Influence of pressure on the solid state phase transformation of Cu–Al–Bi alloy*

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The solid state phase transformation of Cu–Al–Bi alloy under high pressure was investigated by x-ray diffraction, energy dispersive spectroscopy and transmission electron microscopy. Experimental results show that the initial crystalline phase in the Cu–Al–Bi alloy annealed at 750 °C under the pressures in the range of 0–6 GPa is α-Cu solid solution (named as α-Cu phase below), and high pressure has a great influence on the crystallisation process of the Cu–Al–Bi alloy. The grain size of the α-Cu phase decreases with increasing pressure as the pressure is below about 3 GPa, and then increases ($P > 3$ GPa). The mechanism for the effects of high pressure on the crystallisation process of the alloy has been discussed.

Keywords: Cu–Al–Bi alloy, high pressure, microstructure, grain growth
PACC: 6250, 6155H, 6460M

1. Introduction

Aluminum is the second most widely used metal after steel.[1] One of the most technically important applications of Al-based demixing alloys would be self-lubricating sliding bearings for automotive applications which are capable of substituting for conventional bearing material Cu–Sn–Pb if a hard Al/Si or Al–Cu/Si matrix with finely dispersed particles of a soft metal like Bi could be produced.[2] Investigation of the ternary Cu–Al–Bi alloy is important in view of possible technical applications as bearings. However, thick grain is its main defect in Cu–Al–Bi alloy structure, which directly affects its application as an engineering material. It is reported that pressure can significantly affect the transformation behaviour of alloys and often lead to the formation of dense, metastable crystalline phases that were not encountered during transformation at ambient pressure.[3,4] If properly applied, high-pressure annealed alloy was a promising method for synthesising new crystalline phases in multicomponent systems.[5−7] High pressure is a powerful tool for modifying and controlling the nucleation and growth to induce atomic rearrangement in alloys,[8−10] and the knowledge of the pressure effect on the process of phase transformation in Cu–Al–Bi alloys is of high importance in materials science. In the present work, phase transitions and microstructure of ternary Cu–Al–Bi alloys are investigated by x-ray diffraction (XRD), energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM). The relationship between the pressure and the grain size of α-Cu phase annealed under pressures in the range of 0–6 GPa is given.

2. Experimental

Cu–Al–Bi alloy studied in this work was prepared from high-pure Cu, Al and Bi (99.999%) with the composition (atom percent) of 75.96% Cu, 23.99% Al and 0.05% Bi. The alloy rod was cut into disk with 5 mm in diameter and 1mm in thickness. The high pressure annealing was performed in an apparatus with six anvil tops. The samples were embedded into sodium chloride. The reason for selecting powder sodium chloride was its high chemical stability and excellent pressure transmitting behaviour. The heating furnace in the high pressure device is a graphite tube heater. The samples were pre-pressured to a certain value to enhance the homogeneity of the pressurisation and annealed at 750 °C under given pressure (0–6 GPa) for 0.5 hour. Pressure was calibrated at room temperature by means of the phase transitions of Bi

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and Ba. The temperature was determined from its relation with the input electric power. The accuracy in measurment of the temperature of the sample itself under applied pressure was about 1.5 °C. XRD was performed using a MAC M03 XHF diffractormeter with Cu radiation. The microstructure observation of the annealed alloys was carried out by an H-800 transmission electron microscope.

3. Results and discussion

Figure 1 shows the microstructures of Cu–Al–Bi alloys under different conditions. It can be seen that the microstructure of the as-cast Cu–Al–Bi alloy consists of irregular white sticks and black zone. With the increase of pressure, both white fine grainy α-Cu phase and white grain α phase implanted in the black zone were observed. When the value of pressure reached 3 GPa, α-Cu phase with white reseau-structure can be detected, as shown in Fig. 1(d), and also the grain size of the α-Cu phase decreases with increasing pressure at pressures below about 3 GPa, and then increases at $P > 3$ GPa. In order to further investigate the effect of high pressure on the phase composition of Cu–Al–Bi alloy, XRD patterns for the Cu–Al–Bi alloy under different pressures were analysed. According to the XRD patterns shown in Fig. 2, we can see that the as-cast alloy consists of α-Cu phase and β' phase. As we know that α phase is Cu-based solid solution and belongs to faced centred cubic structure, while β' is $AlCu_3$-based solid solution and belongs to the rhombic structure. The results show that with increasing pressure, some un-identified phases can be detected in black zone, which means that there are multiphases in the black zone (such as fine needle-like α phase). This results in various contents of Cu and Al in different black zones. Identifying of new phases in Cu–Al–Bi alloy after annealing under high pressure needs further research. According to the result of the component of every microcosmic zone by EDS shown in Fig. 3, we can see that the content of Cu and Al in the white grainy α phase changed less than that in the black zone.

