DIRECT OBSERVATION OF THERMAL EFFECT APPEARANCE DURING GRAIN BOUNDARIES COMPLETE WETTING TRANSITION IN COPPER-BISMUTH SYSTEM

Ass. Novikov A¹, PhD Kondratiev A., Prof. Dr. Eng. Bokstein D., Prof. Dr. Eng. Petelin A², PhD Novikova E.
National University of Science and Technology «MISIS»
E-mail:¹ novikov@misis.ru, ²alexander-petelin@yandex.ru

Abstract: Grain boundary wetting process takes place during the contact of solid metal phase with the metal melt. The liquid bismuth network formation along grain boundaries (GB) connected with wetting process was investigated in copper polycrystalline samples. The endothermic thermal effect in the temperature range close to complete GBs wetting transition temperature for Cu-Bi system was observed. Thermal effect size of GB wetting per mol of copper passed into bismuth melt during process of forming wetting GB channels was characterized as 21-23 kJ/mol.

KEYWORDS: GRAIN BOUNDARIES, COMPLETE WETTING, COPPER, BISMUTH, THERMAL EFFECT, TRANSITION TEMPERATURE

1. Introduction
Grain boundaries wetting via interaction of solid copper with bismuth melt saturated with copper was investigated in detail in works of several liquid-metal wetting research teams [1, 2]. In particular it has been found that in temperature interval 560 – 620 °C in polycrystal copper samples transition to grain boundaries (GB) complete wetting takes place, wherein GB surface energy (γSL) passes through a value equal to double energy of boundary surface solid copper - melt (2γSL) and by further heating becomes larger than it. Each GB in polycrystal has its own complete wetting transition temperature [3] that is due to the fact that GB surface energy is different in any single case because of individual crystallographic misorientation of bound grains [4]. As a consequence, complete wetting transition temperature range in polycrystal occurs. At temperatures higher than complete wetting temperature, instead of GB a substitutional grain boundary melt channel forms; and it “eats” overtime GB al over it [5].

The morphology of complete wetting growing channels and kinetics of their growth were investigated in [6]. In the work [7] it is marked that via passing to complete wetting negligible positive (absorbing) thermal effect may be observed. The reasons and the value of the effect, as well as the fact of its existence are still opened to question. That is why the aim of this investigation was reliable detection of GB complete wetting transition thermal effect and its quantitative assessment for the system copper – bismuth.

2. Experimental
For the thermic analysis of thermal effect interactability connected with GB wetting with melt the process of polycrystal copper sample should be investigated, i.e. the sample that contains large amount of GBs in contact with bismuth. At temperature close to 271 °C (melting point of pure bismuth) bismuth, saturated with copper, melts, that provides melt interactability with GBs of solid copper sample via further heating. The heating process itself as well as concurrent thermal effects measurement was carried out with the use of differential scanning calorimeter DSC Labsys.

In experiments copper (with purity 99,996 mass %) and chemically pure bismuth (99,99 mass %) were used. Bismuth melt was saturated with copper till the saturation concentration at a temperature of 650 °C.

Studying the process of heating the copper in contact with bismuth was carried out in two variants. They differ in that: in the first case the copper samples with a polycrystal structure with a predetermined grain size were used. In the second case, the copper samples, that were prepared, have the same size and shape as in the first case but which have a monocrystal structure. It helps to identify effects associated only with GBs, because in the first case (a polycrystal) there were enough of them, and at a given grain size we could make an estimate of their total amount in the test sample. In the second case, they were no effects (a monocrystal), and thus GB grooves and channels at complete wetting could not be formed. (Volume dissolution of copper samples in both cases could not occur, because they were in contact with saturated with copper bismuth melt).

For polycrystal and monocrystal versions of copper samples the original copper subjected to preliminary mechanical deformation (sediment under pressure) and subsequent heat treatment. Selection of an appropriate heat treatment conditions in the first case provided the polycrystal samples with an average grain size of 50 microns. Heat treatment in the second case allowed growing to a value of grain diameter of 5-7 mm. The grain size was determined by optical microscope Leica DMILM and scanning electron microscope Hitachi S-800. Using the method of electroerosion cutting, the copper samples were cut from large grain preform to monocrystal containing no more than one of each grain. The size of each copper blanks for runs in the first and second cases was the same. Blanks were made as thin circular disks of thickness 300 mm and 5 mm in diameter, which corresponds to the conditions of their use in the differential scanning calorimeter Setaram «ALexSys».

