Materials Science and Engineering A 403 (2005) 234–240

MATERIALS SCIENCE & ENGINEERING A

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Relationship between temperature dependence of interdiffusion and kinetics of reactive diffusion in a hypothetical binary system

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Accepted 6 May 2005

Abstract

The temperature dependence of the kinetics of reactive diffusion was theoretically analyzed for a hypothetical binary system consisting of one compound phase (β) and two primary solid solution phases (α and γ). The growth rate of the β phase due to the reactive diffusion between the α and γ phases in a semi-infinite diffusion couple was mathematically described as a function of the interdiffusion coefficients and the solubility ranges of the α, β and γ phases. For simplicity, however, the solubility ranges of all the phases were assumed to take an equivalent constant value. On the other hand, the interdiffusion coefficient D^{θ} was expressed as a function of the temperature T by the equation of Arrhenius-form $D^{\theta} = D_0^{\theta} \exp(-Q^{\theta}/RT)$. Here, D_0^{θ} is the pre-exponential factor, Q^{θ} the activation enthalpy, R the gas constant, and θ stands for α, β and γ. Furthermore, we assumed $D_0^{\alpha} = D_0^{\beta} = D_0^{\gamma}$. For the reactive diffusion controlled by the volume diffusion, the square of the thickness l of the β phase is proportional to the annealing time t as $l^2 = Kt$. When $Q^{\alpha} = Q^{\beta} = Q^{\gamma}$, the temperature dependence of K is exactly described by the equation $K = K_0 \exp(-Q_K/RT)$, and Q_K coincides with Q^{α}, Q^{β} and Q^{γ}. Although this equation becomes merely approximation unless Q^{α}, Q^{β} and Q^{γ} are equivalent, it is sufficiently reliable within usual experimental errors for determination of K. Q_K is still close to Q^{β} at $Q^{\alpha} = Q^{\gamma} > Q^{\beta}$, whereas it becomes greater than Q^{β} at $Q^{\alpha} = Q^{\gamma} < Q^{\beta}$. Consequently, the temperature dependence of D^{β} is estimated directly from that of K in the former case but not in the latter case.

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Keywords: Intermetallic compounds; Bulk diffusion; Analytical methods; Kinetics

1. Introduction

Tin–base solder alloys are widely used to interconnect electronic devices and Cu–base conductor alloys in electronic industry. Owing to the reactive diffusion between the conductor and solder alloys, however, binary Cu–Sn compounds are produced at the interface of the interconnection during soldering and then continuously grow during annealing under usual energization heating conditions. Since such compounds are very brittle and possess high electrical resistivities, their growth gradually deteriorates the electrical and mechanical properties of the interconnection. In order to examine the growth behavior of the compounds, the reactive diffusion between Cu and Sn has been experimentally studied by many investigators [1–9]. Most of the studies were carried out using diffusion couples prepared by a soldering technique. For the compounds in such diffusion couples, however, it is not so easy to distinguish the growth rate during annealing from the formation rate during soldering. Thus, the soldering technique may not be appropriate to observe the growth behavior of the compounds due to the reactive diffusion at solid-state temperatures.

The solid-state reactive diffusion between Cu and Sn was experimentally studied by Onishi and Fujibuchi [10]. In their experiment, Cu/Sn diffusion couples were prepared by a diffusion bonding technique and then annealed at temperatures between $T = 463$ and 493 K for various times up to 900 h. After annealing, Cu_3Sn (ε) and Cu_6Sn_5 (η) compound layers were observed to form at the Cu/Sn interface. Their observations indicate that the square of the thickness l is proportional to the annealing time t as $l^2 = Kt$ for both the ε and η layers. Such a relationship is usually called the parabolic relationship. Here, K is the parabolic coefficient with a

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doi:10.1016/j.msea.2005.05.013

dimension of m^2/s. The temperature dependence of the parabolic coefficient K is empirically described by the equation of Arrhenius-form $K = K_0 \exp(-Q_K/RT)$, where K_0 is the pre-exponential factor, Q_K the activation enthalpy, and R is the gas constant. On the basis of the observations, they obtained $K_0^{\varepsilon} = 2.14 \times 10^{-10}\,\mathrm{m}^2/\mathrm{s}$ and $Q_K^{\varepsilon} = 61.1\,\mathrm{kJ/mol}$ for the ε layer and $K_0^{\eta} = 8.06 \times 10^{-11}\,\mathrm{m}^2/\mathrm{s}$ and $Q_K^{\eta} = 53.1\,\mathrm{kJ/mol}$ for the η layer [10]. The parabolic relationship yields that the volume diffusion of the constituent elements in each phase is the rate-controlling process of the reactive diffusion. Hence, they estimated the temperature dependence of the interdiffusion coefficient D of the volume diffusion with the formula $D = D_0 \exp(-Q/RT)$ for the ε and η phases. In their estimation, it is assumed that no diffusional flux exists in the two neighboring phases pinching the growing phase in the diffusion couple. The estimation gives $D_0^{\varepsilon} = 1.43 \times 10^{-8}\,\mathrm{m}^2/\mathrm{s}$ and $Q^{\varepsilon} = 70.7\,\mathrm{kJ/mol}$ for the ε phase and $D_0^{\eta} = 1.55 \times 10^{-8}\,\mathrm{m}^2/\mathrm{s}$ and $Q^{\eta} = 64.9\,\mathrm{kJ/mol}$ for the η phase [10]. Since the growth of the ε and η phases is controlled by the volume diffusion, we may expect that the temperature dependence is almost equivalent between K^{θ} and D^{θ}, and thus Q_K^{θ} is close to Q^{θ} ($\theta = \varepsilon, \eta$). However, their results indicate that Q^{θ} is greater than Q_K^{θ}.

