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A New Technique for Evaluating Diffusion Mobility Parameters

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The development and evaluation of a multicomponent diffusion mobility database for Ni-rich alloys are reviewed. In an effort to directly evaluate the mobility parameters in the database, a method for optimizing the mobility parameters as a function of the experimental composition profiles is proposed. This method is demonstrated for the NiCo system at 1100 °C. The optimization of four diffusion mobility parameters improved agreement between the experimental and calculated composition profiles and decreased the error between the experimental and calculated interdiffusion coefficients from 45 to <5%. This method can easily be expanded to multicomponent systems.

1. Introduction

Much of the processing and performance of Ni-base superalloys is governed by multicomponent diffusion processes. Back-diffusion during solidification defines the degree of segregation in a casting.[1,2] Multicomponent diffusion in the as-cast structure also determines the heat treatment cycle because diffusion must be controlled to avoid incipient melting during heating and to ensure that complete homogenization has been obtained.[3] The size and composition of the γ' (ordered face-centered cubic [fcc], $L1_2$) strengthening precipitates are also dependent on the multicomponent diffusion occurring in the γ (fcc) matrix during the heat treatment cycle.[4,5] Decreasing the amount of interdiffusion between a protective coating and a Ni-base superalloy substrate can increase the lifetime of a coating.[6] Many of these diffusion-driven processes can be modeled using multicomponent thermodynamics and diffusion mobility databases in conjunction with either finite-difference or phase field simulation codes to numerically solve the appropriate flux-balance equations.[7]

While several multicomponent thermodynamic databases for Ni-base superalloys have been developed,[8-10] the development of diffusion mobility databases has been limited until recently. A multicomponent diffusion mobility database for the fcc (γ) phase for Ni-base superalloys was developed[11,12] to model some of the aforementioned diffusion processes. This article reviews the development and evaluation of this multicomponent diffusion mobility database and then proposes a new evaluation technique.

2. Database Development

The development of a diffusion mobility database is based on the assumption that all of the phenomenological diffusion coefficients can be expressed in terms of a diffusion mobility function and a thermodynamic factor, and that a vacancy exchange diffusion mechanism occurs in a crystalline phase. The intrinsic (lattice-fixed frame of reference) diffusion coefficient is a product of the diffusion mobility $M^{\mathrm{L}}_{\mathrm{ki}}$ and $(\partial\mu_{\mathrm{i}}/\partial x_{\mathrm{j}})$, the thermodynamic factor.

$$D^{\mathrm{L}}_{\mathrm{kj}} = \sum_{\mathrm{i}=1}^{\mathrm{n}} M^{\mathrm{L}}_{\mathrm{ki}} \frac{\partial \mu_{\mathrm{i}}}{\partial x_{\mathrm{j}}} \qquad \text{(Eq 1)}$$

The specie j is the diffusing specie, and k is the gradient specie. The partial derivative of the chemical potential μ_{i}, with respect to the mole fraction x_{i}, defines the thermodynamic factors, which can be easily calculated using an appropriate multicomponent thermodynamic database. The $M^{\mathrm{L}}_{\mathrm{ki}}$ matrix, which is both composition-dependent and temperature-dependent, defines the diffusion mobility in the lattice-fixed frame of reference. Following the work of Andersson and Ågren,[13] the off-diagonal terms of the diffusion mobility matrix are assumed to be 0 (i.e., the correlation effects are assumed to be negligible). The diagonal terms of the mobility matrix are assumed to have the following form:

$$M^{\mathrm{L}}_{\mathrm{ki}} = \delta_{\mathrm{ki}} x_{\mathrm{i}} M_{\mathrm{i}} \qquad \text{(Eq 2)}$$

$$M_{\mathrm{i}} = \Theta_{\mathrm{i}} \frac{1}{RT} \exp\left(\frac{\Delta Q^{*}_{\mathrm{i}}}{RT}\right) \qquad \text{(Eq 3)}$$

where δ_{ki} is the Kroncker δ symbol, equaling 1 when $\mathrm{i} = \mathrm{k}$ and 0 when $\mathrm{i} \neq \mathrm{k}$, M_{i} is the mobility of specie i in a given phase, Θ_{i} represents the effects of the atomic jump distance (squared) and the jump frequency (square meters per second), and $\Delta Q^{*}_{\mathrm{i}}$ is the diffusion activation energy of specie i in a given phase (in joules per mole). As $\Delta Q^{*}_{\mathrm{i}}$ and Θ_{i} can be combined into one parameter, it is customary to assume that Θ_{i} is exponentially dependent on the composition[14] and thus can be evaluated with $\Delta Q^{*}_{\mathrm{i}}$.[15]

