was funded at ORNL under the Fossil ARM program. ORNL is managed by UT-Battelle, LLC for the U.S. DOE under contract DE-AC05-000R22725. Y. H. Sohn would also like to acknowledge financial support from NSF CAREER award (DMR-0238556). Assistant from Ms. Ashley Ewch, an undergraduate research assistant at UCF on manuscript preparation is sincerely appreciated.

References

Interdiffusion in (fcc) Ni-Cr-X (X = Al, Si, Ge or Pd) Alloys at 700°C

N. Garimella¹, a, M.P. Brady², b and Y.H. Sohn¹, c

¹Advanced Materials Processing and Analysis Center and Department of Mechanical, Materials and Aerospace Engineering, University of Central Florida, Orlando, FL, USA.
²Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA.
³garimella_n@yahoo.com, bradymp@ornl.gov, ysohn@mail.ucf.edu

Keywords: Boltzmann/Matano analysis, diffusion couples, diffusion coefficients, experimental, interdiffusion, multicomponent alloys, ternary system.

Abstract. Interdiffusion at 700°C for Ni-22at.%Cr (fcc γ phase) alloys with small additions of Al, Si, Ge, or Pd was examined using solid-to-solid diffusion couples. Rods of Ni-22at.%Cr, Ni-21at.%Cr-6.2at.%Al, Ni-22at.%Cr-4.0at.%Si, Ni-22at.%Cr-1.6at.%Ge and Ni-22at.%Cr-1.6at.%Pd alloys were cast using arc-melt and homogenized at 900°C for 168 hours. The diffusion couples were assembled with alloy disks in Invar steel jig, encapsulated in Argon after several hydrogen flushes, and annealed at 700°C for 720 hours. Experimental concentration profiles were determined from polished cross-sections by using electron probe microanalysis with pure standards of Ni, Cr, Al, Si, Ge and Pd. Interdiffusion fluxes of individual components were calculated directly from the experimental concentration profiles, and the moments of interdiffusion fluxes were examined to determine average ternary interdiffusion coefficients. Effects of ternary alloying additions on the interdiffusional behavior of Ni-Cr-X alloys at 700°C are presented in the light of the diffusional interactions and the formation of protective Cr₂O₃ scale.

Introduction

Ni-Cr alloys have been extensively explored for a variety of high-temperature applications and form a basis for a numerous commercial superalloy families [1-3]. They possess a good oxidation resistance and excellent high-temperature strength. Oxidation resistance in these alloys is derived from a continuous, slow-growing, adherent Cr₂O₃ scale [1-3]. Minor alloying additions (< 6.2at.%) can significantly improve the oxidation resistance of these Cr₂O₃ forming alloys although the exact mechanism by which the improvement occurs requires further investigation [1,4-6]. Diffusional influence from minor alloying additions can play a significant role in assessing the oxidation behavior of these alloys [1-8]. Ternary interdiffusion coefficients are important parameters to elucidate the effects of minor alloying additions on the oxidation of Cr₂O₃-forming alloys.

In this work, interdiffusion in Ni-22at.%Cr-X (fcc γ phase) alloys (X = Al, Si, Ge, or Pd) was examined using solid-to-solid diffusion couples annealed at 700°C for 720 hours. The selection basis of minor alloying additions (e.g., Al, Si, Ge and Pd) has been described in previous interdiffusion study carried out at 900°C [9]. Experimental concentration profiles are employed to calculate interdiffusion fluxes of individual components, and to determine average effective interdiffusion coefficients and average ternary interdiffusion coefficients. Interdiffusion coefficients are examined to assess the influence of alloying additions on the interdiffusion behavior of Cr and the Cr₂O₃-forming ability in Ni-22at.%Cr alloys.
Determination of Interdiffusion Coefficients from Ternary Isothermal Diffusion Couples

On the basis of Onsager’s formalism [10], the interdiffusion flux $\bar{J}_i$ of a component $i$ in a ternary system can be written as:

$$\bar{J}_i = -\bar{D}_{ij} \frac{\partial C_j}{\partial x} - \bar{D}_{ij} \frac{\partial C_j}{\partial x} \quad (i, j = 1, 2)$$

(1)

where $\partial C_j / \partial x$ and $\partial C_j / \partial x$ are the two independent concentration gradients, and $\bar{D}_{ij}$ and $\bar{D}_{ij}$ are the ternary interdiffusion coefficients. An experimental determination of the four concentration dependent interdiffusion coefficients requires the use of the Boltzmann-Matano analysis with two independent diffusion couples intersecting at a common composition in the diffusion zone.

Alternatively, the interdiffusion fluxes $\bar{J}_i$ of all components can be determined directly from their concentration profiles of an infinite diffusion couple without the need of the interdiffusion coefficients using the expression [11]:

$$\bar{J}_i = \frac{1}{2t} \frac{C_j}{C_j - C_i} \int (x - x_c) dC_i \quad (i = 1, 2, ..., n)$$

(2)

where $t$ is the time, $C_i$ and $C_j$ are the terminal concentrations of the alloys employed for the couple and $x_c$ refers to the location of the Matano plane. The interdiffusion flux $\bar{J}_i$ can then be integrated with respect to position $x$ to define average effective interdiffusion coefficient $\bar{D}_i^{\text{eff}}$ [12]:

$$\bar{D}_i^{\text{eff}} = \frac{\int J_i dx}{C_i - C_i} \quad (i = 1, 2, 3)$$

(3)

The effective interdiffusion coefficient is a chemical diffusion coefficient of individual species and it incorporates all multicomponent diffusional interactions within the system to provide an effective value for the interdiffusion of a component species as defined by:

$$\bar{D}_i^{\text{eff}} = \bar{D}_i^{\text{eff}} + \sum_{j=1}^{n} \frac{\bar{D}_i^{\text{eff}} C_j}{\partial C_j / \partial x} (i \neq j)$$

(4)

The interdiffusion flux $\bar{J}_i$ can be multiplied by $(x - x_c)^m$ and integrated over a selected region, $x_1$ to $x_2$ one gets [13]:

$$\int_{x_1}^{x_2} (x - x_c)^m dx = -\bar{D}_i^{\text{eff}} \int_{c_i(x_1)}^{c_i(x_2)} (x - x_c)^m dC_1 - D_i^{\text{eff}} \int_{c_i(x_1)}^{c_i(x_2)} (x - x_c)^m dC_2 \quad (i, j = 1, 2)$$

(5)

where $\bar{D}_i^{\text{eff}} (i, j = 1, 2)$ coefficients are the average main and cross interdiffusion coefficients treated as constants over the selected composition range. For ternary interdiffusion with the independent components and infinitely possible moments (e.g., $m=0, 1, 2, ...$), Eq. 5 can provide, at least, four equations involving the four interdiffusion coefficients $\bar{D}_i^{\text{eff}}$. The $\bar{D}_i^{\text{eff}}$ coefficients, characteristic
representations of the diffusion path, can be determined over selected composition ranges that include nonlinear segment of the profiles [13].

Experimental Procedure

Binary and ternary Ni-Cr-X alloys (fcc γ phase) with compositions reported in Table 1 were prepared with 99.9% pure Ni, Cr, Al, Si, Ge and Pd by arc melting under an argon atmosphere. The alloys were chill-cast by water-cooled copper mold into rods with approximately 12 mm in diameter. The alloy rods were placed in a quartz capsules, evacuated to a pressure less than 10⁻⁶ torr, and flushed several times with hydrogen. Ar was filled into the quartz capsules before the final sealing. All these alloy rods enclosed in quartz capsule assemblies, were homogenized at 900°C for 168 hours in a horizontal Lindberg™ 3-zone tube furnace, and water-quenched to preserve the high temperature microstructure. The microstructures and compositions of the alloys were examined by optical microscopy, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and electron microprobe analysis (EPMA). No measurable deviation in the alloy compositions was observed, and all alloys consisted of single phase fcc Ni solid solution (γ-phase).

Table 1. Nominal compositions of Ni-Cr-X alloys employed for solid-to-solid diffusion couples.

<table>
<thead>
<tr>
<th>Alloy Identification</th>
<th>Composition (atom fraction)</th>
<th>Composition (weight fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Cr</td>
</tr>
<tr>
<td>Ni</td>
<td>100.0</td>
<td>-</td>
</tr>
<tr>
<td>Ni-Cr (X = None)</td>
<td>78.0</td>
<td>22.0</td>
</tr>
<tr>
<td>Ni-Cr-Al (X = Al)</td>
<td>72.5</td>
<td>21.3</td>
</tr>
<tr>
<td>Ni-Cr-Si (X = Si)</td>
<td>74.0</td>
<td>22.0</td>
</tr>
<tr>
<td>Ni-Cr-Ge (X = Ge)</td>
<td>76.3</td>
<td>22.1</td>
</tr>
<tr>
<td>Ni-Cr-Pd (X = Pd)</td>
<td>76.1</td>
<td>22.3</td>
</tr>
</tbody>
</table>

Diffusion disks with approximate thickness of 2 mm were sliced from the alloy rods and prepared metallographically by polishing through 0.25 μm diamond paste. Table 2 presents ternary diffusion couples that were assembled with the disks held together in Invar™ steel jig consisting of two end plates and three threaded rods. The couples were placed in quartz capsules, which were sealed at one end, evacuated to a pressure less than 10⁻⁶ torr, and flushed with hydrogen several times. Ar was filled into a capsule before the final sealing. The capsules containing the couples were annealed at 700°C in a horizontal Lindberg 3-zone furnace for 720 hours. After the anneal, the couples were quenched in water to avoid any compositional and/or microstructural changes.

Table 2. List of solid-to-solid diffusion couples annealed at 700°C for 720 hours.

<table>
<thead>
<tr>
<th>Series</th>
<th>Diffusion Couples</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Ni vs. Ni-Cr</td>
</tr>
<tr>
<td></td>
<td>Ni vs. Ni-Cr-Al</td>
</tr>
<tr>
<td></td>
<td>Ni vs. Ni-Cr-Si</td>
</tr>
<tr>
<td></td>
<td>Ni vs. Ni-Cr-Ge</td>
</tr>
<tr>
<td></td>
<td>Ni vs. Ni-Cr-Pd</td>
</tr>
<tr>
<td>II</td>
<td>Ni-Cr vs. Ni-Cr-Al</td>
</tr>
<tr>
<td></td>
<td>Ni-Cr vs. Ni-Cr-Si</td>
</tr>
<tr>
<td></td>
<td>Ni-Cr vs. Ni-Cr-Ge</td>
</tr>
<tr>
<td>III</td>
<td>Ni-Cr vs. Ni-Cr-Pd</td>
</tr>
</tbody>
</table>
The diffusion couple assembly was then mounted, cross-sectioned, metallographically prepared for microstructural observations. Excellent bonding was observed with all diffusion couples. Then, cross-section surface was repolished with 1µm diamond paste for electron probe microanalysis (EPMA). The concentration profiles of elements Ni, Cr, Al, Si, Ge and Pd for the diffusion couples were determined with a JEOL 733 (Tokyo, Japan) EPMA by point-to-point counting techniques using pure Ni, Cr, Al, Si, Ge, and Pd as standards. Intensities of Kα X-radiations for Ni, Cr, Al, Si, Ge, and Lα X-radiations for Pd were measured and converted to their respective concentrations with appropriate ZAF (atomic number, Z; absorption, A; fluorescence, F) corrections.

Concentration profiles obtained from EPMA were smoothened by a smoothing-spline approximation using MatLab (The Math Works, Natick, MA). It is worth to mention that the analytical method used to determine interdiffusion coefficients in this study, is by the integration of interdiffusion fluxes (e.g., Eq. 5). This does not require the use of concentration gradients and therefore it significantly reduces the influence of a smoothening procedure on the determination of interdiffusion coefficients.

Results and Discussions

Excellent diffusion bonding was achieved in all diffusion couples. Fig. 1 presents a typical optical micrograph obtained by etching (Kalling’s reagent) the polished surface of the diffusion couple.

![Typical optical micrograph](image)

**Fig. 1.** Typical optical micrograph of solid-to-solid diffusion couple Ni vs. Ni-Cr-Ge annealed at 700°C for 720 hours.

Fig. 2 presents an example of experimental and smoothened concentration profiles that were used for the determination of interdiffusion fluxes and interdiffusion coefficients. The scatters in the concentration profiles for all diffusion couples were within the experimental uncertainty associated with EPMA. Experimental concentration profiles were smoothened with a smoothing-spline approximation by using MatLab. Consistency in experimental and smoothened concentration profiles of Cr in series III (see for example Fig. 2), owing to similar terminal concentration was examined by multiple EPMA acquisitions (e.g., independent Cr concentration) and by close examination of concentration profiles for Ni and X ternary alloying additions (e.g., dependent Cr concentrations). Consistency in terms of repeatable assessment of all concentration profiles was obtained for determination of interdiffusion fluxes and interdiffusion coefficients.
Fig. 2. Typical experimental and smoothened concentration profiles measured from solid-to-solid diffusion couples (a) Ni-Cr vs. Ni-Cr-Al and (b) Ni vs. Ni-Cr-Ge annealed at 700°C for 720 hours. Note that concentration is given in atf, which stands for atomic fraction.

Table 3. Average effective interdiffusion coefficients determined from Ni vs. Ni-Cr-X diffusion couples annealed at 700°C for 720 hours.

<table>
<thead>
<tr>
<th>Diffusion Couple</th>
<th>Composition Range</th>
<th>$D_{Cr}^{ef}$ [10^{-12} m^2/s]</th>
<th>$D_{Cr}^{ef}$ [10^{-18} m^2/s]</th>
<th>$D_{Ni}^{ef}$ [10^{-18} m^2/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni vs. Ni-Cr (X = None)</td>
<td>$C_{i}^{o} ~ C_{i}^{x}$</td>
<td>1.98</td>
<td>-</td>
<td>1.98</td>
</tr>
<tr>
<td></td>
<td>$C_{i}^{o} ~ C_{i}^{x}$</td>
<td>2.34</td>
<td>-</td>
<td>2.34</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Al (X = Al)</td>
<td>$C_{i}^{o} ~ C_{i}^{x}$</td>
<td>0.50</td>
<td>0.40</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td>$C_{i}^{o} ~ C_{i}^{x}$</td>
<td>0.61</td>
<td>0.86</td>
<td>0.68</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Si (X = Si)</td>
<td>$C_{i}^{o} ~ C_{i}^{x}$</td>
<td>1.22</td>
<td>2.08</td>
<td>1.27</td>
</tr>
<tr>
<td></td>
<td>$C_{i}^{o} ~ C_{i}^{x}$</td>
<td>1.95</td>
<td>2.26</td>
<td>1.99</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Ge (X = Ge)</td>
<td>$C_{i}^{o} ~ C_{i}^{x}$</td>
<td>1.39</td>
<td>2.38</td>
<td>1.43</td>
</tr>
<tr>
<td></td>
<td>$C_{i}^{o} ~ C_{i}^{x}$</td>
<td>2.74</td>
<td>5.17</td>
<td>2.97</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Pd (X = Pd)</td>
<td>$C_{i}^{o} ~ C_{i}^{x}$</td>
<td>6.91</td>
<td>6.06</td>
<td>6.85</td>
</tr>
<tr>
<td></td>
<td>$C_{i}^{o} ~ C_{i}^{x}$</td>
<td>9.86</td>
<td>5.41</td>
<td>9.57</td>
</tr>
</tbody>
</table>
Using Eq. 3, average effective interdiffusion coefficients, $\bar{D}^{\text{eff}}$,s on either side of the Matano plane were determined from the concentration profiles obtained from series I and II diffusion couples (i.e., Ni vs. Ni-Cr and Ni vs. Ni-Cr-X). They are reported in Table 3. These average effective interdiffusion coefficients are two orders lower in magnitude than those determined at 900°C [9]. $\bar{D}^{\text{eff}}$ was generally higher on the $\left(C_i \sim C_i^{\alpha}\right)$ composition range with higher Cr concentration relative to the other side.

Table 3 also reports that Al, Si and Ge diffuse faster than Ni in $\gamma$-phase Ni-Cr-X alloys. In the case of Ni vs. Ni-Cr-Pd, $\bar{D}^{\text{eff}}$s for Ni, Cr and Pd are similar. These results are in general, analogues to previous work [9] carried out at 900°C. At 700°C, Table 3 shows that Al and Si additions to Ni-Cr alloy reduced $\bar{D}^{\text{eff}}$, but Pd additions to Ni-Cr alloy increased $\bar{D}^{\text{eff}}$ significantly, especially in the composition range of $\left(C_i \sim C_i^{\alpha}\right)$.

Concentration profiles obtained from diffusion couple series II and III (i.e., Ni vs. Ni-Cr-X and NiCr vs. Ni-Cr-X) were employed to determine average ternary interdiffusion coefficients, $\bar{D}^{\text{ni}}$, on either side of the Matano plane using Eq. 5. These are reported in Table 4 and 5. The magnitude of these interdiffusion coefficients is approximately two orders lower than those determined at 900°C [9]. The sign of the cross interdiffusion coefficients remained the same with those determined at 900°C.

