

The role of the pre-exponential factor in the segregation profiles of Cu(111)-SnSb and Cu(100)-SnSb ternary alloys

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Abstract. Cu(111) and Cu(100) were thermally doped with the same concentrations of Sn (0.14 at%) and Sb (0.12 at%) in both crystals. Auger electron spectroscopy was used to measure the segregation profiles. The segregation parameters of Sn and Sb were extracted by comparing simulated profiles with the experimental data. The segregation profiles in the two crystals were compared and it was found that the profiles of both Sn and Sb in Cu(111) shifts to lower temperatures than those in Cu(100) samples. The quantified segregation parameters were used to explain the shift. It is argued that changes in the pre-exponential diffusion factors, rather than the activation energies, were the main contributing parameter.

1. Introduction

It has become known from binary alloy studies that an impurity that has lower surface energy, larger atomic size as well as having attractive inter-atomic interaction with the host element, will segregate to the grain boundaries or surfaces towards total energy minimization of the alloy [1,2].

Impurity segregation to the grain boundaries of alloys could cause these alloys to become brittle and fail during use. The effects of undesirable low concentration impurities could be neutralised by introducing other impurities that have higher interaction energy, but have no tendency to segregate due to a low segregation energy. The need to understand and quantify segregation parameters is thus necessary for theoretical considerations, designing and manufacturing.

The energetics involved in impurity segregation in ternary and multi-component alloys as well as other segregation parameters have been discussed theoretically and quantified experimentally [3-5]. Besides the bulk concentration, the parameters that account for kinetics segregation of impurity atoms are the activation energy and pre-exponential diffusion factor [6]. In a recent study, Jafta *et al.* [6] have shown that the pre-exponential factor, in the diffusion coefficient of Sb segregating in Cu, is dependent on the surface orientation of a crystal. In this case the authors considered a binary system of a Sb doped Cu(111/110) bi-crystal.

The current study compare the kinetic segregation behaviours of two elemental impurities (Sn and Sb) in two low index surface orientations of Cu and argued that the orientation dependency, in the temperature range studied, is mainly because of a change in the vacancy formation entropy.

2. Experimental

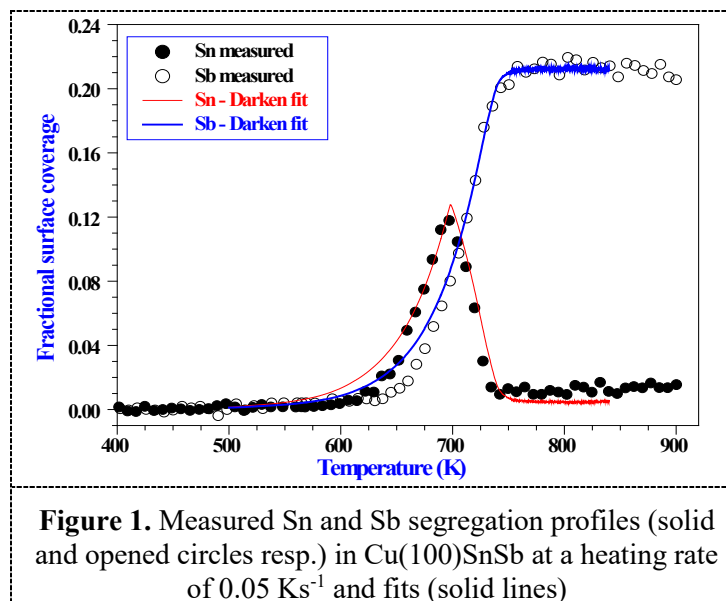
A thin layer of Sn, about 50 kÅ, was evaporated onto pure 99.999 at.% Cu(100) and Cu(111) single crystals. The crystals were sealed in quartz tubes filled with Ar gas and annealed at 920 °C for 44 days to ensure a homogeneous distribution of the elements. The procedures were repeated for Sb (35 kÅ) on the same samples. Atomic adsorption spectroscopy was used to determine the bulk concentrations as 0.14 at.% Sn and 0.12 at.% Sb.

A method of ramping the sample temperature at a constant rate (0.05 K/s) from 400 K to 900 K and at the same time, using AES to measure the surface concentrations in the form of Sn($M_5N_{45}N_{45}$), Sb($M_5N_{45}N_{45}$) and Cu($L_3M_{45}M_{45}$) peaks was followed. Each sample was mounted onto the same resistance heater in a vacuum with base pressure $< 4.0 \times 10^{-9}$ Torr. The temperature was measured with a chromel-alumel thermocouple on the back of the sample.

The measured segregation profiles were simulated with a modified Darken model [7], yielding the segregation parameters.

3. Results and discussion

Figures 1 and 2 show the experimental results and model fits for Sn and Sb segregation in Cu(100) and Cu(111) at a linear temperature ramp of 0.05 K/s. The values of the fitting parameters used are given in Table 1.



