

Local equilibrium in the dissolution and segregation kinetics of Ag on Cu(1 1 1) surface



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ARTICLE INFO

Article history:

Received 22 November 2013

Received in revised form 12 January 2014

Accepted 15 January 2014

Available online 25 January 2014

Keywords:

Local equilibrium

Surface segregation

Dissolution

Kinetics

Modified Darken model

ABSTRACT

The local equilibrium in the kinetic processes of dissolution and segregation of Ag on Cu(1 1 1) surface is addressed. The measured dissolution and segregation kinetic data of Ag on Cu(1 1 1) surface at temperature of 450 °C are well fitted by the modified Darken model. The segregation parameters, i.e. segregation energy, interaction and diffusion parameters, in the Cu(1 1 1)(Ag) binary system are obtained upon fitting. Using the obtained segregation parameters, the discontinuous transition of Ag surface concentration against the bulk concentration of the surface neighboring layers deduced from the local equilibrium model is quantitatively interpreted.

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1. Introduction

The surface segregation of Ag in the low-index Cu single crystals has been studied extensively because a discontinuous transition of Ag surface concentration accompanying an interesting hysteresis effect in isosteric/isothermal surface segregation was observed in the Cu(1 1 1)(Ag) system [1–8]. To interpret such a hysteresis effect in surface segregation, different opinions exist [1–10]. It was firstly proposed that such an effect is related to the so-called 2D-phase separation [3,4]. Then, it was demonstrated by applying the so-called local equilibrium model [1,2] that the discontinuous transition of Ag surface concentration in isothermal segregation could be deduced from a continuous segregation/dissolution kinetics. By the modified Darken model [6–8], the hysteresis effect in surface segregation is explained quantitatively. In the local equilibrium model, it is assumed an existence of the local equilibrium between the surface and its neighboring layer in the dissolution/segregation kinetics, which is the pre-requirement for applying the local equilibrium model. However, the judgment whether the local equilibrium is indeed established could not be made according to the local equilibrium model itself. In this paper, it will be demonstrated that the modified Darken model can be used to explore the local equilibrium in the dissolution/segregation

kinetics and to reproduce the experimental data of the discontinuous transition of Ag surface concentration in the isothermal dissolution/segregation kinetics deduced based on the local equilibrium model.

2. Theory

2.1. The local equilibrium model

The notion of local equilibrium was first suggested in the study of sulphur diffusion in coppers by Pétrino et al. [12] and then formalized by Lagües and Domange [13]. It implies that the existence of a transition area “selvedge” between the surface and the bulk. The solubility and diffusion coefficient of the selvedge are different from the bulk. The dissolution process can be divided into two steps: the diffusion of atoms through the selvedge and the diffusion in the bulk. It is assumed that the diffusion through the selvedge is fast compared with the diffusion in the bulk because of the absence of large potential barrier in the selvedge. In the second step, the local equilibrium is established between the surface layer and its neighboring layer, and the concentration of the layer near the surface depends exclusively on the surface concentration, but weakly on the bulk concentration. The bulk concentration below the selvedge obeys Fick’s diffusion equation [13]:

$$C_v(x, t) = C_v + \int_0^t J_0(t - \tau) \frac{\exp(-x^2/4D_v\tau)}{\sqrt{\pi D_v\tau}} d\tau \quad (1)$$

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when $x=0$, the concentrate near the surface layer is described by:

$$C_v(0, t) = C_v + \int_0^t J_0(t - \tau) \frac{d\tau}{\sqrt{\pi D_v \tau}} \quad (2)$$

$$J_0 = \frac{-dC_s}{dt}, \quad (3)$$

where $C_v(x, t)$ is the bulk concentration at the distance of x to the surface at time t , C_v is the initial bulk concentration, C_s is the surface concentration, D_v is the volume diffusion coefficient of the solute atom, and J_0 is the flux of atoms from the bulk layers into the surface. The dataset $\{C_v(0, t), C_s\}$ represents the isothermal segregation/dissolution equilibrium.

2.2. The modified Darken model

The model based on the Fick's diffusion equation describes only a down-hill diffusion process, but the surface segregation is an uphill diffusion process. Therefore, any attempts to set up a model based on Fick's diffusion equation to describe the surface segregation kinetics will not be consistent with this uphill diffusion process. The problem of uphill diffusion was first addressed by Darken [14] and it was assumed that the driving force for the diffusion process is the gradient of chemical potential instead of the concentration gradient as in Fick's diffusion equation. Followed this assumption, the modified Darken model was proposed for describing the up-hill diffusion process of surface segregation kinetics [15–19]. It is a layer-by-layer model in which the investigated system is regarded as a closed system and is divided into one surface layer in contact with N bulk layers. This modified Darken model has already been successfully applied to describe both equilibrium and kinetic segregation processes [6–8,20–22].