In both cases copper plates in contact with crushed bismuth (saturated with copper) were put into alumina crucible posed in the calorimeter. In the atmosphere of high-purity argon the samples were heated with the rate 5 K/min from room temperature (25°C) to 650 °C, and inverse cooling with the same rate to room temperature. Consequently, calorimetric curves “heating –cooling” became available:- in the first variant – for the polycrystal copper plates in contact with bismuth;- in the second variant – for the monocrystal copper plates in contact with bismuth. Basic materials and experimental regimes in both cases were the same.

3. Results
Fig. 1 shows the thermal heating curves of polycrystal copper samples in bismuth (upper curve) and monocrystal copper samples in bismuth (lower curve). At a temperature of about 270 °C (the exact value of 267 °C) in both curves the deep (substantial) positive thermal effect is observed. It is associated with the melting of bismuth (saturated with copper) that is present in both cases. Further heating to a temperature of 590 °C for both variants occur
without observed thermal effects. When such heating studied melts liquidus point is not achieved [8]. At temperatures of 596-615 °C samples with polycrystal structure demonstrate double positive thermal effect, which is clearly seen in the inset in the right part of Fig. 1 on an enlarged scale. This effect is small in comparison with the effect of melting bismuth, but it appears quite clearly. At the lower curve (monocrystal copper), this effect is absent.

Fig. 1. Thermal heating curves of polycrystal (upper curve) and monocrystal (lower curve) copper samples in the bismuth melt.

It may be noted that cooling occurs in both cases the same, without the observed thermal effects.

The full view of curves "heating - cooling" can be found in a scaled-down view by the example of copper monocrystal samples in contact with bismuth in fig. 3

Fig. 3. Thermal curves "heating-cooling" for monocrystal copper in contact with bismuth.

The presented curves show that the monocrystalline copper in contact with bismuth undergoes no transformations in the "heating - cooling" process in the temperature range 25 – 650 °C. Bismuth melts independently from copper (positive effect on the heat curve) and crystallizes (a negative effect on the cooling curve). Similar curves for polycrystal copper in contact with bismuth differ from those shown in fig. 3 only in the presence of a positive thermal effect at 596 - 615 °C (see Fig. 1), which is inappropriate to show in this scale.

When the experiment had been carried out, metallographic specimen of polycrystal copper in sections perpendicular to the plane were made, i.e., contact surfaces of solid copper and bismuth melt at temperatures above 270 °C. Fig. 4 show photo of the copper microstructure. In picture GBs are clearly visible, which are partially or completely filled with bismuth. Light thin strips of bismuth are grain-boundary channels of penetration of the melt in the complete wetting of the GB. However, it should be noted that only a part of GBs in a polycrystal sample is filled with bismuth, there are a completely "empty" (i.e. without bismuth) GBs as well as partially "empty" GBs.

Fig. 4. Microstructure of polycrystal copper after "heating - cooling" in bismuth melt.

Detailed analysis of microphotographs of specimen of polycrystal copper after the "heating - cooling" in bismuth melt has
given the opportunity to assess the proportion of GBs filled with bismuth, i.e., the proportion of GB channels of bismuth formed during the experiment (fraction of fully wetted with bismuth GBs in samples of polycrystal copper). This proportion is approximately 10% of all GBs in polycrystal samples, which were in contact with bismuth during the experiment.

4. Discussion

Calorimetric study of the copper polycrystal samples heating in bismuth melt showed that in the transition temperature range of the GBs to complete wetting with melt the thermal effect is observed, which is absent in the same conditions in case of monocrystal samples, i.e. in the absence of GBs. As in the polycrystal occurs the growth of deep GB channels, it is natural to assume that this process is the cause of the thermal effect. We can assume that the thermal effect is a consequence of the withdrawal of copper from sample volumes (border volumes), which when GBs were wetted were filled with bismuth. The only way out of copper from the border areas of the grain and making space for melt via formation of channels is the transition (displacement) it in melt, and thus the formation of a supersaturated bismuth-copper melt. Copper dissolution in the melt can be regarded as the cause of the thermal effect when wetted GBs. The fact, that in a subsequent cooling the occurrence of any thermal effects up to the crystallization temperature of bismuth is not marked, is that reversibly reverse formation of dissolved during the formation of GB channels copper does not happen.

