VisiMat-Software for the Visualization of Multicomponent Diffusion in Two and Three Dimensions

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VisiMat is a MATLAB code with a graphical user interface (GUI) that is intended to be used for instructional purposes. It is designed to facilitate understanding of the complex multicomponent diffusion phenomena that may occur in couples of three or more components with a special emphasis on the compositions and locations where maxima, minima, or zero-flux behavior may occur. VisiMat is an implementation of the square-root diffusivity method for predicting and visualizing the diffusion behavior of ternary and quaternary, single-phase, multicomponent diffusion couples with constant diffusivity. The program determines concentration profiles, fluxes including zero-flux conditions, and two- or three-dimensional representations of composition space and diffusion path. Although the code will accomodate any number of components, the three-dimensional visualizations are not possible for more than four components.

1. Introduction

VisiMat software is primarily an implementation of the square-root diffusivity method[1] for exploring the behavior of single-phase, multicomponent diffusion couples with constant diffusivity. The square-root diffusivity method has been used to characterize ternary[2] and quaternary[3,4] diffusion couples and can be extended to any number of components. Couples with more than two components can exhibit very interesting diffusion behavior not seen in two component couples. Some of these behaviors with practical interest include moving and stationary zero-flux planes (ZFPs).[5,6,7] A ZFP occurs when the flux of a particular element becomes zero on a plane in the diffusion couple. This condition may be met anywhere in the couple for moving ZFPs; alternatively, stationary ZFPs are only located at the Matano interface ($x = 0$ herein) where the flux intersects the abscissa.

The software determines right alloy compositions in a diffusion couple that form stationary zero-flux planes given a left alloy composition. With the ZFP compositions known, concentration profiles, fluxes versus distance profiles, and a composition space plots are found for these compositions. These plots may also be generated for any user-specified left

and right alloy compositions in single-phase multicomponent diffusion couples.

VisiMat is a successor to both the Profiler software developed by Brockman and Morral[8] and a MATLAB code with a graphical user interface[9,10] developed at Rensselaer Polytechnic Institute, to implement the equations derived by Glicksman and Lupulescu.[7] VisiMat is written on a more modern platform, which is compatible with many common operating systems. Additionally, this code adds the ability to construct three-dimensional visualizations and performs calculations with many more components than could be handled by the predecessors to this software.

2. Multicomponent Concentration Profiles Obtained with VisiMat

The square-root diffusivity method and a discussion of the properties of the square-root of the diffusivity matrix was first developed by Thompson and Morral.[1] This method has been employed to analyze and characterize multicomponent diffusion couples of n components where $n-1$ components are independent. A summary of the equations relevant to this software is taken from the extensive literature regarding the method.[1,2,3,11,12]

Following Eqs 1–3 of Stalker and Morral,[3] the absolute concentration of the ith component is defined with respect to the average concentration as:

$$C_i(x,t) = C_i^{\text{ave}} + \frac{1}{2}\sum_{j=1}^{n-1}\sum_{k=1}^{n-1}\alpha_{ij}^{-1}\alpha_{jk}\Delta C_k^0 \text{erf}\left(\frac{x}{2\sqrt{E_{jj}t}}\right). \quad \text{(Eq 1)}$$

The transformation matrix $\boldsymbol{\alpha}$ is determined from the spectral decomposition of the diffusivity matrix where

$$\boldsymbol{D} = \boldsymbol{\alpha}^{-1}\widetilde{\boldsymbol{D}}\boldsymbol{\alpha}. \quad \text{(Eq 2)}$$

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Fig. 1 Sample input entered into the VisiMat's System Parameters menu for a four-component CrAlMoNi couple

Thus, $\tilde{D}$ consists of the eigenvalues, E, of the D matrix along the diagonal.[13] The eigenvectors of D are the rows of α^{-1}. The coefficients of Eq 1 can be expressed in a form equivalent to Eq 12 of Stalker and Morral[3] and Eq 19 of Cohen and Glicksman.[12]