The core of this model is that the kinetic process of surface segregation in a binary system is described by a set of coupled rate equations as follow:

$$\begin{aligned} \frac{\partial X^S}{\partial t} &= \frac{DX^{B_1}}{RTd^2} \Delta\mu^{B_1, S} \\ \frac{\partial X^{B_1}}{\partial t} &= \frac{DX^{B_2}}{RTd^2} \Delta\mu^{B_2, B_1} - \frac{DX^{B_1}}{RTd^2} \Delta\mu^{B_1, S} \\ &\vdots \\ \frac{\partial X^{(j)}}{\partial t} &= \frac{DX^{(j+1)}}{RTd^2} \Delta\mu^{(j+1, j)} - \frac{DX^{(j)}}{RTd^2} \Delta\mu^{(j, j-1)} \\ &\vdots \\ \frac{\partial X^N}{\partial t} &= -\frac{DX^{B_N}}{RTd^2} \Delta\mu^{B_N, B_{N-1}}, \end{aligned} \quad (4)$$

where X^S is the surface concentration and $X^{(j)}$ is the j th bulk layer's concentration, R is the gas constant, T is the temperature, d is the interlayer distance, D is the diffusion coefficient ($D = D_0 \exp(-Q/RT)$, Q is the activation energy and D_0 is the frequency factor), $\Delta\mu^{(j+1, j)}$ is the difference of chemical potential between two adjacent layers, i.e. $\Delta\mu^{(j+1, j)} = \mu_1^{(j+1)} - \mu_1^{(j)} - \mu_2^{(j+1)} + \mu_2^{(j)}$. Under the regular solution approximation, the chemical potential is expressed in terms of the standard chemical potential μ^0 , the interaction parameter Ω and the concentration X as:

$$\mu_1^{(j)} = \mu_1^{0(j)} + \Omega(1 - X^{(j)})^2 + RT \ln X^{(j)}, \quad (5)$$

and

$$\mu_2^{(j)} = \mu_2^{0(j)} + \Omega(X^{(j)})^2 + RT \ln(1 - X^{(j)}), \quad (6)$$

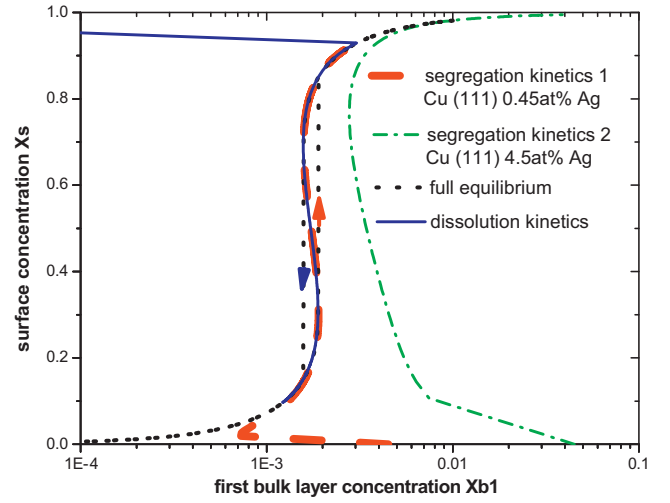


Fig. 1. Two segregation kinetics (dashed and dashed-dotted lines) and one dissolution kinetics (solid line) simulated by the modified Darken model are compared with the full equilibrium segregation curve (dotted line) according to Eq. (7), for $\Delta G = 24.2$ kJ/mol, $\Omega = 14.1$ kJ/mol, $Q_0 = 181$ kJ and $D_0 = 24 \times 10^{-6}$ m²/s at $T = 450$ °C. The initial bulk concentration is 0.45% for segregation kinetics 1 (dashed line) and 4.5% for segregation kinetics 2 (dashed-dotted line).

If an equilibrium state is reached, all the rate equations should equal to zero, resulting $X^{B_1} = X^{B_2} = \dots = X^{B_N} = X^B$. For the first rate equation, it follows

$$\frac{X^S}{1 - X^S} = \frac{X^B}{1 - X^B} \exp \left[\frac{\Delta G + 2\Omega(X^S - X^B)}{RT} \right], \quad (7)$$

where ΔG is the so-called segregation energy and is defined as

$$\Delta G = \mu_1^{OB} - \mu_1^{OS} - \mu_2^{OB} + \mu_2^{OS} \quad (8)$$

where $\mu_{(i)}^{OB}$ and $\mu_{(i)}^{OS}$ are the standard chemical potentials of pure element i for the bulk material and surface region material, respectively. In general, the segregation energy ΔG is independent on the bulk/surface concentration and the temperature.

Eq. (7) is the well-known Bragg–Williams expression for widely describing the equilibrium surface segregation. Thus, the equilibrium surface segregation is a natural consequence of the rate Eq. (4). In order to distinguish the local equilibrium in segregation kinetics, the equilibrium segregation described by Eq. (7) is referred to the so-called *full equilibrium*. It has been demonstrated that, according to Eq. (7), a discontinuous transition of surface concentration can be brought about by a continuous change of sample's bulk concentration [23]. Such a discontinuous transition of surface concentration against the bulk concentration at temperature of 450 °C is shown in Fig. 1 by the dotted line for the segregation energy of 24.2 kJ/mol and the interaction parameter of 14.1 kJ/mol. The two bulk concentration values corresponding to the discontinuous transitions indicated by arrows in Fig. 1 are 0.188 at.% and 0.156 at.%, respectively, upon increasing and decreasing the bulk concentration value. For the segregation parameters of $\Delta G = 24.2$ kJ/mol, $\Omega = 14.1$ kJ/mol, $Q_0 = 181$ kJ and $D_0 = 24 \times 10^{-6}$ m²/s (see Section 3), according to the rate Eq. (4), two isothermal segregation kinetics of surface concentration as a function of first bulk layer concentration are presented in Fig. 1 as dashed and dashed-dotted lines for the initial bulk concentration values of 0.45 at.% and 4.50 at.%, respectively. Clearly, the segregation kinetic curve follows one of the full equilibrium for the case of the initial bulk concentration of 0.45 at.%, indicating that the local equilibrium is indeed established between the surface and the first bulk layers, but not for the case of the initial bulk concentration of 4.50 at.%.

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