Improving the Calculation of Interdiffusion Coefficients

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Least-squares spline interpolation techniques are reviewed and presented as a mathematical tool for noise reduction and interpolation of diffusion profiles. Numerically simulated diffusion profiles were interpolated using a sixth-order spline. The spline fit data were successfully used in conjunction with the Boltzmann-Matano treatment to compute the interdiffusion coefficient, demonstrating the usefulness of splines as a numerical tool for such calculations. Simulations conducted on noisy data indicate that the technique can extract the correct diffusivity data given compositional data that contain only three digits of information and are contaminated with a noise level of 0.001. Splines offer a reproducible and reliable alternative to graphical evaluation of the slope of a diffusion profile, which is used in the Boltzmann-Matano treatment. Hence, use of splines reduces the numerical errors associated with calculation of interdiffusion coefficients from raw diffusion profile data.

I. INTRODUCTION

THE interdiffusion coefficient is a quantity that is useful to both researchers and professional engineers. Improvements in the ability to measure diffusion coefficients or modifications in the numerical techniques used to obtain interdiffusion coefficients from raw diffusion data are expected to improve the accuracy of the data in the interdiffusion data base. Such improvements will influence both basic research and practical applications in metallurgy.

On the theoretical end, the literature on diffusion currently lists two major theories that relate the interdiffusion coefficient to the system thermodynamics and to the phenomenological coefficients. The older theory by Darken[1] is simpler since it assumes that the off diagonal phenomenological coefficients are zero and that vacancies are in local equilibrium in a diffusion couple. Darken's theory leads to the following expression:

$$\tilde{D} = (D_1^* c_2 + D_2^* c_1)\left(1 + \frac{\partial \ln \gamma}{\partial \ln c}\right) \qquad [1]$$

Similarly, the theories of Howard and Lidiard,[2] Manning,[3] and Kirkaldy[4] lead to the following expression:

$$\tilde{D} = \left[(D_1^* c_2 + D_2^* c_1) + \frac{kT}{N}\left(\frac{X_B}{X_{A^*}} L_{AA^*} + \frac{X_A}{X_{B^*}} L_{BB^*}\right)\right] \cdot \left(1 + \frac{\partial \ln \gamma}{\partial \ln c}\right) \qquad [2]$$

From Eqs. [1] and [2], it is clear that the theories differ only in the additional term that is appended in Eq. [2]. The contribution of this term to the interdiffusion coefficient has been estimated to be of the order of 5 pct for isomorphous binary alloys.[4] Since the uncertainty in typical diffusion data can be as high as 20 to 50 pct, it is not possible to compute the contribution of the second term in Eq. [2] for real systems. Thus, despite the availability of a more sophisticated atomistic theory, one is unable to verify it from diffusivity measurements* due to the large errors in the diffusivity data. Hence, efforts directed toward improving the overall accuracy of diffusion data are important from a theoretical standpoint.

*Typically, Kirkendall velocity measurements are used to discriminate between Eqs. [2] and [1], since one may expect as much as a 28 pct difference in the velocities computed from Darken's theory and those computed from the theory by Manning, Howard and Lidiard, and Kirkaldy.

There have been very few changes in the method of obtaining interdiffusion coefficients over the past four to five decades. The Boltzmann-Matano analysis of a diffusion profile, which yields the interdiffusion coefficient as a function of composition, has been extensively used.[4,5] The diffusivity is computed using the following expression:

$$\tilde{D}(c) = \left(\frac{-1}{2t}\right)\left(\frac{1}{\left(\frac{dc}{dx}\right)}\right)\int_0^c (x(c) - x_M)\, dc \qquad [3]$$

Thus, the method relies on the slope of the diffusion profile as well as the area between the diffusion profile and the Matano interface. Both of these quantities must be estimated from discrete measurements of the diffusion profile (pairs of C-x data points). The slope is usually computed graphically.[6] At the ends of a diffusion couple, the slopes are shallow and, consequently, more difficult to estimate graphically. In addition, the integral in Eq. [3] is harder to estimate at the ends. As a result, the diffusivity data representing the terminal compositions are known to contain large errors.

In sharp contrast, considerable advances have been made in the field of numerical analysis over the past four decades. New, improved techniques have emerged for reducing noise from physical measurements; concepts of numerical accuracy and stability have emerged and have led to better algorithms for simple tasks such as estimation of areas under a curve defined by a discrete set of points. Simultaneously, powerful computing tools are now readily available.

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Significant advances have also been made in the accuracy of nondestructive techniques for compositional measurement. Instruments such as the electron microprobe and, more recently, the scanning transmission electron microscope (STEM) have improved not only the accuracy of the compositional measurement but also improved the spatial resolution of compositional measurements. Recent STEM studies on diffusion in the FeNi system[7,8] have attained a spatial resolution that varied between 50 and 400 nm, whereas the compositional measurements were accurate to within 0.5 pct or better. Since electron optical techniques are nondestructive, it is possible to rescan the same area and obtain several diffusion profiles. This further improves the uncertainty in the raw data.

In light of the improvements in the quality of the raw diffusion data (compositions and spatial resolutions), it is now important that more sophisticated numerical techniques be employed for computing the diffusion coefficient from Eq. [3]. Graphical estimation of slopes is subject to human error and must now be superseded by other techniques which offer better reproducibility. It would be unfortunate indeed if the progress made in compositional measurements were offset by poor computational techniques. Instead, efforts must be directed to improving the computational techniques so that eventually one may reduce the overall variation in the diffusivity data to levels that allow one to detect experimentally the differences between Eqs. [1] and [2]. The present paper is a small step along that general direction.