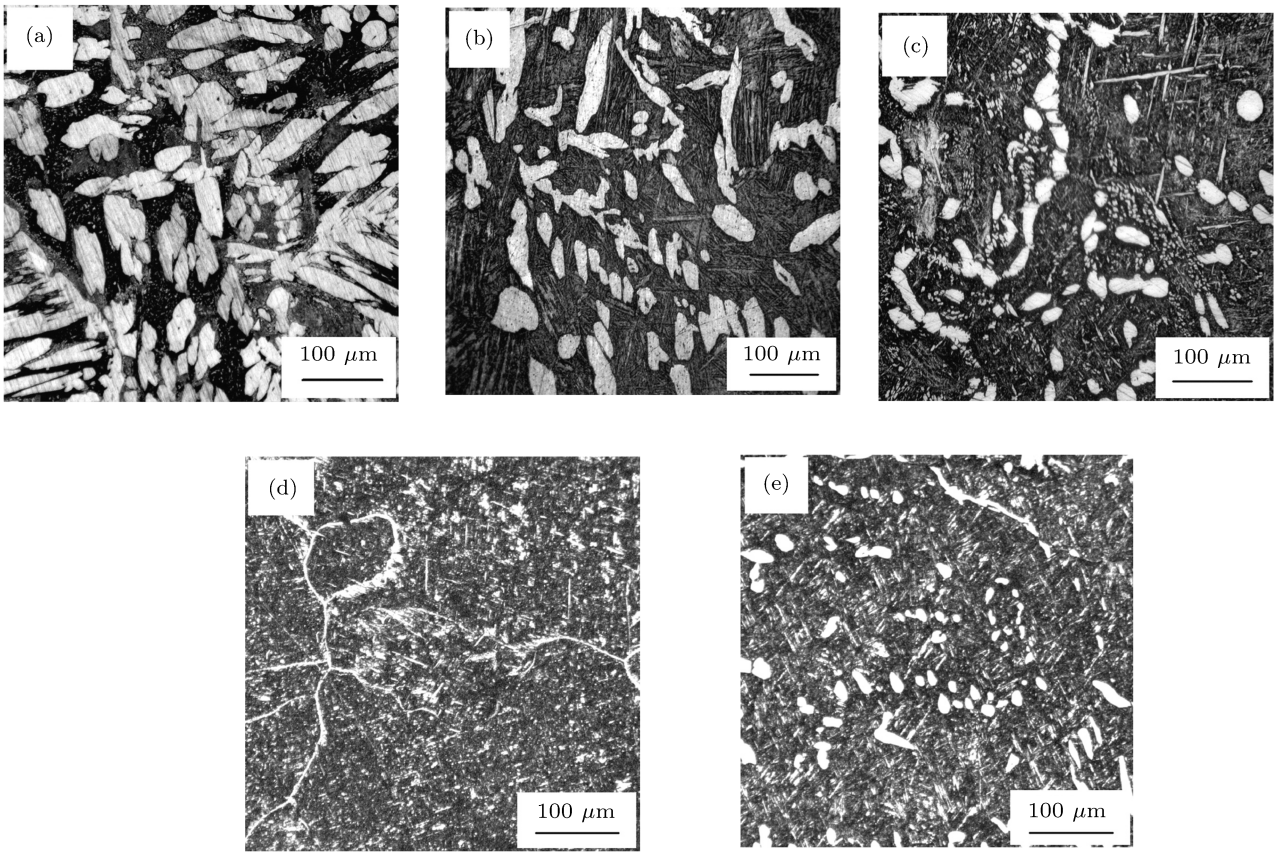


Fig. 1. Microstructure of Cu–Al–Bi alloy under different treatment conditions (a) as-cast (b) annealed at 750 °C for 0.5 hour under 0 GPa (c) annealed at 750 °C for 0.5 hour under 1 GPa (d) annealed at 750 °C for 0.5 hour under 3 GPa (e) annealed at 750 °C for 0.5 hour under 6 GPa.