The concentration scaling factor appearing in Eq 1 is defined as:

$$\Delta C_k^0 = \|\Delta \mathbf{C^0}\| \cos(\Psi_k), \tag{Eq 3}$$

where Ψ_k is the angle between the composition vector and the axis of the ith component in composition space. The length of the composition vector in Eq 3 is defined as:

$$\|\Delta \mathbf{C^0}\| = \sqrt{\sum_{k=1}^{n-1} \left(C_k^R - C_k^L\right)^2}. \tag{Eq 4}$$

The quantities C_k^L and C_k^R in Eq 4 represent the left and right alloy compositions of the kth component.

As a way to validate the methods used in VisiMat, we used the experimental data and the diffusivity matrix determined by Stalker et al.[4] for a CrAlMoNi diffusion couple. Since the couple has $n = 4$ components, composition space can be represented in three dimensions. The tested diffusion couple was an alloy of 1.96 at.% Cr, 6.44 at.% Al, 4.26 at.% Mo, and 87.34 at.% Ni making up the left end of the couple welded to a 5.96 at.% Cr, 6.49 at.% Al, 3.71 at.% Mo, and 83.84 at.% Ni alloy making up the right end of the couple. The experimental couple was annealed for 100 h at 1100°C.[4] Figure 1 shows how the CrAlMoNi couple parameters are input into the VisiMat GUI. The change in measured composition from the left to right end can be described by three angles including one with respect to the Cr axis of $\Psi_1 = 7.86°$, the Al axis of $\Psi_2 = 89.29°$, and an angle oriented at $\Psi_3 = 97.83°$ from the Mo axis. The couple has a total
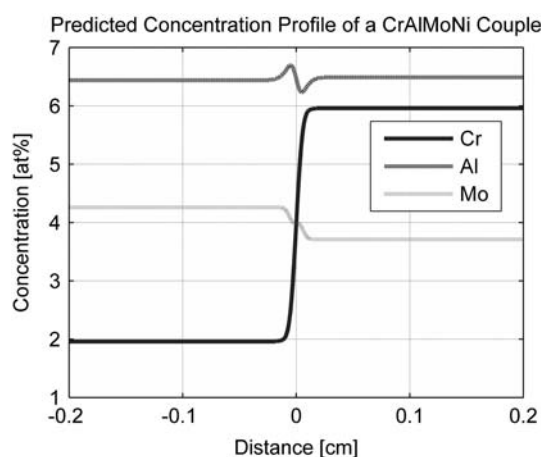

Fig. 2 VisiMat's predicted concentration profile for a CrAl-MoNi couple with conditions that were experimentally investigated.[4] The Ni component (not shown) makes up the balance of the couple

composition change, $\|\Delta \mathbf{C^0}\|$, of 4.04 at.%. The VisiMat predicted concentration profile, shown in Fig. 2, agrees very well with the concentration profile measured by Stalker and Morral.[3]