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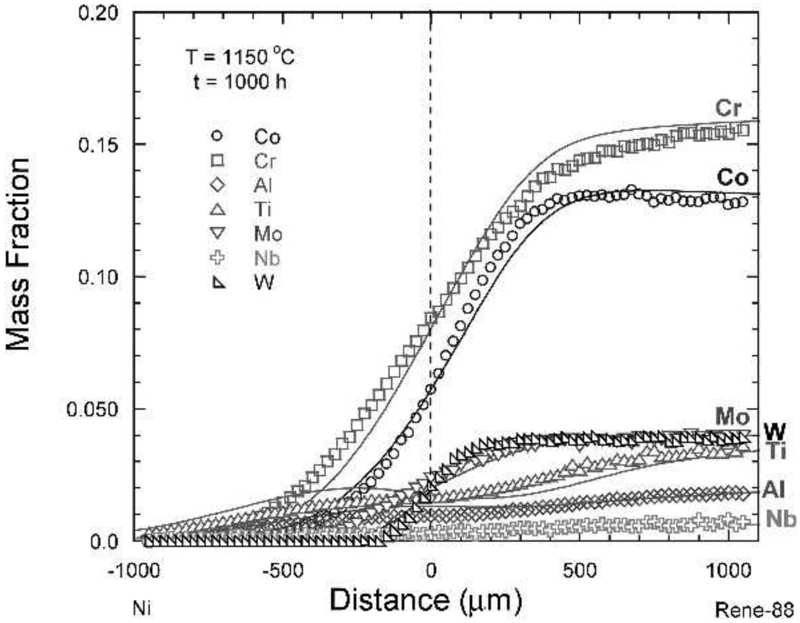

Fig. 1 Ni/René-88 at 1150 °C for 1000 h. Open symbols, experimental profiles; lines, those calculated by the DICTRA simulation. The experimental error is within the size of the data symbols.[12]

Andersson and Ågren,[13] Jönsson,[15,16] Engström and Ågren,[17] Helander and Ågren,[18,19] and Borgenstam et al.[20] expressed the composition and temperature dependence of each ΔQ_i^* in terms of a Redlich and Kister[21] polynomial, as given in Eq 4:

$$\Delta Q_i^* = \sum_j x_j Q_i^j + \sum_p \sum_{j>p} x_p x_j \sum_k {}^k A_i^{pj} (x_p - x_j)^k \qquad \text{(Eq 4)}$$

where the Q_i^j and the ${}^k A_i^{pj}$ are linear functions of temperature. The expansion of the composition dependence is similar to the CALPHAD approach[16,22,23] used in the development of the thermodynamic databases.

If the partial molar volumes are assumed to be constant, the diffusivities in Eq 1 can be transformed to the volume-fixed frame of reference,

$$D_{kj}^V = \sum_{i=1}^{n} (\delta_{ik} - x_k) x_i M_i \frac{\partial \mu_i}{\partial x_j} \qquad \text{(Eq 5)}$$

Note that the tracer diffusion coefficient is not dependent on the thermodynamics and can be expressed as:

$$D_i^* = RTM_i \qquad \text{(Eq 6)}$$

A 13-component diffusion mobility database for the fcc phase for Ni-rich alloys was developed using available tracer, intrinsic, and chemical diffusivity data,[11,12] and previous diffusion mobility assessments.[5,15-17,24] The diffusion mobility optimization was performed using the Ni-base superalloy thermodynamic database assembled by Saunders.[8] Using an optimization program, PARROT[25] (Note: the use of any commercial product does not constitute an endorsement by the National Institute of Standards and Technology), the experimental diffusion data can be used to assess the composition and temperature dependence of the activation energy in Eq 4. The optimization begins by first using initial estimates for the parameters in the mobility equation and by calculating the diffusion coefficients corresponding to the known experimental data. Based on the comparison of the experimental and calculated diffusion coefficients, the mobility parameters are optimized to achieve the best agreement possible. Additional details of the optimization procedure are given in previous work.[11,12]

