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

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Abstract

The discontinuous transition in the Ag equilibrium surface concentration as a function of temperature for a Cu(111) 0.20 at% Ag sample is presented in this paper. The criteria for observing this type of transition are derived, and an expression for the critical bulk concentration, above which no transition is observed, is found. The experimental equilibrium surface concentration values are fitted by the well-known equilibrium segregation equation, yielding a surface segregation energy ΔG of 24.6 ± 0.3 kJ/mol, and a surface interaction parameter Ω^{S} of 13.8 ± 0.3 kJ/mol. These values are discussed in terms of the Cu–Ag phase diagram, and compared with other literature values. In addition, no hysteresis was found, and possible reasons for the absence of this expected feature are also given. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The study of Ag atoms segregating onto the Cu surface has attracted attention from research groups, both theoretically [1–17] and experimentally [18–32]. The system is of particular interest since a discontinuous transition in the surface coverage with temperature was observed for the Cu(111) surface. This type of transition at the Cu(111) surface has been studied by two different research groups: that of Eugène et al. [33] and Liu and Wynblatt [34], using different techniques. Eugène et al. deduced the discontinuous transition indirectly by measuring the isothermal kinetic segregation. Liu and Wynblatt found the discontinuous transition directly by measuring the isosteric equilibrium segregation. However, the interpretation of this sharp transition has been a focus point on which different opinions exist [35–38]. Liu's equilibrium segregation data is displayed in Fig. 1, where a discontinuous transition of Ag surface concentration was observed as the temperature was increased/decreased stepwise. There is a difference between the two transition temperatures (indicated by the arrows in Fig. 1), which is called the hysteresis effect. This effect had also been observed previously for Ni–C [39], Pd(Co)–C [40] and Fe–Si–C [41–43] systems. However, no quantitative treatment for the discontinuous transition with possible accompanying hysteresis effect has been presented until now. It is with this aim that segregation measurements were performed to obtain data under strict experimental conditions

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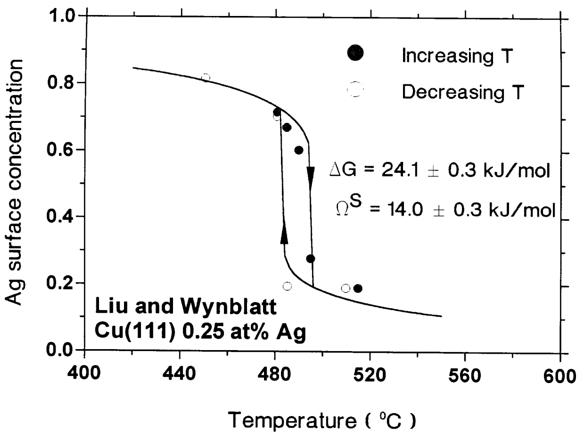

Fig. 1. Equilibrium segregation data of Ag on Cu(111) [26]. The solid lines are the best fit to Eq. (1).

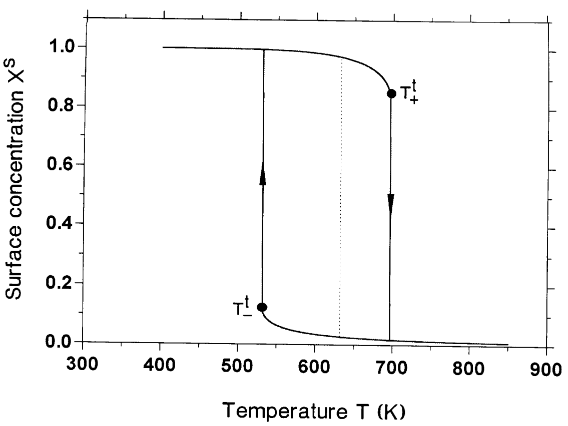

Fig. 2. Hysteresis effect in isosteric segregation for $X^B=0.0005$, $\Delta G=20$ kJ/mol and $\Omega^S=20$ kJ/mol. The sharp transition is observed at $T^t_+=697$ K and $T^t_-=531$ K. The broken line corresponds to the temperature where the two minima in the Gibbs free energy are equal.

in order to give a quantitative explanation for the discontinuous transition in the equilibrium surface segregation and to find the values of the segregating parameters. In particular, the interaction parameter of Ag in the Cu bulk will be compared with that of Ag on the Cu surface.