3. Other Results Obtained with VisiMat

An objective of this software is to be capable of predicting not only concentration profiles, but also the flux at any point and conditions where zero flux of a component is attained. Therefore, the calculation of flux is discussed in detail.
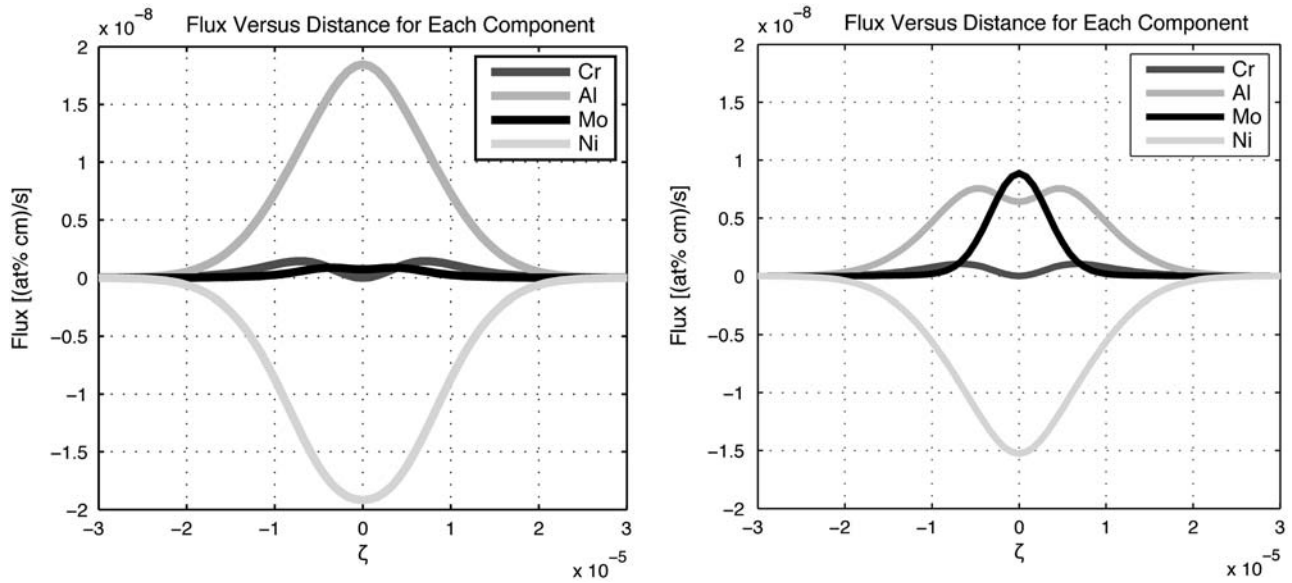
Fig. 3 Two plots showing the calculated flux versus similarity variable (ζ) for a CrAlMoNi couple. Note that this plot shows a stationary ZFP composition for Cr since its flux is zero at $\zeta = 0$. The left plot shows a stationary ZFP located in the Cr-Al search plane while the right plot shows a ZFP located in the Cr-Mo search plane (see sections 3.1 for further explanation)

3.1 Mass Transport-Fluxes

Flux is determined from an analytical expression to ensure accuracy and to allow the flux versus distance to be shown for the user-specified composition, if requested. Using Eq 1 as the expression for concentration, the flux may be expressed as:

$$J_i(x,t) = \sum_{k=1}^{n-1} D_{ik} \frac{\partial}{\partial x} \left[C_i^{\text{ave}} + \|\Delta \mathbf{C^0}\| \left(\sum_{j=1}^{n-1} \sum_{k=1}^{n-1} \alpha_{ij}^{-1} \alpha_{jk} \right. \right.$$
$$\left. \left. \cdot \cos(\Psi_k) \text{erf}\left(\frac{x}{4E_{jj}t} \right) \right) \right]. \quad \text{(Eq 5)}$$

Calculating the derivative as indicated in Eq 5 results in the equation for the flux of component i as:

$$J_i(x,t) = \|\Delta \mathbf{C^0}\| \sum_{j=1}^{n-1} \sum_{k=1}^{n-1} \left(-\frac{D_{ik}\alpha_{ij}^{-1}\alpha_{jk}\cos(\Psi_k)}{\sqrt{\pi E_{jj}t}} e^{\frac{-x^2}{4E_{kk}^2 t}} \right). \quad \text{(Eq 6)}$$

The flux versus distance plots produced by VisiMat show the mass flux, measured in (at.% cm/s), versus distance from the Matano Interface. Distance may also be expressed in terms of the similarity variable:

$$\zeta = \frac{x}{2\sqrt{t \prod_{k=1}^{n-1} E_{kk}}}, \quad \text{(Eq 7)}$$

originally defined by Eq 13 of Cohen and Glicksman,[12] where E_{kk} is the kth eigenvalue of the diffusivity matrix.