3. General Database Evaluation

Evaluation of the database included a comparison with known diffusion correlations, measured ternary and quaternary diffusion coefficients, and measured single-phase and multiphase diffusion couple profiles. Comparisons with known diffusion correlations and measured diffusion coefficients are reviewed by Campbell et al.[11] Diffusion simulations using a developed diffusion mobility database and a multicomponent thermodynamic database[8] have been compared with experimental single-phase[12,26] and multiphase Ni-base superalloy couples.[27] The comparison between the predicted and measured composition profiles for the single-phase (γ) René-88/Ni couple after 1000 h at 1150 °C is shown in Fig. 1. The average (±SD) normalized error between the predicted and measured composition profiles is 13.5% ± 11.5%. This is less than the average experimental error. For multiphase diffusion couples, in which one of the planar layers contains a matrix phase and a significant fraction of a precipitate phase, the predicted matrix phase (γ) composition profiles were compared with the measured composition profiles. An example of one such

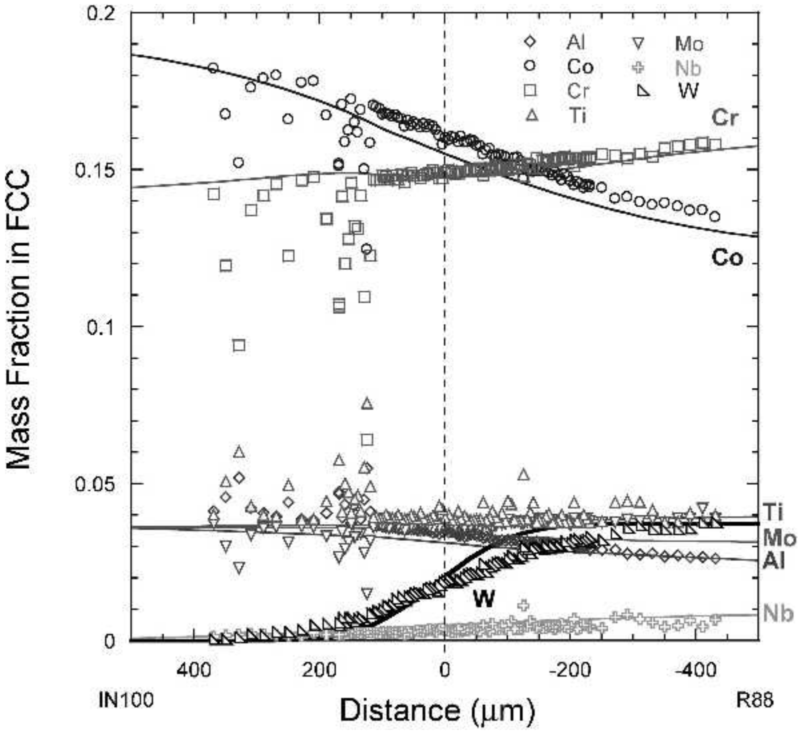

Fig. 2 IN100/René-88 at 1150 °C for 1000 h. Open symbols, experimental profiles; lines, those calculated by the DICTRA simulation. The experimental error is within the size of the data symbols.[27]

couple, René-88/IN100, is shown in Fig. 2.[27] The IN100 alloy has a significant fraction of γ' in the γ matrix: thus, the diffusion couple contains two multiphase planar layers. On the René-88 side, the couple consists of a γ matrix with a small fraction of MC carbide and, on the IN100 side, the couple consists of a γ matrix with a significant fraction (13%) of γ' precipitates and a small fraction of MC carbides.