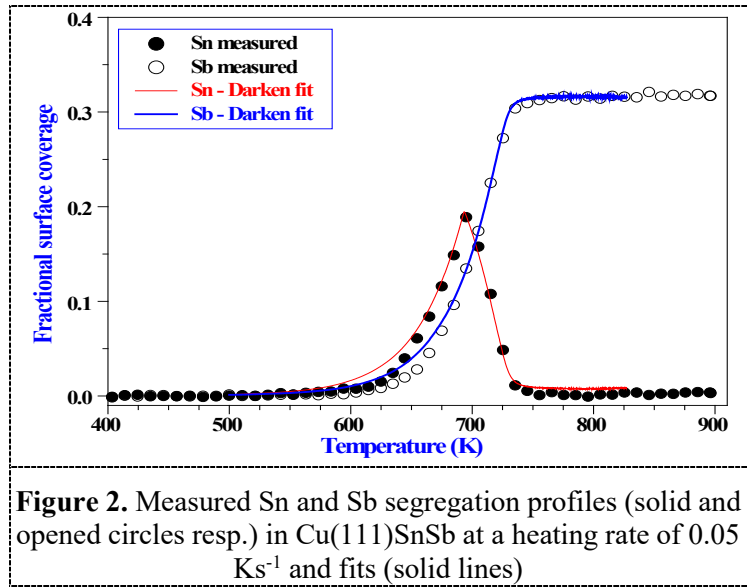


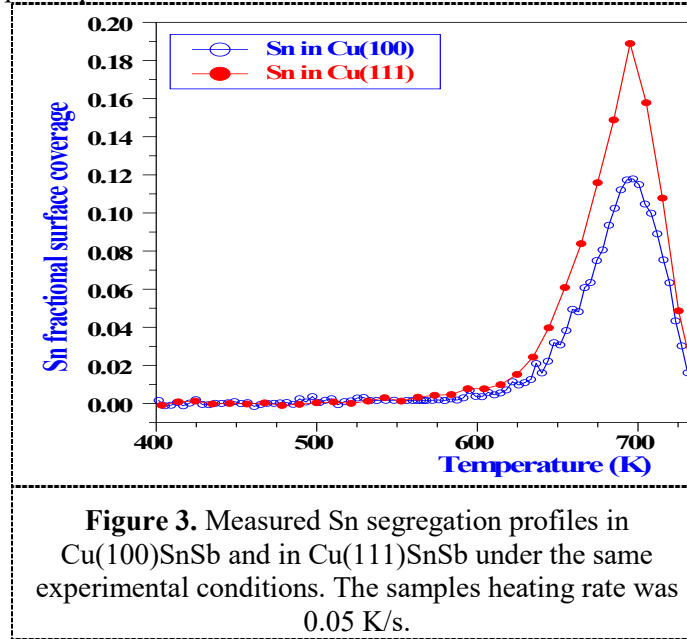
Table 1. Summary of Sn and Sb segregation parameters in Cu(100) and Cu(111).

Orientation	Segregating species	D_0 (m ² s ⁻¹)	E (kJmol ⁻¹)	ΔG (kJmol ⁻¹)	Ω_{Cu-i} (kJmol ⁻¹)	Ω_{Sn-Sb} (kJmol ⁻¹)
Cu(100)	Sn	$(6.3 \pm 0.7) \times 10^{-6}$	175 ± 4	65 ± 5	3.4 ± 0.2	
	Sb	$(2.8 \pm 0.3) \times 10^{-5}$	186 ± 3	84 ± 4	15.9 ± 0.3	-5.4 ± 0.5
Cu(111)	Sn	$(9.3 \pm 0.5) \times 10^{-4}$	196 ± 5	68 ± 4	3.6 ± 0.2	
	Sb	$(3.4 \pm 0.6) \times 10^{-3}$	206 ± 4	86 ± 5	16.2 ± 0.3	-5.3 ± 0.5