The similarity variable, ζ, scales the distances in order to conveniently show the flux of each element on the same plot. Plots of the flux versus ζ for stationary ZFP

compositions in two different planes in the CrAlMoNi couple are shown in Fig. 3. VisiMat also provides concentration profile plots (Fig. 4, left and right) that show the result of evaluating Eq 1 with the similarity variable ζ.

3.2 Location of ZFPs, Composition Space, Diffusion Path

A significant finding of the square-root diffusivity method[1] is that the square-root of the diffusivity matrix (r_{ij}) is related to maximum and minimum flux conditions for multicomponent diffusion couples. In fact, the ith row of the matrix r_{ij} consists of the components of the maximum interdiffusion rate vector j^{th} axis in composition space.[2] Thus, the condition for the presence of a ZFP is that a composition vector and the maximum interdiffusion rate vector must have a scalar product of zero. As shown graphically[7,9,10] in two dimensions ($n = 3$), the ZFP composition is located at right angles to the specified maximum flux vector. In two dimensions, there are two compositions that meet the condition for a stationary ZFP. However, in three dimensions ($n = 4$), there exists an entire plane perpendicular to the maximum flux direction. This allows for the ZFP composition to be any composition vector of length $\|\Delta \mathbf{C^0}\|$ that lies within the plane perpendicular to the maximum flux direction.