The observations by Onishi and Fujibuchi [10] were theoretically analyzed by Mei et al. [11]. In their analysis, the diffusional flux controlling the migration of the interface is explicitly considered for all the phases in the diffusion couple. Using $D_0^{\mathrm{Cu}} = 3.03 \times 10^{-5}\,\mathrm{m}^2/\mathrm{s}$ and $Q^{\mathrm{Cu}} = 177.2\,\mathrm{kJ/mol}$ for the Cu phase and $D_0^{\mathrm{Sn}} = 2.35 \times 10^{-7}\,\mathrm{m}^2/\mathrm{s}$ and $Q^{\mathrm{Sn}} = 32.96\,\mathrm{kJ/mol}$ for the Sn phase, they estimated $D_0^{\varepsilon} = 5.48 \times 10^{-9}\,\mathrm{m}^2/\mathrm{s}$ and $Q^{\varepsilon} = 61.86\,\mathrm{kJ/mol}$ for the ε phase and $D_0^{\eta} = 1.84 \times 10^{-9}\,\mathrm{m}^2/\mathrm{s}$ and $Q^{\eta} = 53.92\,\mathrm{kJ/mol}$ for the η phase. According to their estimation, $Q^{\varepsilon} = 61.86\,\mathrm{kJ/mol}$ and $Q^{\eta} = 53.92\,\mathrm{kJ/mol}$ are close to $Q_K^{\varepsilon} = 61.1\,\mathrm{kJ/mol}$ and $Q_K^{\eta} = 53.1\,\mathrm{kJ/mol}$, respectively. Consequently, it is concluded that the activation enthalpy of the interdiffusion coefficient of the growing compound phase can be evaluated directly from the temperature dependence of its parabolic coefficient for the reactive diffusion in the binary Cu–Sn system.

The kinetics of the reactive diffusion controlled by the volume diffusion was theoretically analyzed for a hypothetical binary system consisting of one compound phase and two primary solid solution phases in a previous study [12]. In that analysis, the growth rate of the compound phase was evaluated for various semi-infinite diffusion couples initially composed of the two primary solid solution phases using an analytical solution of diffusion equations. The analysis indicates that the most predominant parameters determining the growth rate are the diffusion coefficient and the solubility range of the growing compound phase. However, the diffusion coefficients and the solubility ranges of the primary solid solution phases also possess certain effects on the growth rate. As a result, the temperature dependence of the growth rate will be described by a complex function of the diffusion coefficients and the solubility ranges of all the phases. This means that the equation $K = K_0 \exp(-Q_K/RT)$ may not be necessarily valid even for the reactive diffusion in such a hypothetical binary system.

In order to examine the validity of the equation of Arrhenius-form for the parabolic coefficient, the temperature dependence of the growth rate of the compound phase was quantitatively analyzed in the present study. The analysis was carried out for the reactive diffusion in semi-infinite diffusion couples of a hypothetical binary system similar to a previous study [12]. Even in such a case, however, there exist many parameters to control the growth rate. Consideration of all the parameters will cause difficulty for intuitive understanding of the examination. Hence, in the present study, attention was focused on the relationship between the temperature dependency of the growth rate and those of the interdiffusion coefficients of the constituent phases. Interesting results could be obtained under such simplified conditions.

2. Analysis

A hypothetical binary A–B system composed of one compound phase and two primary solid solution phases was adopted in a previous study [12]. The same binary system was utilized also in the present study. In this system, the primary solid solution phases of elements A and B are designated the α and γ phases, respectively, and the compound phase is called the β phase. For the present analysis, we consider a semi-infinite diffusion couple consisting of the α and γ phases with initial compositions of $y^{\alpha 0}$ and $y^{\gamma 0}$, respectively. Here, y is the mol fraction of element B. In such a semi-infinite diffusion couple, the thicknesses of the α and γ phases are semi-infinite and the α/γ interface is flat. Thus, the interdiffusion of elements A and B takes place unidirectionally along the direction perpendicular to the flat interface. Hereafter, this direction is designated the diffusional direction. If the diffusion couple is annealed at temperature T for an adequate time, the β phase will be produced at the interface owing to the reactive diffusion between the α and γ phases. Here, T is high enough for the reactive diffusion to occur sufficiently fast. The concentration profile of element B across the β phase along the diffusional direction is schematically depicted in Fig. 1 [12]. In this figure, the ordinate indicates the mol fraction y, and the abscissa shows the distance x measured from the initial position of the α/γ interface. Dashed lines and solid curves indicate the concentration profiles before and after annealing, respectively, and $z^{\alpha\beta}$ and $z^{\beta\gamma}$ show the positions of the α/β and β/γ interfaces, respectively, after annealing. When the local equilibrium is actualized at each migrating interface during annealing, the compositions of the neighboring phases at the interface coincide with those of the corresponding phase boundaries at temperature T in the phase diagram of the binary A–B system. In such a case, the migration of the interface is controlled by the volume diffusion in the neighboring phases. In Fig. 1, $y^{\alpha\beta}$ and $y^{\beta\alpha}$ are the compositions of the α and β phases, respectively, at the α/β interface, and $y^{\beta\gamma}$

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