

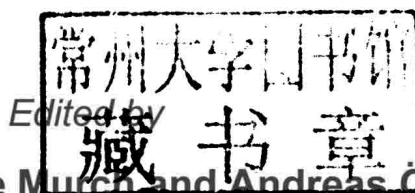
# Diffusion Phenomena in Engineering Materials

**Edited by**

**Irina Belova, Graeme Murch and Andreas Öchsner**

# Diffusion Phenomena in Engineering Materials

Special topic volume with invited peer reviewed papers only.



Irina Belova, Graeme Murch and Andreas Öchsner

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# **Diffusion Phenomena in Engineering Materials**

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## Preface

This volume of Diffusion Foundations entitled Diffusion Phenomena in Engineering Materials captures an important cross section of the contemporary scene of diffusion in solids, ranging from the fundamental science of diffusion through to the application of diffusion concepts in technology. The chapters are written by well-acknowledged experts in their respective areas. In the first chapter, Professor Dayananda provides an in depth overview of some of the important findings from the vast literature on multicomponent diffusion in alloys. In Chapter 2, Professors Belova and Murch and co-workers describe a new solution to the important problem of accurately estimating a tracer diffusivity in a binary alloy, given the other tracer diffusivity, the interdiffusivity and thermodynamic factor. This is followed by Chapter 3 where Professor Lidiard gives a penetrating perspective on the state of knowledge about the Soret effect and thermodiffusion (thermotransport) in solids. In Chapter 4, Professor Kozlowski and colleagues describe important new findings about the critical dimensions of ferromagnetic nanoparticles of iron. This is followed by Chapter 5 where Professor Çimenoglu and co-workers present an in depth overview of surface hardening of titanium and its alloys by way of diffusion of the interstitial atoms of oxygen, nitrogen and boron. In Chapter 6 Professor Morton-Blake describes fascinating new molecular dynamics simulations of sodium and chloride ions in a synthetic ion channel in a membrane. Finally, in Chapter 7, Professor Seetharaman and colleagues describe the important role of diffusion phenomena in process metallurgy. We wish to thank the authors for their prompt contributions and the reviewers for their input.

Professors Irina Belova, Graeme Murch and Andreas Öchsner

March 2015



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## **Chapter I**



## An Overview of Selected Phenomena in Multicomponent Diffusion

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**Keywords:** Uphill Diffusion, Zero-flux Planes, Flux Reversals, Serpentine Diffusion Paths, Interface Instability, Demixing of Phases.

**Abstract.** There exist several interesting phenomena and observations reported in literature for isothermal diffusion in multicomponent systems. Such phenomena include uphill diffusion, development of zero-flux planes and flux reversals for individual components, flux reversals at interfaces, and instability at interfaces and multiphase layer development. In addition, uncommon diffusion structures exhibiting unusual diffusion paths can develop in both single phase and multiphase diffusion assemblies. An overview of such phenomena is presented to highlight the role of interactions among diffusing components with the aid of selected diffusion studies carried out in multicomponent alloy systems, aluminides, silicides, and nuclear fuels.

### Introduction

Isothermal diffusion in multicomponent systems can result in new phenomena and observations not normally expected or encountered in isothermal diffusion in binary systems. Isothermal diffusion in an  $n$ -component system involves  $(n-1)$  independent concentration gradients or chemical potential gradients and is subject to diffusional interactions among  $n$  components. The phenomenological basis for the analysis of multicomponent diffusion has been the extended form of Fick's law, as postulated by Onsager [1]. Onsager's formalism defines  $(n-1)^2$  interdiffusion coefficients that link  $(n-1)$  independent interdiffusion fluxes with  $(n-1)$  independent driving forces and allows a description of diffusional interactions [1-4] among components. Experimental determination of interdiffusion coefficients has been carried out in several ternary alloy systems [4] by employing solid-solid and vapor-solid diffusion couples with intersecting diffusion paths [3]. Alternative approaches for the determination of interdiffusion coefficients from individual diffusion couples over selected composition ranges are also available [5-7] and have been employed for the analysis of ternary and quaternary diffusion couples [8,9].

