PENETRATION KINETIK OF BISMUTH MELT INFO COPPER POLYCRYSTALLINE STRUCTURE

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Abstract: *The liquid bismuth network formation along grain boundaries (GB) and triple junctions (TJ) was investigated in copper polycrystalline samples. The experimental observation in situ technique of Bi penetration through the Cu plate was used. The temperature dependence of the penetration rate of the melt through the wafers of polycrystalline copper and the effective activation energy of penetration of Bi along the GBs are found.*

Keywords: KINETIC, COPPER, BISMUTH, PENETRATION, GRAIN BOUNDARY

1. Introduction

The problem of solid-liquid metal phases interaction described in several tens of theoretical and experimental researches [1,2]. It is well known that liquid-metal grooves formation occurs on the liquid-solid interface at the exiting places of grain boundaries (GBs). This effect can lead to the solid metal embrittlement. The samples destruction along GBs was observed on copper (solid) - bismuth (liquid) system [3]. In polycrystalline samples the wetting GBs transformation is a complex process, which occurs in the area near the wetting temperature – T_w. The triple junctions (TJs) as a GBs are subject to wetting transformation. The spread velocity of the liquid phase along TJs is more than along grain boundaries [4]. Co-wetting of GBs and TJs in polycrystalline metal samples leads to formation and growth of a continuous liquid-metal channel net. The appearance of the liquid phase channels net was observed by GB wetting investigations of liquid bismuth interaction with polycrystalline copper samples [5]. However, until now there were not experimentally obtained kinetic characteristics of molten bismuth penetration into polycrystalline copper structure near the wetting temperature. The aim of present work is the experimentally research of the kinetics of liquid bismuth penetration into polycrystalline copper in the T_w temperature area.

2. Experimental

For the experiments there were used high purity metallic materials, copper - 99.995 wt.% and bismuth - 99.999 wt.%. Copper samples were the plates which were made on electro erosion machine ARTA 200-2. Plate's thickness was from 150 to 500 microns. The average grain size of copper samples was about 40 microns. It was achieved by pre-deformation and following heat treatment of cooper plates.

Deformation of copper was carried out by upsetting (30 – 40 %) after which the samples had two-step recrystallization annealing. Annealing includes exposure for 15 min. at T_1=900 C and then holding for 120 min. at T_2=650 C. Isothermal exposures of copper samples in contact with liquid bismuth were carried out in the temperature range from 560 ºC to 590 ºC.

The experiments were performed in the heating micro-furnace in thermal cell TS1500. This device is accomodated for observations of high-temperature processes *in situ*, i.e. directly during the heating. This method is used for the analysis the process of metal melt penetration along GBs in solid metal matrix for the first time. All treatments were carried out in inert atmosphere - there was used Ar of high purity. During the penetration, on the test surface appeared liquid bismuth points. (Fig. 1).

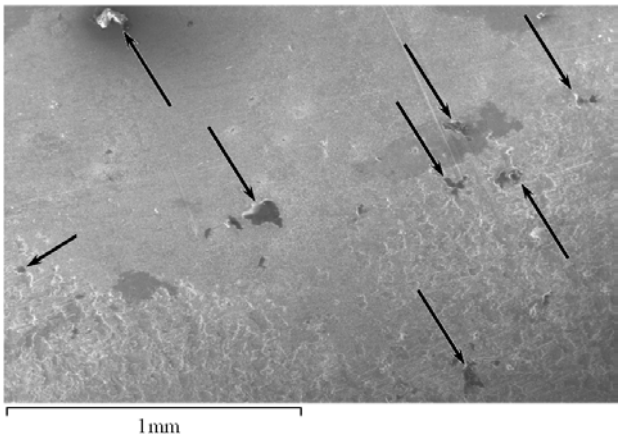

Fig.1. *Appearance of melt on the opposite sample's surface. Arrows show the penetration points*

Bismuth appearance on copper's free surface was observed using a continuous visual microscopic analysis of the surface (using an optical microscopes LEICA-DMILM, LEICA-L2). After experiments copper samples were investigated by scanning electron microscope HitachiS-800, including using electron microprobe analysis.

These results were confirmed the observation data of optical microscopy. The appearing points of bismuth on the free surface of the copper plates correspond to TJs in which there was happened through-penetration. This was confirmed by following chemical etching of the free surface. This fact indicates that the TJs are the fastest ways of the liquid phase penetration through a polycrystalline sample, as previously was noted in [6]. The appearance time of series of bismuth point's on the free cooper surface was fixed during the observation of bismuth penetration process through copper plates at each temperature. Such time was named through-penetration time (t) for definite experimental conditions.

3. Results

To study the morphology of the forming network of melt channels inside the samples of polycrystalline copper after holdings, we prepared transverse slices with planes perpendicular to the contact surfaces of the liquid and solid phases. When investigating the slices, it was established that the melt channels inside copper samples are formed both at GBs and along the lines of TJs. A photograph presented in Fig. 2 shows the region near the separation interface of the bismuth melt (the upper part of the photograph) and solid copper wafer (the lower part of the photograph). Funnel-like melt grooves along the GBs are seen; a thin GB melt channel moves away from one of them and is hampered by the TJ (triangular rosette in the lower part of the photograph). Being branched, it propagates farther into a depth of a copper plate.

