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Effect of Ag addition on the as-cast microstructure of Cu–8 wt.% Fe in situ composites

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ABSTRACT

Ternary copper-based composites consisting of Cu, 8 wt.% Fe and 0.1–6 wt.% Ag were prepared by inductive melting and casting. The effect of Ag addition on the as-cast microstructure was investigated using optical microscopy (OM) and scanning electron microscopy (SEM). The results show that the primary Fe dendrites in the as-cast microstructure are refined significantly with the presence of Ag. Contact angle between Cu–Ag alloy and γ-Fe was measured using sessile drop technique to investigate the refinement mechanism of the primary Fe dendrites. In addition, the effect of Ag addition on the dissolution of Fe atoms in the Cu matrix at high temperature was investigated by means of energy dispersive X-ray spectroscopy (EDS). The results show that the presence of Ag inhibits the solubility of Fe in the Cu matrix at high temperature.

1. Introduction

Due to good combination of strength and conductivity, deformation processed in situ Cu-based metal matrix composites containing a body-centered cubic (bcc) transition metal such as Nb, Fe, Cr have been widely studied in the past two decades [1–10]. The composites are considered as candidate materials in the fields of steady state and long-pulse high-field resistive magnet designs. Upon solidification of these alloys, bcc dendrites form in the copper matrix and the subsequent mechanical reduction reduces the dendrites to aligned filaments with a ribbon-like cross-section. Extensive studies showed the tensile strength of the deformation processed in situ composites could be described by Hall–Petch equation: $\sigma = \sigma_0 + k\lambda^{-1/2}$, where σ is the ultimate tensile strength, σ_0 is the friction stress reported to be near 0 MPa, k is the Hall–Petch coefficient and λ is the filament spacing [4–10]. It is obvious that the ultimate tensile strength increases with the decrease of the filament spacing which depends on the drawing strain and the initial microstructure. Smaller initial dendrites will inevitably lead to finer filament spacing after being deformed to the same extent.

Several methods have been investigated to refine the initial microstructure. Biselli and Morris [1] employed rapid solidification/thermal sprayed technique to produce fairly fine scale initial microstructures. The strength of the composites reached 1.3 GPa at strain of 8. Wu et al. [7] found the homogenizing treatment before cold drawing could refine the primary Fe dendrites of Cu–6 wt.% Fe and Cu–12 wt.% Fe alloys. The average length of dendritic arms shortened from about 6–12 to 4–8 μm for Cu–12 wt.% Fe alloy. The strength of the microcomposites is increased due to homogenizing treatment. Furthermore, Song et al. [11–13] reported that the presence of alloying element was able to refine the primary Fe dendrites in the as-cast microstructure of Cu–9 wt.% Fe–X (X = Cr, Co or Ag). Our previous research also observed the refinement of Fe dendrites after Ag addition [8–9]. Among these methods, the development of ternary alloying techniques was thought of more effective method in refining the initial microstructure. In present work, we investigate the effect of Ag addition on as-cast microstructure of Cu–8 wt.% Fe composites and the refinement mechanism of Ag on Fe dendrites was also discussed.

2. Experimental procedures

The Cu–Fe–Ag alloys have nominal compositions (wt.%) as follows: Cu–8Fe; Cu–8Fe–0.1Ag; Cu–8Fe–0.5Ag; Cu–8Fe–1Ag; Cu–8Fe–3Ag; Cu–8Fe–6Ag. Starting materials containing electrolytic copper, commercial pure iron and analytically pure Ag were put into high-purity Al_2O_3 crucible and then heated to 1600 °C and hold for 5 min in a medium frequency induction furnace under argon atmosphere. The melts were poured into an iron mould preheated to 200 °C. Ingots were of 14 mm in diameter and 100 mm in length. Specimens cut from the ingots were grinded, polished and then etched with mixture of 80 ml H_2O, 10 g $K_2Cr_2O_7$ and 5 ml H_2SO_4. The cross-section microstructures were observed utilizing Olympus-GX41 optical microscopy (OM) and JSM-6460 scanning electron microscopy (SEM). The diameter of primary Fe dendrites was determined using an image analyzer (DT2000 software). The distribution of Fe in Cu matrix was determined by energy dispersive X-ray spectroscopy (EDS). Fe solubility in Cu with the presence of Ag was also calculated using Thermo-calc software for comparing with the experimental results. To compare the dissolution of Fe and Ag in Cu, the supercells containing 32 Cu atoms and 31 Cu atoms plus 1 Fe or Ag atom were constructed using Materials Studio software. The total energy of supercell was calculated via CASTEP module. The optimized planewave cutoff energy was fixed at 270 eV K points sampling was 3 × 3 × 3.