When the sample was annealed under 3 GPa, the composition of white reseau is 54.69%Cu and 45.31%Al (weight percent). EDS further suggests that the primary components of white stick and black zone are Cu and Al, respectively. More Cu is detected in the white stick (about 93.32–94.05%, weight percent) than that in the black zone (about 85.91–87.24%, weight percent). The contents of Cu and Al in different zones tested by EDS in detail are listed in Table 1. Because only a little amount of Bi dissolves in Cu, it can be concluded that the white stick is α phase and most of β' phase is in the black zone, while Bi mainly distributes in the boundary.

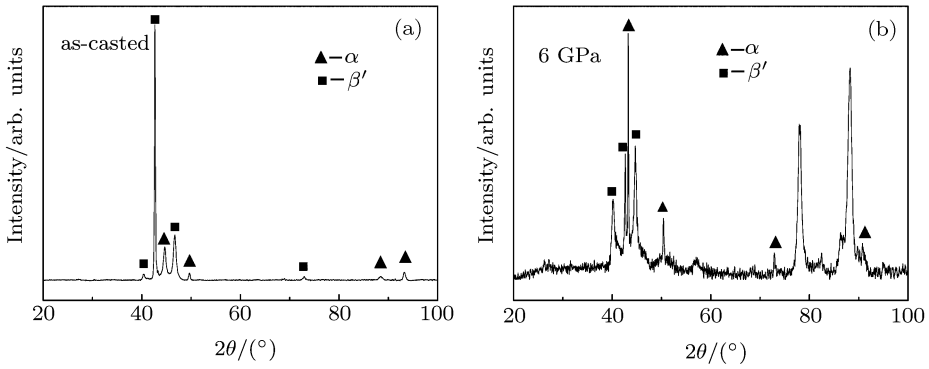


Fig. 2. XRD patterns for the Cu–Al–Bi alloy.

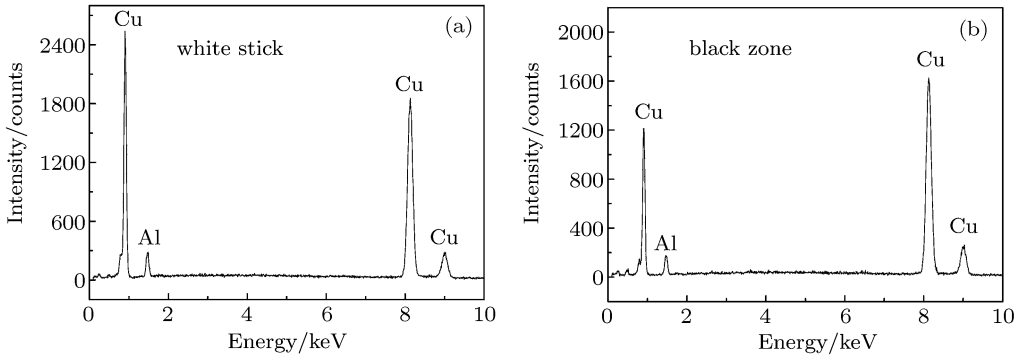


Fig. 3. EDS for the Cu–Al–Bi alloy.

Table 1. Microstructure components of Cu–Al–Bi alloys under different pressures by EDS.

pressure/GPa	zone	Cu/wt.%	Al/wt.%
as-casted	white zone	90.87–91.03	8.97–9.13
	black zone	74.57–81.24	18.76–25.43
0	white zone	90.89–91.19	8.81–9.11
	black zone	72.18-81.68	18.32–27.82
1	white zone	90.84–91.11	8.89–9.16
	black zone	75.67–83.61	16.39–24.33
3	white zone	90.88–91.05	8.95–9.12
	white reseau	54.69	45.31
	black zone	75.64–88.12	11.88–24.36
6	white zone	90.83–91.04	8.96–9.17
	black zone	76.89–85.67	14.33–23.11

According to the phase diagram of Cu–Al alloy[11] shown in Fig. 4, both α and β phase appear in Cu–Al alloy when heated to 750 °C. In the following cooling process, solid phase transformation will take place, which makes change in the quantity of α and β phases. Eutectoid transformation takes place in β phase at the temperature of 565 °C and it transforms into the eutectoid phases ($\alpha + \gamma_2$). Therefore, when the Cu–Al–Bi alloy is cooled down to room temperature, γ_2 (Al_4Cu_9) phase should be found in the alloy. But it was not detected by XRD in our experiment. The possible explanation may be that the content of γ_2 phase is extrmely small or else it is too difficult to achieve a slow enough cooling rate for β phase transformation, so that a metastable phase β' is generated before β phase can decompose in the cooling process of Cu–Al–Bi alloy.