2. Theoretical

2.1. Discontinuous transitions

It is generally accepted that the surface concentration for interacting species may be described by:

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

where X^S and X^B are the surface and bulk concentration, respectively, ΔG is the segregation energy, Ω^S is the surface interaction parameter, T is the temperature, and R is the gas constant.

It has also been shown [44–48] that the hysteresis effect should always accompany the discontinuous transition if the curve of the Gibbs free energy against the surface concentration contains two minima. As an example, the hysteresis effect in the isosteric surface segregation for a given set of (X^B, ΔG, Ω^S) is shown in Fig. 2. The sample's temperature is increased from a low temperature value of 500 K. The system moves through a series of equilibrium states as described in Eq. (1), and the surface concentration decreases from $X^S\approx 1$ as the temperature is increased. Near the temperature $T^t_+=697$ K, the concentration has now decreased to $X^S\approx 0.83$. At the temperature $T^t_+=697$ K, the surface concentration moves discontinuously from $X^S\approx 0.83$ to the low surface concentration $X^S\approx 0.02$. As the temperature is increased further, the surface concentration decreases even further to $X^S\approx 0.01$ at $T=850$ K.

If the temperature is now lowered, the system will stay in the low concentration state and will move back along the curve for temperatures down to $T^t_+=697$ K. At this temperature, however, the surface concentration does not follow the discontinuous transition back to high concentration, but stays in the low concentration state until a much lower temperature $T^t_-=531$ K is reached. Only at this lower temperature does the system move back from the low concentration state at $X^S\approx 0.08$ to the high concentration state $X^S\approx 1$ in a discontinuous transition, similar to the transition from high to low concentration. There is therefore a difference in the temperature values between the high-to-low and low-to-high transitions, having a hysteresis width of $697-531=166$ K in this case.

It is thus that the right branch's solution (indicated by the downward arrow) of the equilibrium segregation equation is obtained with (a) increasing the temperature and (b) high surface coverage as initial value for the solution. The left branch's solution (indicated by the upward arrow) is obtained from a low surface coverage as initial value.

2.2. Criteria for observing the discontinuous transition

It will not be discussed quantitatively at what specific temperatures the discontinuous transition occurs in the equilibrium isosteric segregation measurement. The equilibrium segregation function σ' is defined as in Eq. (2). The function σ' versus surface concentration X^S is plotted in Fig. 3 for the same parameters as described in the caption to Fig. 2. It is clear that the roots of $\sigma'=0$ are the solutions of Eq. (1):

$$\sigma' = \frac{X^S}{1-X^S} - \frac{X^B}{1-X^B}\exp\left[\frac{\Delta G + 2\Omega_{12}(X^S - X^B)}{RT}\right] \tag{2}$$

The two roots of $\sigma'=0$, X_l^S and X_h^S, correspond to the two minima of the Gibbs free energy, and another one, X_c^S, corresponds to the maximum of the Gibbs free energy. These three solutions are possible only if the function σ' has the two extremum points X_-^S and X_+^S, which cause $\sigma'(X_-^S) \times \sigma'(X_+^S) \le 0$, as indicated in Fig. 3. By solving $\partial\sigma'/\partial X^S = 0$, the two extremum points are obtained as:

$$X_\pm^S = \frac{1 \pm \sqrt{1 - T/T^c}}{2} \tag{3}$$

where T^c $(=\Omega_{12}/2R)$ is called the surface critical temperature, and X_+^S and X_-^S are the minimum and maximum points, respectively.

The values for X_+^S and X_-^S will be real only if the temperature T is smaller than the surface critical temperature T^c $(=\Omega_{12}/2R)$, which states the first (but not sufficient) condition for the occurrence of a discontinuous transition:

$$T < T^c = \frac{\Omega_{12}}{2R} \tag{4}$$

The influence of temperature on the function σ' is shown in Fig. 4. As the temperature is increased to $T_+^t = 697$ K, the minimum extremum point merges with the high concentration value X_h^S, as indicated by point P_+ in Fig. 4. Above 697 K the function σ' has only one root, which is equal to the low surface concentration solution X_l^S of Eq. (1). Once the local minimum point X_h^S in Gibbs free energy disappears, the surface concentration X^S will undergo a sharp transition from high to low value — that means a discontinuous transition will take place, and this temperature is defined as the high transition temperature T_+^t.

