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Kinetics near the discontinuous surface transition in the Cu(Ag)(111) binary segregating system

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Abstract

The kinetics of the segregating element silver in the system Cu(111)(Ag) was measured at temperatures close to where the discontinuous transition in the silver surface concentration versus temperature occurs. The seemingly complex kinetic behaviour of two-step diffusion and anomalous segregation processes could be fitted using only the surface segregation energy ΔG, the surface interaction parameter Ω^S and the bulk diffusion coefficient D parameters. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Auger electron spectroscopy; Copper; Low-index single-crystal surfaces; Models of surface kinetics; Silver; Surface segregation

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1. Introduction

The discontinuous surface transition was first observed by Liu and Wynblatt [1] for the system Cu(111)(Ag). In this experiment the silver surface concentration drops discontinuously from nearly monolayer coverage to close to bulk concentration as the temperature is increased above a certain critical value. The experiment was repeated on a similar crystal in this laboratory in order to measure the kinetics of the segregation process. The equilibrium coverage results have been reported previously [2] and are given in Fig. 1. It is clear from the figure that the equilibrium surface concentration shows a discontinuous transition from about 75% of monolayer coverage to 15% coverage as the temperature is increased to values above 460°C. For this system, a (111) single crystal doped to 0.20 at% Ag, the equilibrium data could be fitted adequately by $\Delta G = (24.6 \pm 0.3)$ kJ mol^{-1}

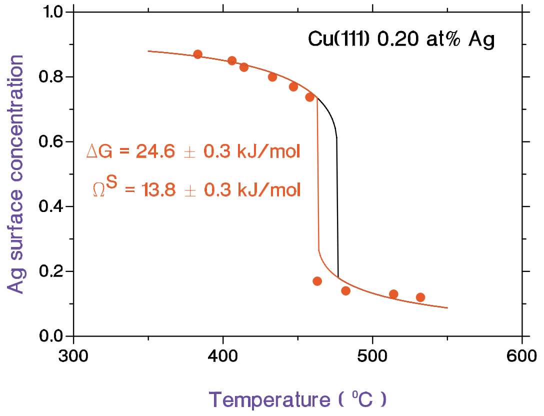

Fig. 1. Silver equilibrium surface concentration at various temperatures. The solid line is the fit of Eq. (8), yielding the values of the segregation energy ΔG and the interaction parameter Ω.

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and $\Omega^S = (13.8 \pm 0.3)$ kJ mol^{-1} which also correspond well to values obtained by Liu and Wynblatt [1] and to bulk interaction parameters obtained from bulk phase diagram calculations [2].

The kinetic data are shown in Fig. 2. It is clear from the outset that the data are more complex than the normal $t^{1/2}$ dependence normally observed for surface segregation kinetics [3–6]. The $t^{1/2}$ dependence does not take any saturation into account. A model to describe saturation was first introduced by McLean [7]. In this case, however, the data show a distinct two-step behaviour and on closer inspection also what could be regarded as *anomalous* segregation since the segregation rate decreases as the temperature is increased to a temperature of 455°C.

It is the aim of this paper to show that the complex segregation behaviour may be fitted by the modified Darken model proposed earlier and that *no additional* fitting parameters are needed except the diffusion coefficient D.

2. Theoretical

In the modified Darken model [8–12] it is assumed that the driving force in the segregating system is the gradient of the chemical potential instead of the concentration gradient as is assumed in the Fick description. The segregation process of a binary system is described by a set of coupled rate equations for a surface S in contact with the bulk consisting of N layers. The rate of change of the concentration in each layer is given by:

$$\frac{\partial X^S}{\partial t} = \left[\frac{M X^{B_1}}{d^2} \Delta\mu^{B_1,S} \right] \tag{1}$$

$$\frac{\partial X^{B_1}}{\partial t} = \left[\frac{M X^{B_2}}{d^2} \Delta\mu^{B_2,B_1} - \frac{M X^{B_1}}{d^2} \Delta\mu^{B_1,S} \right]$$

$$\vdots \tag{2}$$

$$\frac{\partial X^{(j)}}{\partial t} = \left[\frac{M X^{(j+1)}}{d^2} \Delta\mu^{(j+1,j)} - \frac{M X^{(j)}}{d^2} \Delta\mu^{(j,j-1)} \right]$$

