The surface orientation dependence of the pre-exponential factors extracted from the segregation profiles of a Cu(111/110) bi-crystal

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Abstract. Previous experimental investigations have only shown, without explanation, that the pre-exponential factor (D_0), in the diffusion coefficient of Sb segregating in Cu, is dependent on the surface orientation of a crystal. In this study, the surface concentration of Sb in a Sb doped Cu(111/110) bi-crystal was measured using a method combining Auger Electron Spectroscopy (AES) and linear temperature heating. Segregation parameters, including the D_0's are extracted from the experimental data of surface concentration versus temperature using the modified Darken model. The difference in the two pre-exponential factors D_0 (Sb in Cu(111)) and D_0 (Sb in Cu(110)) is explained thermodynamically in terms of entropy change ΔS that is calculated, for the first time, for a Cu(111/110) bi-crystal.

1. Introduction

Bulk-to-surface segregation studies are often carried out to determine the bulk diffusion coefficients (D) of the segregating species using the techniques AES, Low Energy Electron Diffraction (LEED), Ion Scattering Spectroscopy (ISS), etc. [1 – 12]. These diffusion and segregation studies of elements in alloys play a major role in the industrial treatment of alloys.

The need to develop improved catalysts for use in connection with environmental protection and the creation of viable alternative energy systems have led to an increasing use of metal alloys as heterogeneous catalysts, in which surface concentration plays a key role in controlling such important factors as activity and selectivity. Segregation in alloys can be used to engineer the properties of a catalytic surface by allowing the active elements to segregate to the surface [13]. Therefore an understanding of these surface phenomena requires knowledge of not only the structure of the surface, but also of the surface composition. The surface composition, in turn, depends on the surface segregation thermodynamics.

One of the parameters that the surface composition depends on is the diffusion coefficient. The pre-exponential factor (D_0), in the diffusion coefficient, depends on the formation and migration entropies. In this study a Cu bi-crystal was doped with Sb and the segregation behaviour used to measure the differences in D_0 for different surface orientations.

2. Theory

It is shown [14] that the diffusion coefficient can be written as:

$$D = f_c \frac{\rho \gamma_A d^2}{6} \tag{1}$$

where f_c is a factor correlating subsequent atomic jumps ($f_c \leq 1$), ρ a probability factor, γ_A the atomic jump frequency and d the jump distance.

For vacancy diffusion ρ is the probability that there is a neighbouring vacancy available to mediate the jump.

The temperature dependence arises from two distinct thermodynamic factors:

- The vacancy formation energy term (it cost thermal energy to create the vacancy).
- The atomic migration energy term (it cost thermal energy to transfer an atom from one site to another).

The Gibbs free energy of vacancy formation is:

$$\Delta g_v = \Delta h_v - T \Delta s_v \tag{2}$$

where Δh_v is the formation enthalpy, T the temperature and Δs_v the formation entropy.

The probability (ρ) of finding a vacancy adjacent to an atom is:

$$\rho = \exp(-\Delta g_v / k_b T) \tag{3}$$

The migration free energy (Δg_m) can be decomposed into enthalpy and entropy terms as:

$$\Delta g_m = \Delta h_m - T \Delta s_m \tag{4}$$

The probability of having sufficient energy to surmount the energy barrier occurs with a frequency proportional to the Boltzmann factor, $\exp(-\Delta g_m / k_b T)$.

The jump frequency of the atom (γ_A) is now equal to the product of the atomic vibrational frequency (v_A) and the probability of executing a jump:

$$\gamma_A = v_A \exp(-\Delta g_m / k_b T) \tag{5}$$

and therefore the diffusion coefficient D can be expanded and expressed as:

$$D = v_A f_c \frac{d^2}{6} \exp[(\Delta s_m + \Delta s_v)/k_B] \times \exp[-(\Delta h_v + \Delta h_m)/k_B T] \tag{6}$$

$$= D_0 \exp[-Q/k_B T]$$

with

$$D_0 = v_A f_c \frac{d^2}{6} \exp[(\Delta s_m + \Delta s_v)/k_B] \tag{7}$$

which is temperature independent and also known as the pre-exponential factor, and

$$Q = \Delta h_v + \Delta h_m \tag{8}$$

also known as the activation energy.

It is clear from equation (7) that, for the same substrate, the D_0's will be determined by the jump distance and vacancy formations entropy terms.

The D_0 for each surface orientation (xxx) can be written as:

$$D_0^{(xxx)} = v_A f_c \frac{d_{(xxx)}^2}{6} \exp\left[\left(\Delta s_m + \Delta s_v^{(xxx)}\right)/k_B\right] \qquad (9)$$

Using equation (9) for both orientations and a few mathematical manipulations the following equation is derived:

$$\Delta S_{\Delta s} = \Delta s_v^{(111)} - \Delta s_v^{(110)} = k_B\left[\ln\left(\frac{D_0^{(111)}}{D_0^{(110)}}\right) - \ln\left(\frac{d_{(111)}^2}{d_{(110)}^2}\right)\right] \qquad (10)$$

where $\Delta s_v^{(111)} - \Delta s_v^{(110)}$ is the difference in the formation entropies ($\Delta S_{\Delta s}$), which can be calculated if the D_0's are known.