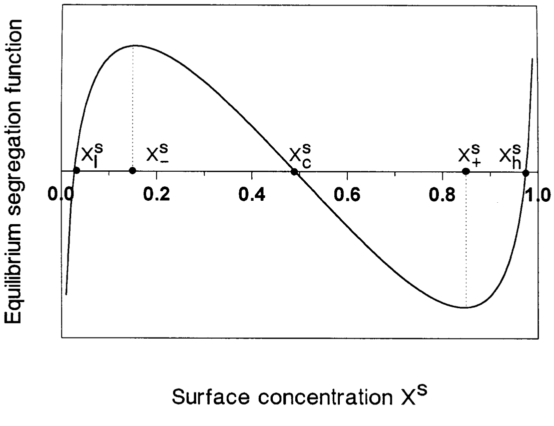

Fig. 3. Equilibrium segregation function σ' for $T=630$ K, $X^B=0.0005$, $\Delta G=20$ kJ/mol and $\Omega_{12}=20$ kJ/mol.

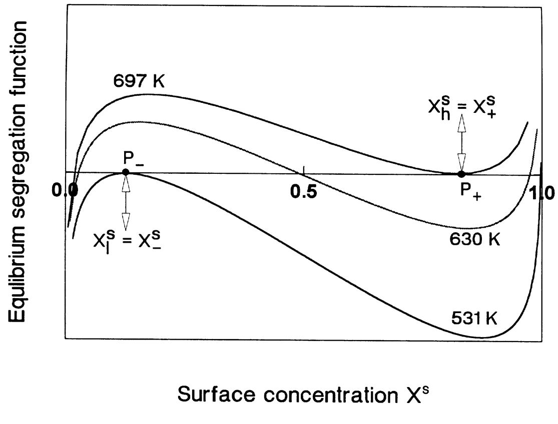

Fig. 4. Equilibrium segregation function σ' for $X^B=0.0005$, $\Delta G=20$ kJ/mol and $\Omega_{12}=20$ kJ/mol at different temperatures.

Clearly, the high transition temperature T^{t}_{+} satisfies:

$$\ln\frac{X^{\mathrm{St}}_{+}}{1-X^{\mathrm{St}}_{+}}=\ln\frac{X^{\mathrm{B}}}{1-X^{\mathrm{B}}}+\frac{\Delta G+2\Omega_{12}(X^{\mathrm{St}}_{+}-X^{\mathrm{B}})}{RT^{\mathrm{t}}_{+}} \tag{5}$$

where X^{St}_{+} is:

$$X^{\mathrm{St}}_{+}=\frac{1+\sqrt{1-T^{\mathrm{t}}_{+}/T^{\mathrm{c}}}}{2}$$

Similarly, if the temperature is decreased to $T^{\mathrm{t}}_{-}=531$ K, X^{S}_{-} merges with $X^{\mathrm{S}}_{\mathrm{l}}$ at point P_{-} as indicated in Fig. 4. Below 531 K the function σ' has only one root, which is equal to the high surface concentration solution $X^{\mathrm{S}}_{\mathrm{h}}$ of Eq. (1). Once the local minimum point $X^{\mathrm{S}}_{\mathrm{l}}$ disappears, the surface concentration X^{S} will undergo a sharp transition from a low to a high value — once again that means the discontinuous transition will take place, and this temperature is defined as the low transition temperature T^{t}_{-}. The low transition temperature T^{t}_{-} satisfies:

$$\ln\frac{X^{\mathrm{St}}_{-}}{1-X^{\mathrm{St}}_{-}}=\ln\frac{X^{\mathrm{B}}}{1-X^{\mathrm{B}}}+\frac{\Delta G+2\Omega_{12}(X^{\mathrm{St}}_{-}-X^{\mathrm{B}})}{RT^{\mathrm{t}}_{-}} \tag{6}$$

where X^{St}_{-} is:

$$X^{\mathrm{St}}_{-}=\frac{1-\sqrt{1-T^{\mathrm{t}}_{-}/T^{\mathrm{c}}}}{2}$$

It should be noted that the two temperatures $T^{\mathrm{t}}_{\pm}$ represent the extreme possible limits of the hysteresis, which actually can be narrower. Once the segregation system is determined, i.e. the segregation energy ΔG and interaction parameter Ω_{12} are fixed, the only other parameter in Eqs. (5) and (6) is the bulk concentration X^{B}. The two transition temperature values $T^{\mathrm{t}}_{\pm}$ will therefore depend on the sample's bulk concentration X^{B} as well, and the surface critical temperature T^{c} cannot be regarded as the transition temperature.

