The Segregation of Bi and S from a Cu(Bi,S) Ternary System

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In this paper the ternary segregation behaviour of Bi and S in a dilute Cu(Bi,S) polycrystalline crystal was investigated by using Auger electron spectroscopy to monitor the surface concentrations of Bi and S during constant temperature segregation measurements that were performed in the temperature range 723 to 973 K at 50 K intervals. It was found that initially both Bi and S segregated to the surface. At first the segregation rate of S was higher than that of Bi. The Bi segregated to the surface until it reached a surface maximum concentration (2-6%) and subsequently the segregation rate of both S and Bi decreased and the Bi started to desegregate. The S replaced the Bi completely on the surface. Diffusion parameters, namely the activation energy \(Q\) and pre-exponential factor \(D_0\) were determined for Bi as 181.6 kJ·mol\(^{-1}\) and 3.7 \times 10^{-5}\text{m}^2\text{s}^{-1}\), respectively. The S concentration in the crystal was unknown and the S segregation profiles were used to estimate the S concentration in the Cu crystal as 122 ± 12 ppm. [DOI: 10.1380/ejssnt.2009.480]

Keywords: Surface segregation; Diffusion; Segregation; Cu; Bi; S; Copper; Bismuth; Sulphur

I. INTRODUCTION

Several authors have studied the Copper-Bismuth system and it is well-documented [1–4]. The low solubility of Bi (Bismuth) in a Cu (Copper) lattice (∼200 ppm) and the affinity of Bi to segregate make this system attractive for investigating basic segregation. Although the Bi segregation from Cu has been investigated extensively, it was surprising that there were only a small number of studies that attempted to determine the diffusion parameters. It is also well known that embrittlement is the result of grain boundary segregation of Bi.

“Temperature embrittlement” is frequently observed with copper and copper-based alloys. This type of embrittlement is seen as a sharp decrease in ductility as the temperature of the sample is gradually increased by a few hundred degrees above room temperature. The onset temperature at which a reduction in ductility begins is in the vicinity of 600 K, and extends over a limited temperature range (∼200 K), above which the ductility increases again. A sharp reduction in ductility of copper and many copper alloys when annealed has serious implications on metal forming processes. These type of materials are normally susceptible to cracking, during deformation or afterwards. The cracking is cause by either residual stress or transient stress that has a thermal origin. (This is generally called “warm shortness” [2].) The “temperature embrittlement” has been linked with the onset of grain boundary sliding which causes voiding at grain boundaries and shifts the fracture mode towards intergranular fracturing [4].

At the atomic scale embrittlement is associated with the weakening of the metal-metal bond strength. If the metal-metal cohesion strength is reduced the metal becomes more brittle and if the cohesion strength is enhanced the metal becomes more ductile. It has been suggested that

the localized charge on the impurity can directly influence the cohesive strength of the metal-metal bonds. If the localized charge of the impurity is more electronegative than the metal host, it will weaken the metal-metal bonds (near the impurity) because fewer electrons are available for the metal-metal bonds. (Most metal embritting elements tend to belong to columns IV to VI of the periodic table and tend to be more electronegative than the host metal [5].) Segregation of impurities to grain boundaries will therefore influence the cohesion strength around these boundaries. Depending on the localized charge of the impurity the interatomic cohesion can be reduced or increased. (Boron in nickel-based alloys is a classical example of a cohesion enhancer [6].) Multicomponent segregation can play a very significant role to engineer the composition at grain boundaries during heat treatments. Segregation may therefore be used to enhance the properties of materials to meet industrial requirements. These alterations of the surface and grain boundary properties are diffusion controlled and it is therefore necessary to study diffusion and segregation.

In an attempted to understand a multicomponent segregation system better it is critical to study the ternary segregation system. In this paper the ternary segregation behaviour of Bi and S in a dilute Cu(Bi,S) polycrystalline sample was investigated. Auger electron spectroscopy was used to monitor the surface concentrations of Bi and S during bulk-to-surface segregation studies. The bulk diffusion parameters of Bi segregation from a Cu crystal and the S concentration in the diluted crystal were determined.