The main purpose of this paper is to present an overview of selected phenomena and observations made with both single phase and multiphase couples in several systems including Cu-based, Ni-based and Fe-based alloys, ternary aluminides and silicides, and nuclear fuels. The phenomena include uphill diffusion, development of zero-flux planes (ZFP) and flux reversals exhibited by individual components in both single phase and multiphase couples, interfacial instability, and demixing of phases in two-phase couples. The types of diffusion couples most suited to observe the various phenomena are presented with examples. Concentration profiles of experimental couples are converted directly to profiles of interdiffusion fluxes without using Fick's law or interdiffusion coefficients. The observed phenomena are discussed in terms of diffusional and thermodynamic interactions among the components and experimental interdiffusion coefficients. In addition, uncommon diffusion paths and diffusion structures that can develop in diffusion couples assembled with single phase as well as two-phase alloys are also presented to highlight the dependence of the diffusion structure development on the terminal alloy compositions.

### Uphill Interdiffusion

**Isoconcentration Couples.** Diffusion couples most suited to examine the phenomenon of uphill interdiffusion for a given component may be identified as *isoconcentration couples*, where the terminal alloys for the couple are chosen to have compositions with similar concentration levels for the given component but dissimilar concentrations for the other components. Such couples can be employed to investigate uphill interdiffusion of a component down or against the concentration gradient of another component. Schematic concentration profiles for two ternary isothermal diffusion couples (Alloy A vs. Alloy B) characterized by similar terminal concentrations for component 1 are presented in Fig. 1, where components, 1 and 2, are taken as independent concentration variables. The original plane of contact between the two alloys is the Matano plane identified as  $x_0$ .  $C_i^+$  and  $C_i^-$  corresponds to the initial concentrations of component  $i$  in the terminal alloys, A and B, respectively. For the couple shown in Fig.1(a), the concentration profile of component 1 develops a minimum on the Alloy A side and a maximum on the Alloy B side and exhibits uphill interdiffusion up its own concentration gradient from left to right (+ direction) but down the concentration gradient of component 2. For the couple shown in Fig. 1(b), the concentration profile of component 1 develops a maximum on the alloy A side and a concentration minimum on the Alloy B side; the uphill interdiffusion of component 1 is from right to left (- direction) against its own gradient as well as the concentration gradient of component 2.

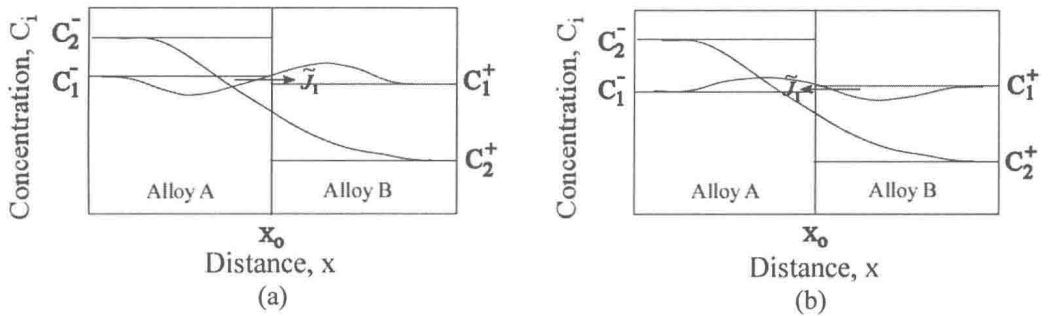


Figure 1. Isoconcentration couples with similar concentrations of a component in the terminal alloys; (a) Isoconcentration couple for component 1 exhibiting interdiffusion up its own gradient but down the gradient of component 2; (b) Isoconcentration couple for component 1 exhibiting interdiffusion up its own gradient and the gradient of component 2;  $x_0$  corresponds to the original contact plane (Matano plane) between the terminal alloys, A and B.

**Onsager's Formalism of Fick's Law.** The diffusional interactions among the components in ternary couples can be appreciated with the aid of Onsager's extended form of Fick's law expressed by [1]

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

where  $\tilde{D}_{i1}^3$  and  $\tilde{D}_{i2}^3$  correspond to the main and cross interdiffusion coefficients relating the interdiffusion flux  $\tilde{J}_i$  of component  $i$  (based on a laboratory-fixed frame of reference) to the two independent concentration gradients of components 1 and 2, respectively. Component 3 is considered as the dependent variable. The main coefficients,  $\tilde{D}_{11}^3$  and  $\tilde{D}_{22}^3$ , are usually positive and the cross coefficients,  $\tilde{D}_{12}^3$  and  $\tilde{D}_{21}^3$ , can be either positive or negative. In Fig. 1(a)  $\tilde{J}_1$  is in the direction from left to right (+), and the concentration gradients  $\partial C_1 / \partial x$  and  $\partial C_2 / \partial x$  are,

respectively, positive and negative in the region of the uphill interdiffusion of component 1. Hence, for uphill interdiffusion of component 1, the second term in Eq. (1) must be a positive number and greater than the first term in magnitude. It also follows that the diffusional interaction expressed by the cross coefficient  $\tilde{D}_{12}^3$  has to be a positive number. A positive  $\tilde{D}_{12}^3$  implies that the interdiffusion flux of component 1 gets enhanced down the gradient of component 2.