Unfortunately, Eqs. (5) and (6) can be solved by a numerical technique only to obtain numerical values for the transition temperatures $T^{\mathrm{t}}_{\pm}$ since these equations are transcendental. Because of a restriction on the transition temperatures $T^{\mathrm{t}}_{\pm}$ in Eqs. (5) and (6), that is $T^{\mathrm{t}}_{\pm}\leq T^{\mathrm{c}}$, there must be a restriction on X^{B} to obtain the solution of $T^{\mathrm{t}}_{\pm}$. Let:

$$\begin{aligned}g_1(x_+)&=\ln\frac{X^{\mathrm{St}}_{+}}{1-X^{\mathrm{St}}_{+}}-\ln\frac{X^{\mathrm{B}}}{1-X^{\mathrm{B}}}\\&\quad-\frac{\Delta G+2\Omega_{12}(X^{\mathrm{St}}_{+}-X^{\mathrm{B}})}{RT^{\mathrm{t}}_{+}}\\&=\ln\frac{1+\sqrt{1-x_+}}{1-\sqrt{1-x_+}}\\&\quad-\ln\frac{X^{\mathrm{B}}}{1-X^{\mathrm{B}}}-\frac{2(q-2X^{\mathrm{B}})}{x_+}\\&\quad-\frac{2(1+\sqrt{1-x_+})}{x_+}\end{aligned} \tag{7}$$

$$\begin{aligned}g_2(x_-)&=\ln\frac{X^{\mathrm{St}}_{-}}{1-X^{\mathrm{St}}_{-}}-\ln\frac{X^{\mathrm{B}}}{1-X^{\mathrm{B}}}\\&\quad-\frac{\Delta G+2\Omega_{12}(X^{\mathrm{St}}_{-}-X^{\mathrm{B}})}{RT^{\mathrm{t}}_{-}}\\&=\ln\frac{1-\sqrt{1-x_-}}{1+\sqrt{1-x_-}}\\&\quad-\ln\frac{X^{\mathrm{B}}}{1-X^{\mathrm{B}}}-\frac{2(q-2X^{\mathrm{B}})}{x_-}\\&\quad-\frac{2(1-\sqrt{1-x_-})}{x_-}\end{aligned} \tag{8}$$

where $x_{\pm}=T^{\mathrm{t}}_{\pm}/T^{\mathrm{c}}$ and $q=\Delta G/\Omega_{12}$.

The curves of $g_1(x_+)$ versus x_+ and $g_2(x_-)$ versus x_- are plotted in Fig. 5 for three different bulk concentration values. For the smallest bulk concentration the function g_1 or the function g_2 has only one root, which is $T^{\mathrm{t}}_{+}/T^{\mathrm{c}}$ or $T^{\mathrm{t}}_{-}/T^{\mathrm{c}}$, respectively, both smaller than unity. For these ratios smaller than unity, the transition concentration values as defined by Eq. (3) are real. However, for the largest bulk concentration there are no distinct roots and a smooth transition will thus be observed. At a certain bulk concentration X^{BC}, both roots may be shown to be equal to unity — the point indicated by the black square

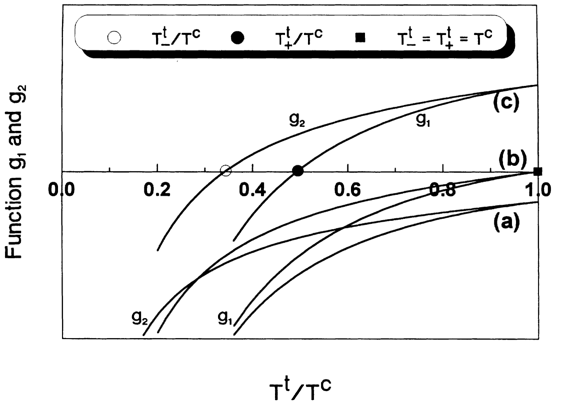

Fig. 5. g_1 and g_2 as functions of T^t/T^c for $q=1$ and at different bulk concentrations: (a) $X^B=0.2$; (b) $X^B=X^{BC}=0.01941$; (c) $X^B=0.0001$.

in Fig. 5. Setting $x_+=x_-=1$ in either Eq. (7) or Eq. (8) and $X^B=X^{BC}$, the equation simplifies to:

$$\ln\frac{X^{BC}}{1-X^{BC}}+2(q-2X^{BC})+2=0 \tag{9}$$

an expression linking the critical bulk concentration X^{BC} to the ratio of the segregation energy ΔG and the interaction parameter Ω_{12} through $q=\Delta G/\Omega_{12}$.

