Algorithm for Predicting Diffusion Paths in Ternary Systems

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Abstract

Diffusion paths in multicomponent systems denote the course of flow of diffusing species and are very important in understanding the behaviour of materials during service or heat treatment. Determining the diffusion paths in ternary systems by experimental means is both tedious and time consuming as it involves making large number of couples with alloys of different compositions and annealing them at various conditions of time and temperature. The diffusion paths, however, can be predicted by suitably modeling various relationships between the compositions of various constituents and the characteristic parameters of the diffusion paths. The present work relates to developing an algorithm to determine and plot the diffusion paths on the Gibbs triangle. It is applied to a very common and very useful system Fe-Ni-Cr. The diffusion paths constructed by the present algorithm match very well with the experimentally determined diffusion paths.

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1. Introduction

Modern technology involves use of variety of multi-component materials in contact with each other, which may interact at ambient or high temperature. The interdiffusion takes place between them in order to attain thermodynamic equilibrium with each other. The constituent components diffuse down the chemical potential gradient. As a consequence of such interdiffusion, the composition may change at the diffusion zone or new phases may appear at the interface with various morphologies. The sequence of phase formation or the composition variation can be represented as a stable diffusion path on the isothermal section of the phase diagram of the system. The diffusion path depicts the nature of change in the composition in the diffusion zone.

The diffusion paths in multi-component systems are generally S-shaped [1]. In some cases it may be double serpentine in nature [2]. The extent of deviation from linearity depends upon the relative magnitudes of the diffusion coefficients and activity of the components. Also it is observed that the diffusion path moves along the constant concentration lines of slowest moving species [3]. Apart from the S-shaped diffusion paths, ternary diffusion may exhibit the zero-flux planes and flux reversals for individual components [1]. Development of two zero-flux planes has also been reported in some systems [2]. Thus it is essential to know the exact nature of the diffusion path that has developed at the diffusion zone. If the system is binary, the diffusion path can be easily deduced from the phase diagram. However, in ternary and multi-component systems, it is possible to construct more than one diffusion path on the isothermal section of the phase diagram. Out of these, only one is stable. This stable diffusion path is essentially governed by the thermodynamic and kinetic properties of the phases involved. Therefore, the stable diffusion path cannot be unambiguously predicted from the phase diagram in ternary and multi-component systems. The experimental observations are the only available direct method to get reliable information about the chemical interactions at the interface and obtain the diffusion path. But experimental determination of diffusion paths in multi-component system requires long diffusion annealing time with large number of diffusion couples.

Many workers have attempted to estimate the nature of the diffusion path [4,5,6,7]. The nature of the diffusion path can be estimated from the values of the ternary diffusion coefficients [4]. But this method is only applicable when the direct and cross diffusion coefficients are concentration independent. The interdiffusion coefficients are invariably concentration dependent and hence estimated diffusion paths may be quite erroneous. The diffusion paths can be described from the ternary tracer diffusion data [5]. However the correlation between the experimental and estimated diffusion paths by this method is rather poor. The nature of the diffusion paths can also be estimated from the eigen properties of the diffusing matrix [6]. This method only predicts the nature of the diffusion as to whether the diffusion path is linear or S-shaped. Dayananda and Kim [1] have described the diffusion path on the basis of only two characteristic parameters.

The paper presents an algorithm to predict the diffusion paths on the basis of these parameters. The algorithm has been developed for predicting the diffusion path obtained in the diffusion couple with any two terminal components of the couple for ternary Fe-Ni-Cr system in the γ- solid solution phase. The predicted diffusion paths compare well with the experimental diffusion paths.

2. Theoretical Analysis

Fig. 1 shows schematically, a diffusion couple made between two alloys in ternary system A-B-C. $C_i^{-\infty}$ and $C_i^{+\infty}$ are the concentrations of component *i* in the terminal alloys. The diffusion couple can uniquely defined by the concentration differences, ΔC_A (= $C_A^{-\infty}$ - $C_A^{+\infty}$) and ΔC_B (= $C_B^{-\infty}$ - $C_B^{+\infty}$) in the terminal alloys.

