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A physico-chemical approach in binary solid-state interdiffusion

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Abstract

A physico-chemical approach is developed, which can be used in binary diffusion couples to determine diffusion parameters of product phases with a wide homogeneity range, as well as phases with a narrow homogeneity range. It is demonstrated that this approach is basically equivalent to the diffusion-based treatment. However, the physico-chemical approach pedagogically sheds light on the chemical reactions occurring during interdiffusion at the interphase interfaces. This theory can be used in any binary system for any end-member condition to explain single-phase or multiphase diffusion-controlled growth. Ni–Al and Ag–Zn systems are considered here to calculate diffusion parameters following the physico-chemical approach. It is evident from our theoretical analysis and experimental evidence that in the case of presence of a stable Kirkendall marker plane one should expect the presence of duplex grain morphology in a particular phase layer.

Keywords: Interdiffusion; Kirkendall effect; Grain morphology; Intermetallics

1. Introduction

Diffusion-controlled interactions in the solid state (when one solid reacts with another solid, liquid or gas to produce solid product layer) are of importance in terms of both academic interest and industrial application. It is well known that the formation of an intermediate product layer and its growth effectively controls the overall performance of the structure in many systems, such as protective coatings, thin film microelectronic devices and bonded structures. It has always been a challenge for materials scientists to develop an understanding of the growth mechanisms and morphological evolution during interdiffusion to predict the life of a structure in application.

Much effort in this area started after the publication of one of the most noted and exciting works by Wagner [1] on metal oxidation. By considering local equilibrium at interphase interfaces, he assumed quasi-steady-state growth to calculate the parabolic growth constant of a single-phase oxide scale on metal. It is apparent that this model is applicable to the growth of intermediate layers with a narrow homogeneity range. However, Hirth and Rapp [2] found that the Wagner's phenomenological theory could also be applied, with a minor error in the calculation, where the intermediate product layer has a wide homogeneity range. This model was extended by Yurek et al. to apply in the case where two phases grow simultaneously in the product layer [3]. In this analysis, partitioning of flux at the interphase interfaces and molar volume of the product phases were considered to develop an expression for the parabolic growth constant of each phase.

In the mean time, Kidson [4], Sauer and Freise [5] and Wagner [6] published their pioneering work on multiphase diffusional growth. Sauer and Freise generalized the Matano–Boltzmann treatment to develop a relation between parabolic growth constant and interdiffusion coefficient. Wagner adopted the Sauer–Freise generalization [5] and followed a much simpler treatment to derive the same relation of interdiffusion coefficient as found by Sauer and Freise. Shatyinski et al. [7] assumed the idea of partitioning of flux at the interphase interfaces in multiphase diffusion growth (which was developed to explain the phenomenological

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process of the formation of oxide layers on metal by Yurek et al.) to combine with Wagner's methodology and obtained an expression of the parabolic growth constant in binary reaction–diffusion couples. This model was used to elucidate multiphase growth in the Ag–Zn binary diffusion couple [8]. Recently, Noolu et al. [9] followed the same procedure to explicate the growth of intermetallic compounds in the Au–Al system.

However, for applications, it is important to develop a predictive capability, which not only visualizes the growth kinetics of different phases in the product layer, but also predicts the location of the Kirkendall plane. The Kirkendall plane provides required information on the relative mobilities of the species and also plays an important role behind morphological evolutions in the product layer. This is the weakest plane in the structure; because all debris (present at the contact interface) and pores (produced because of negative surfaces on the bonding face, such as scratches) will eventually be accumulated along this plane. Kirkendall and his student Smigelkas [10] showed in their revolutionary work that the intrinsic diffusion coefficients of different species in a product layer are not the same but different, contrary to previous notions. This finding changed the viewpoint regarding the diffusion mechanism in the solid state. It was evident that vacancies play an important role in the diffusion process in the solid state. Immediately after this finding, Darken [11] published an extensive mathematical analysis to explain the phenomenological process through a thermodynamical point of view. Heumann [12] and Van Loo [13] determined a relation to calculate the intrinsic diffusion coefficient of species at the Kirkendall marker plane position.