Since a ZFP composition can lie anywhere within a circle of radius $\|\Delta \mathbf{C^0}\|$ in the plane normal to the maximum flux direction, there is no unique ZFP composition for ($n > 4$). As a result, it is convenient to place restrictions on the compositions that may be searched when locating the ZFP. The method employed in this software to locate a ZFP composition takes a quasi two-dimensional approach to the problem by restricting the search to the plane specified by
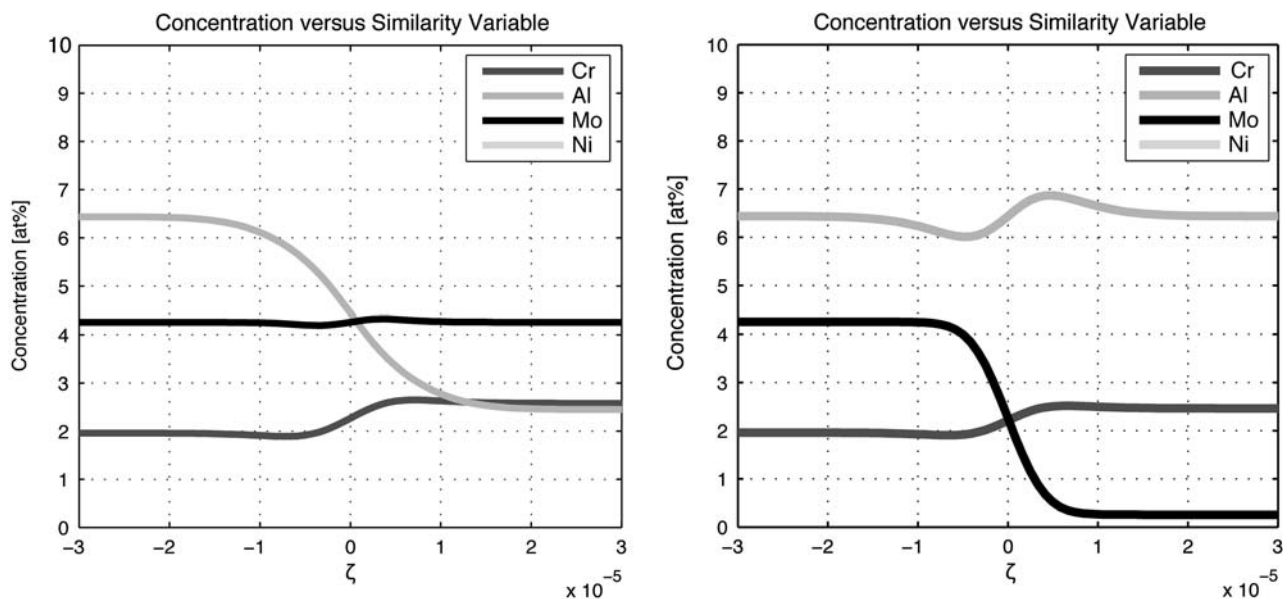
Fig. 4 Two plots showing the calculated absolute concentration versus similarity variable (ζ) from the left to right end alloy in the CrAlMoNi couple. The left plot shows the ZFP located in the Cr-Al search plane, while the right plot shows the ZFP located in the Cr-Mo search plane
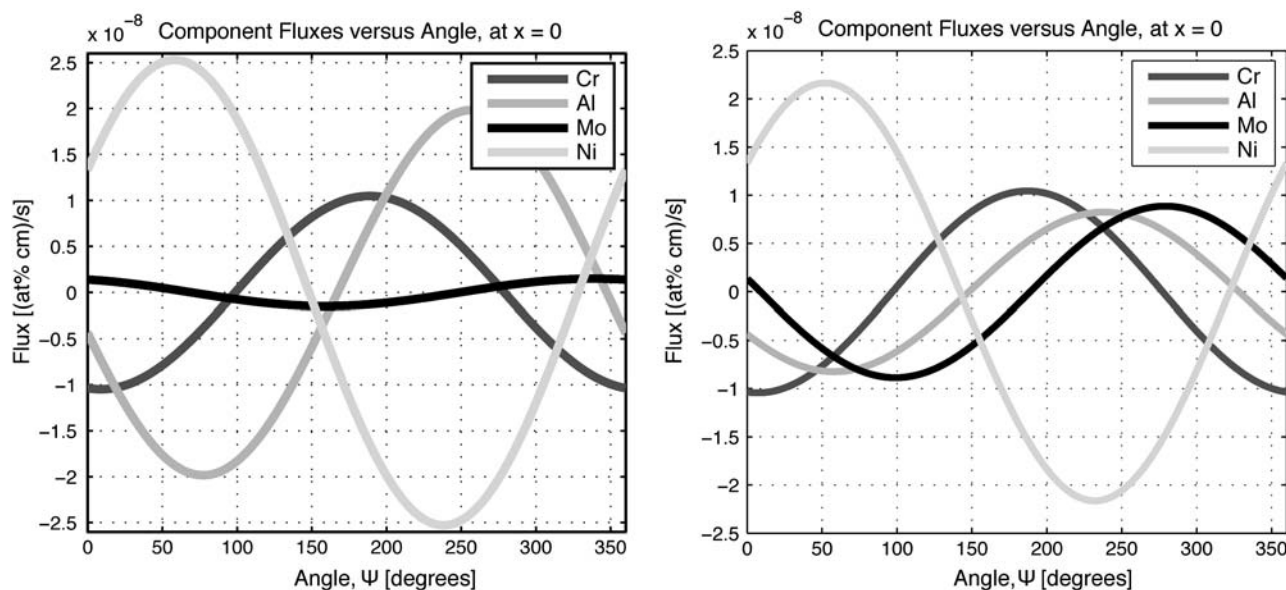

Fig. 5 The flux of each element versus angle from the Cr composition space axis of a CrAlMoNi alloy couple is shown. The flux is calculated by varying the angle in both the Cr-Al search plane (left) by varying the composition of Cr and Al, and in the Cr-Mo search plane (right) by varying the composition of Cr and Mo. In each case, the compositions are varied so that the total composition difference is $\left\|\Delta\mathbf{C^0}\right\|$

the first two components of the GUI input screen shown in Fig. 1. A numerical search algorithm is implemented in order to locate stationary ZFPs by determining the angle at which the flux of the first component becomes zero, as shown in Fig. 5 (left and right). Implementing the search routine allows the software to locate ZFP planes in couples with many components ($n > 4$).