4. New Technique for Database Evaluation

While the comparison of measured and calculated diffusion coefficients and composition profiles has shown good agreement, it is difficult to access the error associated with the optimized mobility parameters used in the diffusion database. As a result, a scheme was developed to optimize a given set of mobility parameters as functions of the experimental composition profiles. This method involves developing an optimizer to work in conjunction with the DICTRA[20,28] software program. The current work will demonstrate the optimization of the diffusion mobility parameters for the Co-Ni system at a constant temperature using Mathematica and Python scripts to interact with the DICTRA program. It should be noted that Höglund[29] performed similar work using a DICTRA-Matlab toolbox.[30]

A NiCo diffusion couple that was heat treated at 1150 °C for 1000 h was chosen for this study because it provides a simple binary in which both elements are completely soluble in one another. The measured and calculated (initial) Co and Ni composition profiles are shown in Fig. 3. To compare the experimental composition profiles to the calculated composition profiles using the existing diffusion mobility database, the Matano interface is calculated for the experimental profiles and equated with the initial interface grid position used in the simulations. The experimental composition dependence of the interdiffusion coefficient can be calculated using the Matano-Boltzmann method,[31] and the results are shown in Fig. 4. The corresponding calculated interdiffusion coefficient composition dependence is also shown in Fig. 4. While the initial comparison of the calculated and measured composition profiles are in good agreement, Fig. 4 reveals significant discrepancies between the experimental and calculate interdiffusion composition dependence. The calculated $\tilde{D}_{\mathrm{CoNi}}$ composition dependence, which is based on the initial diffusion mobility database, has a similar profile shape to that of the experimental curve; however, the calculated values are 45% larger than the experimental values. This leads to the question: Can the diffusion mobility parameters be optimized to improve the agreement between the measured and calculated composition and interdiffusion coefficients profiles?

The diffusion mobility of the Co-Ni system at 1150 °C is represented by the following equations:

$$M_{\mathrm{Co}}^{\mathrm{fcc}} = \frac{1}{RT}\exp\left(\frac{\Delta Q_{\mathrm{Co}}^{*}}{RT}\right) \qquad \text{(Eq 7)}$$

$$^{\mathrm{fcc}}\Delta Q_{\mathrm{Co}}^{*} = x_{\mathrm{Co}}(-393{,}000) + x_{\mathrm{Ni}}(\underline{-380{,}400}) + x_{\mathrm{Co}}x_{\mathrm{Ni}}(\underline{-5570}) \qquad \text{(Eq 8)}$$

$$M_{\mathrm{Ni}}^{\mathrm{fcc}} + \frac{1}{RT}\exp\left(\frac{\Delta Q_{\mathrm{Ni}}^{*}}{RT}\right) \qquad \text{(Eq 9)}$$

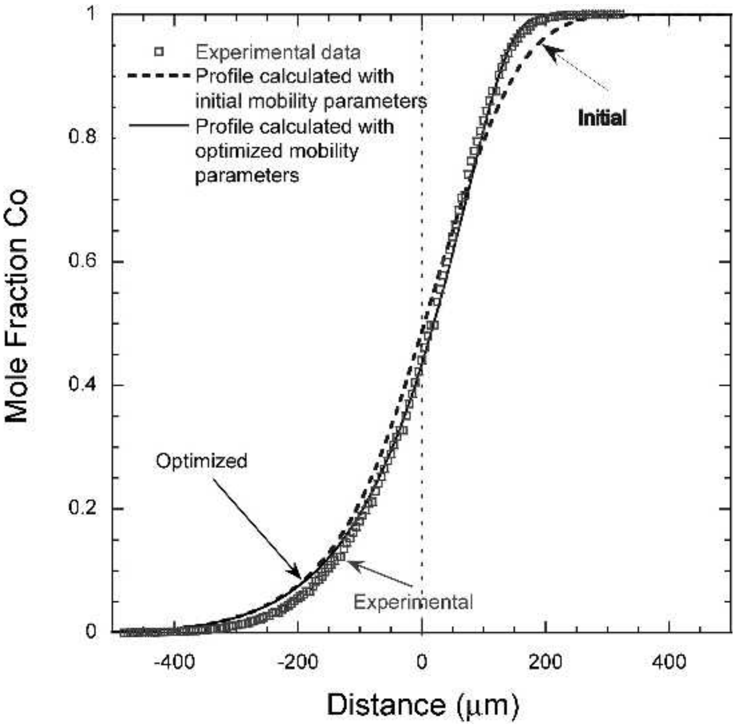

Fig. 3 Experimental and calculated composition profiles as a function of distance for the NiCo system at 1100 °C for 1000 h