Series II diffusion couples were designed to yield the same sign of $\partial C_i / \partial x$ and $\partial C_j / \partial x$ where a positive and negative $\bar{D}^{\text{ni}}$, indicates an increase and a decrease in $\bar{J}_c$, respectively. In general, higher magnitude of $\bar{D}^{\text{ni}}$, and $\bar{D}^{\text{nx}}$ was observed on the $\left(C_i \sim C_i^{\alpha}\right)$ composition range with higher Cr concentration. The Al addition in the Ni-Cr alloy yielded positive $\bar{D}^{\text{ni}}$, and increased $\bar{J}_c$, in agreement with the previous work by Nesbitt [14], Thomson [15] and Garimella [9].

Table 4. Average ternary interdiffusion coefficients determined from Ni-Cr vs. Ni-Cr-X diffusion couples annealed at 700°C for 720 hours.

<table>
<thead>
<tr>
<th>Diffusion Couple</th>
<th>Composition Range</th>
<th>$\bar{D}^{\text{ni}}$</th>
<th>$\bar{D}^{\text{nx}}$</th>
<th>$\bar{D}^{\text{ncr}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni vs. Ni-Cr-Al (X = Al)</td>
<td>$\left(C_i^{\alpha} \sim C_i^{\alpha}\right)$</td>
<td>0.48</td>
<td>0.53</td>
<td>0.06</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Si (X = Si)</td>
<td>$\left(C_i^{\alpha} \sim C_i^{\alpha}\right)$</td>
<td>0.54</td>
<td>0.02</td>
<td>0.10</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Ge (X = Ge)</td>
<td>$\left(C_i^{\alpha} \sim C_i^{\alpha}\right)$</td>
<td>0.96</td>
<td>0.58</td>
<td>0.03</td>
</tr>
<tr>
<td>Ni vs. Ni-Cr-Pd (X = Pd)</td>
<td>$\left(C_i^{\alpha} \sim C_i^{\alpha}\right)$</td>
<td>1.42</td>
<td>0.05</td>
<td>0.05</td>
</tr>
</tbody>
</table>

The Si, Ge and Pd additions to Ni-Cr alloy also increased $\bar{J}_c$, with positive $\bar{D}^{\text{ni}}$, and $\bar{D}^{\text{nx}}$. This effect was stronger when Cr concentration was high on the $\left(C_i \sim C_i^{\alpha}\right)$ side particularly for Ge and Pd. In previous work at 900°C [9], $\bar{D}^{\text{ni}}$, was not significant to this extent. The Si, Ge and Pd additions to...
Ni-Cr alloy also increased $\dot{J}_{Cr}$ with positive $D^{Ni}_{CrX}$. This effect was stronger when Cr concentration is high on the $(C^6_1 \sim C^8_1)$ side, particularly for Ge and Pd. In previous work at 900°C [9], $D^{Ni}_{CrGe}$ was not significant while $D^{Ni}_{CrSi}$ and $D^{Ni}_{CrPd}$ were significantly large. This study at 700°C finds that $D^{Ni}_{CrGe}$ and $D^{Ni}_{CrPd}$ are large positive values while $D^{Ni}_{CrSi}$ is not so significant.

Diffusion couple series III was designed so that the initial $\partial C_{Cr}/\partial x = 0$. Therefore, $\dot{J}_{Cr}$ is mainly due to $\partial C_{X}/\partial x$, and the magnitude and sign of $D^{Ni}_{CrX}$. $\dot{J}_{Al}$ and $\dot{J}_{Si}$ have caused an uphill-diffusion of Cr owing to positive $D^{Ni}_{CrAl}$ and $D^{Ni}_{CrSi}$, respectively. On the other hand, $\dot{J}_{Ge}$ and $\dot{J}_{Pd}$ did not cause any measurable redistribution of Cr ($\dot{J}_{Cr} \approx 0$). However, Ge and Pd are lower in concentration than those of Al and Si, in the Ni-Cr-X alloys, as reported in Table 1. Average ternary interdiffusion coefficients for series-III couples are reported in Table 5.

### Table 5. Average ternary interdiffusion coefficients determined from Ni vs. Ni-Cr-X diffusion couples annealed at 700°C for 720 hours.

<table>
<thead>
<tr>
<th>Diffusion Couple</th>
<th>Composition Range</th>
<th>$D^{Ni}_{CrX}$ $[10^{-18} \text{m}^2/\text{s}]$</th>
<th>$D^{Ni}_{CrGe}$ $[10^{-18} \text{m}^2/\text{s}]$</th>
<th>$D^{Ni}_{CrPd}$ $[10^{-18} \text{m}^2/\text{s}]$</th>
<th>$D^{Ni}_{CrSi}$ $[10^{-18} \text{m}^2/\text{s}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Cr vs. Ni-Cr-Al (X = Al)</td>
<td>$(C^6_1 \sim C^8_1)$</td>
<td>1.98</td>
<td>0.73</td>
<td>1.97</td>
<td>0.78</td>
</tr>
<tr>
<td>Ni-Cr vs. Ni-Cr-Si (X = Si)</td>
<td>$(C^6_1 \sim C^8_1)$</td>
<td>6.91</td>
<td>5.87</td>
<td>0.11</td>
<td>0.62</td>
</tr>
<tr>
<td>Ni-Cr vs. Ni-Cr-Ge (X = Ge)</td>
<td>$(C^6_1 \sim C^8_1)$</td>
<td>2.59</td>
<td>2.22</td>
<td>0.16</td>
<td>1.35</td>
</tr>
<tr>
<td>Ni-Cr vs. Ni-Cr-Ge (X = Ge)</td>
<td>$\Delta C_{Cr}/\Delta x \approx 0$ and cannot be determined</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Based on average effective interdiffusion coefficients and average ternary interdiffusion coefficients determined in both the present study at 700°C and earlier study at 900°C [9], alloying additions of Al, Si, Ge and Pd have yielded positive $D^{Ni}_{CrX}$. Therefore, Cr$_2$O$_3$-forming ability of Ni22at.%Cr alloy should improve with these alloying additions.

### Summary

Experimental concentration profiles, measured after annealing at 700°C for 720 hours, were employed to determine interdiffusion fluxes, average effective interdiffusion coefficients and average ternary interdiffusion coefficients. The, $D^{Ni}_{CrX}$ were observed to be positive with the alloying additions of Al, Si, Ge, or Pd. These results indicate that these alloying additions can facilitate the formation of Cr$_2$O$_3$-scale after scale-spallation and Cr-depletion due to long-term oxidation.

### Acknowledgements

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References


Ternary Interdiffusion in L12-Ni3Al with Ir Alloying Addition

M. Ode1a, N. Garimella2b, M. Ikeda3c, H. Murakami1d, Y.H. Sohn2a

1National Institute of Materials Science, Tsukuba, Japan
2University of Central Florida, Orlando, FL, USA
3Kobe Steel, Co. Ltd. (Formally graduate student of the Univ. of Tokyo), Japan

aODE.Machiko@nims.go.jp; bga825540@pegasus.cc.ucf.edu
caikeda.muneaki@steel.kobelco.co.jp; dmurakami.hideyuki@nims.go.jp
dysohn@mail.ucf.edu

Keywords: Ir, Ni3Al, L12, intermetallics, high temperature alloys, ternary interdiffusion

Abstract. Average ternary interdiffusion coefficients in Ni3Al with Ir additions have been determined using solid-to-solid diffusion couples annealed at 1200°C for 5 hours. Disc shaped alloy specimens were prepared by the vacuum arc melting at compositions of Ni-24Al, Ni-25Al, Ni-26Al, Ni-23.5Al-1Ir, Ni-24.5Al-1Ir, Ni-23Al-2Ir, Ni-23Al-2Ir, Ni-24Al-2Ir, Ni-23Al-3Ir (at.%). Surfaces of alloys were polished down to 1200 grit and diffusion couples were assembled in Si3N4 jig for initial bonding heat treatment at 1200°C for 0.5 hours. Additional diffusion anneal was carried out at 1200°C for 4.5 hours outside of Si3N4 jig so that diffusion couples can be water quenched. Concentration profiles of individual components were measured by electron probe microanalysis using pure standard of Ni, Al and Ir. Interdiffusion flux of individual component was determined directly from the experimental concentration profiles, and the moments of interdiffusion flux were examined to calculate the average ternary interdiffusion coefficients, Dij, either with Al or Ni as dependent component. Calculated interdiffusion coefficients suggest that Ir-alloyed Al3O3-forming oxidation resistant coatings would be beneficial to reduce the interdiffusion flux of Ni from superalloy substrates to the coating, and reduce the interdiffusion flux of Al from the coating to the superalloy substrate.

Introduction

Nickel-base superalloys are extensively used in both aviation and land-based gas turbine environments, and many studies have been devoted to improve their mechanical properties and microstructural stability. Ni-based superalloys are typically composed of L12 γ’-phase (Ni3Al) coherently precipitated in a fcc γ-phase matrix. The diffusion mobility database for Ni-based superalloys is available for fcc phase [1]. However, a limited number of study [2,3] exist on interdiffusion of the γ’-phase, particularly with alloyed with other constituents in superalloys, although the γ’ is the strengthening phase of the Ni-based superalloys. An understanding of multicomponent diffusion processes in these alloys is very important because it is essential to achieve durable microstructure for high-temperature strength and adequate high temperature oxidation resistance. This study is also fueled by recent conceptual development of γ’+γ’ coatings for optimized oxidation resistance, and reduced interdiffusion between the oxidation resistant coatings and structural superalloy substrate (e.g. formation of deleterious phases due to interdiffusion at the interface).
The diffusion mechanism in ordered alloys is recognized to be more complex than for disordered solid solutions [4]. In the case of L1_2 structure, the diffusion mechanism is even more complex than that for B2 structure. Diffusion can occur through the face-centered α-site where Ni atom mainly occupies, and the diffusion coefficient largely depends on the alloy composition, namely the degrees of order [5-7]. Tracer diffusion studies in γ' Ni3Al is difficult since 26Al is not easily available, although the self-diffusion of Ni and chemical/impurity diffusion in Ni3Al binary and Ni3Al-X ternary alloy (X= Co, Cu, Pt, Ti, Si, W, Ge, In, V, Nb, Cr, Fe, Mn) have been studied [2,3].

Murakami and coworkers have proposed Ir-based alloys for oxidation resistant coatings, either as stand-alone coatings or as bond coats [8-16], because Ir has the highest melting temperature (2716K) among platinum group metals, excellent chemical stability and low oxygen diffusivity [17]. Ir addition also increases the melting temperature of Ni-based superalloys [18]. Furthermore, the Ir-Al phase diagram [19, 20] does not contain any intermediate phases between the B2 IrAl phase and the Ir-based fcc solid solution phase. Therefore, Ir-Al-based coatings are expected to be thermodynamically more stable during high temperature applications.

For better understanding of microstructural stability of Ni-base superalloys and potential development of Ir-Al-based oxidation resistant coatings, we examined the ternary diffusional interaction of Ir addition on the L12 Ni3Al phase. Solid-to-solid diffusion couples were assembled and annealed at 1473K for 5 hours. Based on concentration profiles obtained by electron probe microanalysis, average ternary interdiffusion coefficients were determined to assess how Ir addition influences interdiffusion behavior of Ni and Al.

Experimental Details

Binary Ni-Al and ternary Ni-Al-Ir alloys were prepared by the vacuum arc melting of 99.97 wt.% Ni, 99.9 wt.% Al and 99.2 wt.% Ir according to the compositions presented in Table I. The alloys were cast into a semi-cylindrical mold with the diameter of 8 mm in the arc furnace. The alloy rods were homogenized at 1473K for 137 hours in the vacuum furnace evacuated to a pressure less than 10^-2 Pa. The homogenized alloys were then sectioned into discs with the height of 1.5 mm. Surface of alloy discs were polished metallographically up to 1200-grit and cleaned thoroughly prior to diffusion couple assembly.

Table I. Nominal compositions of Ni-Al-Ir alloys employed for solid-to-solid diffusion couples.

<table>
<thead>
<tr>
<th>Alloy Identification</th>
<th>Composition (atom percent)</th>
<th>Composition (weight percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-24.5Al</td>
<td>76 24 0</td>
<td>59.3 40.7 0</td>
</tr>
<tr>
<td>Ni-25Al</td>
<td>75 25 0</td>
<td>58.0 42.0 0</td>
</tr>
<tr>
<td>Ni-26Al</td>
<td>74.5 25.5 0</td>
<td>57.3 42.7 0</td>
</tr>
<tr>
<td>Ni-23.5Al-Ir</td>
<td>75.5 23.5 1</td>
<td>59.5 40.3 0.2</td>
</tr>
<tr>
<td>Ni-24.5Al-Ir</td>
<td>74.5 24.5 1</td>
<td>58.2 41.6 0.2</td>
</tr>
<tr>
<td>Ni-23Al-2Ir</td>
<td>74.5 23.5 2</td>
<td>59.0 40.5 0.5</td>
</tr>
<tr>
<td>Ni-23Al-3Ir</td>
<td>74 23 3</td>
<td>59.2 40.0 0.7</td>
</tr>
</tbody>
</table>
Coupled alloys were put into a Si₃N₄ jig and were annealed at 1473K for 0.5 h in a vacuum furnace to promote initial bonding. Since the metal discs have larger thermal expansion coefficients than the Si₃N₄ jig, the discs can adhere to each other due to the compressive stress by the annealing treatment. A diffusion couple fabricated in this manner was then sealed in an evacuated transparent quartz capsule, and annealed at 1473K for 4.5 hours in an atmosphere furnace. All diffusion couples were water quenched after the high temperature anneal to preserve high temperature microstructure and concentration profiles. In this study, the time required for the diffusion bonding treatment (0.5 hours) was added to the total annealing time. Thus, concentration profiles from all diffusion couple were analyzed with diffusion anneal time of 5 hours.

Microstructures and concentration profiles of the annealed diffusion couples were analyzed by an JEOL-JXA-8900 electron probe microanalyzer (EPMA). The accelerating voltage of 20 kV, the beam current of 50 nA and the probe diameter of 1 μm were employed for data acquisition of Ni Kα x-radiation peak using LIF crystal, Al Kα x-radiation peak using TAP crystal, and Ir Lα x-radiation using LIFH crystal. Pure element standards of Ni, Al and Ir along with ZAF correction were used for quantification of concentrations.

**Determination of Interdiffusion Coefficients in Ternary System**

Based on Onsager’s formalism [21], the phenomenological description of interdiffusion in ternary system requires four concentration-dependent interdiffusion coefficients: two main and two cross-coefficients [22]. For the classical experimental determination, two independent diffusion couples with intersecting diffusion paths are needed to determine four independent interdiffusion coefficient at the intersecting composition.

In the case of intermetallics, an alloying element often show site-preference. For example, Ir atoms mainly substituting for Ni atoms on the a-site in the L1₂ structure. This site preference can lead to concentration profile where \( \nabla C_\text{Ni} = -\nabla C_\text{Ir} \), and may pose a difficulty in determining the ternary interdiffusion coefficient for (Ni,Ir)₂Al based on classical Boltzmann-Matano analysis.

On the basis of Onsager’s formalism [21], the interdiffusion flux \( \vec{j}_i \) of a component \( i \) in a ternary system can be written as:

\[
\vec{j}_i = -\vec{D}_i \frac{\partial C_i}{\partial x} - \vec{D}_j \frac{\partial C_j}{\partial x} \quad (i, j = 1, 2)
\]

(1)

where \( \frac{\partial C_1}{\partial x} \) and \( \frac{\partial C_2}{\partial x} \) are the two independent concentration gradients, and \( \vec{D}_i \) and \( \vec{D}_j \) are the ternary interdiffusion coefficients. An experimental determination of the four concentration dependent interdiffusion coefficients requires the use of the Boltzmann-Matano analysis with two independent diffusion couples intersecting at a common composition in the diffusion zone [22].

Alternatively, the interdiffusion fluxes \( \vec{j}_i \) of all components can be determined directly from their concentration profiles of an infinite diffusion couple without the need of the interdiffusion coefficients using the expression [23]:

\[
\vec{j}_i = -\vec{D}_i \frac{\partial C_i}{\partial x} - \vec{D}_j \frac{\partial C_j}{\partial x} \quad (i, j = 1, 2)
\]
\[
\vec{J}_i = \frac{1}{2t} \int_{x_i}^{x_f} (x - x_o)^m \frac{dC_i}{C_i} (i = 1, 2, ..., n)
\] (2)

where \(t\) is the time, \(C_i^-=\) and \(C_i^+=\) are the terminal concentrations of the alloys employed for the couple and \(x_o\) refers to the location of the Matano plane.