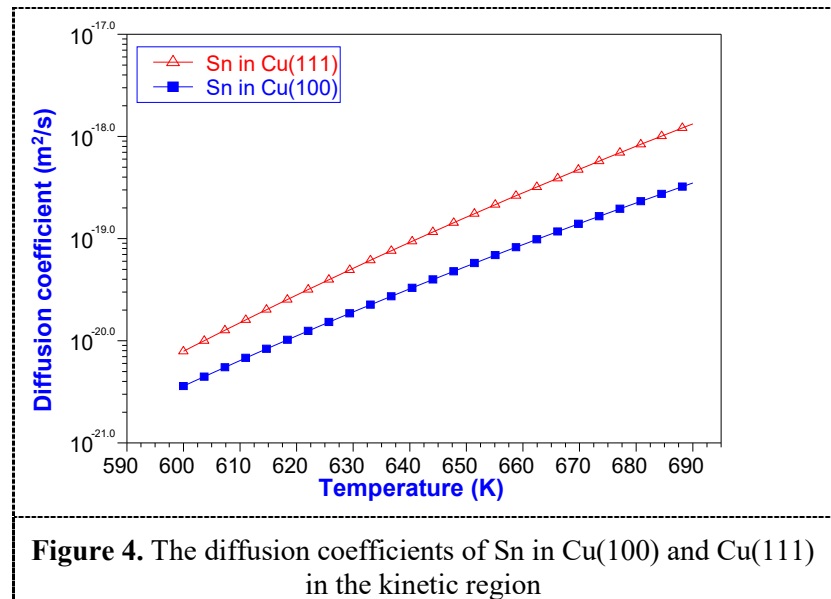
Both figures 1 and 2 clearly show that Sn segregates first, attained some maximum concentration, depending on the orientation, and is then replaced from the surface by Sb [8]. This replacement is because of the lower Sn segregation energy, compared to Sb, as well as the repulsive interaction (Ω_{Sn-Sb}) between the two segregates. The temperature where Sn reaches a maximum coverage on the surface of both orientations is the same and confirms the same bulk concentrations of Sn.

It is well known from thermodynamic segregation theory that the kinetic region of segregation is controlled by the diffusion coefficient of the species. For vacancy diffusion, the activation energy E is the sum of the migration enthalpy, E_m , and the vacancy formation enthalpy E_v . The vacancy formation energy, E_v is defined as the difference between the bulk cohesive and the surface cohesive energies. In a fcc lattice, the vacancy created by a bulk Cu atom has a coordination number of twelfth. On the surface of (100) and (111) orientations the coordination numbers are four and three respectively. The surface cohesive energies of Sn in (100) surface is therefore higher than for the (111) surface. The difference in activation energy between the (100) and (111) orientations for both Sn and Sb is the same (about 20 kJ/mol) see Table 1 indicating that the creation of vacancies is mainly due to Cu atoms. The migration energy is thus a bulk phenomenon and independent of the surface orientations [6]. The two orientations will have different E_v s and are thus orientation dependant. The change in the activation energies between the orientations, is thus because of the change in vacancy formation enthalpies.

The activation energies suggests that, other segregation parameters being equal, the (100) profiles shift to higher temperatures for higher activation energy. However, from the segregation plots of Sn in the two orientations, figure 3, Sn in the Cu(111) profile with $E_{\text{Cu}(111)} = 196 \text{ kJ/mol}$ lies at lower temperatures than the Sn profile in the Cu(100) with $E_{\text{Cu}(100)} = 175 \text{ kJ/mol}$. Similarly, Sb in Cu(111) lies at lower temperatures as compared to Sb in Cu(100). The plausible explanation therefore lies in the differences in the pre-exponential factors.



The pre-exponential factors, D_0 s, depend on the change in entropy of both vacancy formation and migration Gibbs free energies as well as the frequency of vibrations [6]. The values in Table 1, indicate a similar change in entropy between the orientations. This is evident in the ratios of the D_0 s. $D_0(\text{Sn:111})/D_0(\text{Sn:100}) \approx D_0(\text{Sb:111})/D_0(\text{Sb:100})$ resulting in differences in entropy changes of $4.99 k_B$ and $4.79 k_B$ respectively (here $k_B = \text{Boltzmann's constant}$). The entropy change is therefore greater in Cu(111) than in Cu(100). Consequently, Sn in Cu(111) has a higher D_0 ($= 9.3 \times 10^{-4} \text{ m}^2\text{s}^{-1}$) than in Cu(100) with $D_0 = 6.3 \times 10^{-6} \text{ m}^2\text{s}^{-1}$. Noting the same bulk concentration of Sn in the two orientation, the effect of the D_0 s, which is two order of magnitude higher, of Sn in Cu(111) than in Cu(100), could be the plausible way to explain the lower temperature kinetic profile of Sn in Cu(111) as compared to that of Sn in Cu(100). A plot of the diffusion coefficient versus temperature, using the parameters in Table 1, (see figure 4) further confirms the dominant role of the D_0 s in the diffusion coefficient in this temperature region. The same is true for Sb.



4. Conclusion

It has been confirmed experimentally that the segregation parameters of ternary alloys of Cu are orientation dependant if vacancy diffusion plays a role in the kinetics. The changes in diffusion parameters describing the segregation profiles of Sb and Sn in (111) and (100) orientations, proved that the differences are due to different vacancy formation entropies. The changes in the vacancy formation energies are reflected in the changes in activation energies as well as changes in the pre exponential diffusion terms. Both Sn and Sb profiles lie at lower temperatures in Cu(111)SnSb as compared to their profiles in Cu(100)SnSb. In the kinetic temperature range these changes are mainly due to the vacancy formation entropy term differences in the D_0 s which is found to be about $4.8 k_B$ and yielding a higher diffusion coefficient.

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