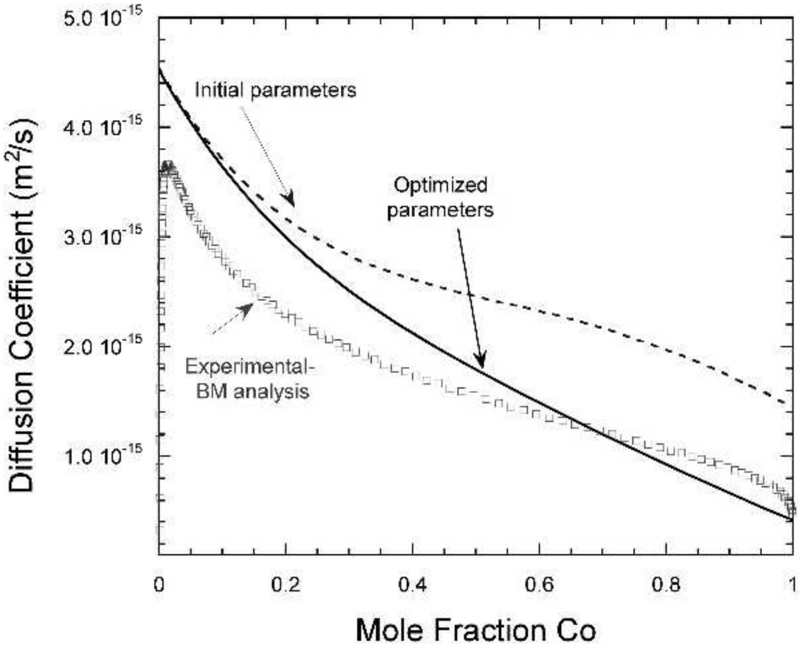

Fig. 4 Experimental and calculated interdiffusion coefficient as a function of composition for the NiCo system at 1100 °C

$$^{\mathrm{fcc}}\Delta Q^{*}_{\mathrm{Ni}} = x_{\mathrm{Co}}(\underline{-394{,}400}) + x_{\mathrm{Ni}}(-386{,}300) + x_{\mathrm{Co}}x_{\mathrm{Ni}}(\underline{-18{,}750}) \quad \text{(Eq 10)}$$

The first term in Eq 8 represents the activation energy for the self-diffusion of Co in pure Co, the second term represents the activation energy for the diffusion of Co in pure Ni, and the third term is a Co-Ni interaction term. Similarly, the first term in Eq 10 represents the activation energy for the diffusion of Ni in pure Co, the second term represents the activation energy for the self-diffusion of Ni in pure Ni, and again the third term is a Co-Ni interaction term. For this

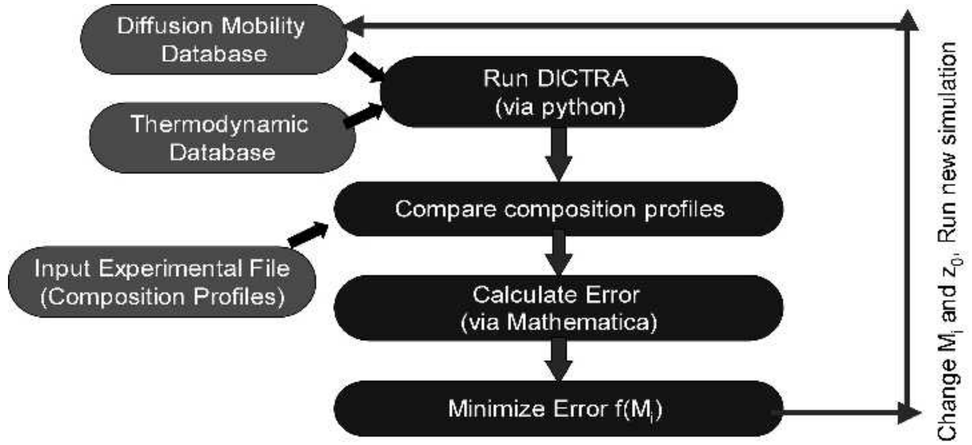

Fig. 5 Schematic of the optimization process

set of diffusion mobility parameters, the second term of Eq 8, the first term of Eq 10, and both interaction parameters are optimized (the four underlined terms in Eq 8 and 10). The parameters representing the self-diffusion of Co in Co and Ni in Ni are not optimized because these parameters are well defined by established tracer diffusivity data. Note that it is for demonstration purposes only that only one composition profile at a constant temperature is considered. Ideally, one would consider all of the experimental diffusion data for the NiCo system at various temperatures for the optimization.