The composition space plot (Fig. 6 left and right) also includes a sphere, shown so that its *surface* represents all possible right alloy compositions attainable from the left alloy composition specified for the couple. The sphere is centered on the left alloy in composition space and generates a surface at a distance $\left\|\Delta\mathbf{C^0}\right\|$ from the left alloy composition. The ZFP search plane (grid of solid lines) also
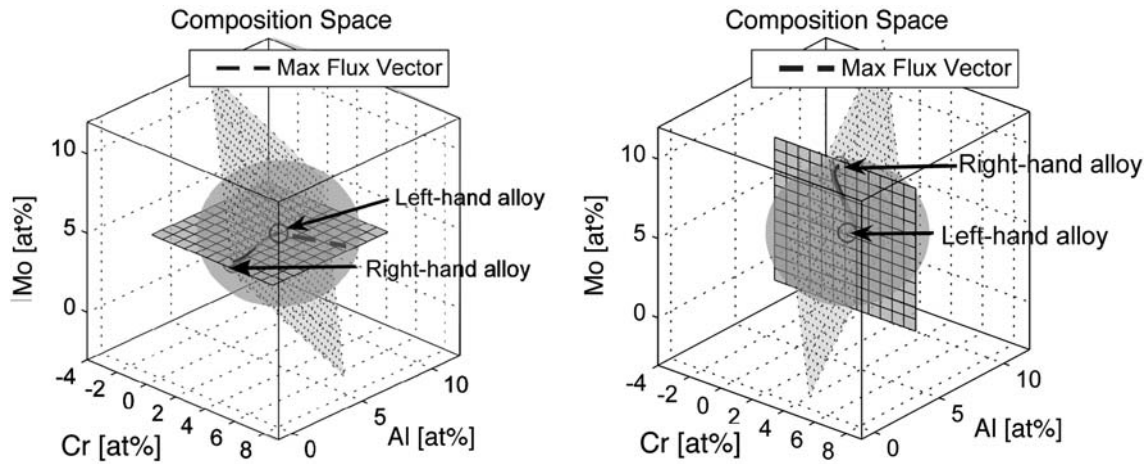
Fig. 6 The composition space plots for ZFPs located in two different search planes are shown in composition space. Each plot shows the diffusion path (solid line) along with the left and right end alloy compositions (dark and light open circles respectively). A sphere is added whose *surface*, located at a distance of $\|\Delta \mathbf{C^0}\|$ from the left alloy composition, represents all possible right alloy compositions attainable from the left alloy composition specified for the couple. The search plane (dark gray with solid lines) also appears in the composition space plot. The left plot shows one of the two ZFPs located in the Cr-Al search plane, and the right plot shows one of the two ZFPs located in the Cr-Mo search plane
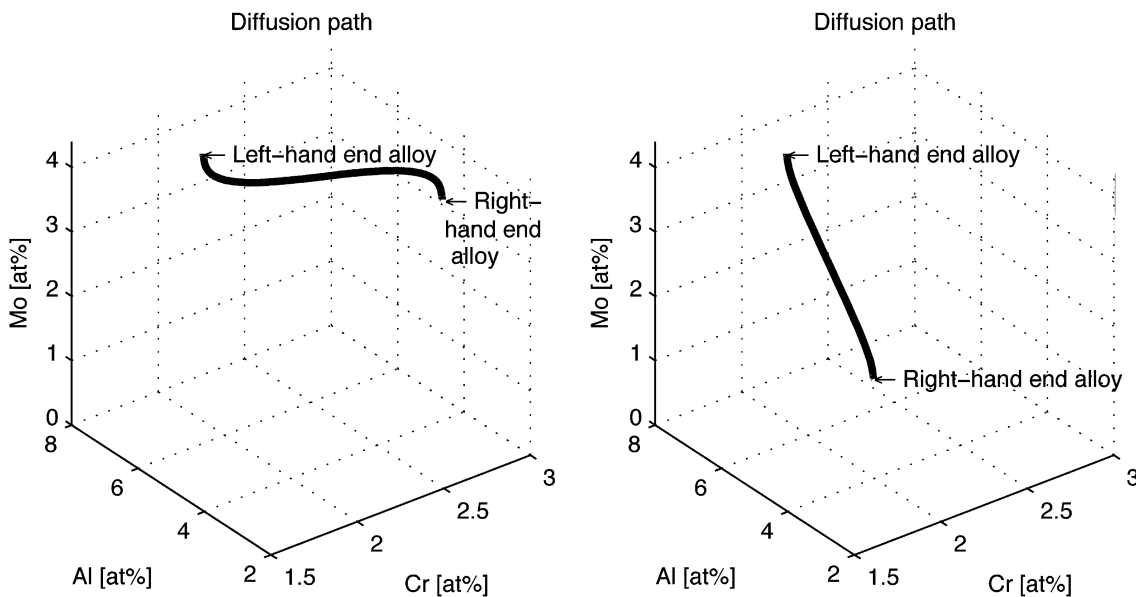