The interdiffusion flux \(\vec{J}_i\) can be multiplied by \((x-x_o)^m\) and integrated over a selected region, \(x_1\) to \(x_2\) one gets [24]:

\[
\int_{x_1}^{x_2} \vec{J}_i (x - x_o)^m \, dx = -\overline{D}_{ij} \int_{C_i(x_1)}^{C_i(x_2)} \frac{dC_i}{C_i} - \overline{D}_{ij} \int_{C_j(x_1)}^{C_j(x_2)} \frac{dC_j}{C_j} (i, j = 1, 2) \tag{5}
\]

where \(\overline{D}_{ij}\) (\(i, j = 1, 2\)) coefficients are the average main and cross interdiffusion coefficients treated as constants over the selected composition range. For ternary interdiffusion with the independent components and infinitely possible moments (e.g., \(m = 0, 1, 2, ..., n\)), Eq. 5 can provide, at least, four equations involving the four interdiffusion coefficients \(\overline{D}_{ij}\). The \(\overline{D}_{ij}\) coefficients, characteristic representations of the diffusion path, can be determined over selected composition ranges that include nonlinear segment of the profiles [24].

**Results and Discussion**

Figure 1 shows typical concentration profiles obtained by EPMA for diffusion couple Ni-25Al vs. Ni-23Al-Ir annealed at 1437K for 5 hours. The x-axis represents the distance from the Matano plane, and the solid lines are smoothed concentration profiles.

![Fig. 1. Concentration profile of diffusion couple, Ni-25Al vs. Ni-23Al-Ir annealed at 1437K for 5 hours.](image)
The average ternary interdiffusion coefficients determined using Eq. [4] with $m = 0$ and $m = 1$ are presented in Table II. The magnitude of $\overline{D}_{\text{AlAl}}$ and $\overline{D}_{\text{NiNi}}$ is much larger than $\overline{D}_{\text{IrIr}}$. In Fig. 2, $\overline{D}_{\text{Ir}}$, determined from only the diffusion couple Ni-25Al vs. Ni-23.5Al-1Ir (square dots) is compared with the reported interdiffusion coefficients in Ni$_3$Al [3]. The magnitude of $\overline{D}_{\text{Ir}}$ is slightly smaller than that of the minimum diffusion coefficient, $\overline{D}_{\text{FeFe}}$, among the Ni-substitute elements.

Table II. Average ternary interdiffusion coefficients determined from diffusion couples of (Ni,Ir)$_3$Al alloys annealed at 1473K for 5 hours.

<table>
<thead>
<tr>
<th>Diffusion Couple</th>
<th>Composition Range</th>
<th>$\overline{D}_{\text{NiNi}}$</th>
<th>$\overline{D}_{\text{NiAl}}$</th>
<th>$\overline{D}_{\text{AlAl}}$</th>
<th>$\overline{D}_{\text{NiIr}}$</th>
<th>$\overline{D}_{\text{AlIr}}$</th>
<th>$\overline{D}_{\text{NiAl}}$</th>
<th>$\overline{D}_{\text{AlNi}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-25Al vs.</td>
<td>C$<em>{25}$-C$</em>{25}$</td>
<td>783</td>
<td>-101</td>
<td>Ngl.</td>
<td>13</td>
<td>783</td>
<td>873</td>
<td>Ngl.</td>
</tr>
<tr>
<td>Ni-23.5Al-1Ir</td>
<td>C$<em>{23.5}$-C$</em>{25}$</td>
<td>646</td>
<td>-101</td>
<td>Ngl.</td>
<td>13</td>
<td>644</td>
<td>73</td>
<td>Ngl.</td>
</tr>
<tr>
<td>Ni-24.5Al vs.</td>
<td>C$<em>{24.5}$-C$</em>{25}$</td>
<td>541</td>
<td>-85</td>
<td>Ngl.</td>
<td>11</td>
<td>541</td>
<td>615</td>
<td>Ngl.</td>
</tr>
<tr>
<td>Ni-24.5Al-1Ir</td>
<td>C$<em>{24.5}$-C$</em>{25}$</td>
<td>816</td>
<td>-76</td>
<td>Ngl.</td>
<td>19</td>
<td>816</td>
<td>871</td>
<td>Ngl.</td>
</tr>
<tr>
<td>Ni-26Al vs.</td>
<td>C$<em>{26}$-C$</em>{25}$</td>
<td>873</td>
<td>-52</td>
<td>Ngl.</td>
<td>15</td>
<td>873</td>
<td>912</td>
<td>Ngl.</td>
</tr>
<tr>
<td>Ni-23Al-2Ir</td>
<td>C$<em>{23}$-C$</em>{25}$</td>
<td>590</td>
<td>-117</td>
<td>Ngl.</td>
<td>13</td>
<td>590</td>
<td>690</td>
<td>Ngl.</td>
</tr>
<tr>
<td>Ni-25Al vs.</td>
<td>C$<em>{25}$-C$</em>{25}$</td>
<td>522</td>
<td>-107</td>
<td>Ngl.</td>
<td>16</td>
<td>522</td>
<td>613</td>
<td>Ngl.</td>
</tr>
<tr>
<td>Ni-23Al-2Ir</td>
<td>C$<em>{25}$-C$</em>{25}$</td>
<td>494</td>
<td>-117</td>
<td>Ngl.</td>
<td>16</td>
<td>494</td>
<td>594</td>
<td>Ngl.</td>
</tr>
<tr>
<td>Ni-25Al vs.</td>
<td>C$<em>{25}$-C$</em>{25}$</td>
<td>440</td>
<td>-93</td>
<td>Ngl.</td>
<td>16</td>
<td>440</td>
<td>522</td>
<td>Ngl.</td>
</tr>
<tr>
<td>Ni-23Al-3Ir</td>
<td>C$<em>{23}$-C$</em>{25}$</td>
<td>441</td>
<td>-136</td>
<td>Ngl.</td>
<td>19</td>
<td>441</td>
<td>548</td>
<td>Ngl.</td>
</tr>
</tbody>
</table>

The $\overline{D}_{\text{NiIr}}$ coefficient is positive and large in magnitude. This suggests that Ir substitutes in Ni-site and influences the interdiffusion of Ni significantly. The $\overline{D}_{\text{AlIr}}$ coefficient is negative and large in magnitude as well. Based on magnitudes and sign of $\overline{D}_{\text{NiIr}}$ and $\overline{D}_{\text{AlIr}}$, Ir can substitute Ni in oxidation resistant coatings (e.g., NiCoCrAlY and Ni-aluminides) to reduce the accumulated interdiffusion fluxes of Ni and Al. Ir addition in coatings would reduce the interdiffusion flux of Ni from superalloy substrates to the coating, and reduce the interdiffusion flux of Al from the coating to the superalloy substrate.

Conclusion

Ternary interdiffusional interaction of Ir addition on the L12 Ni$_3$Al phase was examined using solid-to-solid diffusion couples annealed at 1473K for 5 hours. Average ternary interdiffusion coefficients were determined from integration of interdiffusion fluxes for individual components. The $\overline{D}_{\text{NiIr}}$ coefficient was determined to be positive and large in magnitude: Ir substitutes in Ni-site and influences the interdiffusion of Ni significantly. The $\overline{D}_{\text{AlIr}}$ coefficient was negative and appreciable in magnitude. Findings from this study finds that Ir addition in coatings would be beneficial to reduce the interdiffusion flux of Ni from superalloy substrates to the coating, and reduce the interdiffusion flux of Al from the coating to the superalloy substrate.
Fig. 2. Comparison of interdiffusion coefficients in Ni$_3$Al alloys [3]. Value obtained from this study is presented in square dots.

References

Ternary and Quaternary Interdiffusion in $\gamma$ (fcc) Fe-Ni-Cr-X 
($X = Si, Ge$) Alloys at 900°C

N. Garimella$^{1,a}$, M.P. Brady$^b$ and Y.H. Sohn$^{1,c}$

$^1$Advanced Materials Processing and Analysis Center and Department of Mechanical, Materials and Aerospace Engineering, University of Central Florida, Orlando, FL, USA. 
$^2$Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA. 
$^a$garimella_n@yahoo.com, $^b$bradymp@ornl.gov, $^c$ysohn@mail.ucf.edu

Keywords: Multicomponent diffusion, interdiffusion coefficients, Austenitic alloys

Abstract. Interdiffusion in Fe-Ni-Cr (fcc $\gamma$ phase) alloys with small additions of Si and Ge at 900°C was studied using solid-to-solid diffusion couples. Alloy rods of Fe-24 at.%Ni, Fe-24 at.%Ni-22at.%Cr, Fe-24 at.%Ni-22at.%Cr-4at.%Si and Fe-24 at.%Ni-22at.%Cr-1.7at.%Ge were cast using arc-melt, and homogenized at 900°C for 168 hours. Sectioned alloy disks from the rods were polished, and diffusion couples were assembled with Invar steel jig, encapsulated in Argon after several hydrogen flushes, and annealed at 900°C for 168 hours. Polished cross-sections of the diffusion couples were characterized to determine experimental concentration profiles using electron probe microanalysis with pure elemental standards. Interdiffusion fluxes of individual components were calculated directly from the experimental concentration profiles, and the moments of interdiffusion flux profiles were examined to determine the average ternary and quaternary interdiffusion coefficients. Effects of alloying additions on the interdiffusion behavior of Fe-Ni-Cr-X alloys at 900°C are presented with due consideration for the formation of protective $Cr_2O_3$ scale.

Introduction

Austenitic (fcc-$\gamma$) $Cr_2O_3$ forming Fe-Ni-Cr alloys are of potential interest for many applications due to their combination of good oxidation/corrosion resistance and high temperature strength [1-7]. Minor alloying additions (< 5 wt.%) on these alloys are found to increase the oxidation resistance by forming a slowly growing, adherent, continuous and impervious layer of $Cr_2O_3$ [4,8,9]. In this work, effects of Si and Ge alloying additions on the interdiffusion behavior of quaternary Fe-Ni-Cr-X ($X = Si, Ge$) alloys (fcc $\gamma$-phase) were studied by using solid-to-solid diffusion couples with due respect for the formation and growth kinetics of protective $Cr_2O_3$ scale of these alloys.

Ternary and quaternary interdiffusion coefficients are important tools to explain the effects of minor alloying additions on the oxidation of $Cr_2O_3$-forming alloys. In this work, interdiffusion in Fe-24at.%Ni-22at.%Cr-X (fcc $\gamma$ phase) alloys ($X = Si, Ge$) was examined using solid-to-solid diffusion couples annealed at 900°C for 168 hours. The selection criteria of minor alloying additions (e.g., Si, Ge) for the case of Ni-Cr alloys has been described in earlier interdiffusion studies carried out at 900°C and 700°C [10,11]. Experimental concentration profiles are employed to calculate interdiffusion fluxes of individual components, and determine average effective interdiffusion coefficients and average ternary and quaternary interdiffusion coefficients. Interdiffusion coefficients are examined to assess effects of alloying additions on the interdiffusion behavior of Cr in promoting $Cr_2O_3$ formation in Fe-24at.%Ni-22at.%Cr-X alloys.
Determination of Interdiffusion Coefficients from Ternary Isothermal Diffusion Couples

Onsager’s formalism of Fick’s law [12] provides the interdiffusion flux $\tilde{J}_i$ of a component $i$ in a multicomponent system, written as:

$$\tilde{J}_i = -\sum_{j=1}^{n} D^{i}_{ij} \frac{\partial C_j}{\partial x} \quad (i = 1, 2, \ldots, n - 1)$$  \hspace{1cm} (1)

where, $\partial C_j / \partial x$ is the independent concentration gradient of component $j$, and $D^{i}_{ij}$’s are the $(n-1)^{th}$ composition-dependent interdiffusion coefficients. An experimental determination of 9 composition-specific quaternary interdiffusion coefficients requires the use of the Boltzmann-Matano analysis with three independent diffusion couples that develop a common composition in the diffusion zone. Alternatively, the interdiffusion fluxes $\tilde{J}_i$ of all components can be determined directly from their concentration profiles of an infinite diffusion couple without the availability of the interdiffusion coefficients using the expression [13]:

$$\tilde{J}_i = \frac{1}{2t} \int_{C_i^{-} \rightarrow C_i^{+}}^{x-x_0} (x-x_0) dC_i \quad (i = 1, 2, \ldots, n)$$  \hspace{1cm} (2)

where $t$ is the time, $C_i^{-}$ and $C_i^{+}$ are the terminal concentrations of the parent alloys employed for the couple and $x_0$ refers to the location of the Matano plane.

The interdiffusion flux $\tilde{J}_i$, determined from Eq. 2 can then be integrated with respect to position $x$ to define average effective interdiffusion coefficient, $D_{ij}^{\text{eff}}$ [14]:

$$D_{ij}^{\text{eff}} = \frac{\int_{x_1}^{x_2} \tilde{J}_i \, dx}{C_i^{+} - C_i^{-}} \quad (i = 1, 2, 3)$$  \hspace{1cm} (3)

This average effective interdiffusion coefficient incorporates all multicomponent diffusional interactions for the system, and provides an effective value for the interdiffusion of a component as defined by:

$$D_{ij}^{\text{eff}} = D_{ij}^{*} + \sum_{j} D^{*}_{ij} \frac{\partial C_j}{\partial x} \quad (i \neq j)$$  \hspace{1cm} (4)

The interdiffusion flux $\tilde{J}_i$, determined from Eq. 2 as a function of $x$, can be multiplied by $(x-x_0)^n$ and integrated over a selected region, $x_1$ to $x_2$; in the light of Eq. 1, one gets [15]:

$$\int_{x_1}^{x_2} \tilde{J}_i (x-x_0)^n \, dx = -D_{ij}^{*} \int_{C_i^{-}}^{C_i^{+}} (x-x_0)^n \, dC_i - D^{*}_{ij} \int_{C_i^{-}}^{C_i^{+}} (x-x_0)^n \, dC_j \quad (i = 1, 2)$$  \hspace{1cm} (5)

$$\int_{x_1}^{x_2} \tilde{J}_i (x-x_0)^n \, dx = -D_{ij}^{*} \int_{C_i^{-}}^{C_i^{+}} (x-x_0)^n \, dC_i - D^{*}_{ij} \int_{C_i^{-}}^{C_i^{+}} (x-x_0)^n \, dC_j \quad (i = 1, 2, 3)$$  \hspace{1cm} (6)
for ternary and quaternary interdiffusion, respectively. Eq. 5 provides four equations involving the $\bar{D}_6^i$ interdiffusion coefficients ($n = 0, 1$) and can be set up from interdiffusion fluxes calculated using Eq. 2 from the concentration profiles of a single diffusion couple of the ternary system. Similarly, Eq. 6 provides nine equations involving the $\bar{D}_6^i$ interdiffusion coefficients ($n = 0, 1$ and 2) from the single diffusion couple of the quaternary system. The $\bar{D}_6^i$ coefficients, characteristic of the diffusion path, can be determined over selected composition ranges that include nonlinear segment of the profiles [15].

**Experimental Procedure**

Ternary and quaternary alloys of Fe-Ni-Cr-X (fcc $\gamma$ phase) system with compositions reported in Table 1 were prepared with 99.9% pure Fe, Ni, Cr, Si and Ge by arc melting under an argon atmosphere. These alloys were chill-cast by water-cooled copper molds into rods with approximately 12 mm in diameter. The alloy rods were placed in a quartz capsule, evacuated to pressure below $10^{-5}$ torr, and flushed with hydrogen. The hydrogen-flush procedure was repeated several times, and Ar was finally filled into the capsule before the final encapsulation. They were homogenized at 900°C for 168 hours in a horizontal Lindberg™ 3-zone tube furnace, and water-quenched to retain the high temperature microstructure. The microstructures and compositions of the alloys were examined by optical microscopy, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and electron microprobe analysis (EMPA). No measurable variation in the alloy compositions was found, and all alloys consisted single-phase fcc solid solution ($\gamma$-phase).

<table>
<thead>
<tr>
<th>Alloy Identification</th>
<th>Composition (atom percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Ni</td>
<td>76.3 (0.7) 23.7 (0.7)  -  -</td>
</tr>
<tr>
<td>Fe-Ni-Cr</td>
<td>55.5 (0.7) 23.1 (0.4)  21.4 (0.4)  -</td>
</tr>
<tr>
<td>Fe-Ni-Cr-Si (X = Si)</td>
<td>52.2 (0.7) 22.3 (0.4)  21.4 (0.3)  4.1 (0.4)</td>
</tr>
<tr>
<td>Fe-Ni-Cr-Ge (X = Ge)</td>
<td>53.4 (0.3) 22.3 (0.4)  21.9 (0.3)  1.4 (0.3)</td>
</tr>
</tbody>
</table>

Alloy disks of approximately 2 mm in thickness were sliced from the rods of alloys, and prepared metallographically by polishing through 0.25 μm diamond paste. Table 2 presents ternary and quaternary diffusion couples that were assembled with the disks held together in Invar™ steel jig consisting of two end plates and three threaded rods. The couples were placed in quartz capsules, which were sealed at one end, and evacuated to a pressure less than $10^{-5}$ torr and flushed with hydrogen several times. Ar was filled into a capsule before the final sealing. The capsules containing the couples were annealed at 900°C in a horizontal Lindberg 3-zone furnace for 168 hours. After the diffusion anneal, the couples were quenched in water to preserve the high temperature composition and/or microstructure.