For all bulk concentrations smaller than the critical bulk concentration X^{BC}, a discontinuous transition will be observed. If the bulk concentration X^B is equal to the critical bulk concentration X^{BC}, one finds that the transition temperatures $T^t_\pm$ are equal to the surface critical temperature T^c. Therefore, the surface critical temperature T^c is only the upper limit of the transition temperatures and cannot be regarded as a criterion for the discontinuous transition in the isosteric segregation. The expression obtained here for the critical bulk concentration, X^{BC}, is equivalent to the $T_{0.5}$ criteria in Ref. [14], but is derived with added mathematical rigour.

The influence of ΔG, Ω^S and X^B on the hysteresis effect width in terms of $\Delta=(T^t_+-T^t_-)/T^c$ is displayed in Fig. 6. For a given system (ΔG and Ω^S are fixed), the width of hysteresis effect will first increase and then decrease slowly, as the bulk concentration X^B is decreased. For a given bulk concentration X^B, the width of hysteresis effect

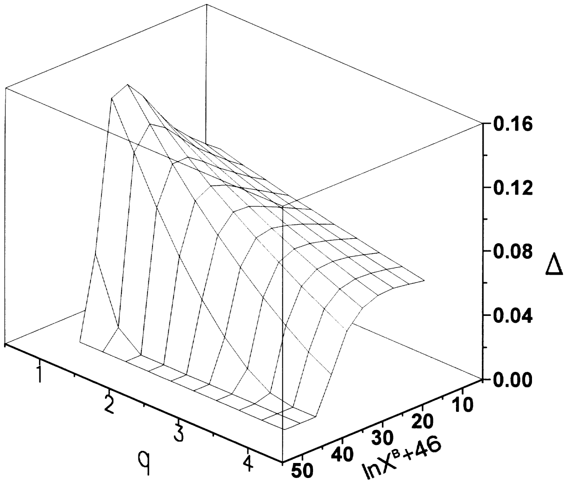

Fig. 6. The dependence of the hysteresis effect (Δ) on q ($=\Delta G/\Omega^S$) and bulk concentration (X^B).

will increase as the value of $q=\Delta G/\Omega^S$ is decreased. The system with smaller segregation energy (ΔG) or larger surface interaction parameter (Ω^S) should be chosen to observe the discontinuous transition in surface segregation experiments. The segregation energy can be compared with the difference between the pure component's sublimation heats [49]. The interaction parameter can be obtained from a phase diagram calculation (see next subsection). Although these comparisons are based on the bulk properties, they are still helpful in surface segregation studies because surface data may be unavailable.

The above analysis is different from existing explanations of the discontinuous transition. The equilibrium surface state [the solution of Eq. (1)] corresponds to the local minimum of the Gibbs free energy of the system in this new analysis, in contrast to the common tangent construction or the absolute minimum point in the Gibbs free energy. By constructing the common tangent on the surface (similar to the equilibrium conditions of bulk phases), Shelton et al. [39] and Guttmann and McLean [50] proposed that the discontinuous transition in surface segregation is associated with the so-called surface miscibility gap. Thus the discontinuous transition would be observed at any temperature smaller than the critical temperature for the system with a positive interaction parameter. However, experimental results do not confirm this suggestion, since the discontinuous transition also depends on the sample's bulk concentration, as can be shown experimentally and theoretically. Wynblatt and Liu [14] also proposed that the discontinuous transition is associated with the surface miscibility gap. In this description the surface equilibrium state corresponds to the absolute minimum point in the Gibbs free energy instead of the common tangent value. Thus only one transition temperature exists at the temperature where the two minimum points in the Gibbs free energy are equal, as indicated by the broken line in Fig. 2. Some experimental results showed [14] that two transition temperatures (hysteresis effect) exist.

2.3. Phase diagram calculation for the Cu(Ag) system

A FORTRAN program [51] was developed to calculate the Cu(Ag) system's phase diagram [52], which consists of a miscibility gap between the two pure element solid phases and the phase boundaries between the solid–liquid phases. Because the regular solution model (with a single interaction parameter) was used for the phase diagram calculation, the phase diagram should be symmetric with respect to the axis $X=0.5$. Since the real system is slightly asymmetric, the Cu-rich side was fitted because the sample in this study was a dilute Cu(Ag) solution.