The compositions of the alloys can be orthogonally transformed to new set of composition Y_A and Y_B. These transformed compositions are defined in such a way that $0 \bullet Y_i \bullet 1$.

$$Y_i = \frac{C_i - C_i^{+\infty}}{C_i^{-\infty} - C_i^{+\infty}} \qquad (1)$$

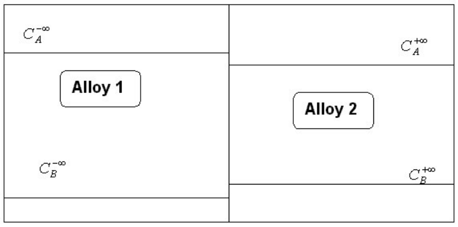

Fig. 1 Schematic diagram of a diffusion couple.

The diffusion path can be obtained by plotting Y_A against Y_B. Such a diffusion path is shown in the Fig. 2. The straight line joining the compositions of the two terminal alloys, would intersect the diffusion path at a point. Let the slope of the diffusion path and the value of Y_A, at the point of inflection of the diffusion path be *1/m* and Y^c respectively. The diffusion path can be uniquely defined by these two characteristic parameters Y^c and m. This point of intersection of the diffusion path with the diagonal divides the diffusion path into two segments. These two segments can be mathematically expressed by the equations:

$$Y_A^m = (Y^c)^{m-1} Y_B \qquad \text{for } (0 \bullet Y_A \bullet Y^c) \qquad (2\text{-a})$$

and

$$(1 - Y_A)^m = (1 - Y^c)^{m-1} (1 - Y_B) \qquad \text{for } (Y^c \bullet Y_A \bullet 1) \qquad (2\text{-b})$$

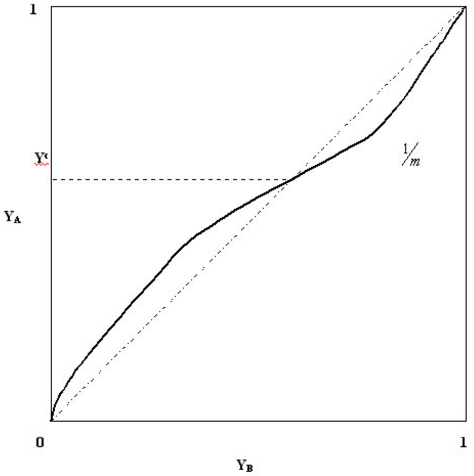

Fig. 2 Plot of Y_A against Y_B showing schematic diffusion path.

Therefore for each diffusion couple we get values of Y^c and m that define the diffusion path uniquely. A set of values for Y^c and m can be experimentally determined for a number of diffusion couples. By fitting the values of these two parameters in suitable relations, one can calculate the Y^c and m for any combination of ΔC_A and ΔC_B which are unique to the diffusion couples.

3. Experimental

Pure iron, nickel and chromium (purity 99.9%) were melted in a non-consumable arc furnace in pure argon atmosphere to prepare buttons of various alloys of γ-phase in the Fe-Ni-Cr system. These buttons were hot rolled to 5 mm thick strips. Rectangular pieces of 10X10 mm^2 were pre annealed at 1273K for 7days for homogenisation and to attain a coarse grained microstructure of grain size 3-5 mm. Chemical homogeneity of the alloys was confirmed by random point analysis with an Electron Probe Micro Analyser (EPMA). The compositions of the alloys prepared are given in Table 1.

The surfaces of the pre-annealed samples were prepared metallographically by grinding on various grades of emery paper and finally polishing on diamond paste of 1μm. The polished surfaces of the two pieces of terminal alloys were clamped in special die under a pressure of 8-10 MPa. Mica spacers were used to isolate the sample from the die material. The whole assembly was heated at 1173 k for a period of 2 ks in a vacuum of 10^{-5} torr. The as bonded samples were analysed by EPMA and was found to have a diffusion width of 2-5 μm.

These bonded samples were wrapped in tantalum foil and were sealed in quartz capsules in He atmosphere. These samples were diffusion annealed in a pre-heated resistance heated furnace. The temperature was controlled within ±1k with a proportional temperature controller. The heat treatment schedule for diffusion annealing for various couples is given in Table 2.