The diffusion couple assembly was then mounted, sectioned and metallographically prepared for microstructural observations. Excellent diffusion bonding in all couples was observed. Then, cross-section surface was polished with 1μm diamond paste for electron microprobe analysis (EPMA). The concentration profiles of Fe, Ni, Cr, Si and Ge for the diffusion couples were determined with a
JEOL 733 (Tokyo, Japan) microprobe by point-to-point counting techniques using pure standards of all the constituent alloying elements. Intensities of $K_a$ X-radiations were measured and converted to concentrations of Fe, Ni, Cr, Si and Ge with appropriate ZAF (atomic number, Z; absorption, A; fluorescence, F) corrections.

Table 2 List of solid-to-solid diffusion couples annealed at 900°C for 168 hours.

<table>
<thead>
<tr>
<th>Series</th>
<th>Diffusion Couples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Ni vs. Fe-Ni-Cr</td>
<td>Fe-Ni vs. Fe-Ni-Cr-Si</td>
</tr>
<tr>
<td>Fe-Ni-Cr-X (Si,Ge)</td>
<td>Fe-Ni vs. Fe-Ni-Cr-Ge</td>
</tr>
</tbody>
</table>

Concentration profiles obtained from EPMA were smoothened by a smoothening-spline-tool using MatLab (The Math Works, Natick, MA). The analytical method used in this study to determine interdiffusion coefficients is by the integration of interdiffusion fluxes (e.g., Eqs. 5 and 6) only. It does not require the determination of concentration gradients that significantly reduces the influence of a smoothening procedure on the determination of interdiffusion coefficients.

Results and Discussion

Figs. 1 and 2 present examples of experimental and smoothened concentration profiles that were used for the determination of interdiffusion fluxes and interdiffusion coefficients. The scatters in the concentration profiles for all diffusion couples were minimal and within the experimental uncertainty associated with EPMA. Consistency in experimental and smoothened concentration profiles of Ni, owing to similar terminal concentration was examined by multiple EPMA acquisitions (e.g., independent Ni concentration) and by close examination of concentration profiles for Cr and X ternary alloying additions (e.g., dependent Ni concentrations).

![Graphs showing concentration profiles for Cr, Ni, Si, and Fe.](image)

Fig. 1. Typical experimental and smoothened concentration profiles from solid-to-solid diffusion couple, Fe-Ni vs. Fe-Ni-Cr-Si annealed at 900°C for 168 hours.
Fig. 2. Typical experimental and smoothened concentration profiles from solid-to-solid diffusion couple, Fe-Ni vs. Fe-Ni-Cr-Ge annealed at 900°C for 168 hours.

From concentration profiles obtained from diffusion couples, average effective interdiffusion coefficients \( \bar{D}_{\text{eff}} \)'s on either side of the Matano plane were determined using Eq. 3, and are reported in Table 3. Fe-Ni vs. Fe-Ni-Cr is considered as a reference to compare and contrast the diffusional interactions of alloying elements Si and Ge. Average effective interdiffusion coefficients reported in Table 3 are comparable in magnitude to those determined for Ni-Cr-X (Si, Ge) alloys at 900°C [12].

Alloying additions have increased the magnitude of average effective interdiffusion coefficients of Cr and Fe on the \( \{ C_i \sim C_{i}^{*} \} \) side with X \( (X = \text{Si or Ge}) \) alloying additions.

Table 3 Average effective interdiffusion coefficients determined from Fe-Ni vs. Fe-Ni-Cr-X (Si, Ge) diffusion couples annealed at 900°C for 168 hours. (Units: \( 10^{-16} \) m\(^2\)/s)

<table>
<thead>
<tr>
<th>Diffusion Couple</th>
<th>Composition Range</th>
<th>( \bar{D}_{\text{eff}} )</th>
<th>( \bar{D}_{\text{eff}}^{X} )</th>
<th>( \bar{D}_{\text{eff}}^{\text{Si}} )</th>
<th>( \bar{D}_{\text{eff}}^{\text{Fe}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Ni vs. Fe-Ni-Cr</td>
<td>( { C_i \sim C_i^{*} } )</td>
<td>0.6</td>
<td>N/A</td>
<td>N/A</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>( { C_i \sim C_i^{*} } )</td>
<td>0.3</td>
<td>N/A</td>
<td>N/A</td>
<td>0.3</td>
</tr>
<tr>
<td>Fe-Ni vs. Fe-Ni-Cr-Si</td>
<td>( { C_i \sim C_i^{*} } )</td>
<td>0.7</td>
<td>1.3</td>
<td>-2.8</td>
<td>0.9</td>
</tr>
<tr>
<td>(X = Si)</td>
<td>( { C_i \sim C_i^{*} } )</td>
<td>0.8</td>
<td>1.2</td>
<td>-2.3</td>
<td>1.0</td>
</tr>
<tr>
<td>Fe-Ni vs. Fe-Ni-Cr-Ge</td>
<td>( { C_i \sim C_i^{*} } )</td>
<td>0.7</td>
<td>2.8</td>
<td>3.9</td>
<td>0.7</td>
</tr>
<tr>
<td>(X = Ge)</td>
<td>( { C_i \sim C_i^{*} } )</td>
<td>1.8</td>
<td>2.7</td>
<td>2.9</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Note: \( \bar{D}_{\text{eff}}^{\text{Si}} \) could not be determined since there was no observable development of concentration gradient (i.e., pseudo-binary).

Dahi's [16] study for interdiffusion in Fe-Ni-Cr alloys at 1100°C reported a decrease in \( \bar{D}_{\text{eff}}^{\text{Cr}} \) values with an increase in Cr at constant Ni concentration. Similar observation was made in this study.
from Fe-Ni vs. Fe-Ni-Cr diffusion couple where $\overline{D}_{\text{Cr}}^\text{eff}$ was determined to decrease on the $(C_0^* - C_1^*)$ region with higher Cr content. However, the influence of Si and Ge alloying additions on quaternary diffusion couples altered this trend by increasing the $\overline{D}_{\text{Cr}}^\text{eff}$ on the $(C_0^* - C_1^*)$ side where the contents of both Cr and X (X = Si or Ge) are higher. The $\overline{J}_{\text{Ni}}$ caused an uphill-diffusion of Ni as shown in Fig. 1, which yielded a negative average effective interdiffusion coefficients of Ni, $\overline{D}_{\text{Ni}}^\text{eff}$, reported in Table 3. This indicates a significant diffusion interaction between Ni and Si in austenitic Fe-based alloys where $\overline{J}_{\text{Ni}}$ would be significantly influence by the concentration gradient of Si, $\overline{c}_{\text{Si}}/\overline{c}_X$. There was no “noticeably-unusual” redistribution of Ni in Fe-Ni vs. Fe-Ni-Cr-Ge diffusion couple as shown in Fig. 2. However, a higher magnitude of $\overline{D}_{\text{Ni}}^\text{eff}$ in Table 3 is noted for all concentration ranges within this diffusion couple.

Concentration profiles obtained from diffusion couples were employed to determine the average quaternary interdiffusion coefficients $\overline{D}_{\text{Ni}}^\text{eff}(i,j)=\text{Cr, Ni, X}$ on either side of the Matano plane using Eq. 5 and Eq. 6. They are reported in Table 4. Average ternary interdiffusion coefficients $\overline{D}_{\text{Ni}}^\text{eff}(i,j)=\text{Cr, Ni}$ could not be determined since there was no observable development of concentration gradient for Ni in Fe-Ni vs. Fe-Ni-Cr diffusion couple (i.e., pseudo-binary). Table 4 reports that the magnitude of these interdiffusion coefficients are comparable to those obtained for Ni-Cr-X alloys at 900°C [11]. These diffusion couples were designed with initial $\overline{c}_{\text{Cr}}/\overline{c}_X$ and $\overline{c}_{\text{Si}}/\overline{c}_X$, so that a positive and negative $\overline{D}_{\text{NiX}}^\text{ref}$ indicates an increase and a decrease in $\overline{J}_{\text{Cr}}$, respectively. Also, the initial $\overline{c}_{\text{Cr}}/\overline{c}_X$ implies that, $\overline{J}_{\text{Ni}}$ is mainly due to $\overline{c}_{\text{Cr}}/\overline{c}_X$ and/or $\overline{c}_X/\overline{c}_X$, and the magnitude and sign of $\overline{D}_{\text{NiX}}^\text{ref}$ and/or $\overline{D}_{\text{NiX}}^\text{ref}$.

Table 4 Average quaternary interdiffusion coefficients determined from Fe-Ni vs. Fe-Ni-Cr-X (X = Si or Ge) diffusion couples annealed at 900°C for 168 hours. (Units: $10^{-16}$ m$^2$/s)

<table>
<thead>
<tr>
<th>Couple</th>
<th>Composition Range</th>
<th>$\overline{D}_{\text{CrX}}^\text{ref}$</th>
<th>$\overline{D}_{\text{CrNi}}^\text{ref}$</th>
<th>$\overline{D}_{\text{NiX}}^\text{ref}$</th>
<th>$\overline{D}_{\text{NiNi}}^\text{ref}$</th>
<th>$\overline{D}_{\text{CrNi}}^\text{ref}$</th>
<th>$\overline{D}_{\text{NiX}}^\text{ref}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Ni vs. Fe-Ni-Cr-Si (X=Si)</td>
<td>$(C_0^* - C_1^*)$</td>
<td>1.1</td>
<td>0.3</td>
<td>-2.1</td>
<td>-0.1</td>
<td>2.7</td>
<td>2.7</td>
</tr>
<tr>
<td>Fe-Ni vs. Fe-Ni-Cr-Ge (X=Ge)</td>
<td>$(C_0^* - C_1^*)$</td>
<td>1.0</td>
<td>0.3</td>
<td>-1.1</td>
<td>-0.3</td>
<td>1.6</td>
<td>4.2</td>
</tr>
</tbody>
</table>

Note: “Neg.” refers to magnitude less than $0.1 \times 10^{-16}$ m$^2$/s.

The $\overline{D}_{\text{CrX}}^\text{ref}$ and $\overline{D}_{\text{NiX}}^\text{ref}$ cross coefficients have been reported small in magnitude and both positive and negative signs in literature [16-18] for Fe-Ni-Cr alloys. This holds true for quaternary cross coefficients, $\overline{D}_{\text{CrNi}}^\text{ref}$ and $\overline{D}_{\text{NiNi}}^\text{ref}$ reported in Table 4. This implies that there is no significant influence of Ni and Cr on each other in austenitic Fe alloys. The magnitude of $\overline{D}_{\text{NiNi}}^\text{ref}$ is lower than that of both
$\tilde{D}_{\text{Ni}}^{\text{Fe}}$ and $\tilde{D}_{\text{Ge}}^{\text{Fe}}$ coefficients for Fe-Ni-Cr-Si alloys. However, the magnitude of $\tilde{D}_{\text{Ge}}^{\text{Fe}}$ and $\tilde{D}_{\text{Ni}}^{\text{Fe}}$ coefficients is comparable to that of $\tilde{D}_{\text{Cr}}^{\text{Fe}}$ and $\tilde{D}_{\text{Si}}^{\text{Fe}}$ coefficients. The large magnitude of $\tilde{D}_{\text{Ni}}^{\text{Fe}}$ would have caused an uphill-diffusion of Ni. The magnitude of $\tilde{D}_{\text{Ge}}^{\text{Fe}}$ coefficient is comparable with that of $\tilde{D}_{\text{Cr}}^{\text{Fe}}$, and slightly lower than that of $\tilde{D}_{\text{Si}}^{\text{Fe}}$ coefficient. Even though the magnitude of $\tilde{D}_{\text{Ge}}^{\text{Fe}}$ is large, an apparent uphill-diffusion of Ni is be absent due to a large $\tilde{D}_{\text{Ni}}^{\text{Fe}}$ despite a very small $\tilde{D}_{\text{Ni}}^{\text{Ni}}/\tilde{D}_{\text{X}}^{\text{X}}$.

**Summary**

Interdiffusion in Fe-Ni-Cr (fcc γ phase) alloys with small additions of Si and Ge was studied using solid-to-solid diffusion couples annealed at 900°C for 168 hours. Alloying addition of Si or Ge altered diffusional behavior of Ni and Cr in austenitic Fe-Ni-Cr alloys. Large magnitude of cross coefficients, $\tilde{D}_{\text{Cr}}^{\text{Fe}}$, $\tilde{D}_{\text{Ge}}^{\text{Fe}}$, $\tilde{D}_{\text{Si}}^{\text{Fe}}$, and $\tilde{D}_{\text{Ni}}^{\text{Fe}}$ were observed in Fe-Ni-Cr-X (X=Si or Ge) alloys. The Si addition has caused on uphill-diffusion of Ni while there was no measurable uphill diffusion of Ni due to an increase in $\tilde{D}_{\text{Ni}}^{\text{Fe}}$ in Fe-Ni-Cr-Ge alloy, despite the large positive $\tilde{D}_{\text{Ni}}^{\text{Fe}}$.

**Acknowledgements**

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**References**


Effects of Ir or Ta Alloying Addition on Interdiffusion of L12-Ni3Al


A. Advanced Materials Processing and Analysis Center, NML, University of Central Florida, 4000 Central Florida Boulevard, Orlando, FL 32816, USA
B. National Institute of Materials Science, Tsukuba, Japan
C. Kobe Steel, Co. Ltd., Japan

1. Introduction

Nickel-base superalloys are extensively used in both aviation and land-based gas turbine environments, and many studies have been devoted to improve their mechanical properties and microstructural stability [1]. Ni-base superalloys are typically composed of L12 + g phase (Ni3Al) coherently precipitated in a fcc g phase matrix. The diffusion mobility database for Ni-base superalloys is available for fcc phase [2]. Although g is the strengthening phase, Ni-base superalloys, a limited number of studies exists on interdiffusion of the g phase [3-9], particularly when alloyed with other constituents in superalloys. An understanding of multicomponent diffusion processes in these alloys is very important because it is essential to achieve a durable microstructure for strength and oxidation resistance at high temperature. This study is also fueled by recent conceptual development of refractory based superalloys with L12 + g precipitates and refractory-modified aluminate coatings [10-15] for optimized oxidation resistance along with reduced interdiffusion between oxide resistant coatings and structural superalloy substrate (e.g., formation of deleterious phases due to interdiffusion at the interface). The crystal structure of Ni3Al is derived from an fcc based Cu3Au prototype lattice with face centered sublattice sites (a-sites) occupied by Ni atoms and corner sublattice sites (b-sites) by Al-atoms. In general, highly electronegative substitutional elements (e.g., Pt, Cu and Co) occupy the a-sites, whereas highly electronegative ones (e.g., Ti, Ta and Nb) occupy the b-sites in Ni3Al [1]. The relative site-preference for some ternary alloying elements can be best illustrated from the direction of the solubility lines for the g-phase within the ternary isotherm of Ni-Al-K (K-alloying addition) system at 1273 K as shown in Fig. 1 [6]. In Fig. 1, Pt (i.e., group VIII metal that includes Ir) and Ta are highlighted with circles. Site-preference of ternary alloying additions to Ni3Al has attracted significant interest, as this true solid solution accepts considerable amount of third element into solution [17-19].

The alloying phenomenon ultimately plays an important role in enhancing the mechanical properties and high-temperature oxidation resistance of this intermetallic [19-25]. The behavior of ternary substitutional alloying additions to Ni3Al was first reported by Guard and Westbrook [17] as Ni-occupiers. Al-occupiers or both Ni- and Al-occupiers. Several studies [26-28] have predicted the change in site-preference of alloying elements as a function of temperature and chemical composition of Ni3Al.

Diffusional interactions of a ternary alloying addition to Ni3Al can be a tool to examine the site-preference. The diffusion mechanisms in ordered alloys is recognized to be more complex than for disordered solid solutions [29]. In the case of L12 structure, the diffusion mechanism is even more complex than that for B2 structure. Diffusion can occur through a- or b-site where Ni or Al-atoms mainly occupy, respectively, and the diffusion coefficient...
largely depends on the alloy composition, namely the degrees of order [30–32]. While tracer diffusion studies in Ni$_3$Al are difficult since Ni is not readily available, self-diffusion of Ni and chemical diffusion of a dilute element in Ni$_3$Al systems have been studied [3–5]. The temperature dependence of the diffusion for a ternary alloying addition is evident from Arrhenius rate law [5,33–35]. The site occupation has been observed to diffuse slower than the a-site occupants [29,36]. This is attributed to the fact that, in Li$_2$-ordered structure, each Ni atom is surrounded by 4 Al atoms and 6 Ti atoms, where as an Al atom is surrounded by 12 Ni atoms. Therefore, the activation enthalpy of alloying element increases mainly due to the antisite defect formation [36].

For an additional insight into the diffusion process in Li$_2$-ordered systems, to enhance microstructural stability of Ni-based superalloys, and to develop refractory-modified alumina oxidation resistant coatings, we examined the ternary diffusion interaction of In and Ta additions to the Li$_2$Ni$_3$Al phase. Solid-to-solid diffusion couples were assembled and annealed at 1473 K for 5 h. Based on concentration profiles obtained, the ternary diffusion coefficients from integration of interdiffusion fluxes, and ternary interdiffusion coefficients via Boltzmann–Matano analysis were determined to assess how In and Ta additions influence interdiffusion behavior of Ni and Al in Li$_2$Ni$_3$Al phase. Additional estimates of binary interdiffusion coefficients in Ni$_3$Al and In$_2$Au and tracer diffusion coefficients of In and Ta in Ni$_3$Al were made.