Figure 5 is a schematic of the method used to optimize the selected mobility parameters. DICTRA, using the initial diffusion mobility parameters listed in Eq 8 and 10 and using the thermodynamic database developed by Saunders,[8] calculates the composition profiles for the Co-Ni diffusion couples at 1100 °C for 1000 h. The calculated profiles are then compared with the experimental profiles using Mathematica to calculate the average error between the two sets of profiles. The average error is calculated as:

$$Error(z_0, M_{Co}, M_{Ni}) = \left\{ \sum_{i=1}^{n} (b-a)^{-1} \int_{a}^{b} W_i(z)(x_i^{meas}(z - z_0) - x_j^{cal}(z; M_{Co}; M_{Ni}))^2 \, dz \right\}^{1/2} \qquad \text{(Eq 11)}$$

where z equals distance; b-a equals the length of couple; $W_i(z)$ is a weighting function, which is currently set to 1; x_i^{meas} and x_i^{cal}, respectively, are the measured and calculated compositions at a given distance z; and z_0 equals the error associated with the position of the initial Matano interface. Mathematica is then used to minimize the error using a least square fit as a function of the M_{Co}, M_{Ni}, and z_0. This procedure involves both changing the mobility parameters and shifting the position of the experimental profile as a function of distance (z_0). The four underlined mobility parameters in Eq 8 and 10 are altered based on the minimization. A Python script is used to modify the diffusion mobility description used by DICTRA, to run a new DICTRA simulation with the modified mobility parameters, and to export the new calculated composition profiles back to the Mathematica script. The average error is recalculated, and the process continues until an acceptable minimum is obtained.

The results of this optimization procedure are shown in Fig. 3 and 4. The agreement between the measured and calculated composition profiles is improved, especially for the Co-rich side of the couple. The measured and calculated interdiffusion coefficient dependence on composition is significantly improved: the coefficients are within 5% of the measured values. A comparison of the initial and optimized mobility parameters is given in Table 1. The largest relative change was for the Co-Ni interaction parameter for the mobility of Co.

In addition to the optimization of the mobility parameters, the current technique allows for possible experimental error in determining the Matano plane, which was used as the reference grid position when comparing the experimental and calculated composition profiles. During the optimization, the experimental profiles are shifted by a distance, z_0. The optimized value of z_0 is the error associated with the Matano plane. For this simple Co-Ni optimization the error was −1.58 μm.

5. Conclusions

This simple example demonstrates that experimental composition profiles can be used to optimize the diffusion mobility parameters. This method can be easily expanded to multicomponent systems and can incorporate multiple experimental profiles at various temperatures. The simplicity of the binary NiCo system provided the opportunity to check the optimization method using both composition and diffusion coefficient profiles. In higher-order systems, checking the interdiffusion coefficients will be more difficult because the experimental interdiffusion coefficients cannot be determined from just one experimental composition profile.

This type of optimization procedure will be used to determine the errors associated with the mobility parameters in the multicomponent diffusion mobility database by optimizing the mobility parameters with respect to various

Table 1 Comparison of initial and optimised diffusion mobility parameters

Parameter	Initial value	Optimized value	Change
Co in Ni	−380,400	−382,600	0.6%
Ni in Co	−394,400	−408,200	3.5%
Co-Ni interaction for Co	−5,570	−6,410	15.1%
Co-Ni interaction for Ni	18,750	18,860	0.6%

single-phase Ni-base superalloy diffusion couples. This technique also provides a method for the assessment diffusion mobility parameters directly from experimental composition profiles, thus avoiding some of the errors associated with determining interdiffusion coefficients using a Matano-Boltzmann-type method.

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