The diffusion annealed couples were sectioned perpendicular to the bond interface using a slow-speed diamond saw. These samples were mounted, ground on various grades of emery papers and then polished on a lapping wheel with 1 μm diamond paste. The polished, unetched diffusion couples were analysed using a CAMEBAX Electron Probe Micro Analyser (EPMA) equipped with three wavelength dispersive spectrometers (WDS). The operating voltage and beam current were kept at 15kV and 100nA respectively. The equipment was calibrated with respect to Fe Kα,• Ni K α and Cr Kα with pure elemental standards of Fe, Ni and Cr respectively. Lithium Fluoride (LiF) crystals were used for diffraction of these lines. The standard ZAF correction program was used for atomic number (Z), absorption (A) and fluorescence (F) corrections. Quantitative analysis on point-to-point basis was done at a regular interval of 1-2μm by scanning the sample across the bonding interface to determine the concentration profile. For each sample, at least three scans were taken at different locations to confirm the consistency of the concentration profiles.

Table 1. Compositions of the alloys prepared.

Alloy No.	Fe	Ni (atom%)	Cr
1	41.4	30.3	28.3
2	31.0	37.5	31.5
3	20.3	42.0	37.7
4	18.6	54.7	26.7
5	11.5	57.3	31.2
6	-	67.4	32.6
7	-	76.1	23.9
8	-	100	-
9	6.8	93.2	-
10	43.2	56.8	-
11	53.3	46.7	-
12	63.7	24.6	11.7
13	51.8	25.1	23.1
14	55.9	44.1	-
15	16.9	79.0	4.1
16	4.3	77.1	18.6
17	4.3	82.9	12.8
18	15.4	72.5	12.1
19	31.0	34.5	34.5

4. Results and Discussions

4.1 Diffusion Paths from Experiments

The concentration profiles acquired from the diffusion zone of the diffusion couples, by EPMA have been plotted on the isotherm of the ternary phase diagram to obtain the diffusion paths. Fig. 3 shows such a ternary isothermal section of the Fe-Ni-Cr system at 1173K, on which the typical diffusion paths of some of the couples are plotted. Almost all the diffusion paths are s-shaped in nature.

Table 2. Diffusion annealing schedule for the couples.

COUPLE	ALLOYS	TEMPERATURE (K)	TIME (ks)
A	8/2	1223	432
B	8/3	1223	432
C	8/5	1223	432
D	8/12	1223	432
E	8/13	1223	432
F	1/6	1223	324
G	1/11	1223	324
H	3/11	1223	324
I	4/14	1223	324
J	7/9	1223	324
K	13/7	1223	324
L	12/19	1223	324
M	7/10	1223	324
N	8/4	1173	324
O	8/2	1173	324
P	13/7	1173	324
Q	8/3	1323	180
R	8/19	1323	180
S	13/7	1323	180
T	15/16	1380	259.2
U	17/18	1380	259.2
V	17/18	1403	180
W	15/16	1403	180

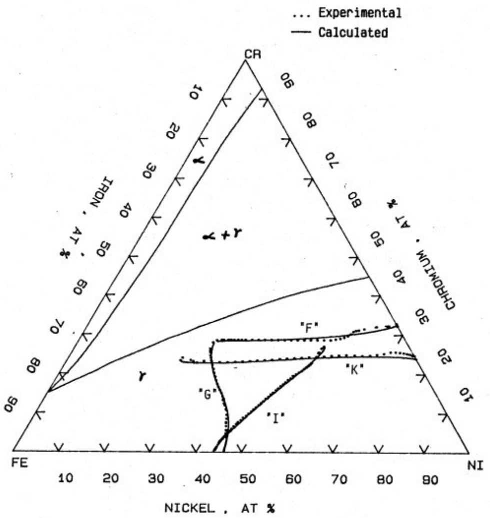

Fig. 3 Diffusion paths for couples F,G,I and K on the Fe-Ni-Cr isotherm.

4.2 Algorithm for diffusion paths

The concentrations of Fe and Ni are orthogonally transformed to Y_{Fe} and Y_{Ni} using the eqn. 1. The diffusion paths are obtained by plotting Y_{Fe} versus Y_{Ni} . The typical diffusion path obtained for orthogonally transformed concentrations is shown in Fig 4. The values of Y^c are obtained from the value of Y_{Fe} or Y_{Ni} at the point of inflection as shown in Fig. 4. The value of 'm' is obtained as inverse of the slope at the point of inflection. These values of Y^c and m are fitted against the ratio ($\Delta C_{Fe}/\Delta C_{Ni}$) for all the couples. The values of 'm' and Y^c as a function of ratio ($\Delta C_{Fe}/\Delta C_{Ni}$) can be described by following equations

$$m=2.72+2.786(\Delta C_{Fe}/\Delta C_{Ni}) \quad \ldots\ldots\ldots\ldots\ldots(3)$$

$$Y^c=3.073+19.22(\Delta C_{Fe}/\Delta C_{Ni}) +36.71(\Delta C_{Fe}/\Delta C_{Ni})^2 +20.27(\Delta C_{Fe}/\Delta C_{Ni})^3. \quad \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