2. Determination of ternary interdiffusion coefficients

From Onsager’s formalism [37,38] and Frick’s law [39], the interdiffusion flux $J_i$ of component $i$ in a ternary system can be expressed in terms of two independent concentration gradients $\nabla C_i$ by:

$$J_i = D_{ij} \frac{\nabla C_i}{\nabla C_j} \frac{\nabla C_j}{\nabla C_k} \hat{v}_{ik}$$

where $D_{ij}$ refers to the ternary interdiffusion coefficients. An independent determination of the four concentration-dependent interdiffusion coefficients is generally carried out by the use of Boltzmann–Matano analysis with two independent diffusion couples that develop a common composition in the diffusion zone where the interdiffusion coefficients can be evaluated [40,41]. Alternatively, the interdiffusion fluxes of individual components can be determined directly from their concentration profiles.

Without the need or use of the interdiffusion coefficients, the interdiffusion flux of any section x can be calculated directly from the concentration profile from the relation [42,43]:

$$J_i = \frac{1}{2} \frac{\partial}{\partial x} C_i (x) \frac{\partial C_i}{\partial x} \hat{v}_{ik}$$

where $i$ is the component, $C_i(x)$ and $C_k(x)$ are the terminal concentrations, and $\hat{v}_{ik}$ refers to the location of the Matano plane. Based on the direct determination of interdiffusion fluxes, diffusion behavior of components can be examined, and observations of zero-flux planes (ZFPs) and flux reversals have been reported for individual components in isothermal ternary interdiffusion studies [42–45]. Furthermore, the calculated interdiffusion fluxes can be related to interdiffusion parameters which can be employed to generate and characterize concentration profiles developed in ternary diffusion couples [46–49].

The interdiffusion fluxes determined from Eq. (2) as functions of x can be integrated over a selected region, $x_1$ to $x_2$, to yield an expression based on Eq. (1) [49]:

$$Z_{x_1} Z_{x_2} \frac{\partial}{\partial x} C_i (x) \frac{\partial C_i}{\partial x} \hat{v}_{ik}$$

where $D_{ij}$ refers to the average value of matrix and cross-interdiffusion coefficients. With $D_{ij}$ taken as constants, Eq. (1) is re-written as:

$$J_i = \frac{1}{2} \frac{\nabla C_i}{\nabla C_j} \frac{\nabla C_j}{\nabla C_k} \hat{v}_{ik}$$

If both sides of Eq. (4) are multiplied by $x_2 - x_1$ and integrated over the diffusion zone between $x_1$ and $x_2$, one obtains in general [49]:

$$Z_{x_1} x_2 \frac{\partial}{\partial x} C_i (x) \frac{\partial C_i}{\partial x} \hat{v}_{ik}$$

$$Z_{x_1} x_2 \frac{\partial}{\partial x} C_i (x) \frac{\partial C_i}{\partial x} \hat{v}_{ik}$$

Table 1: Material composition of alloys employed for diffusion couple studies

<table>
<thead>
<tr>
<th>Alloy identification</th>
<th>Composition (atom percent)</th>
<th>Composition (weight percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_3$Al</td>
<td>70.0</td>
<td>75.3</td>
</tr>
<tr>
<td>Ni$_3$Al-0.1In</td>
<td>70.0</td>
<td>75.3</td>
</tr>
<tr>
<td>Ni$_3$Al-0.1In</td>
<td>70.0</td>
<td>75.3</td>
</tr>
<tr>
<td>Ni$_3$Al-0.1In</td>
<td>70.0</td>
<td>75.3</td>
</tr>
<tr>
<td>Ni$_3$Al-0.1In</td>
<td>70.0</td>
<td>75.3</td>
</tr>
</tbody>
</table>

Table 2: Diffusion couples assembled and analysed after annealing at 1473 K for 5 h

<table>
<thead>
<tr>
<th>Series</th>
<th>Diffusion couple</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_3$Al vs. Ni$_3$Al</td>
<td>Ni$_3$Al vs. Ni$_3$Al-0.1In</td>
</tr>
<tr>
<td>Ni$_3$Al vs. Ni$_3$Al-0.1In</td>
<td>Ni$_3$Al vs. Ni$_3$Al-0.1In</td>
</tr>
<tr>
<td>Ni$_3$Al vs. Ni$_3$Al-0.1In</td>
<td>Ni$_3$Al vs. Ni$_3$Al-0.1In</td>
</tr>
<tr>
<td>Ni$_3$Al vs. Ni$_3$Al-0.1In</td>
<td>Ni$_3$Al vs. Ni$_3$Al-0.1In</td>
</tr>
</tbody>
</table>

Fig. 1: Solubility ranges of selected ternary alloying additions in Ni$_3$Al (adapted from Ohtani et al. [46] at 1373 K)
If the exponent $m$ is chosen to be zero, Eq. (5) becomes identical to Eq. (3). For $m = 1$, Eq. (5) yields [49]:

$\frac{Z_{x_2}}{x_2} \frac{x_1}{x_0} \frac{c_{x_2}}{c_{x_1}} \frac{D_{ij}}{D_{kl}} = \frac{Z_{x_1}}{x_1} \frac{x_2}{x_0} \frac{c_{x_1}}{c_{x_2}} \frac{D_{kl}}{D_{ij}}$

Fig. 2. Concentration profiles of (a) Ni, (b) Al and (c) Ta obtained from diffusion couple Ni-204 vs. Ni-23Al-2Ta annealed at 1473 K for 5 h. Open circles and solid lines represent EPMA measurement and calculated concentration profiles, respectively.

Fig. 3. Concentration profiles of (a) Ni, (b) Al and (c) Ta obtained from diffusion couple Ti-24.5Al vs. Ti-23Al-1.5Ta annealed at 1473 K for 5 h. Open circles and solid lines represent EPMA measurement and calculated concentration profiles, respectively.

Eqs. (3) and (6) provide four equations involving the $D_{ij}$, $D_{kl}$, $D_{ij}$, and $D_{kl}$ interdiffusion coefficients and can be easily set up from experimental concentrations and the corresponding interdiffusion fluxes. Hence, from the concentration profiles of a single diffusion couple, $D_{ij} \equiv \frac{1}{2}$ coefficients, characteristic of the diffusion path, can be determined by using Eqs. (3) and (6) over selected composition ranges in the diffusion zone [49]. Eqs. (3) and (6) provide independent relations when the composition ranges are selected to include non-linear segments of the profiles. This analysis method to determine average ternary interdiffusion coefficients has been directly employed in various studies [550–58]. In addition, the
independence of Eqs. (3) and (5) in solving the average ternary interdiffusion coefficients for the concentration profiles obtained in this study is demonstrated in Section 4. In this paper, the analysis applied to the concentration profiles of experimental ternary diffusion couples in Ti-Ni-Al-X (X = Ir or Ta) intermetallics is carried out for 2 segments, one on either side of the Matano plane; the two chosen composition ranges are $C_1$, $C_2^*$ and $C_2^*$, $C_3$ where $C_2^*$ refers to the concentration at the Matano plane. The average ternary interdiffusion coefficients, $D_{ij}$, determined on either side of the Matano plane are employed to simulate experimental concentration profiles using error-function solution for infinite ternary systems from Fujita and Gosting [59]. For Ni-Al, Ni-Al-Ir diffusion couples, the average ternary interdiffusion coefficients, $D_{ij}$, are found to be consistent with ternary interdiffusion coefficients, $D_{ij}$, determined by Boltzmann-Matano analysis [40,41].

3. Experimental details

Ni-Al, Ni-Al-Ir and Ni-Al-Ta alloys were prepared by the vacuum arc melting of 99.97 wt.% Ni, 99.9 wt.% Al, 99.2 wt.% Ir, and 99.2 wt.% Ta, according to the compositions presented in Table 1. The alloys were cast into a semi-cylindrical mold with the diameter of 8 mm in an arc furnace. The alloy rods were homogenized at 1473 K for 137 h in the vacuum furnace evacuated to a pressure less than $10^{-5}$ Pa. The homogenized alloys were then sectioned into discs with the height of 15 mm. The surfaces of alloy discs were polished metallographically up to 1200 grit and cleaned thoroughly prior to diffusion couple assembly.

Table 2 presents diffusion couples that were assembled and analyzed in this study. Coupled discs were put into a $\text{Si_3N_4}$ jig and annealed at 1473 K for 0.5 h in a vacuum furnace to promote initial bonding. Since the metal discs have large thermal expansion coefficients than the $\text{Si_3N_4}$ jig, the discs can adhere to each other due to the compression during the annealing treatment. Each diffusion couple fabricated in this manner was then sealed in an evacuated transparent quartz capsule and annealed at 1473 K for 4.5 h in an atmosphere furnace. All diffusion couples were water quenched after the high-temperature anneal to preserve high-temperature microstructure and concentrations. In this study, the time required for the diffusion bonding treatment (0.5 h) was added to the total

<table>
<thead>
<tr>
<th>Diffusion couple</th>
<th>Composition range</th>
<th>$D_{ij}$</th>
<th>$D_{kl}$</th>
<th>$D_{lm}$</th>
<th>$D_{km}$</th>
<th>$D_{kl}$</th>
<th>$D_{lm}$</th>
<th>$D_{km}$</th>
<th>$D_{kl}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-25Al vs. Ni-23.5Al-1Ir</td>
<td>C, $\text{Ni}_2\text{Al}_3$</td>
<td>0.231</td>
<td>0.127</td>
<td>0.216</td>
<td>0.278</td>
<td>0.227</td>
<td>0.203</td>
<td>0.278</td>
<td>0.267</td>
</tr>
<tr>
<td>Ni-24.5Al vs. Ni-24.5Al-1Ir</td>
<td>C, $\text{Ni}_2\text{Al}_3$</td>
<td>0.419</td>
<td>0.367</td>
<td>0.430</td>
<td>0.512</td>
<td>0.440</td>
<td>0.392</td>
<td>0.512</td>
<td>0.473</td>
</tr>
<tr>
<td>Ni-26Al vs. Ni-24.5Al-2Ir</td>
<td>C, $\text{Ni}_2\text{Al}_3$</td>
<td>0.819</td>
<td>0.752</td>
<td>0.824</td>
<td>0.897</td>
<td>0.844</td>
<td>0.796</td>
<td>0.897</td>
<td>0.864</td>
</tr>
<tr>
<td>Ni-24.5Al vs. Ni-24.5Al-2Ir</td>
<td>C, $\text{Ni}_2\text{Al}_3$</td>
<td>1.227</td>
<td>1.083</td>
<td>1.227</td>
<td>1.364</td>
<td>1.183</td>
<td>1.128</td>
<td>1.364</td>
<td>1.250</td>
</tr>
<tr>
<td>Ni-26Al vs. Ni-24.5Al-3Ir</td>
<td>C, $\text{Ni}_2\text{Al}_3$</td>
<td>1.696</td>
<td>1.563</td>
<td>1.696</td>
<td>1.849</td>
<td>1.633</td>
<td>1.563</td>
<td>1.849</td>
<td>1.726</td>
</tr>
<tr>
<td>Ni-24.5Al vs. Ni-24.5Al-3Ir</td>
<td>C, $\text{Ni}_2\text{Al}_3$</td>
<td>2.172</td>
<td>1.945</td>
<td>2.172</td>
<td>2.325</td>
<td>2.013</td>
<td>1.909</td>
<td>2.325</td>
<td>2.193</td>
</tr>
</tbody>
</table>

Note: Ngl refers to magnitude less than 0.1 $\times 10^{-13}$ m/s².
annealing time. Thus, concentration profiles from all diffusion couples were analyzed with diffusion anneal time of 5 h.

Microstructures and concentration profiles of the annealed diffusion couples were analyzed by a Jeol-JXA-6000 electron probe microanalyzer (EPMA). An accelerating voltage of 20 kV, a beam current of 50 nA, and a probe diameter of 1 mm were employed for data acquisition of Ni Kα x-ray peak using LiF crystal, Al Kα x-ray peak using TaKα crystal, Ir Lα x-ray peak using LiF crystal, and Ta Lα x-ray peak using LiF crystal. Pure element standards of Ni, Al, Ir, Ta, along with ZAF correction (60), were used for quantification of concentrations via point-to-point count technique.

4. Results and analysis

4.1. Profiles of concentrations and interdiffusion fluxes

Figs. 2 and 3 present typical concentration profiles obtained by EPMA measurements from diffusion couples, Ni–2BAi vs. Ni–23Al-2Ir and Ni–24.5Ni vs. Ni–23Al-15Ir, respectively, annealed at 1473 K for 5 h. The x axes represent the distance from the Matano plane and the open circles are EPMA measurement. Scatter in the concentration profiles for all diffusion couples was minimum and within the experimental uncertainty associated with EPMA. The interdiffusion fluxes of individual components were then determined using Eq. (2) from experimental concentration profiles that were smoothed with a series of weighted splines. While no zero-flux plane was observed, a significant diffusional interaction between Ni and Ir, and Al and Ta was observed when NiAl was diffusion annealed against NiAl alloyed with Ir and Ir, respectively, as shown in Figs. 2 and 3. Clearly, the interdiffusion of Ni was greatly enhanced by the interdiffusion of Ir down the Ir gradient, while Al exhibited an uphill diffusion against its own gradient due to the interdiffusion of Ta. However, diffusion influencing Ir on Al and Ta on Ni is difficult to ascertain from the profiles presented in Figs. 2 and 3. Determination of ternary interdiffusion coefficients can quantify the extent and magnitude of these diffusional interactions, and provide a more complete picture of the composition design and modification of alloys and protective coatings.

4.2. Average ternary interdiffusion coefficients

From profiles of concentration and interdiffusion fluxes in Ni–Al vs. Ni–Al–Ir diffusion couples, average ternary interdiffusion coefficients, $D_{ij}^{p}$, were determined on either side of the Matano plane using Eqs. (3) and (6). Use of Eqs. (3) and (6) provides independent relations for the determination of average ternary interdiffusion coefficients as presented in Fig. 4. In this figure, for diffusion couple Ni–2BAi vs. Ni–23Al-2Ir whose

![Fig. 5: Variation of $D_{ij}^{p}$ against $x_0$](image)

Al-Ta coefficients in Eq. (3), equivalent to Eq. (5) when $m = 0$, and Eq. (6) equivalent to Eq. (6) when $m = 1$. The two lines generated by Eqs. (3) and (6) are sufficiently independent to obtain an approximate solution of $D_{ij}^{p}$ in Al-Ta. Coefficients that are expected for the composition range of $x_0$, $D_{ij}^{p}$ and $x_0$, in Table 4.
concentration profiles are presented in Fig. 2, the variation of \( D_{\text{Al}i}^{m} \) and \( D_{\text{Ni}i}^{m} \) in Eq. (5) where \( m = 0 \), equivalent to Eq. (3), and \( m = 1 \), equivalent to Eq. (6), is presented. The two lines generated by Eqs. (3) and (6) are sufficiently independent to obtain a unique solution of \( D_{\text{Al}i}^{m} \) and \( D_{\text{Ni}i}^{m} \) coefficients that are reported in Table 3.

The main diffusion coefficients, \( D_{\text{Al}i}^{m} \) and \( D_{\text{Ni}i}^{m} \) correspond well to the interdiffusion coefficients of Al and Ni reported in literature for binary Ni-Al at 1473 K [3–9]. Estimation of binary interdiffusion coefficients from the ternary diffusion couples and the comparison to the interdiffusion coefficients of Al and Ni reported in literature for binary Ni-Al are presented in detail in Section 4.4. The magnitudes of these main coefficients for Al and Ni are observed to be larger with higher Al content as well. The main interdiffusion coefficient of \( m = 0 \), \( D_{\text{Al}i}^{m} \), is 20–40 times lower in magnitude than the main coefficients of Ni and Al. Table 3 reports that \( D_{\text{Al}i}^{m} \) coefficients are negative, and smaller in magnitude than \( D_{\text{Ni}i}^{m} \) coefficients, and \( D_{\text{Al}i}^{m} \) coefficients are negligibly small (<0.1 \( 10^{-6} \) m²/s). Thus the interdiffusion flux of Al can be influenced only slightly by the interdiffusion of Ir. However, \( D_{\text{Ni}i}^{m} \) coefficients are positive and large (e.g., larger than the \( D_{\text{Al}i}^{m} \) coefficients in some cases), while \( D_{\text{Ir}i}^{m} \) coefficients are negligibly small (<0.1 \( 10^{-6} \) m²/s). The large positive \( D_{\text{Ni}i}^{m} \) coefficient corresponds well with an enhanced interdiffusion of Ni (e.g., down the gradient of \( i \)). Against the concentration gradient of \( i \), the large positive \( D_{\text{Ni}i}^{m} \) coefficient can therefore reduce the interdiffusion of Ni. The average ternary interdiffusion coefficients reported in Table 3 indicate a strong diffusional interaction between Ni and Ir both occupying the a-site in \( \text{Li}_{2} \) lattice structure.