In recent years, research into the Kirkendall effect in solid-state interdiffusion has taken a new direction due to the experimental discovery of unknown but characteristic behaviour of Kirkendall markers in a multiphase reaction zone. It has been shown that in a binary diffusion couple under volume diffusion-controlled interaction, the Kirkendall marker plane can be stable, as well as unstable [14–16]. With specific end-member compositions, more than one Kirkendall plane can be found in a single phase [15,17] or in different phases [18] in a diffusion-controlled product zone. The different characteristic behaviours of the Kirkendall marker plane has been explained in terms of velocity diagram construction [15].

In the case of a binary diffusion couple of species A and B, the velocity of the markers placed at the bonding interface can be expressed as [15]:

$$v = -(V_B J_B + V_A J_A) = V_B (D_B - D_A) \frac{\partial C_B}{\partial x} \tag{1}$$

where J_i (mol m^{-2} s^{-1}) is the intrinsic flux, D_i (m^{-2} s^{-1}) is the intrinsic diffusion coefficient and V_i (m^{-3} mol^{-1}) is the partial molar volume of the species i. $\partial C_i/\partial x$ (mole m^{-4}) is the concentration gradient measured at the Kirkendall marker plane position and x (m) is the position parameter.

Another way of finding the velocity of the Kirkendall marker plane is directly from the displacement of the Kirkendall markers after annealing for time, t (s) following Ref. [15]:

$$v = \frac{x_K - x_0}{2t} = \frac{x_K}{2t} \tag{2}$$

where x_K and x_0 are the locations of the Kirkendall marker planes after annealing times $t = t$ and $t = 0$.

The location(s) of the Kirkendall marker plane(s) can be found at the point of intersection(s) between the velocity curve $2tv$ vs. x (calculated by Eq. (1)) and the straight line $2tv = x_K$ (determined by Eq. (2)). It was shown that the number, nature and the location(s) of the Kirkendall marker plane(s) in a diffusion interaction zone depend on the number of intersection points and the gradient of the velocity curve at the point of intersection. When the straight line $2tv = x_K$ intersects the velocity curve at a point where the gradient $(\partial v/\partial x)_K$ of the velocity curve $2tv$ vs. x is $\leqslant 0$, one should expect the presence of a stable Kirkendall plane. When the gradient of the velocity curve at the point of intersection $(\partial v/\partial x)_K > 0$, one will find an unstable Kirkendall plane (markers will be scattered over a region without finding any particular plane). Experimental evidence of this previously unknown behaviour of Kirkendall markers was found in different binary systems, such as Fe–Pd [16], Ni–Al [17], Au–Zn [15] and Ag–Zn [18].

In the course of these developments, an exciting fact was noticed in several experimental results: that the position of stable Kirkendall plane(s) could be detected from the morphology developed during the interdiffusion process. There is no need to use any inert markers! Always, duplex grain morphology is found in a phase layer when a stable Kirkendall plane is present [19].

These recent developments helped us to develop a physico-chemical approach to considering chemical reactions at the interphase interfaces [19]. It was possible to use this treatment to calculate diffusion parameters where line compounds grow in an interdiffusion zone. It was noticed that both the approaches, physico-chemical and the diffusion-based model lead to the same results in predicting the thicknesses of the layers and in finding the Kirkendall marker location(s). However, the extra benefit of using the physico-chemical approach over the diffusion-based approach is that it explains the morphological evolution during interdiffusion. Unlike the model developed by Yurek et al. [3], it was shown that in multiphase diffusion phases grow by consuming neighbouring end-member/phases. There is mutual competition in the growth of different phases in the multiphase product zone. But the ultimate thicknesses of different layers will be fixed following the integrated diffusion coefficient of the phases.

However, the use of this approach was restricted to systems where phases grow with a narrow homogeneity range in a binary diffusion couple. Moreover, it was noticed that the data calculated following the physico-chemical approach resemble the data determined by following the