The main purpose of this paper is to review an interpolation technique known as *linear least-squares spline fitting* and to demonstrate its usefulness in treatment of diffusion data. Numerical experiments were conducted to test the usefulness of this technique. Results from these experiments indicate that spline interpolation techniques can be successfully used to compute the interdiffusion coefficient even when the input compositional data are contaminated with noise. The first part of the paper will review spline interpolation, and the second part will describe the numerical experiments.

II. LITERATURE REVIEW

The idea of using polynomial interpolation for computing the interdiffusion coefficient has been studied earlier by Baroody[9] and later by Borovskii *et al.*[10] In both cases, the raw diffusion data (C-x) were subjected to a nonlinear transformation involving the error function. Subsequently, a single high-order polynomial was fitted to the data over the entire composition range. The final expressions directly yielded the interdiffusion coefficient as a sum of a series of polynomials. These polynomials bear a recurrence relationship among themselves.

The approach taken earlier suffers from two drawbacks. First, a single interval (the entire length of the diffusion zone) was chosen for interpolating the diffusion profile. Second, high-order polynomials were used (up to order 9 or 11), which tend to oscillate between two successive data points. In contrast, the present investigation relies on spline interpolation. Splines split the interval of interpolation into several subintervals and fit low-order polynomials over each subinterval. In addition, a spline fit ensures that the derivatives of the interpolant remain continuous at the subinterval boundaries. Thus, the main advantages of spline fitting are (1) an accurate fit to the data, (2) lack of oscillation in the interpolant, and (3) continuity in the derivatives of the interpolant (slopes, curvatures, *etc.*).

The earlier investigators could not have used splines, since splines were an active area of research by mathematicians when Baroody[9] and Borovskii *et al.*[10] examined interpolation as a mathematical tool for computing diffusivities. However, at present, splines are well understood, and the computing facilities, as well as the necessary software, are easily accessible.

III. LINEAR LEAST-SQUARES APPROXIMATION USING SPLINES

This section begins with a discussion on polynomial interpolation techniques, thereby developing the motivation for spline fitting. Next, details on spline fitting are presented. The final topic will cover least-squares approximation techniques with emphasis on least-squares spline fitting. An example of the latter is presented to highlight the technique. The discussion is terse for the sake of brevity. Interested readers are directed to the book by de Boor.[11]

A. *Polynomial Interpolation*

Polynomials are attractive and popular as mathematical models for approximation because they can be evaluated, differentiated, and integrated easily using basic arithmetic operations. However, the use of polynomials for interpolation is not without drawbacks. For example, uniform spacing of data points (common in real experiments) can lead to large oscillations between two successive data points as the order of the polynomial increases. Such oscillations are usually undesirable from a physical standpoint.

Consider a general function $g(x)$ which possesses "r" continuous derivatives. When $g(x)$ is experimentally measured, one collects a set of data points $(x, g(x)]$. Thus, the function $g(x)$ is defined by the data points $[x, g(x)]$. It is desired to approximate this function by use of an n-th order polynomial (which will be a subset of P_n, the space of all n-th order polynomials) over the interval $a \leq x \leq b$. The polynomial will not provide a perfect fit but will approximate the given function. Hence, one may define a quantity $\text{dist}_\infty\ (g, P_n)$, which is a measure of the difference between the function $g(x)$ and the approximating polynomial P_n. Note that the quantity $\text{dist}_\infty\ (g, P_n)$ can only be determined at the x coordinate of each data point. Thus, the quantity $\text{dist}_\infty\ (g, P_n)$ measures the distance between the approximating function and the measured data *ONLY* at discrete points on the interval $[a, b]$. The quantity $\text{dist}_\infty\ (g, P_n)$ does not tell us anything about the quality of the approximation between any two data points since $g(x)$ (and, hence, $\text{dist}_\infty\ (g, P_n)$) is not defined between two datum points.

Approximation theory provides precise statements about the ability of polynomials to model other functions. It

can be shown that the error, when using polynomials to model a general function $g(x)$, which has r continuous derivatives, is bounded by the following upper bound:

For $g \in c^{(r)}[a,b]$ and $n > (r+1)$

$$\text{dist}_\infty(g, P_n) \leq (\text{constant}) \left(\frac{b-a}{n-1}\right)^r w\left(g^{(r)}; \frac{(b-a)}{2(n-1-r)}\right) \quad [4]$$

where g = measured quantity or function being modeled by a polynomial;
P_n = the space of all polynomials of order n;
$[a,b]$ = domain of the independent variable;
n = order of the polynomial;
$w(r)$ = modulus of continuity; and
$g \in c^{(r)}$ = implies that g has r continuous derivatives on $[a,b]$.

The important point to note here is that the error is bounded by $[(b-a)/(n-1)]^r$. This relationship relates the error in the approximation process to two distinct variables that one can control: (1) $(b\text{-}a)$, the interval size, and (2) n, the order of the polynomial.

Thus, there are two ways to reduce the error: (1) reduce the interval length, $(b\text{-}a)$, and (2) increase the order of the polynomial, n. Increasing n, the polynomial order, certainly reduces the error between the approximating polynomial and the function g (at those points on the interval $[a,b]$ where $g(x)$ has been measured). But as n increases, the polynomial tends to oscillate between two successive data points. Such oscillations are often undesirable, since physical quantities are not known to show numerous oscillations. Hence, a better way to improve the approximation process would be to choose a smaller interval. In other words, the main interval, $[a,b]$, should be split into several subintervals, and the function should be approximated over each subinterval with a unique polynomial (usually of low order). A simple example of such an approximation scheme would be a piecewise linear approximation to a given set of datum points $(x_i, g_i(x))$. The process of splitting the main interval into several subintervals and fitting a polynomial on each subinterval is called *piecewise polynomial interpolation*.