$$\vdots \tag{3}$$

where X^S is the surface concentration of the segregant and X^{B_1} is the first bulk layer concentration of the segregant. The rest of the bulk therefore consists of the $N-1$ layers and the interlayer distance is given by d. The quantity M is the mobility of the segregant. For *dilute alloys*, the mobility is related to the diffusion coefficient via $D = MRT$ where R is the universal gas constant and T the temperature. Furthermore, $\Delta\mu^{(j+1,j)} = \mu^{(j+1)} - \mu^{(j)} - \mu_m^{(j+1)} + \mu_m^{(j)}$, where $\mu^{(j)}$ is the chemical potential of the segregant in layer j and $\mu_m^{(j)}$ is the chemical potential of the solvent in layer j. For a regular solution only pairwise interactions between the atoms are taken into account and the chemical potential for binary alloys may then be expressed in terms of the standard chemical potential μ^0, the interaction coefficient Ω and the concentration X as in

$$\mu_1 = \mu_1^0 + \Omega X_2^2 + RT \ln X_1 \tag{4}$$

and

$$\mu_2 = \mu_2^0 + \Omega X_1^2 + RT \ln X_2 \tag{5}$$

The interaction coefficient Ω is defined by

$$\Omega = Z[\epsilon_{12} - \tfrac{1}{2}(\epsilon_{11} + \epsilon_{22})] \tag{6}$$

where ϵ_{ii} is the interaction energy between the same species and ϵ_{ij} is the interaction between different atom species. The coordination number of an atom in the solid is given by Z. In this regard, the interaction parameter Ω is similar to

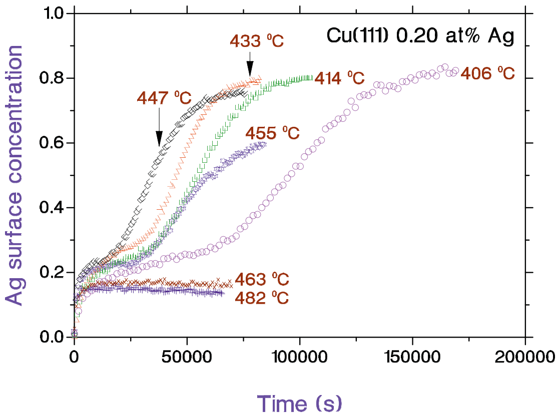

Fig. 2. Surface segregation kinetics of silver in Cu(111) at various temperatures. Note the smaller rate of segregation at 455°C when compared with temperatures lower than 447°C.

the effective pair interaction V used by Saúl et al. [13]. Their model makes use of an analogous system of coupled rate equations, derived previously by Martin [14], using the diffusion coefficient D, transition probabilities γ and the concentration c. The transition probabilities include the segregation enthalpies and implicitly also the interaction terms γ. In both models, the mobility M and diffusion coefficient D are respectively taken as the proportionality constant, and the driving force is therefore proportional to the energy gradient. Both models, depending on a simple pairwise interaction, should therefore lead to very similar time dependencies. The difference, however, lies in the value attributed to the proportionality constants. In a pure Fickian description the flux J_{F} is given in terms of the diffusion coefficient D and the concentration gradient $\partial C/\partial x$ only. On the other hand, the flux J_{D} in a purely Darken description is given by the mobility M, the concentration and the gradient of the solute chemical potential. Setting equal these two fluxes, a relationship between M and D may be derived

$$D = MRT\left(1 + \frac{\partial f}{\partial X}\right) \tag{7}$$

where f is the activity coefficient. This last expression reduces to $D=MRT$ for a dilute alloy for which $f=$constant. Only under these conditions is it possible to move from one description to the next and to assign values to the diffusion coefficient obtained from fits of the Darken equations, for example. If the flux equations are modified, as per Martin [14] or Du Plessis and van Wyk [8–12], the relationship between the mobility M or the Martin diffusion coefficient D_{M} and the "true" diffusion coefficient D_{F} becomes more complicated, and care should be exercised in assigning values to the generally accepted diffusion coefficient D_{F} (or D). A detailed comparison between these models is, however, beyond the scope of this short paper.