By comparing the computed phase diagram (thick lines in Fig. 7) with the published phase diagram (thin lines in Fig. 7), the interaction parameter Ω^B of Ag in bulk Cu was estimated as 29.2 kJ/mol, which will be compared with the surface interaction parameter Ω^S obtained by the equilibrium surface segregation measurement later.

3. Experimental

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 a UHV chamber. At the same time a high purity (99.999%) copper polycrystal (as dummy sample) was also doped to the same silver concentration. The crystal and dummy samples were then sealed in a quartz tube under argon gas atmosphere and annealed at 920°C for 25 days to obtain a uniform distribution in the alloy sample. The bulk concentration was determined by dissolving the dummy sample for atomic absorption measurements. This dopant level is well below the solubility limit for silver in copper, 0.3 at% at 400°C. The annealing time to obtain a uniform distribution alloy sample was obtained from the diffusion time for a thin layer on a finite substrate as found in Ref. [53]. The uniformity of this sample corresponded to 99.999% after annealing.

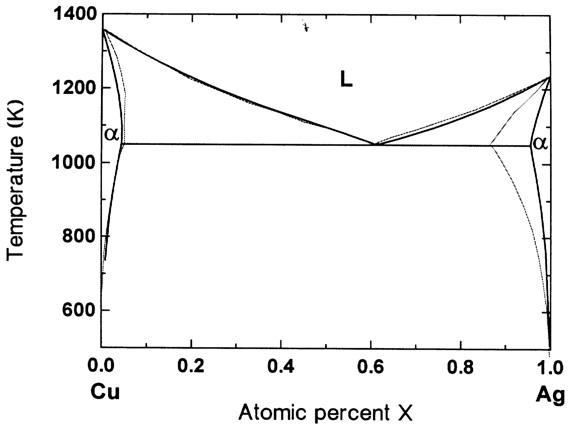

Fig. 7. Comparison between the computed phase diagram (thick lines) and the published phase diagram (thin lines) for the Cu(Ag) system.

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 another dummy copper sample.

The surface concentration of the silver atoms segregating the (111) surface of the copper single crystal was monitored by Auger electron spectroscopy in the temperature range 380 to 550°C. At each constant temperature measurement, the surface was cleaned by argon ion sputtering at 3 keV and ion beam current of 0.35 μA for 240 s. Data acquisition was started at the end of sputtering and was done by a computer in a multiplexing Auger peak-to-peak height (APPH) mode of a locally developed VisiScan program. The Auger peak-to-peak heights APPH(t) for silver (340–360 eV) and copper (900–935 eV) were recorded at a beam voltage of 3 keV and beam current of 15 μA and scanning rate of 3 eV/s as a function of time t. Full Auger spectra were recorded before and after each run. After each run the sample was annealed for 1 h at 600°C to remove any concentration gradient. An Auger spectrum in Fig. 8 showed no segregating elements other than silver, even after 50 h measurement at 406°C. At temperatures above 500°C, the sample surface remained clean for a few hours, although eventually a small amount of sulphur was found to segregate to the surface. However, the kinetics of silver segregation above 500°C were found to be much faster than those of sulphur, so that useful measurements could be made before any sulphur appeared at the surface.

The quantification of surface concentration was based on the Seah scheme [54], in which it is assumed that the segregation is restricted to a monolayer for an interlayer distance of $d=0.208$ nm for the copper (111) planes, that the electron inelastic mean free paths may be approximated by the universal expression of Tanuma et al. (TPP-2) [55], and that the backscattering factors may be calculated from Shimizu [56]. The AES measurements were also made on the standard samples of pure Ag and pure Cu under identical experimental conditions to obtain the ratio of AES intensity of pure Ag to that of pure Cu.

4. Results and discussion

The silver equilibrium surface concentration as a function of temperature is given in Fig. 9 by the closed circles. The characteristic discontinuous transition from a high coverage of $X^{\mathrm{S}}_{\mathrm{Ag}} \approx 0.9$ to $X^{\mathrm{S}}_{\mathrm{Ag}} \approx 0.2$ at around 470°C is the single feature of this curve. As all the data points in the equilibrium curve correspond to the values attained by segregating from a low surface coverage, the points should therefore be fitted with the left branch and the hysteresis therefore lies to the right of the experimental data points. Using the least-squares method, the data are fitted by the equilibrium segregation Eq. (1), as indicated by the solid lines in Fig. 9, for $\Delta G = 24.6 \pm 0.3$ kJ/mol, $\Omega^{\mathrm{S}} = 13.8 \pm 0.3$ kJ/mol, and $X^{\mathrm{B}} = 0.2$ at%. Two transition temperatures are also estimated from the equilibrium data fits, which are the low transition temperature T^{t}_{-} of 463 ± 5°C and the high transition temperature T^{t}_{+} of 477 ± 5°C. The critical bulk concentration for observing the discontinuous transition is estimated as 0.38 ± 0.01 at% in the Cu(111)(Ag) sample.

