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Grain boundary wetting and premelting in the Cu–Co alloys

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ABSTRACT

The complete and incomplete wetting of Cu/Cu grain boundaries (GBs) by the Co-containing melt has been observed. The GB wetting in a peritectic system, where the GB wetting layer is depleted by a second component and not enriched like in the conventional cases, has been observed for the first time. The submicrograined structure in Cu–2.2 wt.% Co and Cu–4.9 wt.% Co alloys has been produced by the high pressure torsion. The melting process of both HPT-treated alloys was studied by the differential scanning calorimetry (DSC). The DSC melting curves were very asymmetric and have been deconvoluted into 2 and 4 different components, respectively. The positions of onsets and minima of high-temperature component peaks for both alloys correspond well with respective liquidus and solidus temperatures in the Cu–Co bulk phase diagram. The low-temperature component peaks were interpreted as GB premelting. The respective GB solidus line was constructed. The step-wise viscosity change of Cu–Co solid solutions was previously observed below the bulk solidus line. The viscosity changes 40–50 °C below the GB solidus line observed in this work. This difference can be explained by the difference in the GB character distribution or (alternatively) by the premelting in dislocations cores.

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1. Introduction

Cu–Co is a well-known peritectic system [1,2], which has attracted considerable interest due to its magnetic properties (giant magnetoresistance [3]) and its application as catalyst in the synthesis of higher alcohols [4]. Therefore, the Cu–Co phase diagram has been recently extensively studied and reconsidered [5,6 and references therein]. The high positive mixing enthalpy leads not only to the interesting phenomena connected with metastable miscibility gap in the range of the undercooled melt [7,8 and references therein]. In the systems with positive mixing enthalpy the so-called grain boundary (GB) phase transformations; in particular GB wetting transitions can take place. In the Co-rich alloys (i.e. close to the eutectic temperature) such phenomena have been observed recently [9]. However, the GB wetting transitions have never been studied before in peritectic systems. From this point of view the Cu-rich Co–Cu alloys are very attractive and promising.

The GB phase transformations can drastically modify the properties of polycrystals [10,11]. Most important GB phase transformation is the transition from incomplete to complete wetting of a GB by a second phase. The wetting phase can be either liquid or solid. In case of incomplete wetting the contact angle between second phase and GB is non-zero $\theta > 0^\circ$, and the wetting phase forms the lenticular particles separated by the “dry” GB portions. It is because the enthalpy of a GB unit area σ_{GB} is lower than that of two interphase boundaries σ_{IB} , namely $\sigma_{GB} < 2\sigma_{IB}$. In case of complete wetting $\sigma_{GB} > 2\sigma_{IB}$, $\theta = 0^\circ$, and a layer of wetting phase completely substitutes a GB. The transition from incomplete to complete wetting of a GB by a liquid phase (melt) at a certain temperature T_w is described by a horizontal tie-line in the two-phase “solid solution + liquid” area of a bulk phase diagram [12,13]. Such tie-line connects the points at solidus and liquidus lines at T_w . According to simple thermodynamic calculations, this tie-line cannot finish in its intersection with solidus line at T_w but has to continue in the one-phase “solid solution” area of a bulk phase diagram as a GB solidus line (or solvus line, if the second phase wetting the GB is solid) [14,15].

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By the intersection of the GB solidus or solvus lines the sudden change of GB properties can occur. In particular, the diffusivity drastically increases in the liquid-like GB layer [11,16], GB mobility becomes one order of magnitude higher [17], the multilayer segregation films form [18,19]. The first (temperature) derivative of GB energy breaks at the GB solidus line. It means that the prewetting/premelting is the phase transition of first order [19]. The measurements on the Cu–Bi samples showed that the electrical conductivity abruptly increased when the network of Bi-rich layers isolating the copper grains one from another had broken [18]. The extreme superplasticity of ultra-fine-grained Al–Zn–Mg alloys (with elongation to failure up to 2500%) in the narrow temperature interval just below the bulk solidus [20–25] is also driven by the formation of a liquid-like GB film [26,27] as a result GB wetting phase transition. The thin layers of the liquid-like Ni-rich phase were recently observed in the W–Ni system [14,28]. Such liquid-like GB layers phase appear because of the complete wetting of GBs in W and Mo by the liquid phase with lower melting point containing Ni, Co, Fe or Cu [29]. Thus, the GB solidus or solvus lines appear in the solid solution area of a bulk phase diagram if the melt of the second solid phase can completely wet the GBs in the respective two-phase areas of the same bulk phase diagram [11,13,26–30]. The second phase wetting GB in a first phase can be not only liquid but also solid [31].

Recently the creep behaviour of polycrystalline copper-based solid solutions and their surface tension has been studied under the solidus line of Cu–Co phase diagram [32,33]. The activation enthalpy for creep of pure copper was close to that of copper bulk self-diffusion. The activation enthalpy of creep of Cu–Co solid solutions was always lower than that of pure copper. Moreover, the experimental points for viscosity of Cu–Co solid solutions in Arrhenius coordinates can be approximated by the two straight lines with a break at a certain temperature. Such unusual creep behaviour of Cu–Co solid solutions has been explained by the change in grain boundary (GB) properties in studied coarse-grained polycrystals [32].

The goal of the present work is to prove the hypothesis that the abrupt increase of viscosity happens due to the intersection of GB solidus line in the Cu–Co phase diagram. First, we checked whether the Cu–Co melt can completely wet the GBs in Cu-based solid solution. Second, we investigated the melting heat release in the temperature interval close to the solidus line in Cu–Co alloys using the differential scanning calorimetry (DSC). The heat effects of the GB wetting and premelting phase transformations has been successfully observed previously in the Al-based alloys [34]. In order to increase possible input of GB wetting and premelting phenomena in DSC curves we applied the severe plastic deformation (SPD) to the studied Cu–Co alloys. SPD is known as a very powerful method of grain refinement and increase of the GB area in the unit volume [35,36].