B. *Spline Interpolation*

Spline interpolation is a subset of piecewise polynomial interpolation. The main objection to a piecewise approximation is the lack of continuity of the derivatives of the function at the boundaries beween two subintervals. Often, there are physical reasons to demand that the approximation to a physical quantity possess several continuous derivatives. For example, the slope and curvature of a diffusion profile (C-x data) are related to the flux and to the instantaneous depletion rate. Therefore, discontinuities in the derivatives of the composition-distance data are undesirable. To avoid such discontinuities, one seeks an approximation process that will ensure continuity of the derivatives across subinterval boundaries. An approximation process that splits the main interval of interest $(a < x < b)$ into several subintervals and fits a polynomial on each subinterval such that the derivatives of the approximating polynomial are continuous at the boundary between two subintervals is called spline fitting. A subset of spline fitting is least-squares spline fitting.

In spline fitting terminology, the subintervals are known as spans, and the end points of each span are termed knots. A k-th order spline fit to a given data set ensures the following: (1) the resultant polynomial of order k (degree k-1) interpolates (passes through) all the given data points on that span, and (2) (k-2) derivatives of the interpolant are continuous at the breakpoints. In other words, the interpolant is differentiable (k-3) times.

To construct a spline fit, one needs not only the given data set but also some additional input. Consider a data set comprising of N data points, *i.e.*, N (x,y) pairs. In the simplest case, one desires to fit a k-th order spline on N spans; that is, one considers the distance between two successive data points to constitute a subinterval.* The total number of unknowns in fitting a k-th order polynomial on each subinterval is kN (k unknowns on each of the N subintervals). The constraints from the interpolation conditions are $2(N\text{-}2) + 2 = 2(N\text{-}1)$.** Additionally, continuity of (k-2) derivatives imposes (N-2) (k-2) constraints. Thus, the total number of unknowns are (k-2). In other words, to uniquely specify the k-th order spline, one needs to provide (k-2) pieces of information in addition to the data set. Usually, these are supplied as the values of the function or one of its derivatives at either end. Often, the derivatives at either end can be set to zero based on physical considerations. An example would be the fitting of a diffusion profile from an infinite diffusion couple. In this case, it is known that the slope and curvature of the diffusion profile are zero at points far from the diffusion zone.

It should be noted that in the general case, the breakpoints or knots are fewer in number than the total number of data points. Further, the knots need not coincide with the data points. This is particularly true for least-squares approximation using splines.

*The result to be presented is true even when the number of spans does not coincide with the number of data points.

**Disregarding the two endpoints, one has (N-2) interior data points. At each data point, two polynomials, one from each adjacent subinterval, must pass through the given data point. Hence, 2(N-2) constraints result. In addition, one has two constraints at either end for a total of 2(N-2) + 2 constraints.

C. *Least-Squares Approximation Techniques*

Measurements of physical quantities are usually contaminated by the inherent noise associated with the measuring technique. The term "noise" refers to the errors in the measuring technique related to the uncertainty of the measuring instrument. Thus, the measured quantity is a sum of the noise (which is presumed to be random) and the true value of the physical property. Least-squares approximation techniques attempt to separate the noise from the true values of the physical quantity. All least-squares techniques assume a certain functional form that describes the physical quantity. Often the functional form is known from the physical understanding of the process. For example, in electric circuits, it is known that the current through a resistor is proportional to the potential

drop across the resistor. The mathematical model selected reflects a compromise between the accuracy of the fit and the ability to separate noise from the data. Ideally, the function chosen should possess just enough degrees of freedom to model the underlying variation of the physical quantity. Excessive degrees of freedom will certainly improve the accuracy of the fit, but the function will also include some contamination from the noise.

The first step in least-squares approximation involves choosing a certain mathematical model (trigonometric, polynomial, exponential, *etc.*) to describe the variation of the physical quantity under consideration. The second step consists of defining a least-squares error function* by using the mathematical model. The third step consists of backing out the necessary coefficients which constitute the mathematical model by minimization of the least-squares error with respect to the unknown coefficients. Typically, the number of observations or measurements far exceeds the number of unknowns that constitute the mathematical model. This results in an overdetermined system of equations (in the linear case) from which the unknown parameters are estimated. In the nonlinear case, the resultant least-squares error function (sum of the squares) must be minimized using an iterative procedure.

*Note that the least-squares error function referred to here is distinct from the mathematical error function, erf (z), which occurs in the standard solution to the diffusion equation. The error function referred to here is also known as the chi-squared (χ^2) function and is defined as the sum of the squares of the distances between each measured data point (x_i, y_i) and the value of the approximating function at the point x_i.

Specifically, consider a data set comprising of N data points (x_i, y_i) to which one desires to fit a model function f. Assume that k parameters $(\alpha_1, \ldots, \alpha_k)$ are needed to describe the function f in addition to the independent variable x. In other words, one may express the function f as follows:

$$f = f(\alpha_1, \ldots, \alpha_n, x)$$

For each measured data point (x_i, y_i), there exists a corresponding value of the approximating function. This value is given by

$$f(\alpha_1, \ldots, \alpha_n, x_i)$$

Thus, at the i-th datum point, the square of the distance between the measured datum point and the value of the approximating function is

$$[y_i - f(\alpha_1, \ldots, \alpha_n, x_i)]^2$$

One may sum these values for all of the data points to obtain the overall least-squares error function, which is given by the following equation:

$$E^2 = \sum_1^n \{[y_i - f(\alpha_1, \ldots, \alpha_k, x_i)]w_i\}^2 \qquad [5]$$

where w_i, the weighing function, reflects the certainty (inverse of spread) in the i-th datum point (x_i, y_i) and accounts for the spread (uncertainty, error bars) at each datum point.