II. THEORY

Segregating kinetics depends on the rate at which atoms move from the bulk to a surface. The segregation rate is coupled to the bulk mobility of the segregating atoms [7, 8]. If one assumes that there is no interaction between the segregating atoms, then the rate at which atoms are transferred from near the surface to on the surface is independent of the surface concentration of the segregated atoms. It is as if the segregating atoms are being
removed from the surface as soon as they arrive. Mathematically the surface concentration \( C(x=0) \) is kept at a zero value for all time. It is also assumed that the bulk concentration of the segregating species is uniform in the bulk initially (at time \( t = 0 \)). The boundary and initial conditions are:

\[
C(x) = 0 \quad \text{at} \quad x = 0 \quad \text{for} \quad t \geq 0;
C(x) = C(B) \quad \text{at} \quad x > 0 \quad \text{for} \quad t = 0.
\] (1)

Atoms that segregate to the surface of a crystal have to diffuse from the bulk. The diffusion in the bulk can be described with Fick’s second law:

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}.
\] (2)

With the help of Laplace transformations and the conditions set (Eq. (1)) it is possible to solve Fick’s second law (Eq. (2)). The solution (Eq. (3)) describes how the bulk concentration changes with time, due to the diffusion. The full derivation may be found in “The Mathematics of Diffusion” by Crank [9]:

\[
C_t^{(x)} = C(B) \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right),
\] (3)

where \( C_t^{(x)} \) is the concentration of the diffusing species at time \( t \) at a distance \( x \), \( C(B) \) is the initial concentration of the diffusing species in the bulk and \( D \) is the diffusion coefficient.

From Eq. (3) it is possible to derive an expression for the flux of atoms that are moving through the surface at \( x = 0 \). The total number of atoms that have left the crystal through an area \( A \) at \( x = 0 \) during time \( t \) can be calculated by integrating the flux and multiplying it with the area. The surface concentration is calculated by assuming that all the atoms that have left the crystal are situated on the surface. The surface concentration is equal to the total amount of atoms on the surface divided by the surface volume. The full derivation may be found in “Solid State Phenomena–Surface Segregation” [10]:

\[
C_t^\phi = C(B) \left[ 1 + 2 \left( \frac{Dt}{\pi} \right)^{\frac{1}{2}} \right],
\] (4)

where \( C_t^\phi \) is the surface concentration of the diffusing species at time \( t \).

This expression is widely used to describe the time dependence of the segregated surface concentration [11–14]. The derivation is partially shown here to emphasised that the initial bulk concentration in the crystal must be constant when a segregation measurement is started. (Experimentally it is difficult to comply with this initial condition.) Two procedures may be followed to measure the change in surface concentration as a function of time \( t \) in order to determine the segregation parameters:

**Procedure 1:**

The sample is sputter cleaned at low (room) temperature and then the temperature is increased to the desired segregation temperature where the surface concentration is recorded as a function of time \( t \). Since the sample heater response is slow, some time is required to reach the desired temperature. During this time the segregating atoms start to segregate at temperatures that are not well defined (or known) and the condition for the constant diffusion constant \( (D) \), for which Eq. (4) is valid, is violated.

**Procedure 2:**

The sample is heated to the desired segregation temperature and then sputter cleaned. During the cleaning process, the segregating atoms segregate to the surface causing the bulk concentration near the surface to change and the initial condition (constant bulk concentration) for Eq. (4) is violated.

Du Plessis et al. [15] define a time scale (\( t' \)) for the segregation to start simultaneously with the sputtering. The total time that the sample is sputtered is \( t'_0 \). The time scale for the surface concentration measurements is \( t \). The segregation has started at \( t' = 0 \) and at this stage the bulk concentration is constant and the temperature is also constant for the rest of the time that segregation takes place. It is therefore acceptable to use Eq. (4) to calculate the surface concentration in the time scale \( t' \). It is clear that \( t' = t + t'_0 \).