The heat effect magnitude, accompanying the transition to complete wetting of the GBs and the formation of GB channels, can be estimated from the known heat of bismuth melting - $ΔH_{S → L}$ (Bi). The area on the thermal curve corresponding to the thermal effect on bismuth melting is proportional to the total heat absorbed by the sample containing a known amount of moles of bismuth. The magnitude of the thermal effect upon GB wetting (596-615 °C) may be determined by the ratio of areas of the GB melting thermal peak and the peak at the bismuth melting. Using this fact thermal effect of GB wetting, divided by the total mass of the sample, was calculated. It was equal to 0.0327 J.

To compare the magnitude of the observed thermal effect with the magnitude of changes in the surface energy of the transition to the complete wetting of the GBs was estimated surface area of GBs filled with bismuth melt. For this purpose it was assumed that the copper grains in the sample have the form of cubes (calculation in the first embodiment) or icosahedron (in the second embodiment). Geometric analysis allowed in both cases by the proportion of wetting GBs (10%) to determine the surface area of the GBs wetting, which was found to be $1.7 \cdot 10^5 \text{ m}^2$ in the first case and $1.8 \cdot 10^5 \text{ m}^2$ in the second case. Thus, the magnitude of the thermal effect per surface unit of GBs wetted by bismuth melt is about $2 \cdot 10^3 \text{ J/m}^2$. This is thousands of times greater than the possible values of the surface energy associated with the GB and the boundary of solid and liquid phases in the Cu - Bi (the value of the surface energy at the boundaries of Cu, - Bi, is 0.2 - 0.4 J/m$^2$ [9]). This indicates that the observed thermal effect is not associated with capillary processes at GBs.

We can assume that the absorbed heat when GBs were wetted is associated with the transition of the copper to the bismuth melt - this is the heat of dissolution. Dissolution of copper in bismuth by GBs is stimulated by the process of wetting. The solubility of copper in liquid bismuth increases with temperature, the wetting process "imitates" the temperature increase near the GBs and initiates a transition of the copper into the melt. All the heat that would absorb when copper was dissolved in bismuth with temperature increase is being recorded in a narrow temperature range in the transition to complete wetting of the GBs.

Then the effect of the heat on 1 mole of copper, passed into the melt was estimated. The volume of GB formed channels (thickness of bismuth in the channels was assumed to be 2 microns), and the amount of copper in the moles, repressed in the melt when wetted were determined. As a result, the thermal effect value was obtained equal to 23 kJ/mol (cubic grain shape for copper) and 21 kJ/mol (for the icosahedral shape of grains of copper). It is of the same order of magnitude as the fusion heat of pure copper which equals to 13 kJ/mol. Received "specific" values of the thermal effect, as can be seen, not very sensitive to the method of description of the grain structure of the sample. But they may undergo significant changes due to the influence of the two factors that require a reliable experimental confirmation. This is the value of the thickness in the GB layer of bismuth channels which, as shown by microarray analysis, may vary for different channels and at different depths within a wide range (0.1 to 10 microns). Furthermore, this is proportion value of bismuth fill GBs of all GB network of the sample. Both of these quantities cannot be defined exactly, the interval value depends on the depth of the statistical analysis of the sample structure after thermal tests. Those are why the values of the thermal effect of wetting the GBs should be regarded as tentative, and require clarification.

5. Conclusion

In consequence of the experiments on copper GB complete wetting with bismuth melt study that were carried on, it was found that:

- thermal effect due to process of passing to copper GB complete wetting was found which is proved by carrying out a parallel investigation of monocrystal copper behavior in bismuth melt when heated;
- thermal effect size of GB wetting per mol of copper passed into bismuth melt via process of forming wetting GB channels was characterized as 21-23 kJ/mol.

6. References