By differentiating with respect to each α_k and setting the result to zero, one ends up with the normal equations that must be solved for each α_k. This is accomplished by standard procedures of linear algebra (Gaussian elimination, LU factorization).[12]

In the case of least-squares spline fitting, one must specify *a priori*, the spline order, the number of knots, the knot sequence, and the $(k\text{-}2)$ additional unknowns. The spline function is defined in terms of the unknown coefficients, α_k, which define the interpolating polynomials. Thus, during the minimization process, one seeks the numerical values of the unknown coefficients, α_k. The least-squares spline interpolant does *not* pass through each datum point exactly but offers a least-squares fit to the data set, thereby filtering out the noise from the data.

It should be noted that varying the number and location of the knots (*i.e.*, changing the number and length of the subintervals) can significantly affect the accuracy of the fit. Hence, least-squares spline fitting schemes must incorporate an algorithm that optimizes the number and location of the knots. The spline routines used in this work accomplish this by a two-step process. In the first stage, the number of polynomial pieces is continuously increased. For each value of the number of polynomial pieces, a complete spline fit is evaluated. For each spline fit, the least-squares error at the minimum (also termed residual) is obtained and monitored as a function of the number of polynomial pieces. It will be shown in the example to follow that a plot of residual as a function of number of polynomial pieces depicts a fairly flat minimum or a plateau. The number of polynomial pieces is chosen to correspond to the plateau on the graph; *i.e.*, one chooses just enough number of polynomial pieces (degrees of freedom) to minimize the least-squares error with respect to the number of polynomial pieces. For a given number of polynomial pieces, the algorithm automatically selects the optimal knot locations. The optimal knot locations are selected based on examination of the k-th root of the k-th derivative of the data set.[11]

D. *Example of Spline Fit*

Figure 1 depicts the chemical interdiffusion coefficient in the Ni-Pt system. The data were obtained by digitizing one of the figures in Reference 10. Clearly, the input data are contaminated by high wave number noise arising from the digitizing process. It was decided to fit a spline of order 4 (cubic spline) to this data. The input to the programs included the data set depicted in Figure 1 and the two breakpoints at either end of the interval (*i.e.*, a single span).

The programs increased the number of polynomial pieces continuously and monitored the least-squares error. A plot of the least-squares error is depicted in Figure 2 as a function of the number of polynomial pieces. The error plateau is clearly seen. A value of 17 was selected for the number of polynomial pieces, and the spline coefficients constituting the fit were computed. Figure 3 depicts the fitted function along with the raw digitized data for comparison. The fit appears to be satisfactory. Also depicted in Figure 3 are the locations of all of the breakpoints. A more stringent evaluation of the fit involves examination of the residual at each datum point. In other words, one examines the difference between the fitted value and the measured (digitized) value of the function. If the fit is a good one, then the residual should

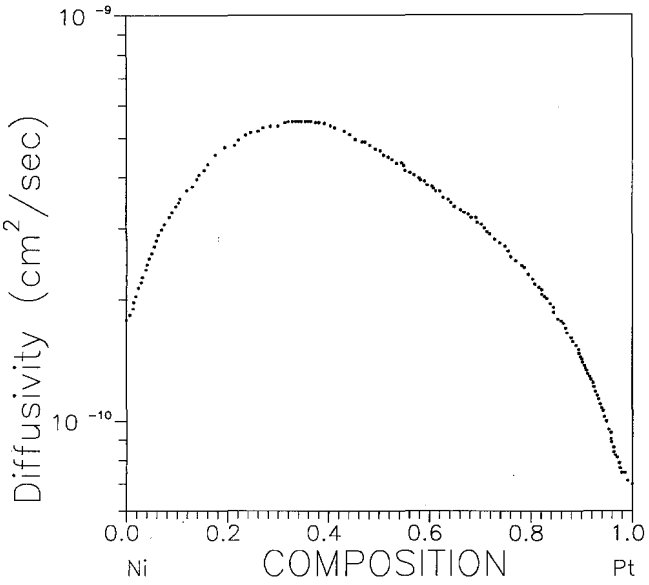

Fig. 1—Raw digitized diffusivity data for the NiPt system at 1296 °C (digitized from Ref. 10).

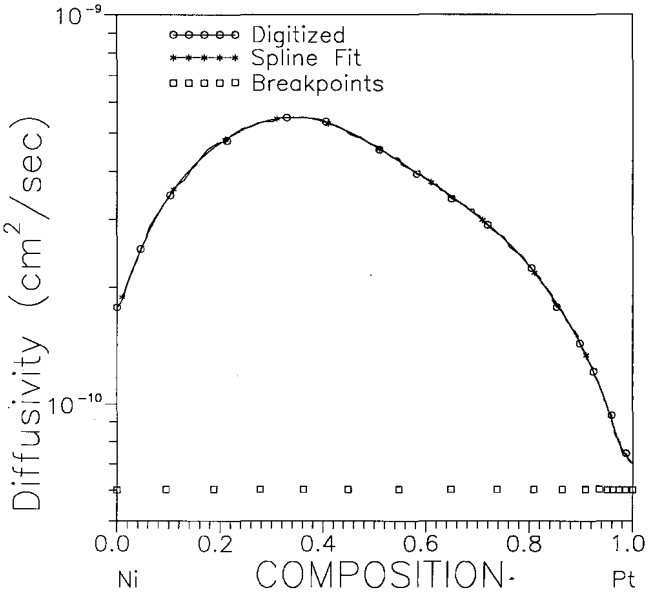

Fig. 3—Raw and spline-fitted diffusivity data for the NiPt system at 1296 °C. The spline order was 4.

represent the noise which is presumed to be random. This difference is plotted as a function of the composition in Figure 4. It is clear that the residual experiences several changes in sign. This suggests that the residual is indeed random and, hence, may be presumed to represent noise. Hence, the fit is believed to be a good one.