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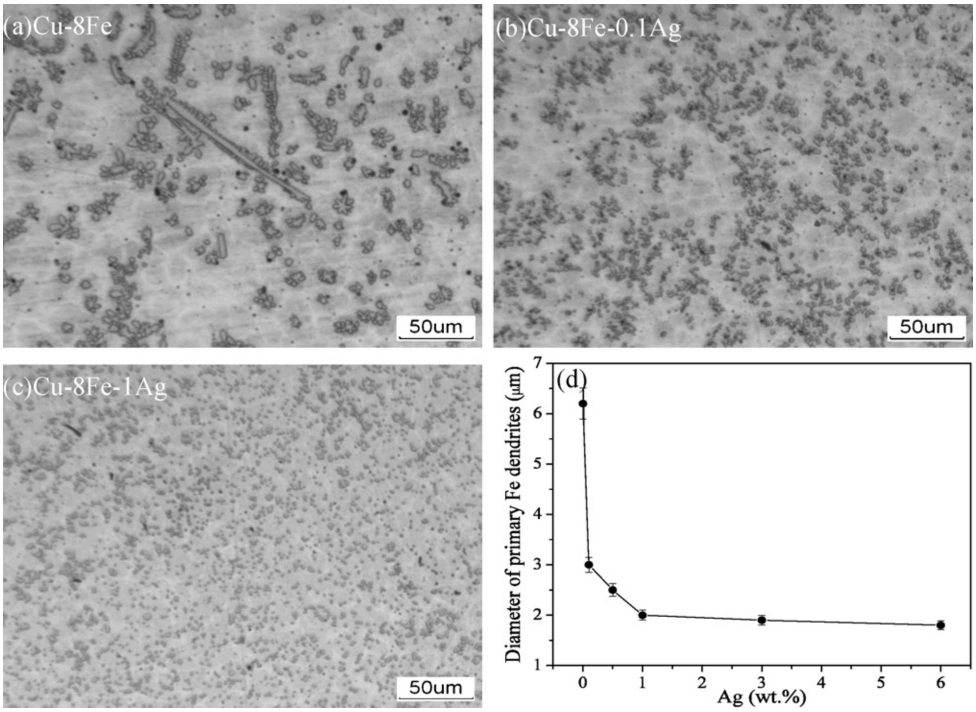

Fig. 1. Typical microstructure and the variation of diameter of primary dendrites with Ag.

The contact angles between Cu–Ag alloy and Fe were measured using sessile drop technique on Digidrop system (DGD-DS) to investigate the wetting properties between liquid Cu–Ag and γ-Fe. The prepared Cu–Ag alloys with 0.1–6 wt.% Ag were placed on a polished pure Fe substrate and heated to 1100 °C together and then cooled to room temperature for measurement.

3. Results and discussion

Fig. 1 shows the effect of Ag addition on the as-cast microstructure and diameter of primary dendrites of Cu–8 wt.% Fe in situ composites. As indicated in the figure, the primary Fe dendrites are refined significantly with the increase of Ag, but rather slowly after Ag content exceeds 0.1 wt.%. The average diameter of primary dendrite is decreased from about 5–6 μm for Cu–8Fe to about 2–3 μm for Cu–8Fe–0.1Ag and 1.5–2 μm for Cu–8Fe–6Ag.

The refinement mechanism can be explained based on the classical nucleation theory. We assume that the homogeneous nucleation of γ-Fe takes place during the solidification. The critical radius of γ-Fe nuclei can be described using the following equation: $r^* = -2\sigma/\Delta G_V$, where σ is the interfacial energy between γ-Fe and liquid Cu–Ag system and ΔG_V is the unit volume free energy change and herein is regarded as constant. The interfacial energy can be estimated by contact angles between Cu–Ag alloys and γ-Fe. Fig. 2 shows the variations of contact angles of Cu–Ag alloys and γ-Fe with Ag. It is observed that the contact angles trend to decrease with increasing Ag. As Ag content is lower than 1.0 wt.%, the tendency is even obvious. Considering the refinement effect, 1.0 wt.% Ag addition is enough. The contact angle is determined as 13.7° between Cu and γ-Fe, 8° between Cu–0.5Ag and γ-Fe and 4.3° between Cu–6Ag and γ-Fe, respectively. The above experimental results indicate that the Ag plays an important role on reducing the interfacial energy of liquid Cu–Ag and γ-Fe, i.e. the interfacial energy between liquid Cu–Ag and γ-Fe decreases with increasing amount of Ag added. According to the equation mentioned above, the critical radius of γ-Fe will decrease with the presence of Ag and the nucleation of γ-Fe in liquid Cu–Ag should becomes easier than in liquid pure Cu. That is to say the primary Fe dendrites will be further refined with the increase of Ag.