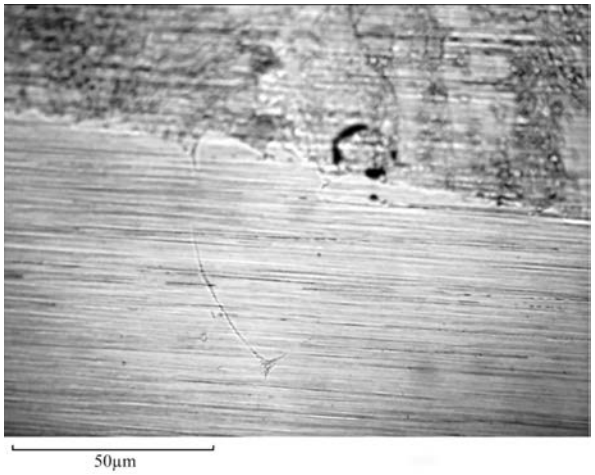

Fig. 2. *Morphology of the liquid bismuth penetration*

The experimental results for all temperatures conditions - through-penetration times (t) and the total average lengths of liquid bismuth channels (h_1) which were determined by measuring of the copper plate's thicknesses (h) with account of copper polycrystalline structure – are present in Table 1. An average velocity of liquid metal channel net formation was determined using the results of measurements of through wetting penetration.

Under the assumption that the rate-limiting stage of channels formation has the diffusion nature there were made the estimations of the effective diffusion coefficients (D*) by the correlation $h_1 \approx \sqrt{D^* \cdot t}$.

The estimations of D* were made for all experimental temperatures (see Tabl 2). The base equation of the diffusion coefficient temperature dependence $D^* = D_0^* \exp\left(-\frac{E^*}{RT}\right)$, where E* - is the effective activation energy, D_0^* - is the effective pre-exponential factor, allows to estimate the E* with the help of graphic dependence Ln(D^*)÷1/T (Fig.3).

Table 1: *The experimental results of average velocity of liquid metal channel net formation into polycrystalline copper structure*

T, °C	V, μm/min
550 ± 1	20 ± 5
560 ± 1	23 ± 5
570 ± 1	27 ± 5
580 ± 1	35 ± 5
590 ± 1	42 ± 5

Table 2: *The experimental results of liquid Bi spreading into polycrystalline copper structure*

T, K	t, min	h_1, μm	D^*, m^3/s
550	13	$1{,}0\cdot10^{-4}$	$8{,}7\cdot10^{-11}$
560	13	$9{,}4\cdot10^{-5}$	$1{,}2\cdot10^{-10}$
570	9	$8{,}2\cdot10^{-5}$	$1{,}1\cdot10^{-10}$
580	7	$7{,}0\cdot10^{-5}$	$1{,}4\cdot10^{-10}$
590	6	$8{,}4\cdot10^{-5}$	$1{,}8\cdot10^{-10}$

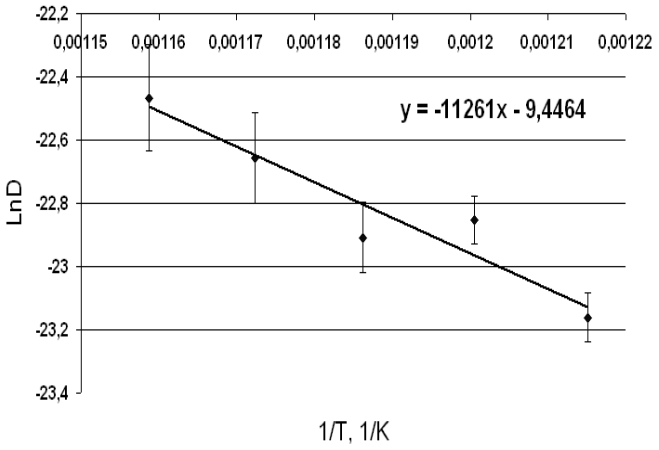

Fig3. *Estimation of E* with the help of linear temperature diffusion coefficient dependence*

The effective activation energy (E*) was defined from the slope of the linear dependence. It's significant is equal 94±22 kJ/mol. This value correlates with the activation energy of GB Bi-Cu hetero diffusion - 156.2 kJ/mol [7]. But obtained experimental data of activation energy is less than the activation energy of GB diffusion of bismuth in copper. This may be connecting with the contribution of the TJs bismuth diffusion in the copper polycrystalline samples.

4. Conclusions

1) The fact of complete liquid bismuth penetration through the copper plate was established in conditions of GBs and TJs complete wetting.

2) The average effective rate of liquid Bi penetration along GBs was determined. It increased from 20 to 42 μm/min with temperature increasing from 550 to 590ºC.

3) The activation energy of Bi penetration process is equal to 94±22 kJ/mol. It was assumed that the GB diffusion is the limiting process of GB wetting. Low value of activation energy may be due to the Bi diffusion along TJs.

5. References

[1] B.B. Straumal, Grain boundary phase transitions, Nauka publishers, Moscow, 2003.

[2] B.S. Bokstein, N,A. Dolgopolov, A.L Petefin et at., Izvestiya vuzov tsvetnaya metallurgiya 6 (2006) p.42 (in Russian).

[3] I.V. Apykhtina, S.A. Gulevskii, N.A. Dolgopolov et al., Defect and Diffusion Forum. Vol. 237240 (2005) p.855.

[4] S.A. Gulevskii, N.B. Emelina, A.L. Petelin, Russian Journal of Non-Ferrous Metals 47 (2006) p.38.

[5] B.S. Bokstein, N.B. Emetina et al., Materiallovedenie 8 (2007) p.13 (in Russian).

[6] S.A. Gulevskii, L.M. Klinger, A.L. Petelin, Tekhnologiya metallov 8 (2007) p.13 (in Russian).

[7] S.V. Divinski, M. Lohmann, Chr. Herzig et al., Phys. Rev. B.71 (2005) p.104104.