E. *Software for Spline Fitting*

Software for the implementation of splines is readily available for spline orders up to $k = 4$, *i.e.*, cubic splines. Popular Fortran libraries such as the NAG[13] library offer routines for cubic splines. During this research project, it became necessary to use splines which possessed a minimum order of 5 and sometimes even 6. The book by de Boor[11] contains several programs for this purpose. The routines by de Boor allow one to increase the number of breakpoints and determine the optimum knot placement given a certain number of knots. In particular, the routine L2MAIN and associated subroutines are very helpful in least-squares spline fitting. These routines are available in the public domain and may be easily obtained by using the NetLib facility over InterNet.[14]

IV. NUMERICAL EXPERIMENTS

A numerical experiment was conducted to test the ability of spline interpolation in extracting the correct interdiffusion coefficients from noisy diffusion profile data.

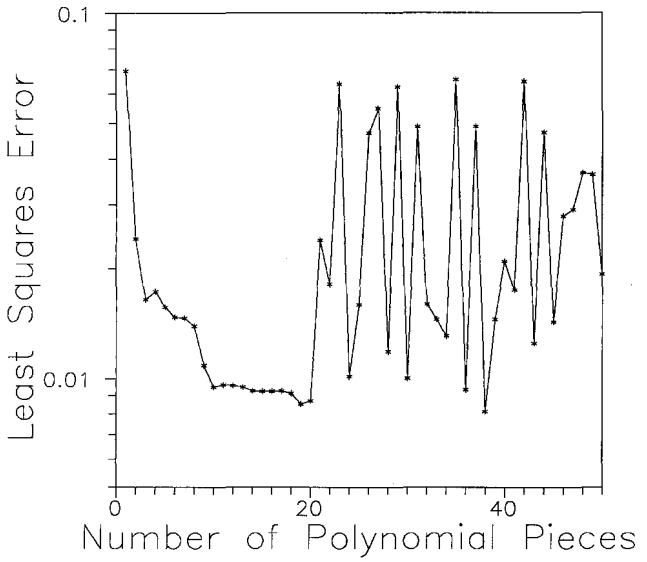

Fig. 2—Least-squares error as a function of the number of polynomial pieces for spline fitting the diffusivity data of Fig. 1. Note the error plateau in the curve.

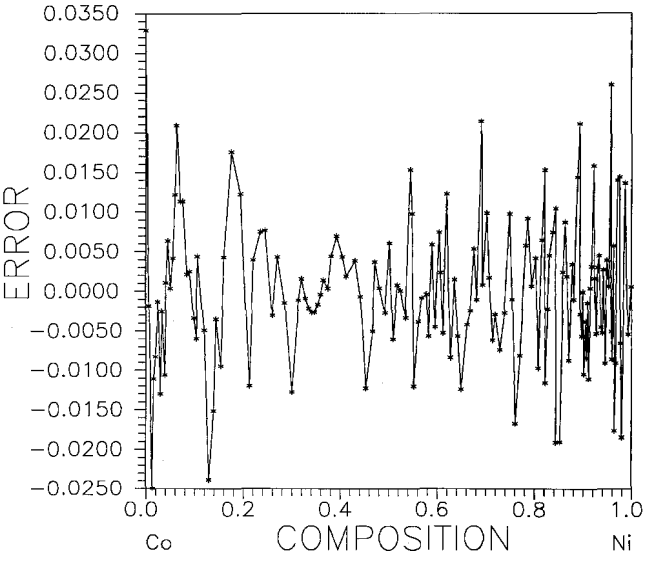

Fig. 4—Difference (residual) between the raw digitized data and the spline-fitted diffusivity data. The random nature of the residual is clearly evidenced in the large number of sign changes, indicating that it is representative of noise.

The basic idea behind the experiment was to fit the diffusion profile with a least-squares spline. The spline approximation would involve splitting the diffusion zone into subintervals and fitting polynomials over each subinterval while ensuring that the derivatives of the interpolant were continuous at the subinterval boundaries. The spline approximation could then be used to evaluate the slope and the area under the diffusion curve. These quantities, in conjunction with the Boltzmann-Matano treatment, would allow one to compute the $\tilde{D}$-c relationship from the compositional profile data.

Instead of obtaining experimental diffusion profiles from the literature (or from experiments), it was decided to numerically simulate a diffusion couple by solving the one-dimensional diffusion equation. Thus, the experiment consisted of the following stages:

(1) Isothermal interdiffusivity data for an isomorphous binary system (AuNi) was obtained from the literature and fitted with a fourth-order spline.
(2) An equidistant finite difference grid was used to simulate numerically an isothermal diffusion couple between pure Au and pure Ni. Diffusion profiles were computed for various annealing times.
(3) Random noise was added to the computed profiles using a random number generator. The amplitude of the noise was varied.
(4) A least-squares spline of order 6 was fit to the composition-distance data.
(5) The Boltzmann-Matano treatment was used to compute the interdiffusion coefficient from the least-squares spline approximation to the diffusion profile.

The main advantage of this scheme was that it allowed a direct comparison between the input diffusivity data and the computed diffusivity data. It is expected that the quality of the computed diffusivity data will deteriorate as the amplitude of the random noise (simulated experimental errors in the composition-distance data) increases. Since one possessed the capability to monitor the difference between the computed and input diffusivity data, a direct correlation between the noise level in the composition-distance (C-x) data and the resultant error in the computed interdiffusivity data could be made. Thus, the scheme used was more advantageous than using experimental diffusion profile data, since in the present scheme, one clearly knows the exact value of the input $\tilde{D}$-c data, the noise level in the C-x data, and the final $\tilde{D}$-c data computed from the C-x data. This allows one to clearly and critically evaluate the usefulness of spline interpolation for the present application. The computed interdiffusivity-composition relationship was compared with the diffusivity data [input at stage (1)] used to simulate the profile.