3. Experimental

Electron beam physical vapour deposition was used to deposit a thin layer ($\approx$ 20 kÅ) of Sb on the back face of a Cu(111/110) bi-crystal[15], which was purchased from MaTeck GmbH in Germany. The crystal was annealed in a custom build annealing system as described in reference [16]. The homogeneously distributed Sb in the crystal was 0.1 at%. A unique experimental setup and measuring procedure [17] was used to determine the concentration of the segregant as a function of temperature.

A Perkin Elmer Auger spectrometer with a PHI 15-110B single pass cylindrical mirror analyzer was used to measure the Sb surface composition on the bi-crystal. The primary electron beam was alternatively deflected from one orientation to the other as the temperature was ramped and the surface compositions of both orientations were recorded almost simultaneously. Two different linear temperature rates of 0.1 K.s^{-1} and 0.075 K.s^{-1} were used.

The setup ensures the same experimental conditions for both orientations, allowing direct comparison of the segregation data on two different surface orientations. A modified Darken segregation model was used to fit the measured segregation profiles where the segregation parameters were extracted.

4. Results and Discussion

Figure 1 shows the experimental results and segregation model fits for Sb segregation in the Cu(111/110) bi-crystal at a linear temperature ramp of 0.1 K. s^{-1}.

The pre-exponential values used in the segregation model, for the best fits, are summarized in table 1.

From equation (7) it is clear that D_0 is a function of the change in entropy ($\Delta s_m + \Delta s_v$), which includes the terms for, (i) the change in entropy for the migration of an atom in the bulk (Δs_m) and (ii) the change in entropy for vacancy formation (Δs_v). The change in entropy for the migration of an atom in the bulk is assumed to be the same for the (111) and (110) surfaces. The change in entropy for vacancy formation, on the contrary, is different for the two surfaces due to the number of vacancies in the surfaces which results in different pre-exponential factors. It is now possible to calculate the difference in the formation entropies ($\Delta S_{\Delta s}$) between the two surfaces.

Using the parameters in table 1 the difference in formation entropies between (111) and (110) orientations in Cu is calculated as 4.32 k_B ($= 3.7 \times 10^{-4}$ eV.K^{-1}.atom^{-1}).

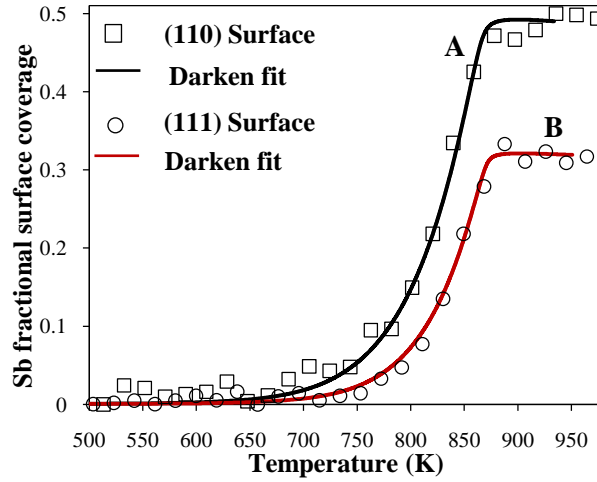**Figure 1.** The measured Sb segregation profiles in (A) Cu(110) and (B) Cu(111) at a heating rate of 0.1 K. s^{-1} and their corresponding modified Darken fits.

Table 1. A summary of the pre-exponential factors experimentally extracted.

Orientation	Rate (K.s^{-1})	D_0 (m^2.s^{-1}) ($\pm 5\%$)	Average D_0 (m^2.s^{-1})
Cu(110)	0.075	2.3×10^{-5}	2.2×10^{-5}
	0.1	2.0×10^{-5}	
Cu(111)	0.075	1.1×10^{-3}	1.1×10^{-3}
	0.1	1.1×10^{-3}	

5. Conclusion

Pre-exponential factors for a Sb doped Cu(111/110) bi-crystal was extracted for the first time. The experimental D_0's measured in this study are in the same range as were calculated and reported by Wynblatt [18].

Comparison of the theoretical calculations of vacancy formation entropy of copper, evaluating the effect of the surface, shows clearly an influence on the formation entropy and that the presence of the surface decreases the entropy approximately by 0.4 k_B [18].

From the pre-exponential factors $D_0^{(110)} = 2.2 \times 10^{-5}$ m^2.s^{-1} and $D_0^{(111)} = 1.1 \times 10^{-3}$ m^2.s^{-1} the difference in the formation entropies was found to be 4.32 k_B. Although the atom jump distance, $d_{(111)}$ and $d_{(110)}$, also contribute to the change in pre-exponential factors, it was demonstrated thermodynamically that the difference is mainly due to the difference in vacancy formation entropy.

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