Fig. 7 Two plots showing the diffusion path in composition space from the left to right end alloys of the CrAlMoNi couple for the same angles used in the calculation of Fig. 2. The left plot shows the diffusion path taken for the ZFP located in the Cr-Al search plane, while the right plot shows the case where the ZFP is located in the Cr-Mo search plane. The ZFP compositions are those indicated in the left and right plots of Fig. 6, respectively

appears in the composition space plot. The search plane is specified by the first two elements in the *ZFP Search Plane* section of the GUI input screen. The left plot of Fig. 6 shows a ZFP found by searching in the Cr-Al plane (while holding the composition of Mo fixed) and the right plot shows a ZFP found by searching in the Cr-Mo search plane (with the Al composition held fixed). The calculated ZFP angles, $\Psi_{ZFP_{il}}$, are located in this plane. The ZFP plane (grid of broken lines) shows the plane on which all compositions

are capable of generating ZFPs lie. Observe that the ZFP plane is necessarily perpendicular to the maximum flux direction (heavy dashed line). The compositions shown in Fig. 6 (left and right) are necessarily ZFP compositions because they lie in the ZFP plane at the surface of the sphere of possible compositions.

The composition space plot, Fig. 6 (left and right), represents the CrAlMoNi couple using the diffusivity matrix determined by Stalker and Morral.[3] The parameters used
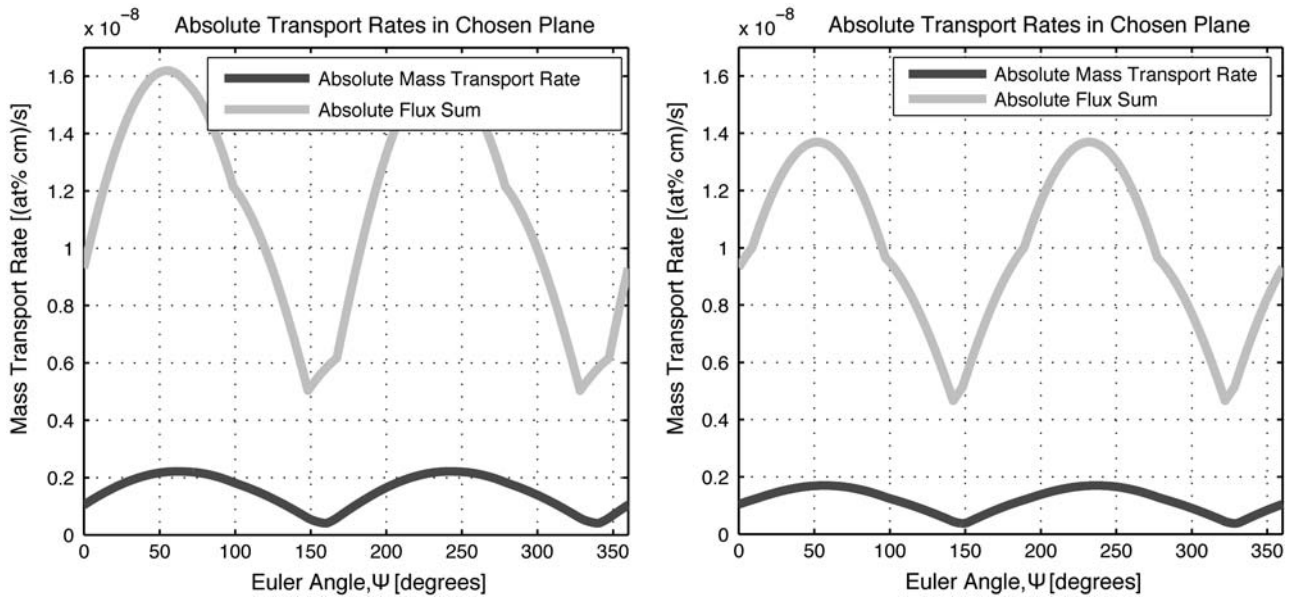
Fig. 8 Absolute mass transport rate and the absolute flux sum are plotted versus angle in a CrAlMoNi alloy couple calculated by varying the only the composition of Cr and one other element. The angle (Ψ) is measured from the Cr axis in the Al-Mo plane of composition space. The left plot shows the absolute flux sum and absolute mass transport rate when varying the composition in the Cr-Al plane. The right plot shows the absolute flux sum and absolute mass transport rate when varying the composition in the Cr-Mo plane. Compositions are varied such that the total composition change remains $\left\|\Delta \mathbf{C^0}\right\|$ for all compositions investigated