In the regular solution model, the interaction

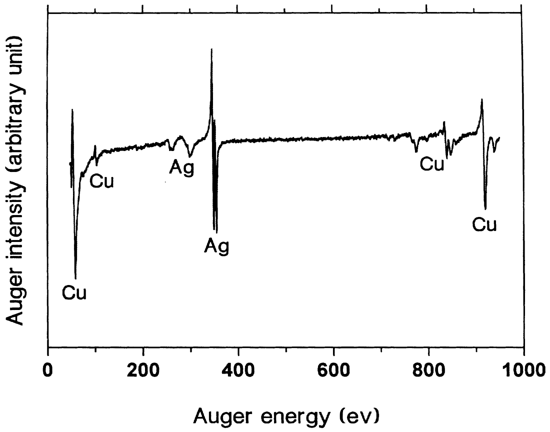

Fig. 8. A typical Auger electron spectrum taken from the Cu(111)(Ag) surface after 50 h at 406°C.

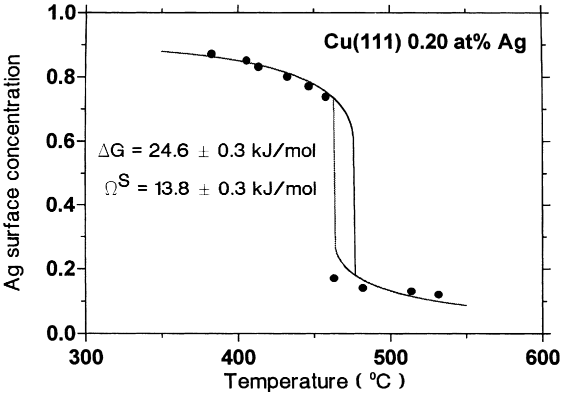

Fig. 9. Fits of Ag equilibrium surface concentration at different temperatures by Eq. (1).

parameter is defined as:

$$\Omega=Z\omega=Z\left[\epsilon_{AB}-\frac{1}{2}(\epsilon_{AA}+\epsilon_{BB})\right]$$

where Z (coordination number) is the nearest-neighbour of atom A or B, ω is the interaction energy per atom pair in one mole, and ϵ_{AB} is the interaction energy per mole between atoms A and B (similarly for ϵ_{AA} and ϵ_{BB}).

The comparison between the surface interaction parameter and the bulk interaction parameter is tabulated in Table 1. It is found that the interaction energy per atom pair (ω) of Ag on the Cu(111) surface is similar to that of Ag in the copper bulk. The interaction energy per atom pair mainly depends on the distance of the two interacting atoms. The fact that the interaction energy per atom pair of Ag on the Cu(111) surface is close to that of Ag in the Cu(111) bulk implies that the distance between interacting atoms on the surface is similar to that in the bulk. So it may be concluded that silver atoms segregated on the Cu(111) surface form the same structure as that of silver atoms in the bulk. It is well known that the alloy of Cu(Ag) is substitutional, so the lattice structure of Ag atoms in the Cu(111) bulk is a Ag(111)-like structure, which is consistent with the LEED pattern to form a $p(9\times9)$, i.e. Ag(111)-like, superstructure on the Cu(111) surface.

The fact that the surface interaction parameter is smaller than the bulk interaction parameter is in contrast to Helms' [57] and Tréglia et al.'s [58] treatments, but similar to Liu and Wynblatt's findings [26].