Fig. 3 shows the microstructure of the as-cast Cu–8Fe–6Ag alloy. It is observed that a lamellar shape Cu–Ag eutectic could be seen clearly distributed along the copper boundaries. Cu and Ag have limited mutual solubility, their equilibrium phase diagram reveals the maximum solubility of Ag in Cu is 7.9 wt.% at the eutectic temperature 780 °C and down to zero at room temperature. During non-equilibrium solidification, as Ag content is approaching 7.9 wt.%, the eutectic reaction is likely to take place during chill cooling.

Fig. 4 shows variation of Fe content in Cu matrix with Ag, which is determined by EDS. To improve measurement precision, selected areas of 10 μm × 5 μm in the matrix were analyzed at higher magnification observations of 2000× and 10 measurements were recorded for each specimen. The average results are used. According to Cu–Fe phase diagram, the peritectic reaction takes place at 1096 °C. During non-equilibrium solidification, most Fe atoms will exist in the "matrix" either in the form of solid solution or Fe precipitates (matrix refers to structures other than dendrites here).

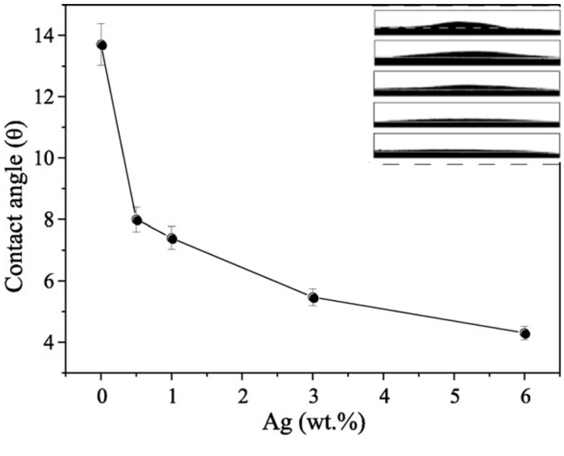

Fig. 2. Dependence of contact angles between Cu–Ag and γ-Fe on Ag content.

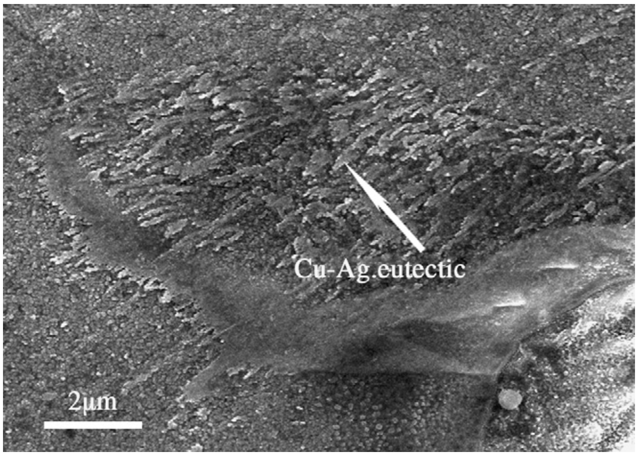

Fig. 3. Microstructure of as-cast Cu–8Fe–6Ag alloy.

Therefore, the Fe content in the “matrix” can reveal the solubility of Fe in copper matrix at high temperature. As indicated in Fig. 4, the amount of Fe in matrix decreases obviously with increasing Ag content in as-cast Cu–Fe–Ag alloys. The Fe content is determined as 4.4 wt.% for Cu–8Fe and 3.5 wt.% for Cu–8Fe–6Ag, respectively. This indicates that Ag can reduce the solubility of Fe at high temperature, which is significant for improving the conductivity of Cu–Fe deformation processed in situ composites. The effect of Ag on solubility of Fe in Cu matrix can be interpreted based on first principle calculations.

Table 1
Results of first principle calculations.

Configuration	32 Cu	31Cu–1Fe	31Cu–1Ag
Total energy (eV)	−43,090	−42,330	−42,770
Energy increment (eV)	–	760	320

Table 2
Effect of Ag addition on solid solubility of Fe.