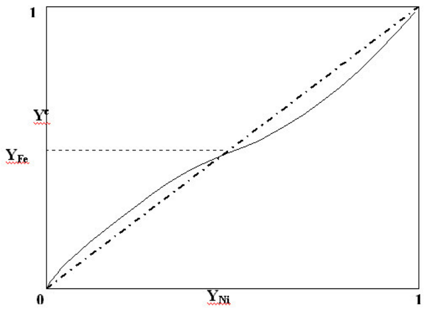

Fig. 4 Plot of Y_{Fe} against Y_{Ni} showing diffusion path for the couple G.

The algorithm has been written which requires the ratio of ($\Delta C_{Fe}/\Delta C_{Ni}$) for a diffusion couple as input. The algorithm estimates the value of m and Y^c from the equations 3 and 4 respectively for the couple. The values of Y_{Ni} are computed for the assumed values of Y_{Fe} ranging from zero to 1 at the intervals of 0.1 using appropriate equations (eq. 2a or 2b). The values of C_{Fe} and C_{Ni} are obtained from corresponding values of Y_{Fe} and Y_{Ni} using eq. 1. The flow diagram for the algorithm is shown in Fig. 5. The values of C_{Fe} and C_{Ni} are used to plot diffusion path on the isotherm.

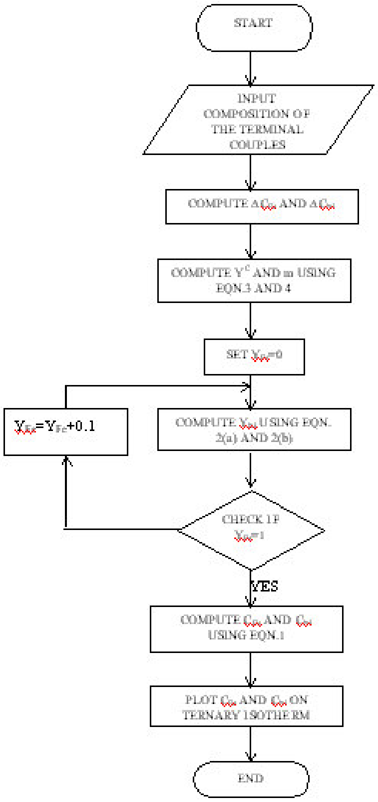

Fig. 5 Flow sheet of the algorithm for predicting diffusion path.

4.3 Predicting the diffusion paths

The algorithm has been used to predict the diffusion paths for the diffusion couples. The predicted diffusion paths have also been plotted on the isotherm in Fig. 3. The predicted diffusion paths match very well with the experimental diffusion paths. The predicted diffusion path matches well with the experimental one even in the couples developing zero flux planes. The algorithm may also be useful for predicting diffusion path in the couple made between commercial Fe-Ni-Cr alloys such as steels, Inconel etc as these alloys contain major components Fe, Ni and Cr and minor alloying elements do not influence the diffusion path drastically.

5. Conclusions

The algorithm can be used to predict the diffusion path for ternary diffusion couple made between any two alloys of Fe-Ni-Cr system. Predicted and experimental diffusion paths match very well.

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References

1. M. A. Dayananda and C. W. Kim, Met. Trans., 10 (1979) 1333.
2. M. A. Dayananda, Solid State Phenomenon, Vol. 72 (2000) 123.
3. A. G.Guy, V. Leroy and T. B. Lindmer, Trans. ASM, Vol. 59(1966) 517.
4. G. W. Roper and D.B. Whittle, Mat. Sci. 14 (1980) 541.
5. 4.C.C. Wan and R. T. D'Hoff, Acta. Met. 25 (1977) 287.
6. M. S. Thompson and J. E. Morral, Acta Met. 34(1986) 339.
7. M. A. Dayananda and C.W. Kim. Scripta Met. 16(1982) 815.