The above system of equations, called the rate equations, can only be solved numerically by using a suitable routine such as a variable-step, variable-order Gear routine [15]. If the equilibrium state is reached all the rate equations are equal to zero, which gives [8–12]:

$$\frac{X^S}{1-X^S} = \frac{X^B}{1-X^B}\exp\left[\frac{\Delta G + 2\Omega^S(X^S - X^B)}{RT}\right] \tag{8}$$

This equation is the well-known equilibrium segregation equation. Thus, the equilibrium segregation is a natural consequence of the rate equations. When compared with the rate equations only one extra parameter, the mobility M (or diffusion coefficient D), is needed to provide a full description of the segregation process.

The modified Darken model has been successfully used in equilibrium and kinetic surface segregation, linear heating and sputtering yield measurements [16–22].

3. Experimental

The experimental procedure is briefly given here. A high-purity (99.999%) copper single crystal oriented to the (111) surface was doped to 0.20 at% Ag by electron-beam evaporation of silver onto the back face of the crystal in an ultrahigh vacuum chamber. After evaporation it was sealed in a quartz tube under argon gas atmosphere and annealed at 920°C for 25 days.

The crystal was then mounted on a resistance heater. A stainless steel disc, to which a thermocouple had been attached, was inserted between the sample and the heater. The disc temperature was calibrated in terms of the true surface temperature by means of a thermocouple inserted in a small hole drilled into the face of a dummy copper sample.

The surface concentration of the silver atoms segregating to the (111) surface of the single crystal was monitored by Auger electron spectroscopy in the temperature range 380°C to 550°C. At each temperature, the surface was first cleaned by argon-ion sputtering, then the Auger peak-to-peak heights APPH(t) for silver (351 eV) and copper (920 eV) were recorded as a function of time t. After each run the sample was annealed for 1 h at 600°C to remove any concentration gradient. The quantification of surface concentration is based on the Seah scheme [23].

4. Results and discussion

The equilibrium surface segregation data were obtained from the saturation values of the kinetic data and could be presented as such. However, it is instructive and of some fundamental consequence to discuss the phenomenon from equilibrium to kinetics.

4.1. Equilibrium Cu(111)(Ag) segregation

The silver equilibrium surface concentration as a function of temperature is given by the closed circles in Fig. 1 and the data are fitted by the equilibrium segregation Eq. (8), as indicated by the solid lines in Fig. 1, for $\Delta G=(24.6\pm 0.3)$ kJ mol^{-1}, $\Omega^S=(13.8\pm 0.3)$ kJ mol^{-1} and $X^B=0.20$ at%. The high-to-low transition temperature is estimated at (463 ± 5)°C.

The characteristic discontinuous transition from a high coverage of $X^S_{\mathrm{Ag}}\approx 0.75$ to $X^S_{\mathrm{Ag}}\approx 0.15$ at around 463°C is the single feature in Fig. 1. The interpretation of the similar data presented by Wynblatt and Liu [24] amongst others has led to two views and a difference of opinion on the origin of the discontinuous transition. Other authors have chosen to interpret the discontinuous transition in terms of a so-called surface miscibility gap whereas the present authors have elected to treat the problem as a two open but fixed sized systems [8–12]. The surface is regarded as a single layer, and the bulk in contact with the surface as being very large but still finite. Under these restrictions it is possible to impose the conservation of atoms and to derive independent equilibrium conditions. (This assumption is quite different from ordinary bulk equilibrium considerations where phases can nucleate and grow at the expense of the other phases present. For a detailed discussion see the references in [8–12].)

4.2. Kinetics of Cu(111)(Ag) segregation

Great care was taken in recording the surface segregation kinetics of silver to the Cu(111) surface. Segregation runs varied from 5 to 50 h per run. The results are given in Fig. 2 in which the obvious features for the kinetic segregation measurements are: the two-step diffusion process, the anomalous segregation process in which the segregation rate decreases as the temperature is increased to 455°C, and the discontinuous transition. Surface segregation kinetics with a two-step diffusion process were also found in the Ag(111)(Pb) [25] and Ge(111)(Sn) [26] systems, but the data were not fitted.

