THE RELATIONSHIP BETWEEN GRAIN BOUNDARY SEGREGATION AND THE SOLIDUS LINE IN THE Cu–Bi SYSTEM

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Abstract

The temperature dependence of the grain boundary segregation of Bi in Cu polycrystals containing 6, 13, 25, 50, 75 and 102 at ppm Bi has been studied. It was found that the segregation behaviour of Bi in Cu is connected with the solidus line of the bulk Cu–Bi phase diagram. A prewetting model was developed to explain this behaviour. A grain boundary solidus line calculated in the framework of the prewetting model is presented.

Introduction

In previous works about the grain boundary (GB) segregation in the Cu–Bi system it is often discussed whether the observed GB adsorption of Bi exceeding one monolayer can be explained by the formation of a two-dimensional GB phase. For answering this question, the knowledge of the bulk phase diagram is needed. Only when the Cu–Bi alloy is in the single-phase region of the bulk phase diagram, the Bi enrichment on the GB can be considered as a real GB segregation. In the two-phase region of the phase diagram the precipitation of a new phase on the GB is possible. Recently, we re-investigated the Cu-rich side of the Cu–Bi phase diagram in the temperature interval 600–1050°C [1]. The determined solidus line in a narrow range of Bi concentrations up to 200 at ppm is drawn as a thick solid line in Fig. 1. The other symbols and lines in Fig. 1 will be discussed later in the following paragraphs.

In order to establish a relationship between the bulk phase diagram and Bi segregation on GBs in the Cu–Bi system, we investigated the GB segregation of Bi in six Cu–Bi alloys in the temperature interval 400–1050°C.

Experimental and Results

Experiments were carried out in Cu-Bi specimens containing 6, 13, 25, 50, 75 and 102 at ppm Bi. After the annealing of polycrystalline Cu–Bi specimens and the in-situ fracture in the ultra-high vacuum chamber of the PHI 600 Scanning Auger Multiprobe, the Bi adsorption was measured at 20–30 various sites of the fracture surfaces via Auger electron spectroscopy (AES). Under the usual assumption that the
fracture crack propagates along general high-energy GBs, one obtains the Bi adsorption for general GBs from the calculation of the average adsorption value. The amount of segregation as presented throughout this work is given in the unit of monolayers (ML). One ML of pure Bi contains 9.3 atoms/nm².

The temperature dependence of Bi adsorption for three alloys studied is shown in Fig. 2. It is seen that the average value of Bi adsorption changes abruptly from about 2 ML down to a value between 1 and 1.5 ML. The temperature dependencies of the Bi adsorption for the other alloys are quantitatively similar to those shown in Figs. 2a and b. In specimens containing 102 at ppm Bi (Fig. 2c) two jumps of the GB segregation were observed: at a temperature between 900 and 950°C the Bi adsorption decreases from a value of 2 ML to a value of 1.5 ML with increasing temperature, while at a temperature between 1000 and 1020°C an opposite jump

![Graph showing temperature dependence of Bi adsorption](image)

Fig. 1. Comparison of the segregation data with the solidus line on the Cu-rich side of the Cu–Bi phase diagram.
takes place. This is a proof that the GB segregation in a binary system can increase with increasing temperature. The lower values of the Bi adsorption in Cu–6 at.ppm Bi at 400 and 500°C indicate that the annealing times were not long enough for reaching the equilibrium and they are drawn in parentheses.

Figure 1 presents the Cu-rich side of the Cu–Bi phase diagram together with the data of GB segregation. At Bi bulk concentrations below 25 at.ppm the jump temperature agrees well with the solidus temperature of the alloy. Above 25 at.ppm Bi the jump temperature deviates from the solidus line. The difference between the jump temperature and solidus temperature increases as the Bi concentration increases.

![Graphs showing GB segregation with Bi concentration and temperature](image)

**Fig. 2.** Temperature dependence of the GB segregation of Bi in Cu–Bi alloys containing 6, 25 and 102 at.ppm Bi.

**Discussion**

The phenomena described above cannot be explained by a classical segregation model (McLean model or Fowler model). Both models as well as a more realistic model from Sutton and Balluffi [2], which permits a spectrum of segregation enthalpies at various GB sites, can only predict a decrease of the GB adsorption with increasing temperature. The non-equilibrium segregation discussed by Muschik et al. [3] can explain an increase of the GB adsorption with increasing temperature, however, the magnitude of the effect is negligibly small (less than 0.01 ML).
Therefore, we have developed a new thermodynamic prewetting model for the description of the GB segregation [4, 5]. In this model a thin film of a quasi-liquid phase can form at the GB to reduce the high chemical energy of the interface between the bulk solid and GB phase. The formation of the quasi-liquid phase can be considered as a GB phase transition. Because the liquid Cu–Bi phase contains much more Bi than the Cu-based solid solution, this phase transition is connected with an abrupt change of the Bi adsorption at the GB. A quantitative consideration shows that this phase transition occurs in the vicinity of the bulk solidus line.

The lines in Fig. 2 represent the calculated temperature dependence of the Bi adsorption at the GB by the prewetting model. The jump temperatures of the GB segregation at the calculated curves agree well with the experimental values. Below 25 at ppm Bi the coincidence between the jump temperature and solidus line can also be explained in the framework of this model (see Fig. 1). The quantitative discrepancy between the model and experiment at high temperatures and Bi concentrations results from a variable thickness of the quasi-liquid film. The thin line in Fig. 1 shows the calculated jump temperatures in dependence of the Bi bulk concentration. On the left side of this line the GB adsorption is below 1.5 ML (open squares) or the specimens were not intergranular fractured (cross), while on its right side the GB adsorption exceeds 2 ML (filled squares). In the framework of the prewetting model a GB segregation of two or more ML is related with the formation of a quasi-liquid phase at the GB. Because of its similarity with the bulk solidus line the dashed line is called grain boundary solidus line. In conclusion, on the left side of the line only the GB phase is stable at the location of a GB, while on the other side both the GB and quasi-liquid phase co-exist in a sandwich-like form. In other words, only on the left side of the GB solidus line the Bi enrichment can be considered as a real GB segregation. However, even in the region between the bulk and GB solidus lines this enrichment results not only from the real GB segregation but also from the quasi-liquid phase.

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