For the uphill interdiffusion of component 1 shown in Fig. 1(b),  $\tilde{J}_1$  is negative (from right to left) and is against the negative  $\partial C_2 / \partial x$ . Hence, the second term in Eq. (1) has to be negative and bigger in magnitude than the positive first term in the region of uphill interdiffusion. It also means that  $\tilde{D}_{12}^3$  cross coefficient is a negative number and that the interdiffusion flux of component 1 gets enhanced against the gradient of component 2. Alternatively,  $\tilde{J}_1$  is decreased down the concentration gradient of  $C_2$ .

**Direct Determination of Interdiffusion Fluxes without Fick's Law.** The interdiffusion flux  $\tilde{J}_i$  at any section  $x$  is normally based on a laboratory-fixed frame of reference, such as  $x_0$  in Fig. 1. For solid-solid diffusion couples similar to those in Fig. 1, Dayananda [10,11] has shown that the flux gradient of a component  $i$  can be related to its concentration gradient through the continuity equation by

$$\begin{aligned} \left( \frac{\partial J_i}{\partial x} \right)_t &= - \left( \frac{\partial C_i}{\partial t} \right)_x \\ &= v(C_i) \left( \frac{\partial C_i}{\partial x} \right)_t \end{aligned} \quad (2)$$

where  $v(C_i)$  is the instantaneous velocity of propagation of the concentration level identified with  $C_i$  at a section  $x$  at time  $t$ .  $v(C_i)$  can be expressed by [11]

$$v(C_i) = \frac{(x - x_0)}{2t}. \quad (3)$$

On substituting Eq. (3) in Eq. (2) and integrating over a range of  $x$ , concentration profiles can be converted into  $\tilde{J}_i$  vs  $x$  plots from the relation [11],

$$\tilde{J}_i(x) = \frac{1}{2t} \int_{C_i^+ \text{ or } C_i^-}^{C_i(x)} (x - x_0) dC_i \quad (i = 1, 2, \dots, n). \quad (4)$$

### Determination of Interdiffusion Coefficients

Equating Eqs. (1) and (4), one gets for a ternary system

$$\int_{C_i^+ \text{ or } C_i^-}^{C_i(x)} (x - x_0) dC = -2t \left[ \tilde{D}_{i1}^3 \frac{\partial C_1}{\partial x} - \tilde{D}_{i2}^3 \frac{\partial C_2}{\partial x} \right] \quad (i = 1, 2). \quad (5)$$

For the determination of the four  $\tilde{D}_{ij}^3$  ( $i, j = 1, 2$ ) as a function of composition, Eq. (5) needs to be solved by setting up 4 equations at a composition common to a pair of diffusion couples. Experimentally, two couples with intersecting diffusion paths [3] are normally set up and Eq. (5) is solved for  $\tilde{D}_{11}^3$ ,  $\tilde{D}_{12}^3$ ,  $\tilde{D}_{21}^3$ , and  $\tilde{D}_{22}^3$  at the common composition of intersection of diffusion paths. If

$\tilde{D}_{ij}^3$  ( $i, j = 1, 2$ ) are assumed as constants, the concentration profiles of solid-solid and vapor-solid ternary diffusion couples with constant boundary conditions can be fitted to error function solutions [2,3,4] and the four constant interdiffusion coefficients can be determined with just one couple. However, in general, a set of constant  $\tilde{D}_{ij}^3$  ( $i, j = 1, 2$ ) may not be valid for the representation of a system over a wide range of composition. Hence, an alternative approach has been proposed by Dayananda and coworkers [5-9], where average values of  $\tilde{D}_{ij}^n$  ( $i, j = 1, 2, \dots, (n-1)$ ) are determined over selected composition ranges of the diffusion zone of a diffusion couple in an  $n$ -component system. This approach has been the basis of a program called "MultiDiFlux", which has been used for the determination of interdiffusion fluxes as well as interdiffusion coefficients from individual couples in systems with three or more components.[6-9]