In Ref. [26], Liu and Wynblatt found evidence for the existence of a mild bulk concentration gradient with the Ag concentration being highest near the surface and dropping off towards the centre of the sample. They decreased their sample's Ag bulk concentration gradually by the periodic spark erosion technique. After several applications of this technique (apparently, at least three), they were able to observe the hysteresis effect in their Cu(111)(Ag) sample. The Ag bulk concentration of their original sample is 0.30 at%, but it may be reasonable to assume that it becomes on the order of 0.25 at% after several spark erosions. Using this bulk concentration value and fitting their equilibrium data by the equilibrium segregation Eq. (1), as shown by the solid lines in Fig. 1, gives the segregation energy ΔG of 24.1 ± 0.3 kJ/mol and the surface interaction parameter Ω^S of 14.0 ± 0.3 kJ/mol, which are the same, within experimental error, as those of the equilibrium data fits in this study for the Cu(111) 0.020 at% Ag sample: ΔG of 24.6 ± 0.3 kJ/mol and Ω^S of 13.8 ± 0.3 kJ/mol.

Table 1
Comparison between the surface interaction parameter and the bulk interaction parameter

Ag in Cu(111)	Nearest neighbours Z	Interaction parameter Ω (kJ/mol)	Interaction per atom pair ω (kJ/mol)
Surface	6	13.8	2.3
Bulk	12	29.2	2.4

Even though the data could be well fitted using Eq. (1), and a good correspondence between the phase diagram calculation values and the fitted segregation parameters could be obtained, a crucial question still remains: why has the hysteresis effect predicted to accompany the discontinuous transition not been observed?

The normal thermodynamic treatment, which has been employed here, treats stability in terms of small fluctuations. For this case, two open systems in contact and one of the systems (the surface) being limited in size, the total energy curve exhibits two minima [44–48]. Small fluctuations around these minima will result in the system returning to the equilibrium state. However, large fluctuations will move the system out of the region of positive curvature and a discontinuous transition from say high to low coverage will occur. These larger fluctuations refer to the statistical variations in surface coverage and not to other parameters such as temperature. They are both unknown and not included in this thermodynamic treatment.

In order to assess the effect of the other variations such as temperature drift, a kinetic model of the surface segregation of the interaction species has since been developed and is reported in detail elsewhere [59]. One feature is shown in Fig. 10.

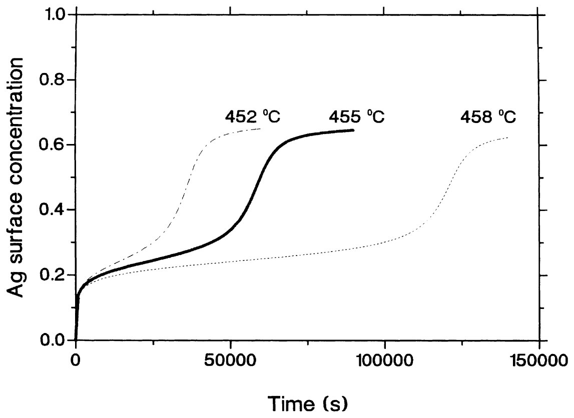

Fig. 10. Kinetic modelling at temperatures close to the transition temperature. A small increase in temperature causes a large increase in the time needed to attain equilibrium, making hysteresis measurements difficult if not impossible.

As the temperature approaches the transition temperature, the kinetics become very slow. This is not due to low temperature, i.e. low diffusion coefficient effects, but as the transition temperature is approached, the Gibbs free energy curve becomes flat and the driving force approaches zero. Any variation in temperature will also tilt the Gibbs free energy curve and result in a discontinuous transition.

Another feature of the kinetic approach is that the system does indeed move from one local equilibrium to the next: the surface concentration is in equilibrium with the subsurface concentration and the surface concentration can only increase once the subsurface concentration reaches a critical level. This is in contrast to previous segregation systems studied. The existence of a local equilibrium therefore depends critically on the segregation parameters (segregation energy ΔG and interaction parameter Ω_{12}) for bulk to surface segregation measurements, but is always observed in dissolution experiments. Criteria for observing local equilibria will be provided in a separate paper.

5. Conclusion

The discontinuous transition of Ag equilibrium surface concentration is observed in the isosteric segregation experiment for the Cu(111) 0.20 at% Ag sample. Contrary to what was expected, no hysteresis was observed, which may have been wiped out by large fluctuations in the surface concentration. Two basic segregation parameters, the surface segregation energy ΔG and interaction parameter Ω^{S} in the equilibrium segregation model, are obtained by the equilibrium segregation data fits as 24.6 ± 0.3 kJ/mol and 13.8 ± 0.3 kJ/mol, respectively. The critical bulk concentration for observing the discontinuous transition is estimated as 0.38 at% for the Cu(111)(Ag) system.

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