

# Formation of multiple stoichiometric phases in binary systems by combined bulk and grain boundary diffusion: Experiments and model

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## Abstract

The thermodynamic extremal principle has been used by the authors to treat the evolution of binary and multicomponent systems under the assumption that all phases are nearly stoichiometric. Up to now only bulk diffusion has been taken into account. The concept is now extended to combined bulk and grain boundary diffusion possible in each newly formed phase. The grains are approximated by cylinders allowing interface diffusion along the top and bottom of the grains and grain boundary diffusion along the mantle with different interface/grain boundary diffusion coefficients. A consistent analysis yields an effective diffusion coefficient taking into account the combined interface/grain boundary and bulk diffusion of each individual component. The current concept is applied to the Cu–Sn couple which has been studied by a number of researchers. The results of simulations are compared with experiments at 200 °C on solid systems reported in the literature as well as with our experiments at 250 °C with liquid Sn.

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## 1. Introduction

If two different alloys come into contact, e.g. by soldering or welding, several intermetallic layers usually form and grow at elevated temperatures in the region of the original interface. Interdiffusion is responsible for this phenomenon, and a significantly pronounced Kirkendall effect can result in the formation of pores and cracking. In addition, splitting of the Kirkendall plane has been observed and studied theoretically in such systems—see e.g. the extensive work by van Loo and co-workers [1–3], who introduced an average interdiffusion coefficient for each phase and with the ratio of the intrinsic diffusion coefficients of the species in each phase being a fitting constant. This approach can

thus treat the parabolic growth of layers controlled by diffusion as well as the splitting and motion of the Kirkendall planes. In addition, other theoretical concepts have been used, such as the quasi-steady-state concept proposed by Mei et al. [4] for sharp interfaces and by Danielewski et al. [5] for thick interfaces. A strong impact on modelling the Kirkendall effect has come also from the multiphase-field approach—see e.g. Steinbach and coworkers [6] and the adaption to the current soldering problem proposed by Park and Arróyave [7,8].

Recently Svoboda et al. (e.g. [9,10]) introduced a thermodynamic model based on the application of the thermodynamic extremal principle (TEP), using the fixed chemical composition of individual stoichiometric phases, their molar volumes, their molar Gibbs energies and tracer diffusion coefficients of all components in individual phases as input parameters. The model simulates the growth of an

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optional number of layers in the system as well as the motion of the split Kirkendall plane. The model also proposes a realistic image of how the Kirkendall plane splits. This approach works with standard thermodynamic quantities such as Gibbs energies, interface energies and diffusivities, and requires no fitting parameters. It even allows the tracer diffusion coefficients to be determined from measurements if these coefficients are unknown. Incoherent interfaces are considered to have infinite mobility and to act as ideal sources and sinks for vacancies (no dissipation occurs due to interface migration and due to generation/annihilation of vacancies at the interface). The bulk of the phases is taken as free of sources and sinks for vacancies. With respect to bridging of the TEP to the phase field method, the reader is referred to Ref. [11].

In nearly all the modelling studies, only bulk diffusion is assumed. A typical example is a solid Cu–solid Sn couple, as was studied in detail by Paul in his thesis [12] and by Paul et al. [13,14] and most recently by Kumar et al. [15]. However, soldering systems exist in which the nucleation and growth of the intermetallic phases is extremely fast. The phases have rather the microstructure of fine polycrystals than a single crystal, and grain boundary diffusion interacts strongly with bulk diffusion. The effect of interacting bulk and grain boundary diffusion occurs predominantly in the  $\eta$ -phase  $\text{Cu}_6\text{Sn}_5$ . The  $\eta$ -phase shows a “scaloped” morphology (e.g. [7,8,12,16,17]), which can only be explained by intensive nucleation of the  $\eta$ -phase and cooperative diffusion through the bulk and along the grain boundaries.

The goal of this paper is to present a model in which the macroscopic diffusive fluxes of the components A, B in some of the newly formed phases between the parent phases consist of bulk and grain boundary contributions. The TEP, as used in Refs. [9,10], is used to analyze the individual contributions to the fluxes as well as the kinetics of the system.