A minor modification was made to the Boltzmann-Matano expression. The variable of integration was altered from the compositional variable to the spatial variable, resulting in the following expression:

$$\tilde{D}(c) = \left(\frac{-1}{2t}\right)\left(\frac{1}{\left(\frac{dc}{dx}\right)}\right)\int_0^{x(c)} (x(c) - x_M)\frac{dc}{dx}\,dx \quad [6]$$

The modification is advantageous since the diffusivity is now expressed as a function of the slope alone, and hence, all errors will arise from a single source only; that is, from the slope of the diffusivity data. The slope of the diffusion profile can be easily computed from the spline fit by differentiating the piecewise polynomial comprising the spline. To compute the integral in Eq. [6], the integrand was computed at discrete points, and a third-order finite difference scheme was used to evaluate the integral. Subroutine D01GAF from the NAG[13] Fortran library was used for this purpose.

Estimation of Errors

For any physical measurement, it is important to have an upper bound or at least an estimate of the error involved in that measurement. In a diffusion experiment, the errors that accrue may be classed under two broad categories: (1) intrinsic and (2) extrinsic. Intrinsic errors would include errors related to the change in the molar volume due to diffusion, errors due to large-scale deformation of the sample, Kirkendall porosity, *etc.* The experimentalist has little control over these variables once the alloy system and the temperature have been chosen. On the other hand, there are additional errors that one introduces based on one's treatment of the numerical data from the experiment. These may be termed extrinsic errors, since they arise from sources external to the actual experiment.

From the form of Eq. [6], it is clear that the numerical value of the diffusion coefficient depends strongly on the estimated slope of the diffusion profile (dc/dx). For example, it is well known that errors in the estimation of the slope cause significant errors in $\tilde{D}$ at either end of the diffusion couple. Hence, estimation of the extrinsic relative error in $\tilde{D}$ demands an estimation of the errors in the slope of the diffusion profile.

Error bounds for estimation of dc/dx from least-squares fitted c-x data have been reported by Ragozin.[16] Unfortunately, Ragozin's results are applicable only to least-squares splines for which the knot sequence is predefined by the user and unchanged during the fitting process. Hence, Ragozin's results do not apply to the present treatment, since the routines used in this investigation use knot optimization techniques that continually add and redistribute the knots on a given interval. This makes the problem nonlinear. The authors are not aware of any other investigations that provide error bounds for spline-fitted data. Hence, a rigorous estimation of the errors in $\tilde{D}$ is presently not possible and must await further developments in the field of numerical analysis.

V. RESULTS

Figure 5 depicts the diffusion profile computed using the diffusivity data at 900 °C for the AuNi system.* The finite difference grid used contained 800 equidistant points for a diffusion couple 2 cm in extent. Euler's method[15] was used to solve the diffusion equation with insulating boundary conditions at either end. The original interface between the two pure metals (plane of joining) was chosen to correspond to a location 0.5 cm from the Ni end of the diffusion couple.** The diffusion times corresponding to the profile are astronomically large (4.32 ×

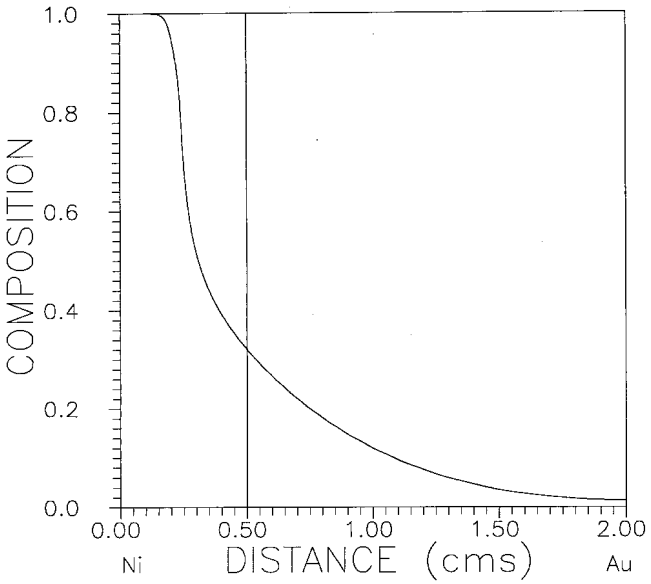

Fig. 5—Computed diffusion profile for the AuNi system. The initial plane of separation corresponded to the location $x = 0.5$ cm.

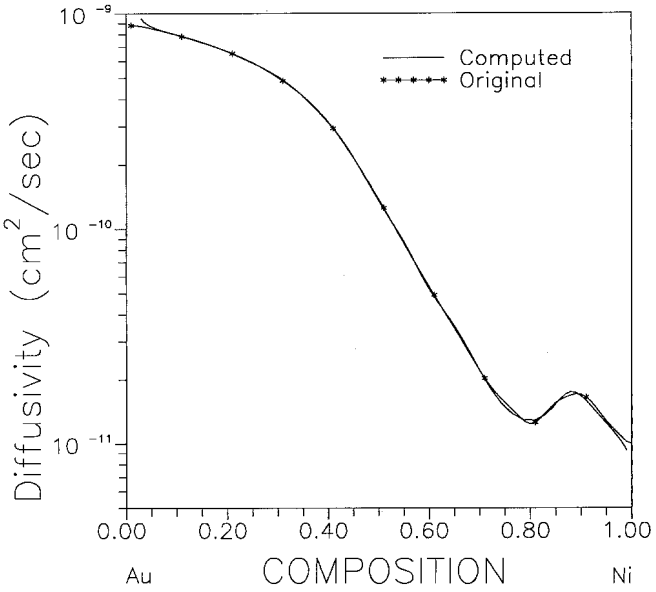

Fig. 6—Interdiffusion coefficient computed by applying the modified Boltzmann-Matano treatment to a noise-free simulated diffusion profile. The compositional data were represented to 8 digits.