**Darken's Isocarbon Diffusion Couple.** A classic example of uphill interdiffusion corresponding to Fig. 1(a) was presented by Darken [12] as early as 1949 through his study of a ternary diffusion couple assembled with a ternary Fe-3.8%Si-0.48%C (wt.%) steel bonded to a binary Fe-0.44%C steel. The couple corresponded to an isoconcentration couple for carbon and was annealed for 13 days at 1050°C. The carbon concentration profile after diffusion is presented in Fig. 2 as a smooth curve showing a minimum and a maximum with a loss of carbon on the ternary steel side and a gain of carbon on the binary steel side. The interdiffusion of carbon from left to right up the steep carbon gradient was attributed to the presence of Si in the ternary steel and the related increase in the chemical potential or the thermodynamic activity of carbon on the ternary steel side. Thus, carbon was considered to interdiffuse down its own chemical potential gradient, as Si interdiffused from

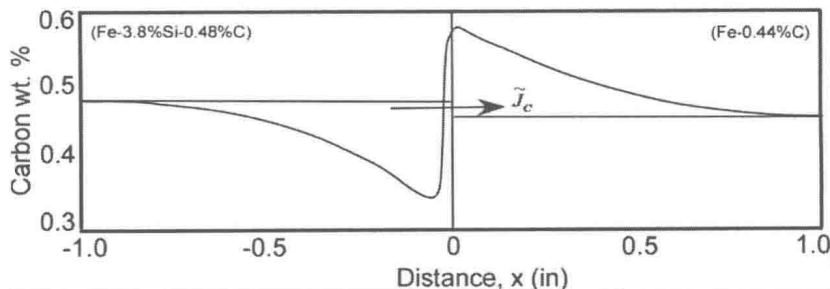


Figure 2. Interdiffusion of carbon up its own concentration gradient but down the gradient of silicon in a Fe-Si-C vs. Fe-C diffusion couple annealed at 1050°C for 13 days. [12]

left to right in the positive direction. However, on the basis of Eq. (1), the interdiffusion flux of carbon  $\tilde{J}_C$  can be related to the concentration gradients of C and Si by

$$\tilde{J}_C = -\tilde{D}_{CC}^{Fe} \frac{\partial C_C}{\partial x} - \tilde{D}_{CSi}^{Fe} \frac{\partial C_{Si}}{\partial x}. \quad (6)$$

From an analysis of the carbon concentration profile on the basis of error function solutions [2], Kirkaldy [13] estimated the values of  $\tilde{D}_{CC}^{Fe} = 4.8 \times 10^{-11} \text{ m}^2/\text{s}$  and  $\tilde{D}_{CSi}^{Fe} = 0.34 \times 10^{-11} \text{ m}^2/\text{s}$ , and reported the enhancement of carbon interdiffusion down the gradient of Si. Similar enhancements of carbon interdiffusion have been reported down the gradients of Ni and Co in Fe-C-Ni and Fe-C-Co systems, respectively, with positive values for  $\tilde{D}_{C Ni}^{Fe}$  and  $\tilde{D}_{C Co}^{Fe}$  cross interdiffusion coefficients [14].

**Isoconcentration Couples in Selected Ternary Systems.** There are many other ternary systems where uphill interdiffusion with positive cross interdiffusion coefficients have been reported [4]; these include Cu-Zn-Sn [15,16], Fe-Co-Ni [17,18], Ni-Al-Cr [19], V-Co-Fe [20] and U-Pu-Zr [21] systems. A few experiments carried out with isoconcentration couples are given below.