The average ternary interdiffusion coefficients, \( D_{\text{Al}i}^{m} \), \( D_{\text{Ir}i}^{m} \), \( D_{\text{Ir}i}^{m} \), and \( D_{\text{Ir}i}^{m} \), determined on either side of the Matano plane for Ni-Al vs. Ni-Al-Ta couples are reported in Table 4. For diffusion couple Ni–24.5Al vs. Ni–24.5Al–1.5Ta where concentration profiles are presented in Fig. 3, the variation of \( D_{\text{Al}i}^{m} \) and \( D_{\text{Ni}i}^{m} \) in Eq. (5), equivalent to Eq. (6), where \( m = 0 \), and Eq. (6), equivalent to Eq. (5), where \( m = 1 \) is presented in Fig. 5. The two lines generated by Eqs. (3) and (6) are again sufficiently independent to obtain an unique solution of \( D_{\text{Al}i}^{m} \) and \( D_{\text{Ni}i}^{m} \) coefficients that are reported in Table 4.

The main diffusion coefficients, \( D_{\text{Al}i}^{m} \) and \( D_{\text{Ir}i}^{m} \), again correspond well to the interdiffusion coefficients of Al and Ni reported in literature [3–9] for Ni-Al at 1473 K. As aforementioned, estimation of binary interdiffusion coefficients from the ternary diffusion couples along with the comparison to the interdiffusion coefficients of Al and Ni reported in literature for binary Ni-Al is presented in detail in Section 4.4. The main interdiffusion coefficient of Ta, \( D_{\text{Ta}i}^{m} \), is 10–40 times lower in magnitude than the main coefficients of Ni and Al. Table 4 reports that \( D_{\text{Al}i}^{m} \) coefficients, are positive, and comparable in magnitude to \( D_{\text{Ni}i}^{m} \) coefficients, while \( D_{\text{Ta}i}^{m} \) coefficients are negligibly small (<0.1 \( 10^{-6} \) m²/s). Thus, the large positive \( D_{\text{Ta}i}^{m} \) coefficient corresponds well with an interdiffusion flux of Al (e.g., uphill diffusion) against the gradient of Ta. The \( D_{\text{Ni}i}^{m} \) coefficients are positive, but much smaller than the \( D_{\text{Ta}i}^{m} \) coefficients. Thus the interdiffusion flux of Ni can be influenced only slightly by the interdiffusion flux of Ta. The average ternary interdiffusion coefficients reported in Table 4 indicate a strong diffusional interaction between Al and Ta both occupying the b-site in \( \text{Li}_{2} \) lattice structure.

The average ternary interdiffusion coefficients reported in Tables 3 and 4 were employed to generate concentration profiles using error function solution provided by Fugita and Gotoh [59]. Excellent agreement between EPMA measurement and calculated concentration profiles were found for all couples. Typical examples are presented in Figs. 2 and 3 where open circles are the EPMA measurements and solid lines are the calculated concentration profiles.

4.3. Ternary interdiffusion coefficients determined by Boltzmann–Matano analysis

For the diffusion couples Ni–Al vs. Ni–Al–Ir, several intersecting compositions were found along the diffusion paths. Intersecting diffusion paths in Fig. 6 represent typical difficulties in determining interdiffusion coefficients by Boltzmann–Matano analysis for ordered intermetallics with ternary alloying addition. Two diffusion paths of interest can intersect at a shallow angle or with negligible Ir concentration gradient. These are due to site-preference of Ir and Ni on a-site in \( \text{Li}_{2} \) lattice structure, and small interdiffusion

![Fig. 6. Typical intersecting diffusion path of Ni–Al vs. Ni–Al–Ir diffusion couple as needed at 1473K for Ir. Compositions at these intersections were employed for the determination of ternary interdiffusion coefficients based on Boltzmann Matano analysis.](image-url)
Table 5
Ternary interdiffusion coefficients (10^-18 m^2/s) determined by Boltzmann–Matano analysis from Ni–Al vs. Ni–Al–Ir diffusion couples annealed at 1473 K for 5 h.

<table>
<thead>
<tr>
<th>Diffusion couples with intersecting diffusion paths</th>
<th>Intersecting composition (atom fraction)</th>
<th>$D_0$</th>
<th>$D_{2g}$</th>
<th>$D_{5g}$</th>
<th>$D_{10g}$</th>
<th>$D_{15g}$</th>
<th>$D_{20g}$</th>
<th>$D_{25g}$</th>
<th>$D_{30g}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-25Al vs. Ni-23Al-19</td>
<td>Al: 0.24</td>
<td>101.3</td>
<td>21.0</td>
<td>30.9</td>
<td>12.5</td>
<td>695.4</td>
<td>583.0</td>
<td>32.0</td>
<td>52.4</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23Al-19</td>
<td>Ir: 0.006</td>
<td>404.7</td>
<td>36.3</td>
<td>N.G.</td>
<td>17.2</td>
<td>489.6</td>
<td>512.7</td>
<td>N.G.</td>
<td>18.1</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23Al-19</td>
<td>Ir: 0.009</td>
<td>563.9</td>
<td>33.0</td>
<td>N.G.</td>
<td>12.3</td>
<td>664.0</td>
<td>581.0</td>
<td>N.G.</td>
<td>12.3</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23Al-19</td>
<td>Ir: 0.010</td>
<td>634.6</td>
<td>5.4</td>
<td>N.G.</td>
<td>11.5</td>
<td>634.5</td>
<td>621.4</td>
<td>N.G.</td>
<td>11.6</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23Al-19</td>
<td>Ir: 0.001</td>
<td>419.3</td>
<td>117.6</td>
<td>N.G.</td>
<td>21.0</td>
<td>419.3</td>
<td>311.0</td>
<td>N.G.</td>
<td>25.0</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23Al-19</td>
<td>Ir: 0.009</td>
<td>504.0</td>
<td>19.5</td>
<td>N.G.</td>
<td>11.0</td>
<td>504.0</td>
<td>360.6</td>
<td>N.G.</td>
<td>20.0</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23Al-19</td>
<td>Ir: 0.001</td>
<td>627.2</td>
<td>28.1</td>
<td>N.G.</td>
<td>16.2</td>
<td>627.2</td>
<td>284.3</td>
<td>N.G.</td>
<td>19.2</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23Al-19</td>
<td>Ir: 0.007</td>
<td>623.0</td>
<td>26.9</td>
<td>N.G.</td>
<td>13.7</td>
<td>623.0</td>
<td>326.2</td>
<td>N.G.</td>
<td>13.7</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23Al-19</td>
<td>Ir: 0.0002</td>
<td>644.4</td>
<td>72.2</td>
<td>N.G.</td>
<td>12.0</td>
<td>644.4</td>
<td>398.6</td>
<td>N.G.</td>
<td>12.1</td>
</tr>
</tbody>
</table>

Note: N.G. refers to magnitude less than 0.1 \times 10^{-18} m^2/s.

Coefficient of Ir, respectively, in order to determine the ternary interdiffusion coefficients at these compositions, Boltzmann–Matano analysis was employed using a variety of concentrations and distances that are certain with respect to EPMA measurement. The values of ternary interdiffusion coefficients determined in this study are reported in Table 5, and correspond well to the average ternary interdiffusion coefficients on either side of the Matano plane presented in Table 3.

Several relative maxima and minima in concentration profiles (e.g., $C_{Al}$ vs. $C_{Ir}$) were also observed for Ni in Ni–Al vs. Ni–Al–Ir couples and for Al in Ni–Al vs. Ni–Al–Ta couples as shown in Figs. 2 and 3. Ternary interdiffusion coefficients at these compositions were also determined since one of the terms in Eq. (1) becomes zero. These values are reported in Table 6 for Ni–Al vs. Ni–Al–Ir couples, and correspond well to the average ternary interdiffusion coefficients on either side of the Matano plane reported in Table 3, and ternary interdiffusion coefficients determined by Boltzmann–Matano analysis reported in Table 5. Unfortunately, for Ni–Al vs. Ni–Al–Ta couples, the concentration and its gradient for Ta, where the concentration gradient of Al becomes zero (e.g., relative maxima and minima of Al), were uncertain (e.g., $C_{Al}$ vs. 0 and $C_{Ir}$ vs. 0) to determine any ternary interdiffusion coefficients.

4.4. Estimation of binary interdiffusion coefficients in Ni–Al

The ternary interdiffusion coefficients $D_{2g}$ and $D_{5g}$ approach the binary $D_i$ for Ni–Al as the concentration of Ir or Ta decreases to zero. Hence, values of $D_{2g}$ or $D_{5g}$ for Ni or Al were estimated from ternary diffusion couples where Ir or Ta concentration was negligible. Small segments of the diffusion zone (e.g., Hicks' law for substitutional binary alloy) were found in all couples since $D_{2g}$ and $D_{5g}$ are much smaller than $D_{2g}$ and $D_{5g}$. The $D_i$ values extrapolated from the ternary couples with large enough concentration difference (e.g., $D_{2g}$ or $D_{5g}$ $> 2 \times 10^{-18}$ m^2/s) in terminal alloys are presented in Fig. 7. The magnitude of $D_i$ appears consistent with the available binary diffusion data (3–9) for Ni–Al. However, the composition dependence could not be evaluated correctly since this estimation is carried out near the terminal end of the concentration profiles with high uncertainty in the magnitude of concentration gradients for Al, and assumes that the Ir or Ta concentration less than 2 at % do not influence the value of $D_i$.

4.5. Estimation of tracer diffusion coefficient of Ir and Ta in Ni–Al

For component $i$ diffusing into a binary alloy, $j-k$, the cross-interdiffusion coefficient $D_{ijk}$ becomes negligible at infinite dilution of component $i$ in $j-k$ alloy [65]. Then the value of the main coefficient $D_{ijk}$ approaches that of the tracer diffusion coefficient $D_{ij}$

$$C_i / C_j \leq 0.05$$

Thus, the tracer diffusion coefficients of Ir and Ta in Ni–Al alloy can be estimated from the main interdiffusion coefficient of Ir $D_{ij}$.

Table 6
Ternary interdiffusion coefficients (10^-18 m^2/s) determined at relative maxima and minima of concentration profiles in Ni–Al vs. Ni–Al–Ir diffusion couples annealed at 1473 K for 5 h.

<table>
<thead>
<tr>
<th>Couple</th>
<th>Interdiffusion coefficients at diffusion couples (atom fraction)</th>
<th>Ternary interdiffusion coefficients at diffusion couples (atom fraction)</th>
<th>Extent composition (atom fraction)</th>
<th>Ternary interdiffusion coefficients at diffusion couples (atom fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-25Al vs. Ni-23Al-19</td>
<td>Al: 0.242</td>
<td>Ir: 0.0007</td>
<td>727.4</td>
<td>12.5</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23Al-19</td>
<td>Ir: 0.0006</td>
<td>156.0</td>
<td>12.0</td>
<td>Al: 0.241</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23Al-19</td>
<td>Ir: 0.0005</td>
<td>686.5</td>
<td>10.9</td>
<td>Al: 0.241</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23Al-19</td>
<td>Ir: 0.0001</td>
<td>552.2</td>
<td>12.4</td>
<td>Al: 0.241</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23Al-19</td>
<td>Ir: 0.0004</td>
<td>778.3</td>
<td>26.8</td>
<td>Al: 0.241</td>
</tr>
</tbody>
</table>
or \( D_{\text{NAl}} \) and \( D_{\text{TAl}} \) using Eq. (7), provided that the concentration of Ir or Ta approaches zero within the diffusion zone so that the cross-interdiffusion coefficients, \( D_{\text{NAl}} \) or \( D_{\text{TAl}} \) and \( D_{\text{NiAl}} \) or \( D_{\text{TiAl}} \), become negligible. Such regions were found in all couples since \( D_{\text{NAl}} \) and \( D_{\text{TAl}} \) coefficients are much smaller than \( D_{\text{NiAl}} \) and \( D_{\text{TiAl}} \). Values of tracer diffusion coefficients of Ir, \( D_{\text{Ir}} \) and Ta, \( D_{\text{Ta}} \), were extrapolated from the main interdiffusion coefficients, \( D_{\text{Ir}} \) or \( D_{\text{Ta}} \), and \( D_{\text{NiAl}} \) or \( D_{\text{TiAl}} \), as the concentration of Ir and Ta, respectively, becomes zero. The extrapolations for \( D_{\text{Ir}} \) and \( D_{\text{Ta}} \) from the ternary interdiffusion coefficients on the basis of Eq. (7) are presented in Figs. 8 and 9, respectively. The estimated values of \( D_{\text{Ir}} \) and \( D_{\text{Ta}} \) are reported in Table 7.

The estimated tracer diffusion coefficient for the b-site-occupying Ta (2.6 \( \times \) 10\(^{-11}\) m\(^2\) s\(^{-1}\)) is lower than that for the a-site-occupying Ir (14.7 \( \times \) 10\(^{-11}\) m\(^2\) s\(^{-1}\)). More importantly, at these dilute concentrations of Ir and Ta, the magnitude of tracer diffusion coefficients of both Ir and Ta are very similar to ternary interdiffusion coefficients, namely \( D_{\text{Ir}} \) (or \( D_{\text{Ta}} \)) and \( D_{\text{NiAl}} \) (or \( D_{\text{TiAl}} \)).

5. Concluding remarks

Ternary interdiffusion interactions of Ir and Ta addition on the L1\(_2\) NiAl phase were examined using solid-to-solid diffusion couples annealed at 1473 K for 5 h. Average ternary interdiffusion coefficients were determined from an integration of interdiffusion fluxes for individual components. The magnitude of \( D_{\text{NiAl}} \) and \( D_{\text{TiAl}} \) coefficients was determined to be much larger than that of \( D_{\text{Ir}} \) and \( D_{\text{Ta}} \). The \( D_{\text{Ir}} \) coefficient was determined to be positive and large in magnitude; Ir substitutes in Ni-site and influences the interdiffusion of Ni significantly. The \( D_{\text{Ta}} \) coefficient was determined to be negative and moderately large in magnitude; Ta substitutes in Al-site and influences the interdiffusion of Al significantly. Ternary interdiffusion coefficients were also determined at compositions of intersecting diffusion paths, and at relative maxima and minima in concentration profiles for Ir-alloyed NiAl. Consistency among ternary interdiffusion coefficients was observed. Profiles of concentration were also examined to estimate binary interdiffusion coefficients in NiAl. The results agreed well with published values. Tracer diffusion coefficients of Ir and Ta in NiAl were also estimated as \( D_{\text{Ir}} \) (14.7 \( \times \) 10\(^{-11}\) m\(^2\) s\(^{-1}\)) and \( D_{\text{Ta}} \) (2.6 \( \times \) 10\(^{-11}\) m\(^2\) s\(^{-1}\)) at 1473 K.

The experiment and analysis reported herein demonstrate the practical use of analytical technique for multicomponent interdiffusion based on the determination and an integration of interdiffusion fluxes. The large magnitude of \( D_{\text{Ir}} \) and \( D_{\text{Ta}} \) coefficients also signifies a correlation in ternary diffusional interactions and site-preference of ordered ternary intermetallic
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Interdiffusion in L1₂-Ni₃Al Alloyed with Re

N. Garimella¹, M. Ode², M. Ikeda³, H. Murakami², Y.H. Sohn¹,*

¹ Advanced Materials Processing and Analysis Center
Department of Mechanical, Materials and Aerospace Engineering
University of Central Florida, Orlando, FL, USA
² National Institute for Materials Science, Tsukuba, Japan
³ Kobe Steel, Co. Ltd., Japan
* Corresponding Author

Keywords: Re, Ni₃Al, L₁₂, intermetallics, high temperature alloys, ternary interdiffusion

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Abstract

Ternary interdiffusion in L12-Ni3Al with ternary alloying addition of Re was investigated at 1473K using solid-to-solid diffusion couples. Interdiffusion flux of Ni, Al and Re were directly calculated from experimental concentration profiles, and integrated for the determination of average ternary interdiffusion coefficients. The magnitude of main interdiffusion coefficients $\overline{D}_{NiNi}$ and $\overline{D}_{AlAl}$ was determined to be much larger than that of the main interdiffusion coefficient $\overline{D}_{ReRe}$. A moderate tendency for Re to substitute for Al sites was reflected by its influence on interdiffusion of Al, quantified by large and positive $\overline{D}_{AlRe}$ coefficients. An excellent agreement was found with ternary interdiffusion coefficients determined by Boltzmann-Matano analysis. Profiles of concentrations and interdiffusion fluxes were also examined to estimate binary interdiffusion coefficients in Ni3Al, and tracer diffusion coefficients of Re ($5.4 \times 10^{-16} \pm 2.3 \times 10^{-16}$ m$^2$/sec) in Ni3Al.
1. Introduction

Ni$_3$Al precipitation and the associated coherency through tetragonal distortion with the γ-matrix is the key point behind the extensive use of Ni-base superalloys for high temperature applications [1]. Multicomponent diffusion plays an important role in processing and degradation of these alloys that must possess exceptional high temperature strength, microstructural stability and oxidation resistance. Multicomponent diffusion mobility database [2] for γ-phase, together with the alloying studies [3-10] to modify coherent precipitate (γ') have yielded an excellent design criteria to develop advanced superalloys. Recent development of refractory-based superalloys with L1$_2$ precipitates, and refractory-modified aluminate coatings [11-16] warrant a better understanding of interdiffusion in Ni$_3$Al with alloying additions.