10^8 s). However, such large times were necessary to ensure that the slope and the curvature of the diffusion profile do not attain very large numerical values. In a practical experiment, one would split the entire compositional interval and prepare a series of diffusion couples, each covering a narrow composition range.† In such a case, one would obtain shallow profiles in a realistic time span. Thus, in a real experiment, each diffusion couple would provide diffusivity information over a narrow range of compositions. By using a single diffusion couple in the present simulations, the computational effort has been greatly reduced. However, the use of a single diffusion couple covering the entire range of composition from 0 pct B to 100 pct B is not recommended for a real experiment.

In stage (2) of the numerical experiment, the compositional profile was computed to 10-digit accuracy, which is clearly unrealistic. To simulate a real diffusion couple, the data were rounded to a lower accuracy, and random noise was added to the profiles. Equation [6] was then used to compute the interdiffusion coefficient.

Figure 6 depicts the diffusion coefficient computed using 10-digit diffusion profile data. Also depicted in Figure 6 are the original diffusivity data for the AuNi system. The close match between the computed and the original data confirms that the modified computational scheme of Eq. [6] was correctly implemented. Thus, given highly precise and accurate diffusion profile data, it is possible to recover the original $\tilde{D}$-c data. However, in a real experiment, uncertainties in measuring composition (noise) are inevitable, and so the true measure of the proposed computational scheme can only be obtained if it is tested on data contaminated by noise. Hence, the subsequent experiments rounded the diffusion profile data to low precision and superimposed noise onto the rounded profile data.

To implement the proposed scheme, the diffusion profile was rounded to two digits (in other words, the compositional data varied from 0.990 to 0.010). Noise was also added to the profile by using a random number generator. The noise possessed a maximum amplitude of 0.01. Figure 7 depicts the computed and original diffusivity data for the noisy profile data. The computed diffusivity differs slightly from the original diffusivity, although the general trend is preserved. In particular, the maxima and minima around $X_{Ni} = 0.8$ are lost due to the rounding of the profile and the addition of noise. Thus, diffusion profile composition data that are precise to two digits and have a noise level of 0.01 result in some loss of accuracy in the computed $\tilde{D}$-c data.

Similarly, Figure 8 compares the computed and original diffusivities for the case when the profiles were rounded to three digits (in other words, the compositional data varied from 0.999 to 0.001) and the maximum amplitude of the noise was 0.001. In this case, an excellent match was obtained between the computed and the original diffusivities. Comparison of Figures 6 and 8 indicates that the least-squares spline technique is able to filter out all noise with a maximum amplitude less than 0.001 when given 3-digit profile data.

*The Au-Ni system exhibits complete solid solubility at the temperature for which the diffusivity data were obtained. It should be noted that the hump in the diffusivity data at $X_{Ni} = 0.8$ was experimentally obtained by Cohen *et al.*[4] but is not consistent with the thermodynamic data on the AuNi system. For the present purpose, the hump at $X_{Ni} = 0.8$ is advantageous, since it makes the $\tilde{D}$-c relationship more complex and, hence, is a stricter test of the spline fitting technique.

**Preliminary runs were conducted with a coarse grid which suggested that $x = 0.5$ cm would be a good choice for the plane of joining. The lack of symmetry in the diffusion couple is a result of the large variation of the diffusivity in the AuNi system. At the Au-rich end, the diffusivity is about two orders of magnitude larger than the diffusivity at the Ni-rich end.

†A narrow compositional range in a diffusion couple is necessary to ensure the validity of the phenomenological expressions (derived from irreversible thermodynamics).

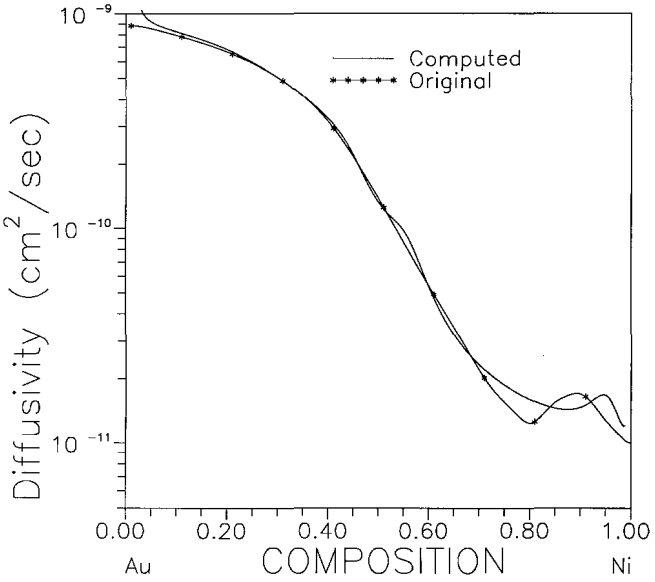

Fig. 7—Diffusion coefficient computed using noisy profile data. The compositional data were rounded off to two significant digits, and random noise of maximum amplitude 0.01 was superposed on the compositional data.

VI. DISCUSSION

The simulation results clearly indicate that spline interpolation can be successfully used in computing interdiffusion coefficients. It is also clear that 3-digit data with a maximum noise amplitude of 0.001 are good enough to obtain highly accurate diffusivity data. With 2-digit data and 0.01 level noise, some loss of reproducibility is clearly seen.