The segregation kinetics at temperatures up to 447°C were fitted and are given in Fig. 3; these are examples of the normal segregation processes. Although the fit is not perfect, it reproduces the first step at $X^S_{\mathrm{Ag}}\approx 0.22$. It should be kept in mind that:

(1) only the diffusion coefficient D was adjusted to obtain the fit. No additional information or parameter was needed to produce the step at $X^S_{\mathrm{Ag}}\approx 0.22$. It follows naturally from the solutions of the rate equations using $\Delta G=24.6$ kJ mol^{-1} and $\Omega^S=13.8$ kJ mol^{-1} as determined from the equilibrium data fits;

(2) no additional information was provided on the length of the step. Just as in the case of the step height (i.e., $X^S_{\mathrm{Ag}}\approx 0.22$), the step length follows automatically from the solution of the rate equations too;

(3) the effect of sputtering has been accounted for by allowing segregation and silver removal before the measurements were started; and

(4) the regular solution model with one interaction parameter is probably an oversimplification but provides an excellent fit to the data.

The quantitative explanation for the two-step diffusion process found in Fig. 3 for a temperature of 447°C is given in Fig. 4. Here the Gibbs free energy (of the surface and bulk) is plotted as a function of time. The Gibbs free energy was calculated by

$$G=\sum_{j=1}^{N}\sum_{i=1}^{2} X_i^j \mu_i^j \tag{9}$$

thereby summing over all the layers (surface and bulk) and over all species.

For small times, the Gibbs free energy decreases rapidly with time, indicating that the supply of atoms to the surface is high. As the intermediate concentration of 0.22 is reached at about 10 000 s, the chemical potential gradient between the first

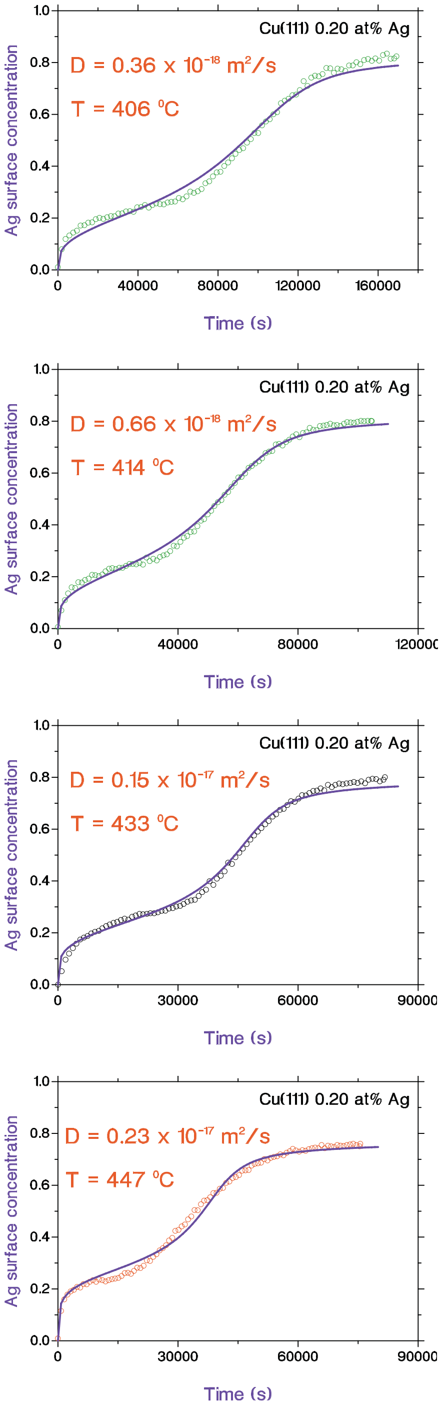

Fig. 3. The fits of surface segregation kinetics of silver in Cu(111) at various temperatures. The points are the experimental data and the solid lines are calculated from the rate equations adjusting only the diffusion coefficient *D*.

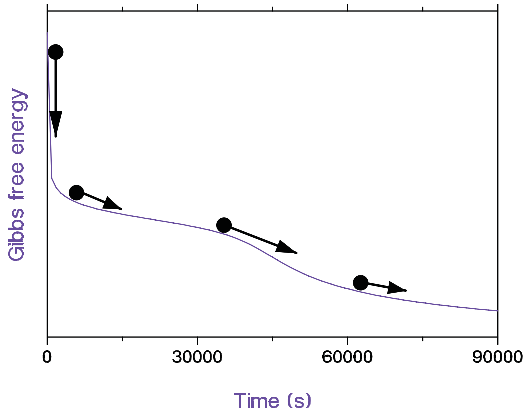

Fig. 4. The total Gibbs free energy curve at 447°C for the Cu(111)(Ag) system.

bulk layer and the surface all but vanishes and the segregation rate drops to nearly zero. The Gibbs free energy therefore stays nearly constant as only a few atoms segregate onto the surface. As more atoms slowly accumulate on the surface, the total Gibbs free energy of the surface is lowered via the interaction between the segregating atoms, and once the gradient between surface and bulk becomes larger at about 30 000 s, the segregation rate increases once again. As the equilibrium coverage is reached at about 60 000 s, the gradient between surface and bulk vanishes and the segregation rate drops to nearly zero again.