The number of sputtered atoms removed from the surface by sputtering is given by

\[
C_{\text{sputter}}^\phi = C_t^\phi - C_{0}^\phi,
\] (5)

where \( C_t^\phi \) is the number of segregated atoms that were not removed by the sputtering. The concentration on the surface after time \( t' \) would therefore be given by:

\[
C_{\text{nett}}^\phi = C_t^\phi - C_{\text{sputter}}^\phi.
\] (6)

Substitution of Eq. (5) into Eq. (6) gives

\[
C_{\text{nett}}^\phi = C_{t}^\phi - (C_{t}^\phi - C_{0}^\phi),
\] (7)

and then substitution of Eq. (4) into Eq. (7) and transforming the time scale to \( t \) gives that

\[
C_t^\phi = C_{0}^\phi + C^B \left[ 1 + \frac{2}{d} \left( \frac{D(t + t_0)}{\pi} \right)^{\frac{1}{2}} \right] - C_{0}^\phi \left[ \frac{2}{d} \left( \frac{D(t_0)}{\pi} \right)^{\frac{1}{2}} \right].
\] (8)

This equation is well adapted to compensate for the segregation that occurs during sputtering. A more detailed derivation can be found in the publication by du Plessis et al. [15].

One of the main shortcomings of Eq. (8) is it inability to predict equilibrium concentrations, although it is very good in describing the kinetic segregation. A better model that can be used to model both kinetic and equilibrium segregation is the Darken model. A huge disadvantage of the Darken model is difficulty in solving the large set of coupled stiff differential equations. The numerical solution procedures are calculation time intensive and take up large amounts of computer time. If the bulk concentrations are very low (as is the case here) it is virtually impossible to solve the Darken model. However it is possible to make some predictions regarding the segregation parameters from the form of the segregating profiles.
A. The modified Darken

The modified Darken model [10, 16] is based on the assumption that the driving force for segregation is the minimization of the total energy of the crystal. (Fick used the concentration gradient as the force for diffusion.) The segregating atoms (in this case S and Bi) will therefore move from a position with a higher chemical potential (the bulk) to a position with a lower chemical potential (the surface), and as a result the total energy of the crystal will be lowered. In the modified Darken model the crystal (in this case a Cu single crystal) is divided into \((N+1)\) layers of thickness \(d\) parallel to the surface and the flux of atoms from the \((j+1)\)-th layer to the \(j\)-th layer is given by [10]

\[
J_{i}^{j+1-j} = M_{i}C_{i}^{(j+1)}\left(\frac{\Delta \mu_{i}^{(j+1-j)}}{d}\right),
\]

where \(M_{i}\) is the mobility of the segregating species \(i\) in the bulk (related to the diffusion coefficient), \(C_{i}^{(j+1)}\) is the concentration of species \(i\) in the \((j+1)\)-th layer, \(d\) is the layer thickness and \(\Delta \mu_{i}^{(j+1-j)}\) is the change in chemical potential when species \(i\) move from the \((j+1)\)-th layer to the \(j\)-th layer, which is calculated using

\[
\Delta \mu_{i}^{(j+1-j)} = \left[\mu_{i}^{(j+1)} - \mu_{i}^{(j)}\right] - \left[\mu_{m}^{(j+1)} - \mu_{m}^{(j)}\right],
\]

where \(\mu_{i}^{(j+1)}\) is the chemical potential of species \(i\) in layer \((j+1)\) and \(\mu_{m}^{(j+1)}\) is the chemical potential of the matrix element in layer \((j+1)\). Using Eq. (9) for the flux of atoms between the different layers, a system of coupled non-linear differential equations (11) can be derived. This system of differential equations describes the rate at which the concentration of species \(i\) changes with time in terms of the chemical potential and the mobility of the segregating atoms:

\[
\begin{align*}
\frac{\partial C_{i}^{0}}{\partial t} &= \left(\frac{M_{i}^{(B_{i}-\phi)}C_{i}^{B_{i}}}{d^{2}}\right)\Delta \mu_{i}^{(B_{i}-\phi)}; \\
\frac{\partial C_{i}^{B_{1}}}{\partial t} &= \left(\frac{M_{i}^{(B_{2}-B_{1})}C_{i}^{B_{2}}}{d^{2}}\right)\Delta \mu_{i}^{(B_{2}-B_{1})} - \left(\frac{M_{i}^{(B_{1}-\phi)}C_{i}^{B_{1}}}{d^{2}}\right)\Delta \mu_{i}^{(B_{1}-\phi)}; \\
\vdots \\
\frac{\partial C_{i}^{j}}{\partial t} &= \left(\frac{M_{i}^{(j+1-j)}C_{i}^{j+1}}{d^{2}}\right)\Delta \mu_{i}^{(j+1-j)} - \left(\frac{M_{i}^{(j-j-1)}C_{i}^{j}}{d^{2}}\right)\Delta \mu_{i}^{(j-j-1)}.
\end{align*}
\]

Equation (11) can describe the entire segregation profile (kinetic as well as equilibrium part). Swart et al. [17] solved Eq. (11) and calculated the kinetic and equilibrium surface concentration for a ternary system (two impurities plus the matrix element). These calculations were preformed systematically to illustrate the effects of the different parameters on a segregation profile. The effect of the impurity concentration in the bulk on the segregation rate was clearly pointed out by Swart et al. The role of the difference in Bi and S concentration will also be illustrated in this paper.

III. EXPERIMENTAL

The copper crystal doped with Bi and S was mechanically polished down to 1 \(\mu m\) using a diamond suspension. The polished crystal was mounted on a resistance heater (inside the UHV chamber) with a built-in chromel–alumel thermocouple (Type K) directly at the back of the crystal. The temperature measured at the back of the crystal was calibrated in terms of the true surface temperature. The calibration was preformed by pressing a second calibration thermocouple against the surface of the sample. Once the calibration was completed the sample was placed in front of the Auger analyzer. The Auger system was equipped with a single-pass cylindrical mirror analyzer (Physical Electronics PHI 25–110) with a co-axial 10 keV electron gun (Physical Electronics PHI 18–085) and an ion gun (Perkin Elmer 04–303). The Auger data was recorded with an electron beam energy of 5 keV and a beam current of 5 \(\mu A\). The angle between the electron beam and the normal to the sample surface was 30°. The modulation voltage was 2 eV for all the measurements and the UHV chamber was ion pumped to a base pressure of \(2 \times 10^{-9}\) Torr.

Segregation measurements at constant temperatures were carried out between 723 K and 973 K at 50 K intervals. The sample was heated to the desired temperature, and after stabilisation of the temperature the sample was sputter cleaned with a 2 keV argon ion beam for exactly 300 s. Data acquisition was started immediately after sputtering by recording the Auger peaks for Cu (66 eV), Bi (105 eV), S (153 eV) and Cu (922 eV). The Auger peak-to-peak heights (APPH) were extracted from the data afterwards. The Bi (105 eV) peak is relatively close to the Cu (110 eV) peak and therefore a peak isolation technique was employed to separate the Bi peak before
determining its APPH. The APPH data was quantified using the method of Ichimura [18] and our own elemental standards.

IV. RESULTS AND DISCUSSIONS

A few of the segregation profiles that were recorded at constant temperature are shown in Fig. 1. From these profiles it is clear that initially both Bi and S segregated to the surface. At first the segregation rate of S was larger than that of Bi. This is an indication that the bulk concentration of S is much larger than that of Bi since the diffusion coefficient of Bi is actually larger that that of S (see Fig. 2). The diffusion coefficients that are shown in Fig. 2 for Bi and S as function of temperature were calculated by using diffusion data from literature [19, 20]. The Bi segregated to the surface until it reached a maximum concentration (~8%) as can bee seen in Fig. 1. At this point the segregation rate of S decreased and the Bi started to desegregate. This type of behaviour is explained completely by Swart et al. [17]. From the graphs it is also clear that the desegregation rate of Bi is lower than its initial segregation rate. There is also a decrease in the segregation rate of S. The S segregation continued until the Bi was completely replaced on the surface. The maximum S concentration at equilibrium was ~50%. From literature it is known that the segregation energy of Bi is ~54.1 kJ·mol$^{-1}$ [21]. Since the S reaches a higher equilibrium concentration it may be that the S has an even lower segregation energy (more negative). The fact that the Bi is completely replaced from the surface by the S is an indication that there is a strong interaction between the Bi and S (see [17]).