The ordered crystal structure of Ni$_3$Al consists of face-centers (α-sites) occupied by Ni-atoms and corners (α'-sites) of the unit cell occupied by Al-atoms. Highly electronegative substitutional elements (e.g. Pt, Cu and Co) occupy the α sites, whereas highly electropositive ones (e.g. Ti, Ta and Nb) occupy the α' sites in Ni$_3$Al [1]. The relative site-preference for a ternary alloying element can be best illustrated from the direction of the solubility lobes for the δ phase on the ternary isotherm of Ni-Al-X (X = alloying addition) system at 1273K as shown by Figure 1 [17]. Site preference of ternary alloying additions to Ni$_3$Al has attracted significant interest as this true solid solution accepts considerable amount of third elements into solution [18-22].

The alloying phenomenon ultimately plays an important role in enhancing the thermomechanical properties and high temperature oxidation resistance of this intermetallic phase [19-26]. The substitutional ternary alloying additions to Ni$_3$Al was first classified by Guard and Westbrook [18] as Ni-occupiers or Al-occupiers or those with no preference. Several
studies [27-29] have examined the change in site preference of alloying elements as a function of
temperature and chemical composition of Ni$_3$Al.

The diffusion mechanism in ordered alloys is more complex than disordered solid
solutions [30]. Diffusion can occur preferentially through $\beta$ or $\beta$ site where Ni or Al atoms
mainly occupy, respectively, and the diffusion coefficient largely depends on the alloy
composition related to the degree of order [31-33]. While tracer diffusion studies in $\beta$ Ni$_3$Al are
difficult since $^{26}$Al is not readily available, self-diffusion of Ni and chemical/impurity diffusion
in Ni$_3$Al binary and Ni$_3$Al-X ternary alloys (X = Ir, Ta, Pt, Nb, Mo, Cr, Fe, Ti) have been studied
[3-6]. The temperature dependency of the diffusion for a ternary alloying addition is evident
from Arrhenius rate law [34-36]. The $\beta$-site occupiers have been observed to diffuse slower than
the $\beta$-site occupiers [30,37]. In L1$_2$-ordered structure each Ni atom is surrounded by 4 Al and 8
Ni atoms as nearest neighbors, where as an Al atom is surrounded by 12 Ni atoms as nearest
neighbors. The $\beta$-sublattice forms a continuous network of nearest neighbors while the $\beta$-
sublattice does not. Consequently, the activation enthalpy of alloying element can change due to
the antisite-defect formation [37].

To further understand the diffusion process in L1$_2$ structure, to help improve the
microstructural stability of Ni-base superalloys, and to help develop refractory-modified
aluminide oxidation resistant coatings, we examined the ternary diffusional interaction of Re
additions to the L1$_2$ Ni$_3$Al phase. Solid-to-solid diffusion couples were assembled with various
Ni$_3$Al-Re alloys, and annealed at 1473K for 5 hours. Average ternary interdiffusion coefficients
from an integration of interdiffusion fluxes, and ternary interdiffusion coefficients via
Boltzmann-Matano analysis were determined from concentration profiles obtained by electron
probe microanalysis (EPMA). In addition, binary interdiffusion coefficients in Ni₃Al, and tracer
diffusion coefficients of Re in Ni₃Al were estimated.

2. Determination of ternary interdiffusion coefficients

Based on Onsager’s formalism [38,39] and Fick’s law [40], the interdiffusion flux \( \vec{J}_i \) of
comp
ter component \( i \) in a ternary system can be expressed in terms of two independent concentration
gradients, \( \partial C_i / \partial x \) by:

\[
\vec{J}_i = -\vec{D}^3_{ij} \frac{\partial C_i}{\partial x} - \vec{D}^2_{ij} \frac{\partial C_j}{\partial x} \quad (i = 1, 2)
\]

where \( \vec{D}^3_{ij} \)’s refer to the ternary interdiffusion coefficients. An experimental determination of the
four concentration-dependent interdiffusion coefficients can be carried out by the use of

Boltzmann-Matano analysis with two independent diffusion couples that develop a common
composition in the diffusion zone where the interdiffusion coefficients can be evaluated [41,42].

Instead, the interdiffusion flux at any section \( x \) can be calculated directly from the
concentration profile from the relation [43,44]:

\[
\vec{J}_i = \frac{1}{2t} \int_{C_i, x_{eq}}^{C_i, x} \frac{c_i}{\partial C_i / \partial x} \, dC_i \quad (i = 1, 2, \ldots, n)
\]

where \( t \) is the time, \( C_i \) and \( C_i^{\text{eq}} \) are the terminal concentrations, and \( x_{eq} \) refers to the location of the
Matano plane. Use of Eq. (2) allows quantitative assessment of diffusional behavior for any
components including zero-flux-planes (ZFPs) and flux-reversals that can develop during

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multicomponent interdiffusion [43-46]. In addition, the calculated interdiffusion fluxes can be related to interdiffusion parameters that can be employed to model and characterize concentration profiles [47-50].

The interdiffusion flux \( \tilde{J}_i \) determined from Eq. (2) can be integrated over a selected region, \( x_1 \) to \( x_2 \), to yield an expression based on Eq. (1) [50]:

\[
\int_{x_1}^{x_2} \tilde{J}_i \, dx - \frac{c_{i,h}}{c_{i,h}} \int \frac{\partial \tilde{C}_i}{\partial t} \, dx - \frac{c_{i,h}}{c_{i,h}} \int \frac{\partial \tilde{C}_j}{\partial t} \, dx \quad (i = 1, 2)
\]

\[
= \overline{D}_{ij} \int_{x_1}^{x_2} f_{x_1} \int_{x_1}^{x_2} C_i f_{x_1} f_{x_2} h_{x_1} f - C_i f_{x_1} f_{x_2} h_{x_1} f \quad (i = 1, 2)
\]

where \( \overline{D}_{ij} \)'s correspond to the average values of main and cross interdiffusion coefficients.

With \( \overline{D}_{ij} \)'s taken as constants, Eq. (1) is re-written as:

\[
\int_{x_1}^{x_2} \tilde{J}_i \, dx - \frac{c_{i,h}}{c_{i,h}} \int \frac{\partial C_i}{\partial x} \, dx = \frac{c_{i,h}}{c_{i,h}} \int \frac{\partial C_j}{\partial x} \, dx \quad (i = 1, 2)
\]

If both sides of Eq. (4) are multiplied by \( f_{x_1} \int_{x_1}^{x_2} f \) and integrated over the diffusion zone between \( x_1 \) and \( x_2 \), one obtains in general [50]:

\[
\int_{x_1}^{x_2} \int_{x_1}^{x_2} \int_{x_1}^{x_2} \tilde{C}_{ij} f_{x_1} \, dx \int_{x_1}^{x_2} \frac{\partial \tilde{C}_i}{\partial t} \, dx \int_{x_1}^{x_2} \frac{\partial \tilde{C}_j}{\partial t} \, dx = \overline{D}_{ij} \int_{x_1}^{x_2} \int_{x_1}^{x_2} \int_{x_1}^{x_2} C_{ij} f_{x_1} \, dx \int_{x_1}^{x_2} \frac{\partial C_i}{\partial x} \, dx \int_{x_1}^{x_2} \frac{\partial C_j}{\partial x} \, dx \quad (i = 1, 2)
\]
If the exponent $m$ is chosen to be zero, Eq. (5) becomes identical to Eq. (3). For $m=1$, Eq. (5) becomes [50]:

\[
\begin{align*}
\frac{\partial}{\partial t} \rho_i \left[ \mathbf{I} \frac{\partial \rho_i}{\partial x_i} \right] + \nabla \cdot \left[ \mathbf{D}_i \rho_i \mathbf{E} \right] &= \nabla \cdot \left[ \mathbf{j}_i \right] + \frac{\partial}{\partial t} \left[ \rho_i \mathbf{C}_i \right] \\
&= 2 \sigma \left[ \mathbf{D}_1 \mathbf{J}_1 \left[ \mathbf{C}_1 \right] \mathbf{F} + \mathbf{D}_2 \mathbf{J}_2 \left[ \mathbf{C}_2 \right] \mathbf{F} \right] \quad (i = 1, 2)
\end{align*}
\]  

(Eq. 6)

Eqs. (3) and (6) provide four equations to solve for $D_{11}$, $D_{12}$, $D_{21}$, and $D_{22}$ interdiffusion coefficients, and can be easily set up from experimental concentrations and the corresponding interdiffusion fluxes. Thus, from the concentration profiles of a single diffusion couple,

$D_{ij}$ (i, j = 1, 2) coefficients, characteristic of the diffusion path, can be determined over selected composition ranges in the diffusion zone [50]. This analysis method has been directly employed in various studies [51-59] to determine average ternary interdiffusion coefficients. In this paper, this analysis applied to the experimental concentration profiles for 2 segments, one on either side of the Matano plane; the two chosen composition ranges are $[C_1^o]$ $C_1^o$ and $[C_2^o]$ $C_2^o$, where $C_1^o$ refers to the concentration at the Matano plane. The average ternary interdiffusion coefficients, $D_{ij}$'s, determined on either side of the Matano plane are employed to model experimental concentration profiles using error-function solution for infinite ternary system given by Fujita and Gosting [60].
3. Experimental details

Ni-Al and Ni-Al-Re alloys were prepared by the vacuum arc melting of 99.97 wt.% Ni, 99.9 wt.% Al, and 99.2 wt.% Re, according to the compositions presented in Table I. The alloys were cast into a semi-cylindrical mold with the diameter of 8 mm. The alloy rods were homogenized at 1473K for 137 hours in the vacuum furnace that was evacuated to a pressure lower than $10^{-2}$ Pa. The homogenized alloys were then sectioned into discs with an approximate height of 1.5 mm. The surfaces of alloy discs were ground metallographically down to 1200-grit and cleaned thoroughly prior to diffusion couple assembly.

Table II presents diffusion couples that were assembled and analyzed in this study. To promote initial bonding, coupled alloys were placed in a Si$_3$N$_4$ jig and annealed at 1473K for 0.5 hour in a vacuum furnace. The metal discs have larger thermal expansion coefficients than the Si$_3$N$_4$ jig, and the discs can adhere to each other due to the compression during the annealing treatment. Each diffusion couple fabricated in this manner was then sealed in an evacuated transparent quartz capsule, and annealed at 1473K for 4.5 hours in an atmosphere furnace. All diffusion couples were water quenched after the high-temperature anneal to preserve high temperature microstructure and concentrations. In this study, the time required for the diffusion bonding treatment (0.5 hour) was added to the total annealing time. Thus, concentration profiles from all diffusion couples were analyzed with diffusion anneal time of 5 hours.

Microstructural analysis by optical microscopy confirmed excellent bonding in all diffusion couples without any precipitation of other phases. Concentration profiles of the annealed diffusion couples were analyzed by JEOL-JXA-8900 EPMA. An accelerating voltage of 20 keV, a beam current of 50 nA, and a probe diameter of 1 μm were employed for data acquisition of Ni K$_\alpha$ x-radiation peak using LiF crystal, Al K$_\alpha$ x-radiation peak using TAP
crystal, and Re L₂ x-radiation using LIFH crystal. Elemental standards of Ni, Al and Re along with ZAF [61] correction were employed for quantification of concentrations via point-to-point count technique.

4. Results and analysis

4.1. Profiles of concentrations and interdiffusion fluxes

Figure 2 presents typical concentration profiles obtained by EPMA from the diffusion couple, Ni-25Al vs. Ni-23.5Al-0.5Re annealed at 1473K for 5 hours. The x-axis is the distance from the Matano plane and the open circles represent EPMA measurement. Scatter in the concentration profiles for all diffusion couples were minimum and within the experimental uncertainty associated with EPMA. The interdiffusion fluxes of individual components were then determined using Eq. (2) from experimental concentration profiles that were smoothened with a series of weighted splines. Although no zero-flux plane was observed, a significant diffusional interaction between Al and Re was observed when Ni₃Al was diffusion annealed against Ni₃Al alloyed with Re. As shown in Figure 2, interdiffusion of Al was reduced by the interdiffusion of Re against the gradient of Al. But, the diffusional influence of Re on Ni is difficult to ascertain from the profiles presented in Figure 2. Determination of ternary interdiffusion coefficients can quantify the extent of these diffusional interactions, and provide competent approaches to compositional design and modification of alloys and protective coatings.

4.2 Average ternary interdiffusion coefficients
From profiles of concentration and interdiffusion fluxes in Ni-Al vs. Ni-Al-Re diffusion couples, average ternary interdiffusion coefficients, $\bar{D}^\text{Ni}_i|j, k \mu \text{Al-Re}$ and $\bar{D}^\text{Ni}_i|j, k \mu \text{Ni-Re}$, were determined on either side of the Matano plane using Eqs. (3) and (6). They are reported in Table III. The magnitudes of main diffusion coefficients, $\bar{D}^\text{Ni}$. and $\bar{D}^\text{Al}$. are similar to the interdiffusion coefficients of Al and Ni reported in literature for binary Ni$_3$Al at 1473K [3-10]. Estimation of binary interdiffusion coefficients from the ternary diffusion couples and the comparison to the interdiffusion coefficients of Al and Ni reported in literature for binary Ni$_3$Al are presented in detail in section 4.4. The main interdiffusion coefficient, $\bar{D}^\text{Ni}$. is approximately 100 times smaller in magnitude than $\bar{D}^\text{Ni}$. and $\bar{D}^\text{Al}$. Table III reports that $\bar{D}^\text{Ni}$.'s are positive and comparable to the magnitude of $\bar{D}^\text{Ni}$. while $\bar{D}^\text{Ni}$. coefficients are negligibly small ($< 0.1 \times 10^{-14}$ m$^2$/sec). Thus the interdiffusion of Al can be strongly influenced by the interdiffusion of Re.

The $\bar{D}^\text{Al}$.' coefficients are also positive, but 2 to 13 times smaller in magnitude than the $\bar{D}^\text{Al}$.'s.

The average ternary interdiffusion coefficients reported in Table III were employed to generate concentration profiles using error-function solution provided by Fujita and Gosling [60]. Excellent agreement between EPMA measurement and calculated concentration profiles were found for all couples. Typical examples are presented in Figure 2 where open circles are the EPMA data, and solid lines are the calculated concentration profiles.

4.3. Ternary interdiffusion coefficients determined by Boltzmann-Matno analysis

From the diffusion couples Ni-Al vs. Ni-Al-Re listed in Table II, several intersecting compositions were found within the diffusion paths. Intersecting diffusion paths in Figure 3 represent typical diffusion paths with one of the paths intersecting with its terminal end. In other
words, Re concentration of that end remained constant with no concentration gradient. These
intersection composition points may be used for the determination of interdiffusion coefficients
using Boltzmann-Matano analysis. The values of ternary interdiffusion coefficients determined
in this study are reported in Table IV, and correspond well to the average ternary interdiffusion
coefficients presented in Table III. Slight deviation in values and change in signs of the \( \bar{D}_{\text{NiAl}} \)
coefficients are attributed to the uncertainty in concentration gradient of Re.

4.4. Estimation of binary interdiffusion coefficients in Ni<sub>3</sub>Al

The ternary interdiffusion coefficients \( \bar{D}_{\text{NiAl}} \) and \( \bar{D}_{\text{NiNi}} \) approach the binary \( \bar{D}_{i} \) for Ni<sub>3</sub>Al
as the concentration of Re decreases to zero. Hence, values of \( \bar{D}_{i} \) (i.e., Ni or Al) were estimated
from ternary diffusion couples where Re concentration was negligibly small in segments of the
diffusion zone (e.g., Fick's law for substitutional binary alloys). Such regions were found in all
couples since \( \bar{D}_{\text{ext}} \) coefficients are much smaller than \( \bar{D}_{\text{NiAl}} \) and \( \bar{D}_{\text{NiNi}} \). The \( \bar{D}_{i} \)'s extrapolated
from the ternary couples with large enough concentration difference (e.g., \( \mu_{\text{Al}} \) or \( \mu_{\text{Ni}} > 2 
at. \% \)) in terminal alloys is presented in Figure 4. These values appear consistent with the
available binary interdiffusion data [3-10] for Ni<sub>3</sub>Al.