for this system and all plots in this manuscript are seen in the GUI input screen of Fig. 1. The composition space plot illustrates many important features of the couple studied. Fig. 6 (left and right) includes the diffusion path (solid line) in composition space along with the left and right alloy compositions (dark and light open circles respectively) that result in a stationary ZFP. The diffusion path [Fig. 7 (left and right)] indicates the composition as it varies from the left to right alloy at a particular time.

3.3 Absolute Mass Transport Rates

The absolute mass transport rate is an important factor in the design and analysis of interfaces between alloys. Although the zero-flux planes occur only for very specific compositions, a design goal of limiting diffusion between alloys may also be met by limiting the absolute mass transport rate, $\dot{M}$, for all components rather than that of a single component. The definition of the absolute mass transport rate given in Eq 28 of Glicksman and Lupulescu[7] states that

$$\dot{M} = \int_{-\infty}^{\infty} \sum_{i=1}^{n} |J_i(x,t)| dx. \tag{Eq 8}$$

Another measurement of the mass transport occurring in the couple is the absolute flux sum. The absolute flux sum is converted from Eq 22 of Glicksman and Lupulescu[7] to a composition space angle (Ψ) dependent form as:

$$J_{\text{sum}}(\Psi, x, t) = \sum_{i=1}^{n-1} |J_i(\Psi, x, t)|. \tag{Eq 9}$$

This software calculates absolute mass transport rates by varying the composition of the first two elements listed in the Systems Parameters menu of the graphical user interface (GUI) shown in Fig. 1, with the composition of the other component fixed. Note that this amounts to varying Ψ in the ZFP search plane (which is shown in Fig. 4). The absolute flux sum and the absolute mass transport rate are calculated at ($x = 0$), and shown in Fig. 8.

4. Conclusions

VisiMat is a MATLAB code and a successor to Brockman and Morral's[8] Profiler and the previous MATLAB code with graphical user interface developed at Rensselaer Polytechnic Institute.[9,10] This software features increased functionality, improved visualization, ability to model couples with many components, and implementation in a modern and portable platform.

VisiMat is designed as an educational tool to assist in learning about many important concepts related to multicomponent diffusion couples, including the conditions for the presence of zero-flux planes. A unique component of this software is the ability to visualize diffusion paths and the conditions necessary for the presence of a stationary ZFP in three-dimensional composition space. In addition, the software can accept a user-specified composition to generate concentration profiles, and flux versus angle plots. In addition, alternative measures of mass transport such as the absolute mass transport rate and the absolute flux sum are also available for plotting.

Acknowledgments

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