**Isoconcentration Couples in Fe-Co-Ni and U-Pu-Zr Systems.** In Fig. 3(a) are presented concentration profiles for a Ni-isoconcentration couple investigated in the Fe-Co-Ni system by Vignes and Sabatier [18] showing uphill interdiffusion of Ni down the Co gradient.  $\tilde{D}_{NiCo}^{Fe}$  and  $\tilde{D}_{NiNi}^{Fe}$  coefficients were determined to be  $5.1 \times 10^{-14} \text{ m}^2/\text{s}$  and  $9.3 \times 10^{-14} \text{ m}^2/\text{s}$ , respectively, from a pair of couples at the composition of 26Fe-25Co-49Ni (at.%) [18]. In Fig. 3(b) is presented a U-Pu-Zr diffusion couple investigated by Petri and Dayananda [21]; it exhibits uphill interdiffusion of U down the gradient of Zr. From a pair of diffusion couples with diffusion paths intersecting at the composition of 75U-13Pu-12Zr, the interdiffusion coefficients,  $\tilde{D}_{Uzr}^{Pu}$  and  $\tilde{D}_{ZrU}^{Pu}$ , were calculated to be about  $1.3 \times 10^{-12} \text{ m}^2/\text{s}$  and  $0.3 \times 10^{-12} \text{ m}^2/\text{s}$ , respectively. Uphill interdiffusion of U down the Zr gradient has also been reported [22] in the (U,Zr)Ni<sub>2</sub> phase developed in a multiphase diffusion couple assembled with a 83.6Ni-16.4Cr alloy bonded to an U-23Zr alloy and annealed at 700°C for 4 days.

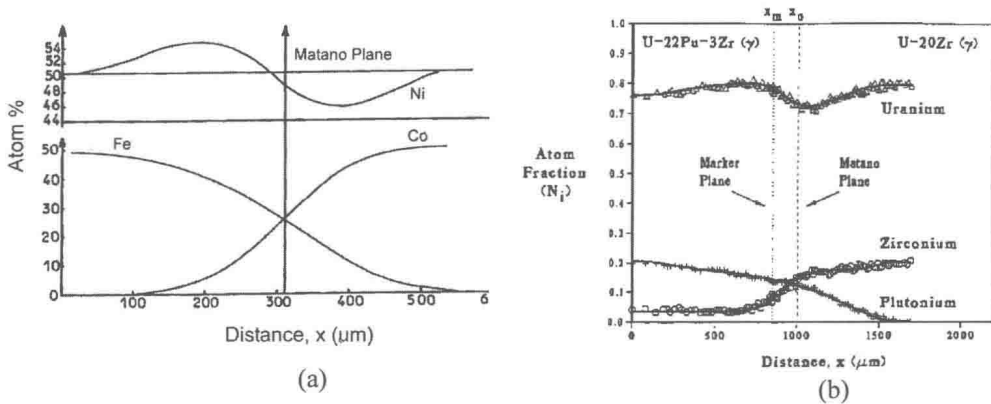


Figure 3. (a) Ni-isoconcentration couple [17,18] in the Fe-Ni-Co system annealed at 1315°C for 17 h ; (b) U-isoconcentration couple [21] in the U-Pu-Zr system annealed at 750°C for 16.5 hours.

**A Ni-isoconcentration Couple in the Cu-Ni-Zn System.** An example of uphill interdiffusion of a component up its own concentration gradient and against the concentration gradient of another component as in Fig.1(b) is presented in Figure 4 for a Ni-isoconcentration couple investigated in the Cu-Ni-Zn system at 775°C [23]. The concentration profiles shown in Fig. 4(a) were converted into interdiffusion flux profiles on the basis of Eq. (4) and are shown in Fig. 4(b) [23,11]. Since the negative  $\tilde{J}_{Ni}$  is related to the negative gradients of  $\partial C_{Ni}/\partial x$  and  $\partial C_{Zn}/\partial x$  in the region of uphill interdiffusion by

$$\tilde{J}_{Ni} = -\tilde{D}_{NiNi}^{Cu} \frac{\partial C_{Ni}}{\partial x} - \tilde{D}_{NiZn}^{Cu} \frac{\partial C_{Zn}}{\partial x} \quad (7)$$

it follows that  $\tilde{D}_{NiZn}^{Cu}$  has to be a negative number. A relatively large  $\tilde{D}_{NiZn}^{Cu}$  of  $-6.9 \times 10^{-15} \text{ m}^2/\text{s}$  compared to a  $\tilde{D}_{NiNi}^{Cu}$  of  $0.6 \times 10^{-15} \text{ m}^2/\text{s}$  has been reported by Sisson and Dayananda [23]. The uphill interdiffusion of Ni occurring against a Zn gradient towards Zn rich regions implies that the thermodynamic activity of Ni gets reduced by Zn in the alloy [23].