Ag	Solid solubility of Fe
0.1	3.4
1.7	3.1
3.3	2.4
5.0	1.9
6.0	1.4

Fig. 5 shows the supercell configurations constructed by Materials Studio software, which consist of 32 Cu atoms and 31 Cu atoms plus 1 Fe/Ag atom, respectively. The result of first principle calculations is shown in Table 1. The total energy increment of supercell containing 31 Cu atoms plus 1 Ag atom is 320 eV, which is greatly lower than that of supercell containing 31 Cu atoms plus 1 Fe atom (760 eV). This indicates that Ag atoms have more priority to dissolve in copper compared with Fe. The dissolution of Ag in the Cu matrix results in large lattice distortion of Cu. For large radius of Fe atoms, it is difficult to relax the distorted solid solution structure by dissolving Fe atoms. Therefore, the distorted structure may inhibit dissolution of Fe atoms.

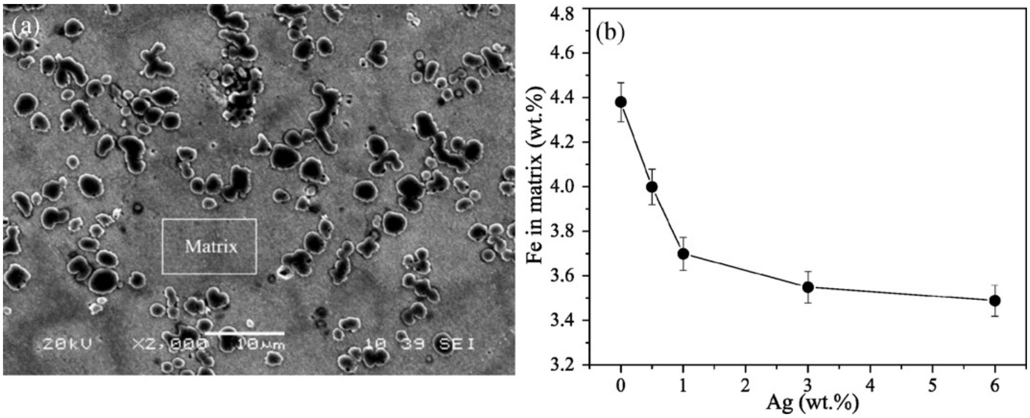

Fig. 4. The SEM and Fe content in matrix.

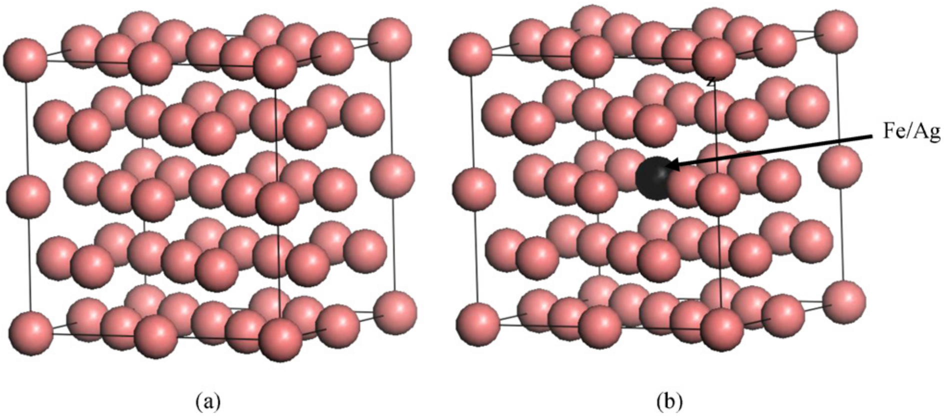

Fig. 5. Supercell configurations.

Table 2 shows effect of Ag on solid solution of Fe in Cu, which is calculated by Thermo-calc software. It also indicates that the maximal solubility of Fe in Cu matrix decreases with increasing Ag addition. The maximal solubility of Fe atoms in Cu matrix is reduced from 3.4 to 1.4 wt.% as the Ag addition increases from 0.1 to 6 wt.%. The calculated results are in accordance with the above experimental results, which indicate Ag inhibits the solution of Fe atoms in Cu matrix based on thermodynamics. However, it is observed that the calculated solubility of Fe in Cu matrix is slightly lower than that of experimental results. This is because the slow kinetics of Fe atoms at low temperature, which leads to large amounts of solid solution Fe atoms in Cu matrix.

4. Conclusions

The primary Fe dendrites in as-cast microstructure of Cu–8 wt.% Fe–*x*Ag alloys are dramatically refined with the addition of Ag element. With the increase of Ag the interfacial energy between liquid Cu and γ-Fe decreases, which results in the refinement of the Fe dendrites. Moreover, the presence of Ag reduces the solubility of Fe at high temperature.

Acknowledgments

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