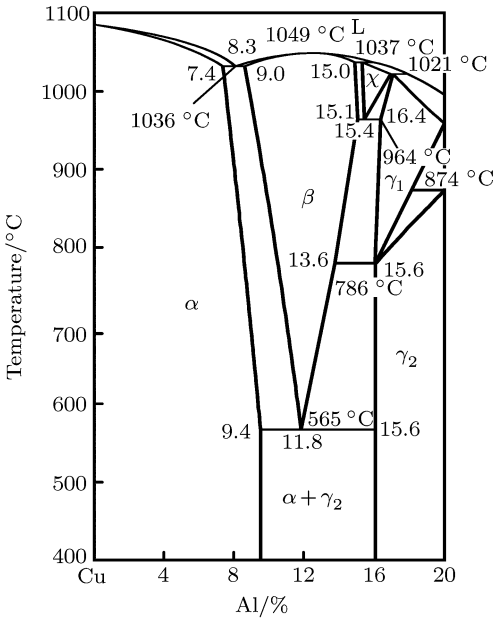


Fig. 4. Binary Cu–Al alloy phase diagram.

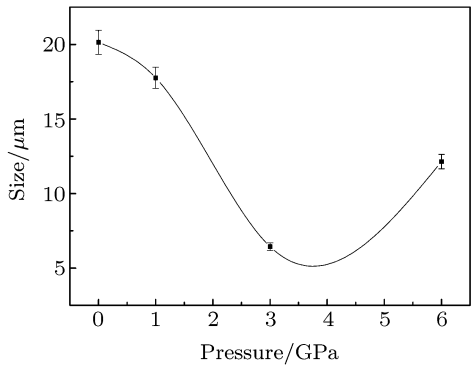


Fig. 5. Dependencies of the grain size of α phase on pressure.

Figure 5 shows the influence of pressure on the size of α phase. It can be seen that the grain size of it decreases with increasing pressure in the pressure range below about 3 GPa, and then increases ($P > 3$ GPa). For Cu–Al–Bi alloy, the growth of α-Cu phase during the crystallisation is dependent on atomic diffusion.[12] According to the theory of diffusion,[13] the size of crystalline phase, d, is approximately given by

$$d = \lambda\sqrt{Dt}, \tag{1}$$

where λ is a constant, D is the atomic diffusion coefficient, and t is the time of diffusion. For alloys annealed under high pressure, the atomic diffusion coefficient D is given by[14]

$$D = D_0 \exp(-P\Delta V^*/RT), \tag{2}$$

where D_0 is a constant, P is the pressure, R is the gas constant, T is the temperature, and ΔV^* is the activation volume. Equations (1) and (2) can be combined to give

$$\ln d = -P\Delta V^*/2RT + (1/2)\ln t + \varphi, \tag{3}$$

where

$$\varphi = \ln\lambda + (1/2)\ln D_0, \tag{4}$$

$$\Delta V* = \Delta V_{\rm f} + \Delta V_{\rm m}. \tag{5}$$

Here $\Delta V_{\rm f}$ is vacancy formation volume, $\Delta V_{\rm m}$ is the volume of vacancy movment which is always positive; however, $\Delta V_{\rm f}$ can be both positive and negative. For vacancy-controlled diffusion $\Delta V_{\rm f} > 0$ and for interstice-controled diffusion, $\Delta V_{\rm f} < 0$. Only when $\Delta V^* > 0$, the size of crystalline phase decreases with increasing pressure. According to the above experimental results (Fig. 2) we know that there is a critical pressure when the diffussion mechanism changes from vacancy to interstice; using the experimental data we calculate the critical pressure to be 3.5 GPa.

4. Conclusions

After annealing in the temperature range of 25–750 °C and pressure range of 0–6 GPa, the microstructure in Cu–Al–Bi alloy is composed mainly of α-Cu phase and β' phase. With the increase of pressure, the grain size of α-Cu phase decreases and accompanied by white reseau in its microstructure for the composition of 54.69%Cu and 45.31%Al (weight percent). However, high pressure causes less effect on the composition of α phase.

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