2. Experimental

The Cu–Co alloys with 2.2 and 4.9 wt.% Co in form of 10 mm diameter rods were prepared by a vacuum induction melting and casting from the high-purity 5 N Cu and Co. The 0.6 mm thick as-cast disks of studied alloys obtained after grinding, sawing and chemical etching were subjected to high pressure torsion (HPT) at room temperature under the pressure of 6 GPa in a Bridgman anvil type unit (5 torsions, 1 rpm). Samples for structural and calorimetric investigations were cut from the HPT-processed discs at a distance of 3 mm from the sample centre. For the investigations of GB wetting behaviour a set of the as-cast Cu–2.2 wt.% Co alloys samples was sealed into evacuated silica ampoules with a residual pressure of approximately 4×10^{-4} Pa at room temperature. Samples were annealed at temperatures between 1085 and 1100 °C for 30 min, and then quenched in water. The accuracy of the annealing temperature was ± 1 °C. The HPT-treated samples were studied with use of the DSC 404 F1 Pegasus, Netzsch in argon atmosphere and of TA Instruments calorimeter (model Q1000) in dry helium, at cooling and heating rates of 10 °C/min. In order to record the DSC curves, the samples were heated from 50 to 1300 °C. The complicated DSC peaks were first approximated with polynomials and

than deconvoluted using the Netzsch Peak Separation program version 2008.05. For each deconvoluted peak the temperature of onset T_{onset} , minimum T_{min} and endset T_{endset} was determined (Tables 1 and 2). According to the standard procedure, the temperature T_{onset} and T_{endset} of the peak was marked as the point of intersection of the tangent drawn through the inflection point of the curve with the extrapolated baseline. For the metallographic investigations the samples were ground by SiC grinding paper, polished with 6, 3, and 1 μm diamond pastes and etched for 5–10 s in 1:1 solution of H_2O and HNO_3 . Light microscopy (LM) was performed on a Zeiss Axiophot microscope. Scanning electron microscopy (SEM) investigations were carried out on a Philips XL30 scanning microscope equipped with a LINK ISIS energy-dispersive spectrometer produced by Oxford Instruments. X-ray diffraction (XRD) data were obtained on a Siemens diffractometer (Co $K\alpha$ radiation). Grain size was estimated by the XRD line broadening using the Scherrer formula [37].

3. Results and discussion

In Fig. 1a the SEM micrograph of Cu–2.2 wt.% Co sample annealed at 1094 °C is shown. According to the bulk phase diagram [5,6,38], the solidus and liquidus temperature for this alloy are 1091 and 1097 °C, respectively. Almost all GBs in Fig. 1a are completely wetted ($\theta = 0^\circ$). In Fig. 1b the Co concentration profile across completely wetted Cu GB is shown. In this plot the position of Cu GB corresponds to the minimum of Co content. It is because the peritectic transformation takes place in the Cu-rich alloys, and melted wetting phase contains less Co than the Cu-based solid solution. Therefore, the complete and incomplete GB wetting in the peritectic system has been observed for the first time, where the GB wetting layer is depleted by a second component and not enriched like in the conventional cases [11–13,26,27,34].

The microstructure of as-cast alloys contains the supersaturated Cu-based solid solution and Co precipitates [15]. The size of (Cu) grains in both alloys is between 15 and 22 μm . A certain tendency to the faceting of Co/Cu interphase boundaries was present [19,39]. After HPT the grain size drastically decreases to about 100 nm for the Cu-grains and 30 nm for the Co-precipitates. Cu grains are almost equiaxial; the Co-particles are uniformly distributed among Cu grains. HPT leads also to the partial dissolution of Co precipitates in Cu-based matrix. The rate of this dissolution was very high (about a half of existed Co precipitates dissolved in 5 min of HPT treatment), despite of the known fact that the application of high pressure, even without deformation always decreases the diffusivity and grain boundary mobility [40,41]. The heating of HPT-treated alloys in the DCS apparatus at a rate of 10 °C/min leads to a certain grain growth. Below bulk solidus line the grain size was about 10–30 μm .

In Fig. 2a the temperature dependence of heat flow (DSC curve) is shown for the HPT-treated Cu–2.2 wt.% Co alloy heated from 50 to 1300 °C at a rate of 10 °C/min. Only the high-temperature part between 1066 and 1116 °C is shown in Fig. 2a. The integral heat effect of melting (melting enthalpy) was about 104% of that for pure copper (208.7 J/g [42,43]). In Fig. 2b the temperature dependence of heat flow (DSC curve) is shown for the HPT-treated Cu–4.9 wt.% Co alloys heated from 50 to 1300 °C at a rate of 10 °C/min. Only the high-temperature part between 1078 and 1122 °C is shown in Fig. 2b. The integral heat effect of melting (melting enthalpy) was about 98.4% of that for pure copper.

Both DSC curves shown in Fig. 2 have complicated form, with overlapping peaks. These DSC peaks were first approximated with polynomials (thin line) and then deconvoluted using the Peak

Table 1

Results of deconvolution of melting curve for the DSC melting curve for the Cu–2.2 wt.% Co alloy (Fig. 2a).

Curve in Fig. 2	Onset (°C)	Minimum (°C)	Endset (°C)	Symbol in Fig. 3
2 (dotted)	1077.1	1082.3	1094.9	Open circles
1 (dashed)	1085.8	1098.0	1103.4	Filled diamonds

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