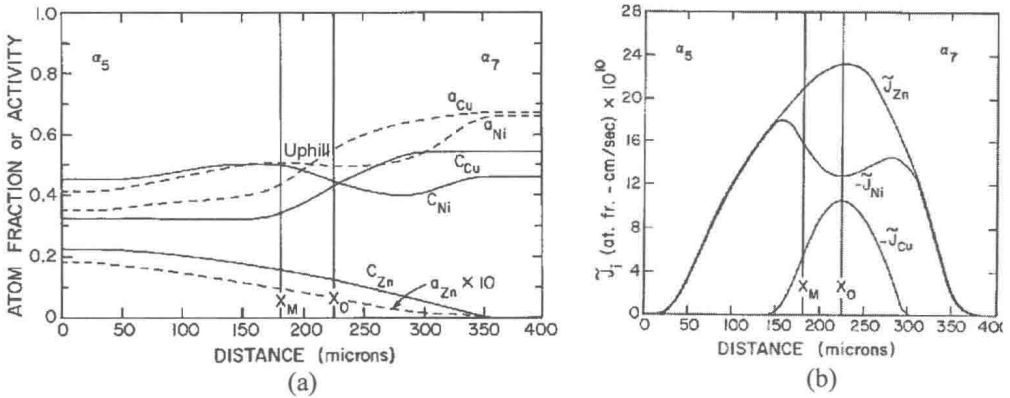


Figure 4. Uphill interdiffusion of Ni against a Zn concentration gradient in a Ni-isoconcentration couple investigated in the Cu-Ni-Zn system at 775°C. [23,11]

**Isoconcentration Couples in the Cu-Ni-Zn-Mn System.** Isoconcentration couples have been employed to explore uphill interdiffusion in multicomponent alloys with more than 3 components [9,24,25]. In Fig. 5 are presented profiles of concentrations and the calculated interdiffusion fluxes of the components for two Cu-Ni-Zn-Mn quaternary diffusion couples investigated at 775°C for 2 days [9,24]. The uphill interdiffusion of Ni shown in Fig. 5(a) is towards the Mn rich side of the

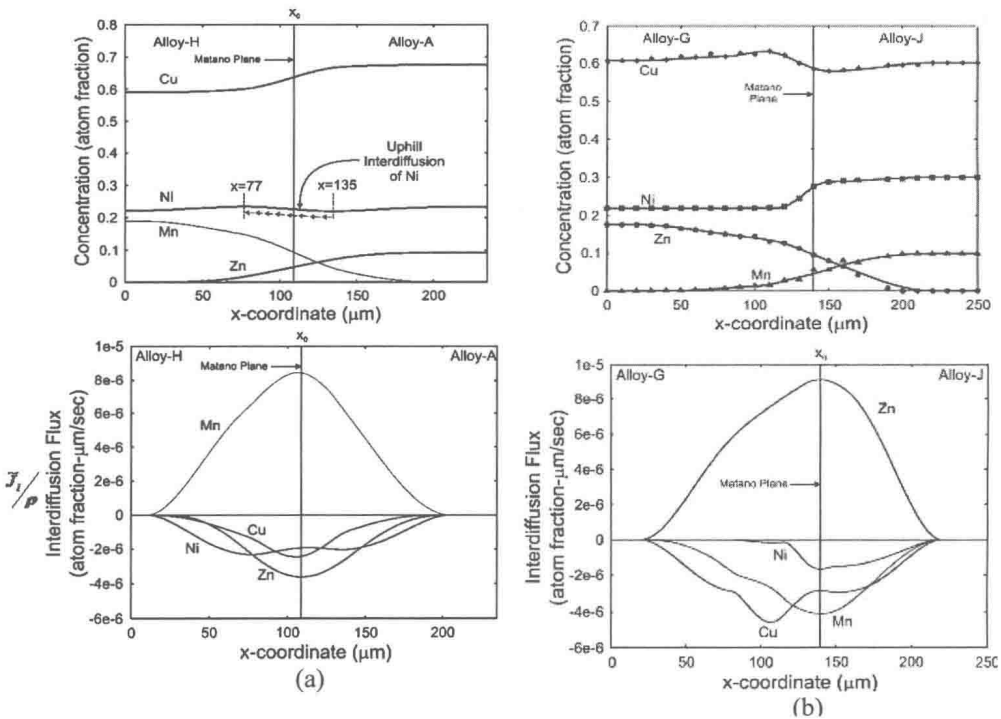


Figure 5. Concentration profiles and flux profiles for (a) a Ni-isoconcentration couple and (b) a Cu-isoconcentration couple in the Cu-Ni-Zn-Mn system annealed at 775°C for 2 days.[24,9]