In a real experiment, the accuracy of compositional measurement will vary with the composition. At very small compositions, the absolute error will be smaller, but the relative error will be larger.[4] The simulations presented here are a stricter test of the method, since the noise added was invariant with composition. Thus, for compositions less than 0.01, the 0.01 level noise will completely swamp out the compositional data. On the other hand, a real experiment introduces several other errors in the data, such as errors in measuring the spatial variable, porosity in the diffusion couple, *etc.*

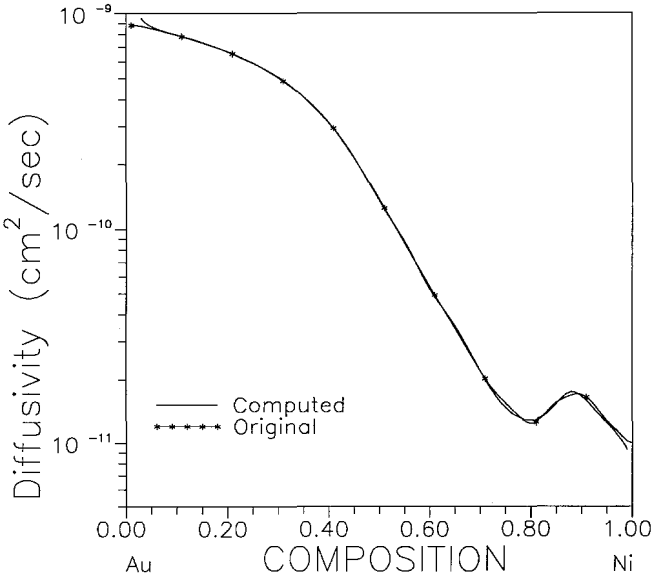

Fig. 8—Diffusion coefficient computed using noisy profile data. The compositional data were rounded off to three significant digits, and random noise of maximum amplitude 0.001 was superposed on the compositional data.

It is important to note that, currently, a real experiment is capable of achieving much better spatial resolution than the simulation data. With proper calibration, the STEM can offer compositional data good to at least two digits and possibly three digits, with noise levels approximately 0.01. An example is the work of Goldstein and co-workers.[7,8] Hence, the experimental capabilities presently available lie between the two cases investigated in this paper. These cases bracket the regime where the contamination from noise in the profile data begins to have a detrimental effect on the computed interdiffusion coefficient. Since the present experimental capabilities lie in this region, it is important that established numerical techniques be used while computing the interdiffusion coefficient. This will minimize any errors arising from the computational technique itself. This implies that graphical evaluation of slopes must be superseded by other more reliable techniques.

It is hoped that, in the future, established numerical techniques will replace graphical evaluations of the quantities used to determine diffusivities and lead to improvements in the accuracy of basic diffusion data.

VII. CONCLUSIONS

Least-squares spline fitting techniques were reviewed and presented as a technique to filter out the noise in the measured composition data. These techniques can be successfully applied to a diffusion profile to estimate the slope of a diffusion profile which is needed to compute the interdiffusion coefficient as a function of composition. Simulation results indicate that the technique can extract the correct diffusivity data given compositional data containing only three digits of information and contaminated with noise levels of 0.001. Some loss of accuracy was seen on using compositional data containing only two digits of information and contaminated by a noise level of 0.01. Since current techniques for compositional measurement lie between these two limits, it is important that graphical estimation of the slope of the diffusion profile be superseded by more reliable and reproducible numerical techniques, such as least-squares spline fitting.

SYMBOLS

$\tilde{D}$	chemical interdiffusion coefficient
D_i^*	tracer diffusivity for element i
γ	activity coefficient
c	chemical composition
L_{AA^*}, L_{BB^*}	phenomenological coefficients

X_{A^*}, X_{B^*}, X_A, X_B	mole fraction
k	Boltzmann's constant
N	Avogadro number
T	absolute temperature
dc/dx	slope of the diffusion profile
t	time
x	spatial variable
x_M	location of the Matano interface

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REFERENCES

1. L.S. Darken: *Trans. AIME*, 1948, vol. 174, pp. 184-201.
2. R.E. Howard and A.B. Lidiard: *Rep. Prog. Phys.*, 1964, vol. 27, p. 161.
3. J.R. Manning: *Diffusion Kinetics for Atoms in Crystals*, Van Nostrand Reinhold, 1968.
4. J.S. Kirkaldy and D.J. Young: *Diffusion in the Condensed State*, The Institute of Metals, London, 1987.
5. P.G. Shewmon: *Diffusion in Solids*, McGraw-Hill, New York, NY, 1963.
6. C. Wells: *Atom Movements*, ASM, Metals Park, OH, 1950, pp. 26-50.
7. D.C. Dean and J.I. Goldstein: *Metall. Trans. A*, 1986, vol. 17A, pp. 1131-38.
8. K.B. Reuter, D.B. Williams, and J.I. Goldstein: *Metall. Trans. A*, 1989, vol. 20A, pp. 719-25.
9. E.M. Baroody: *J. Met., Trans. AIME*, 1957, pp. 819-22.
10. I.B. Borovskii, K.P. Gurov, I.D. Marchukova, and Y.E. Ugaste: *Interdiffusion in Alloys*, Nauka Publishers, Moscow, NTIS Document PB86-245495, 1986.
11. Carl de Boor: *A Practical Guide to Splines*, Applied Mathematical Sciences Series, Springer-Verlag, New York, NY, 1985.
12. Gene Golub and Van Loan: *Matrix Computations*, Johns Hopkins University Press, Baltimore, MD, 1983.
13. NAG Fortran Library Manuals, Mark 13, Numerical Algorithms Group, Downers Grove, IL, 1987.
14. Jack J. Dongarra and Eric Grosse: *Commun. ACM*, 1987, vol. 30 (5), p. 403.
15. J.C. Butcher: *The Numerical Analysis of Ordinary Differential Equations*, John Wiley & Sons, Inc., New York, NY, 1987.
16. D.L. Ragozin: *J. Approximation Theory*, 1983, vol. 37 (4).