The above explanation of the shape of the segregation curves provides an explanation for the anomalous segregation as well. As the temperature approaches the transition temperature, the driving force for atoms to move from the first bulk layer onto the surface becomes zero, the length of the intermediate plateau increases and the total segregation time increases. The segregation kinetics at 455°C are fitted and shown in Fig. 5. Also shown are calculations at temperatures close to 455°C. For a few degrees variation in temperature, the plateau length changes from about 50 000 s to 100 000 s. Any variation in temperature during this long measurement will affect the segregation kinetics and is probably the reason why the fit is not as good as for the lower temperatures.

From all of the kinetic data fits, the values of the pre-exponential factor $D_0=(24\pm2)\times10^{-6}$

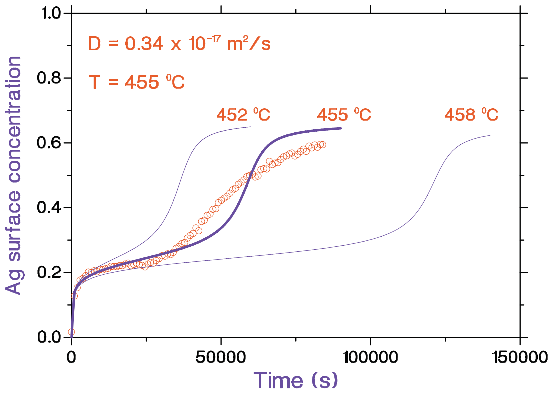

Fig. 5. Comparison between the model calculation results at three different temperatures using the same fit parameters.

$m^2\,s^{-1}$ and activation energy $E=(179\pm5)$ kJ mol^{-1} were determined from the Arrhenius plot as shown in Fig. 6 for the Cu(111) 0.20 at% Ag sample. These values differ from the extrapolated values from radiotracer measurements [27] of $D_0=0.63\times10^{-4}\,m^2\,s^{-1}$ and $E=194.4$ kJ mol^{-1} by a factor of nearly 10. The thermocouple was inserted at the back of the crystal and although great care was taken to measure the temperature as accurately as possible, a sufficiently large systematic error in the temperature determination may lead to this deviation in diffusion coefficient values.

It must also be pointed out that two-step processes are normally associated with structural transitions in the segregated overlayer; see, for example, [28]. These structural transitions are observed with low-energy electron diffraction (LEED) measurements. It was, however, not possible to measure the LEED images for the particular crystal and surface structure transitions can therefore not be excluded as a possible cause for the two steps observed in the surface segregation kinetics. The present explanation appears to provide satisfactory answers to all the observed detail of the two steps, anomalous segregation rates and the discontinuous transition, using a minimum of fit parameters.

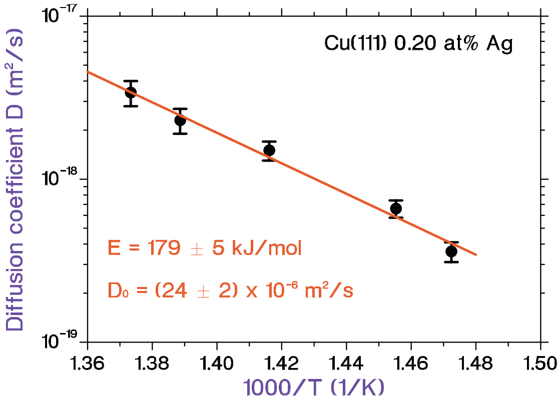

Fig. 6. Arrhenius plot of silver diffusion in Cu(111).

5. Conclusion

This is the first time that the two-step diffusion and anomalous segregation processes at temperatures close to the transition temperature have been observed in the surface kinetic segregation measurements for the Cu(111) 0.20 at% Ag sample, and have been fitted using simple rate equations.

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