## 2. The model

### 2.1. General mass balance and interface velocities

We briefly outline here the background to the problem as this has already been presented in Refs. [9,10]. Therefore, we avoid repeating corresponding figures and refer the reader to Refs. [9,10]. Details with respect to the applied equations (kinematics, mass balance) can also be taken from Refs. [9,10].

Let us assume a binary system of components A and B forming  $n$  stable stoichiometric phases  $A_{r_i}B_{1-r_i}$  with  $r_i$  being the mole fraction of the component A in the phase  $i$ ,  $0 \leq r_i \leq 1$ ,  $i = 1, \dots, n$ , and  $r_i$  increasing with  $i$ .

As a starting configuration we have a diffusion couple of unit cross-section consisting of the phases  $A_{r_1}B_{1-r_1}$  at the left side and  $A_{r_n}B_{1-r_n}$  at the right side of the interface with inert markers on it. We assume that during a negligible time interval very small nuclei of all other phases are formed at the original interface and these grow into a

sequence of phases. All newly nucleated phases contain some markers originally deposited at the interface of the diffusion couple. The assumption of stoichiometry guarantees a constant chemical composition and a constant molar volume  $\Omega_i$  in each phase. As an approximation

$$\Omega_i = r_i\Omega_A + (1 - r_i)\Omega_B \quad (1)$$

can be taken, where  $\Omega_A$ ,  $\Omega_B$  are the molar volume of A, B, respectively.

We assume that all interfaces act as ideal sources and sinks for vacancies and are ideally mobile. In this case the sources and sinks for vacancies in the bulk are not activated [18]. This implies that both macroscopic diffusive fluxes  $j_{Ai}$  and  $j_{Bi}$  as well as the material velocity must be constant in each region occupied by an individual phase. The reason for the existence of fluxes is due to the fact that a very small alteration of the mole fraction in each phase causes large changes in the chemical potentials of both components. The treatment of this complicated task can, however, be avoided by application of the TEP. The macroscopic diffusive fluxes may consist of two contributions: flux through the bulk of grains and flux along the combined path of the grain boundaries and interfaces.

Let us analyze the behavior of an interface between the phases  $i$  and  $i + 1$  where the macroscopic diffusive fluxes  $j_{Ai}$ ,  $j_{Bi}$  and  $j_{Ai+1}$ ,  $j_{Bi+1}$  occur. The splitting of the diffusive fluxes into a bulk contribution and a grain boundary/interface contribution is treated in Section 2.2. The balance between the fluxes at each interface is coupled with both the interface migration and the thickening or thinning (deposition or removal of new atomic layers) at the interface. The second effect causes a motion of the lattices of the individual phases relative to each other.

Let  $u_i$  be the velocity of the interface between the phases  $i$  and  $i + 1$  relative to the lattice of the phase  $i$ , and  $v_{i+1}$  be the velocity of the interface between the phases  $i$  and  $i + 1$  relative to the lattice of the phase  $i + 1$ . The mass conservation for both the A and B components leads to the equations:

$$\frac{u_i r_i}{\Omega_i} - \frac{v_{i+1} r_{i+1}}{\Omega_{i+1}} = j_{Ai} - j_{Ai+1}, \quad i = 1, \dots, n - 1, \quad (2)$$

$$\frac{u_i(1 - r_i)}{\Omega_i} - \frac{v_{i+1}(1 - r_{i+1})}{\Omega_{i+1}} = j_{Bi} - j_{Bi+1}, \quad i = 1, \dots, n - 1. \quad (3)$$

The velocities  $u_i$  and  $v_i$  can be calculated from Eqs. (2) and (3) as:

$$u_i = \frac{\Omega_i}{r_i - r_{i+1}} [(j_{Ai} - j_{Ai+1})(1 - r_{i+1}) - (j_{Bi} - j_{Bi+1})r_{i+1}], \quad i = 1, \dots, n - 1, \quad (4)$$

$$v_{i+1} = \frac{\Omega_{i+1}}{r_i - r_{i+1}} [(j_{Ai} - j_{Ai+1})(1 - r_i) - (j_{Bi} - j_{Bi+1})r_i], \quad i = 1, \dots, n - 1. \quad (5)$$

We consider a closed system with no deposition of matter at the surface of the system, yielding the boundary conditions:

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