Although this segregation system is a ternary system (Cu, Bi, S), the initial segregation (when the surface concentration is low) acts like a classical binary system. The initial parts of the segregation profiles can therefore be used to extract the segregation parameters ($D_0$ and $Q$).

Two objectives were set, firstly to determine the diffusion parameter for Bi diffusing in Cu and secondly to determine the bulk concentration of S in the crystal.

A. Bismuth Segregation

The Bi segregation profiles were plotted as a function of $t^{1/2}$ (Fig. 3). The initial parts of the segregation profiles do not show a linear relationship with $t^{1/2}$. It is clear that the segregation that occurred during sputtering significantly altered the bulk concentration profile. It is therefore not possible to use Eq. (4) to extract the diffusion coefficients from the experimental data. BNALib (Basic Numerical Analysis Library for Personal Computers) mathematical routines were used for the profile fits. The solid lines in Fig. 3 are the fits performed on the experimental data utilizing Eq. (8), which is more appropriate to use since it compensates for the segregation that altered the bulk concentration profile during the pre-cleaning (sputtering) step. The diffusion coefficients ($D$) that were extracted are listed in Table I.

The temperature dependence of the diffusion coefficient is normally described by the Arrhenius equation (12)

$$D = D_0 e^{-\frac{Q}{RT}}.$$  (12)
B. Sulphur Concentration

The S diffusion coefficient is known from previous measurements, making it possible to estimate the S bulk concentration by utilizing Eq. (8). Equation (8) was used for the same reasons that were emphasised in the previous section. Examples of the segregation profiles are shown in Fig. 5. The solid lines are best fits of Eq. (8). By using diffusion coefficients for S calculated with $D_0 = 2.3 \times 10^{-5}$ m$^2$s$^{-1}$ and $Q = 205.9$ kJ mol$^{-1}$ [20], the S bulk concentration was calculated for each segregation profile. The results are shown in Table II. The average bulk concentration for S was determined as $122 \pm 12$ ppm.

V. CONCLUSION

The BNALib (Basic Numerical Analysis Library for Personal Computers) mathematical routines was used to fit the derived diffusion equation on the experimental data and the diffusion parameters for Bi and as well as the bulk concentration for S were extracted. The activation energy ($Q$) and the pre-exponential factor ($D_0$) were determined as 181.6 kJ mol$^{-1}$ and $3.7 \times 10^{-5}$ m$^2$s$^{-1}$, respectively. The S bulk concentration was calculated to be $122 \pm 12$ ppm. The shape and trends that were observed in the segregation profiles suggest that S has an even lower segregation energy (more negative) that Bi and that there is a strong interaction between the Bi and S. The interaction parameters will be determined in a follow-up paper.

### Table I: The diffusion coefficients for Bi diffusion in Cu calculated form the segregation profiles, Fig. 3, recorded for varies temperatures.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Diffusion coefficient (m$^2$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>723</td>
<td>$1.9 \times 10^{-18}$</td>
</tr>
<tr>
<td>773</td>
<td>$1.7 \times 10^{-17}$</td>
</tr>
<tr>
<td>823</td>
<td>$2.2 \times 10^{-16}$</td>
</tr>
<tr>
<td>873</td>
<td>$6.3 \times 10^{-16}$</td>
</tr>
<tr>
<td>923</td>
<td>$2.7 \times 10^{-16}$</td>
</tr>
<tr>
<td>973</td>
<td>$3.3 \times 10^{-16}$</td>
</tr>
</tbody>
</table>

### Table II: The S bulk concentration calculated from the segregation profile recorded at varies temperatures.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>S bulk concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>723</td>
<td>223</td>
</tr>
<tr>
<td>773</td>
<td>112</td>
</tr>
<tr>
<td>823</td>
<td>126</td>
</tr>
<tr>
<td>873</td>
<td>96</td>
</tr>
<tr>
<td>923</td>
<td>78</td>
</tr>
<tr>
<td>973</td>
<td>97</td>
</tr>
</tbody>
</table>

Average S bulk concentration: 122