4.5. Estimation of tracer diffusion coefficient of Re in Ni<sub>3</sub>Al

For a ternary component \( i \) diffusing into a binary alloy \( j-k \), the cross interdiffusion
coefficient \( \bar{D}_{ij} \) (i.e., \( j \)) becomes negligible at infinite dilution of component \( i \) in a \( j-k \) alloy [62].
Then the value of the main coefficient \( \bar{D}_{ii} \) approaches that of the tracer diffusion coefficient
\( \bar{D}_{i}^{t} \) for component \( i \):

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Thus, the tracer diffusion coefficients of Re in Ni<sub>3</sub>Al alloy can be estimated from the main interdiffusion coefficient of Re, \( \overline{D}_{\text{main}}^{\text{NiAl}} \), using Eq. (7), provided that the concentration of Re approaches zero within the diffusion zone so that the cross interdiffusion coefficients, \( \overline{D}_{\text{main}}^{\text{NiAl}} \) or \( \overline{D}_{\text{main}}^{\text{AlNi}} \), become negligible. Such regions were found in all couples since \( \overline{D}_{\text{main}}^{\text{NiAl}} \) coefficients are much smaller than \( \overline{D}_{\text{main}}^{\text{AlNi}} \) and \( \overline{D}_{\text{main}}^{\text{AlNi}} \). Values of tracer diffusion coefficients of Re, \( D_{\text{Re}}^{\text{Ni}} \), were extrapolated from the main interdiffusion coefficients, \( \overline{D}_{\text{main}}^{\text{NiAl}} \) or \( \overline{D}_{\text{main}}^{\text{AlNi}} \), as the concentration of Re, becomes zero. The extrapolations for \( D_{\text{Re}}^{\text{Ni}} \) from the ternary interdiffusion coefficients on the basis of Eq. (7) are presented in Figure 5 for Ni-24.4 to 24.8 at.% Al. The estimated values of \( D_{\text{Re}}^{\text{Ni}} \) are reported in Table V.

5. Concluding remarks

Ternary interdiffusion interactions of Re addition on the L1<sub>2</sub> Ni<sub>3</sub>Al phase was examined by using solid-to-solid diffusion couples annealed at 1473K for 5 hours. Average ternary interdiffusion coefficients were determined from an integration of interdiffusion fluxes for individual components. The magnitude of \( \overline{D}_{\text{main}}^{\text{NiAl}} \) and \( \overline{D}_{\text{main}}^{\text{AlNi}} \) coefficients was determined to be much larger than that of \( \overline{D}_{\text{main}}^{\text{AlNi}} \) coefficients. The \( \overline{D}_{\text{main}}^{\text{AlNi}} \) coefficient was determined to be positive and large in magnitude; Re substitutes in Al-site and influences the interdiffusion of Al significantly. The \( \overline{D}_{\text{main}}^{\text{AlNi}} \) coefficient was also positive but relatively low in magnitude; Re shows
a lower tendency to occupy Ni-sites. Consistency among ternary interdiffusion coefficients was observed from ternary interdiffusion coefficients determined by Boltzmann-Matano analysis. Profiles of concentrations were also examined to estimate binary interdiffusion coefficients in Ni$_3$Al. The results agreed well with published values. Tracer diffusion coefficient of Re at 1473K was also estimated as $D_{Re}^* = 5.4 \times 10^{16} \pm 2.3 \times 10^{16}$ m$^2$/sec for Ni$_3$Al phase with Al concentration range of 24.4 to 24.8 at.%.

Acknowledgements

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3. Typical intersecting diffusion paths of Ni-Al vs. Ni-Al-Re diffusion couples annealed at 1473K for 5 hours. Compositions at these intersections were employed for the determination of ternary interdiffusion coefficients based on Boltzmann-Matano analysis.

4. Interdiffusion coefficients in Ni$_3$Al at 1473K compiled from this investigation and literature review.

5. Extrapolation of $D_{Re}$ coefficient for the estimation of tracer diffusion coefficient of Re in Ni$_3$Al at 1473K.
Table I: Nominal composition of alloys employed for diffusion couple studies.

<table>
<thead>
<tr>
<th>Alloy Identification</th>
<th>Composition (atom percent)</th>
<th>Composition (weight percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Al</td>
</tr>
<tr>
<td>Ni-24.5Al</td>
<td>75.5</td>
<td>24.5</td>
</tr>
<tr>
<td>Ni-25Al</td>
<td>75.0</td>
<td>25.0</td>
</tr>
<tr>
<td>Ni-26Al</td>
<td>74.0</td>
<td>26.0</td>
</tr>
<tr>
<td>Ni-23.5Al-0.5Re</td>
<td>76.0</td>
<td>23.5</td>
</tr>
<tr>
<td>Ni-23.5Al-0.7Re</td>
<td>75.8</td>
<td>23.5</td>
</tr>
</tbody>
</table>
Table II: Diffusion couples assembled and analyzed after an anneal at 1473K for 5 hours.

<table>
<thead>
<tr>
<th>Diffusion Couples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-24.5Al vs. Ni-23.5Al-0.5Re</td>
</tr>
<tr>
<td>Ni-24.5Al vs. Ni-23.5Al-0.7Re</td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23.5Al-0.5Re</td>
</tr>
<tr>
<td>Ni-26Al vs. Ni-23.5Al-0.7Re</td>
</tr>
</tbody>
</table>
Table III. Average ternary interdiffusion coefficients ($10^{16}$ m$^2$/s) determined from Ni-Al vs. Ni-Al-Re diffusion couples annealed at 1473K for 5 hours.

<table>
<thead>
<tr>
<th>Diffusion Couple</th>
<th>Composition Range</th>
<th>$\bar{D}_{Ni}$</th>
<th>$\bar{D}_{Al}$</th>
<th>$\bar{D}_{Re}$</th>
<th>$\bar{D}_{Ni}$</th>
<th>$\bar{D}_{Al}$</th>
<th>$\bar{D}_{Re}$</th>
<th>$\bar{D}_{Ni}$</th>
<th>$\bar{D}_{Al}$</th>
<th>$\bar{D}_{Re}$</th>
<th>$\bar{D}_{Ni}$</th>
<th>$\bar{D}_{Al}$</th>
<th>$\bar{D}_{Re}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-24.5Al vs. Ni-23.5Al-0.5Re</td>
<td>$-C_{i}^{-} \sim C_{i}^{o}$</td>
<td>417.7</td>
<td>380.2</td>
<td>Ngl.</td>
<td>3.8</td>
<td>417.7</td>
<td>33.7</td>
<td>Ngl.</td>
<td>3.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-24.5Al vs. Ni-23.5Al-0.7Re</td>
<td>$-C_{i}^{-} \sim C_{i}^{o}$</td>
<td>509.9</td>
<td>463.4</td>
<td>Ngl.</td>
<td>4.5</td>
<td>509.9</td>
<td>42.0</td>
<td>Ngl.</td>
<td>4.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-25Al vs. Ni-23.5Al-0.5Re</td>
<td>$-C_{i}^{-} \sim C_{i}^{o}$</td>
<td>362.8</td>
<td>304.1</td>
<td>Ngl.</td>
<td>3.4</td>
<td>362.8</td>
<td>55.3</td>
<td>Ngl.</td>
<td>3.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-26Al vs. Ni-23.5Al-0.7Re</td>
<td>$-C_{i}^{-} \sim C_{i}^{o}$</td>
<td>463.2</td>
<td>294.6</td>
<td>Ngl.</td>
<td>3.8</td>
<td>463.2</td>
<td>164.8</td>
<td>Ngl.</td>
<td>3.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-26Al vs. Ni-23.5Al-0.5Re</td>
<td>$-C_{i}^{-} \sim C_{i}^{o}$</td>
<td>668.3</td>
<td>477.4</td>
<td>Ngl.</td>
<td>2.4</td>
<td>668.3</td>
<td>188.5</td>
<td>Ngl.</td>
<td>2.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: Ngl refers to magnitude less than $0.1 \times 10^{-16}$ m$^2$/sec.
| Diffusion Couples with Intersecting Diffusion Paths | Intersecting Composition (atom fraction) | \( D_{\text{NiAl}}^{\text{NiAl}} \) | \( D_{\text{NiAl}}^{\text{NiRe}} \) | \( D_{\text{NiRe}}^{\text{NiAl}} \) | \( D_{\text{NiRe}}^{\text{NiRe}} \) |
|---|---|---|---|---|
| Ni-24.5Al vs. Ni-23.5Al-0.5Re | Re: 0.005 | 682.5 | 928.5 | 832.5 | 988.8 |
| Ni-24.5Al vs. Ni-23.5Al-0.5Re | Re: 0.005 | 241.2 | 216.0 | 241.2 | 250.0 |
| Ni-24.5Al vs. Ni-23.5Al-0.5Re | Re: 0.005 | 726.1 | 734.9 | 726.1 | -11.9 |

Note: Ng1 refers to magnitude less than 0.1 x 10^-6 m²/s. The table shows the interdiffusion coefficients (10^-16 m²/s) determined by a Boltzmann-Matano analysis from Ni-Al vs. Ni-Al-Re.
Table V. Tracer diffusion coefficients ($10^{-6}$ m$^2$/s) of Re in Ni$_3$Al extrapolated from ternary interdiffusion coefficients of diffusion couples annealed at 1473 K.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Tracer Component</th>
<th>$D'$ (10$^{-6}$ m$^2$/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75.2Ni-24.8Al</td>
<td>Re</td>
<td>4.0</td>
</tr>
<tr>
<td>75.6Ni-24.4Al</td>
<td>Re</td>
<td>8.1</td>
</tr>
<tr>
<td>75.5Ni-24.5Al</td>
<td>Re</td>
<td>4.1</td>
</tr>
<tr>
<td>Average Values</td>
<td></td>
<td>5.4 ± 2.3</td>
</tr>
</tbody>
</table>
Solubility ranges of selected ternary alloying additions in γ iron at 1173 K [11].
Concentration profiles of (a) Ni, (b) Al and (c) Re obtained from diffusion couple Ni-b5Al vs. Ni-b0.5Al-Re. Samples annealed at 1170K for 5 h old. Open circles and solid lines represent the experimental and calculated concentration profiles, respectively.

1r1cbo (or corr sp1)
APPENDIX B : MATLAB PROGRAM FOR INTERDIFFUSION ANALYSIS
B.1 Matano Plane Determination

```matlab
% EXPORT TEXT FILE%
% NAME THAT DATA FILE AS 'A'%
% SPECIFY 'DF'. THAT IS LENGTH OF THE DATA POINTS DF= NUMBER %
DF1=DF-1;
rev=DF+1;
for i=1:DF;
    D(i,1)=i-1;
end;
for i=2:DF;
    D1(i,1)=0;E1(i,1)=0;
    D1(i,1)=(D(i)-D(i-1))*((C1(i))+(C1(i-1)))/2;
    E1(i,1)=(D(i)-D(i-1))*((C2(i))+(C2(i-1)))/2;
end;
F1=(sum(D1(1:DF))-(D1(DF)*D(DF)))/(C1(1)-C1(DF));
F2=(sum(E1(1:DF))-(E1(DF)*D(DF)))/(C2(1)-C2(DF));
xx=(F1+F2)/2;
ND=D-xx;
for i=1:DF;
    x(i,1)=xx;
c1(i,1)=C1(rev-i);
c2(i,1)=C2(rev-i);
end;
for i=2:DF;
    d1(i,1)=0;e1(i,1)=0;
    d1(i,1)=(D(i)-D(i-1))*((c1(i))+(c1(i-1)))/2;
    e1(i,1)=(D(i)-D(i-1))*((c2(i))+(c2(i-1)))/2;
end;
f1=(sum(d1(1:DF))-(d1(DF)*D(DF)))/(c1(1)-c1(DF));
f2=(sum(e1(1:DF))-(e1(DF)*D(DF)))/(c2(1)-c2(DF));
xr=(f1+f2)/2;
nd=D-xr;
```
B.2 Diffusion Coefficients Determination

% INPUT TIME OF THE ANNEAL IN HOURS, AS e.g. time=168 %
% INPUT MULTI TO DISPLAY DIFFUSION COEFFICIENT VALUES IN MULTI TIMES 10^-8 % cm^2/sec' e.g. multi=10000; %
for i=2:DF;
    for n=1:100; G(1,n)=0;
        G(i,n)=(C1(i)-C1(i-1))*((ND(i)^n)+(ND(i-1)^n))/2;
    end;
end;
for i=2:DF;
    for n=1:100; H(1,n)=0;
        H(i,n)=(C2(i)-C2(i-1))*((ND(i)^n)+(ND(i-1)^n))/2;
    end;
end;
for i=1:DF;
    G1(i,1)=G(i,1);
    H1(i,1)=H(i,1);
end;
for i=2:DF;
    for n=1:100; O(1,n)=0; P(1,n)=0;
        O(i,n)=(ND(i)-ND(i-1))*((J1(i)*ND(i)^n)+(J1(i-1)*ND(i-1)^n))/2;
        P(i,n)=(ND(i)-ND(i-1))*((J2(i)*ND(i)^n)+(J2(i-1)*ND(i-1)^n))/2;
    end;
end;
for i=2:DF;
    for n=1:100; g(1,n)=0;
        g(i,n)=(c1(i)-c1(i-1))*((nd(i)^n)+(nd(i-1)^n))/2;
    end;
end;
for i=2:DF;
    for n=1:100; h(1,n)=0;
        h(i,n)=(c2(i)-c2(i-1))*((nd(i)^n)+(nd(i-1)^n))/2;
    end;
end;
for i=1:DF;
    gl(i,1)=g(i,1);
    hl(i,1)=h(i,1);
end;
for i=2:DF;
    j1(1)=0+(g1(1)*(1/(2*time*3600)));
    j1(i,1)=j1(i-1)+(g1(i)*(1/(2*time*3600)));
end;
for i=2:DF;
    j2(1)=0+(h1(1)*(1/(2*time*3600)));
    j2(i,1)=j2(i-1)+(h1(i)*(1/(2*time*3600)));
end;
\[ j_2(i,1) = j_2(i-1) + (h_1(i) * (1/(2\times time\times 3600))); \]
end;

for i=2:DF; j1d(1)=0; j2d(1)=0;
    j1d(i,1)=(nd(i)-nd(i-1))*(j1(i)+j1(i-1))/2;
    j2d(i,1)=(nd(i)-nd(i-1))*(j2(i)+j2(i-1))/2;
end;

for i=2:DF;
    for n=1:100; o(1,n)=0; p(1,n)=0;
        o(i,n)=(nd(i)-nd(i-1))*((j1(i)*nd(i)^n)+(j1(i-1)*nd(i-1)^n))/2;
        p(i,n)=(nd(i)-nd(i-1))*((j2(i)*nd(i)^n)+(j2(i-1)*nd(i-1)^n))/2;
    end;
end;

for n=1:100;
    D12R(n,1)=multi*(((sum(o(1:k1,n)))/ sum(-g(1:k1,n)))-( sum(j1d(1:k1))/ (c1(k1)-c1(k1))))/(( (sum(-h(1:k1,n)))/ (sum(-g(1:k1,n))))-( (c2(1)-c2(k1))/ (c1(k1)-c1(k1)))));
end;

for n=1:100;
    D11R(n,1)=multi*(((sum(o(1:k1,n)))/ sum(-g(1:k1,n)))-( sum(j1d(1:k1))/ (c1(k1)-c1(k1))))/(( (sum(-h(1:k1,n)))/ (sum(-g(1:k1,n))))-( (c2(1)-c2(k1))/ (c1(k1)-c1(k1)))));
end;

for n=1:100;
    D21R(n,1)=multi*(((sum(p(1:k1,n)))/ sum(-g(1:k1,n)))-( sum(j2d(1:k1))/ (c2(k1)-c2(k1))))/(( (sum(-h(1:k1,n)))/ (sum(-g(1:k1,n))))-( (c1(1)-c1(k1))/ (c2(k1)-c2(k1)))));
end;

for n=1:100;
    D22R(n,1)=multi*(((sum(p(1:k1,n)))/ sum(-g(1:k1,n)))-( sum(j2d(1:k1))/ (c2(k1)-c2(k1))))/(( (sum(-h(1:k1,n)))/ (sum(-g(1:k1,n))))-( (c1(1)-c1(k1))/ (c2(k1)-c2(k1)))));
end;

for n=1:100;
    D12(n,1)=multi*(((sum(o(1:k,n)))/ sum(-g(1:k,n)))-( sum(j1d(1:k))/ (C1(k1)-C1(k1))))/(( (sum(-h(1:k,n)))/ (sum(-g(1:k,n))))-( (c2(1)-c2(k))/ (C1(k1)-C1(k1)))));
end;

for n=1:100;
    D11(n,1)=multi*(((sum(o(1:k,n)))/ sum(-g(1:k,n)))-( sum(j1d(1:k))/ (C1(k1)-C1(k1))))/(( (sum(-h(1:k,n)))/ (sum(-g(1:k,n))))-( (c2(1)-c2(k))/ (C1(k1)-C1(k1)))));
end;

for n=1:100;
    D21(n,1)=multi*(((sum(p(1:k,n)))/ sum(-g(1:k,n)))-( sum(j2d(1:k))/ (C2(k1)-C2(k1))))/(( (sum(-h(1:k,n)))/ (sum(-g(1:k,n))))-( (C1(1)-C1(k))/ (C2(k1)-C2(k1)))));
end;

for n=1:100;
    D22(n,1)=multi*(((sum(p(1:k,n)))/ sum(-g(1:k,n)))-( sum(j2d(1:k))/ (C2(k1)-C2(k1))))/(( (sum(-h(1:k,n)))/ (sum(-g(1:k,n))))-( (C1(1)-C1(k))/ (C2(k1)-C2(k1)))));
end;