Effects of high-pressure heat treatment on the solid-state phase transformation and microstructures of $Cu_{61.13}Zn_{33.94}Al_{4.93}$ alloys

Wang Hai-Yan(王海燕)[a], Liu Jian-Hua(刘建华)[b], Peng Gui-Rong(彭桂荣)[b]†, and Wang Wen-Kui(王文魁)[b]

[a] *Provincial Key Laboratory of Applied Chemistry, Yanshan University, Qinhuangdao* 066004, *China*
[b] *State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao* 066004, *China*

(Received 23 March 2010; revised manuscript received 17 May 2010)

The phase transformation activation energy of the $Cu_{61.13}Zn_{33.94}Al_{4.93}$ alloys, which were treated at 4 GPa and 700 °C for 15 minutes, was calculated by means of differential scanning calorimetry curves obtained at various heating and cooling rates. Then, the effects of high-pressure heat treatments on the solid-state phase transformation and the microstructures of $Cu_{61.13}Zn_{33.94}Al_{4.93}$ alloys were investigated. The results show that high-pressure heat treatments can refine the grains and can change the preferred orientation from (111) to (200) of α phase. Compared with the as-cast alloy, the sample with high-pressure heat treatment has finer grains, lower $\beta' \rightarrow \beta$ and $\beta \rightarrow \beta$' transformation temperature and activation energy. Furthermore, we found that high cooling rate favours the formation of fine needle-like α phase in the range of 5–20 °C/min.

Keywords: $Cu_{61.13}Zn_{33.94}Al_{4.93}$ alloy, high-pressure heat treatment, solid-state phase transformation, microstructures

PACC: 6250, 8140G

1. Introduction

Cu–Zn alloy is widely used in modern industry. How to improve the overall properties of Cu–Zn alloys by means of grain refinement is one of the overriding concerns in this field.[1−3] It is known that high pressure can improve nucleation, reduce atomic diffusion coefficient, and restrain the grain growth.[4−6] Thus, investigations on grain refinement by means of high-pressure treatments have been attracting more and more attention in recent years. So far, investigations on Cu–Zn alloy high pressure treatment are mainly focused on its solidification process under high pressure.[7−10] As is known, microstructures of many kinds of alloys depend on solid-state phase transformation; therefore, high pressure heat treatment might be an effective way to change the microstructures of alloys and to improve their overall properties. In addition, high pressure heat treatments have some other advantages, such as relatively low temperature and simple operations, etc. In this paper, the influence of high pressure heat treatments on the microstructures and solid-state phase transformation of $Cu_{61.13}Zn_{33.94}Al_{4.93}$ is investigated.

2. Experimental

The as-cast $Cu_{61.13}Zn_{33.94}Al_{4.93}$ (atomic fraction, %) alloy samples were sealed into graphite heaters, and then were pressurized to 4 GPa and heated to 750 °C for 15 min on the CS–IIB type six-anvil high-pressure equipment which uses pyrophyllite as the pressure-transmitting medium. The pressure was released after the samples were cooled down to room temperature. For comparison, the as-cast $Cu_{61.13}Zn_{33.94}Al_{4.93}$ alloy samples were also treated at 700 °C for 15 min in air at ambient pressure in order to clarify the effects of high pressure on microstructure evolution. The as-cast samples and the high-pressure heat treated samples were then subjected to the differential scanning calorimetry (DSC) measurements (STA449C, Jupiter, Netzsch, Germany), in which the sample was heated to 700 °C and kept at this temperature for 1 min and then cooling down to room temperature at heating and cooling rates of 5 °C/min, 10 °C/min, and 20 °C/min respectively. The temperature and the duration of the solid-state phase transformation of the alloys during heating and cooling process were measured according to the DSC curves. The

†Corresponding author. E-mail: gr8599@ysu.edu.cn

© 2010 Chinese Physical Society and IOP Publishing Ltd

phase transformation activation energy (E_c) of the sample was calculated by the Kissinger equation:[11] $\ln(BT^{-2}) = -E_c(RT)^{-1}$+constant, where B is the heating or cooling rate, R is the gas constant, T is the temperature. The microstructures of the samples were observed on the Axiovert200MAT-type optical microscope. And D/MAX-rB type x-ray diffraction (XRD) was used for the identification of different phases.

3. Results and discussions

3.1. Microstructures

Figure 1 shows the microstructures of $Cu_{61.13}Zn_{33.94}Al_{4.93}$ alloy under different conditions. It can be seen that the as-cast $Cu_{61.13}Zn_{33.94}Al_{4.93}$ alloy is composed of α (solid solution of zinc in copper) and β' phase (Electron compound CuZn based solid solution). The α phase shows as thick irregular white strips and the β' phase mainly exists in the black zones. The microstructure of the $Cu_{61.13}Zn_{33.94}Al_{4.93}$ alloy after heat treatment at ambient pressure is the same as that of the as-cast alloy except that the heat treated sample shows finer grains than the original one. For the sample after heat treatment under high pressure, the grain refinement phenomenon can be clearly observed. In addition, the thick irregular white strip-like α phase disappears, and fine granular α phase with grain diameter of 5–10 μm appears. As shown in the XRD patterns in Fig. 2, the preferred orientations of both the as-cast $Cu_{61.13}Zn_{33.94}Al_{4.93}$ alloy and the alloy after heat treatment at ambient pressure are $\alpha(111)$ and $\beta'(110)$, while the preferred orientation of the α phase in the $Cu_{61.13}Zn_{33.94}Al_{4.93}$ alloy after heat treatment at 4 GPa changes into $\alpha(200)$ and that of the β' phase keeps at $\beta'(110)$. In Fig. 2, it can also be seen that the relative peak intensity of β' phase increases whereas that of the α phase decreases after high-pressure heat treatement, and no new peak emerges in the XRD pattern. It can be concluded that high-pressure heat treatment can obviously refine the microstructures of $Cu_{61.13}Zn_{33.94}Al_{4.93}$ alloy.

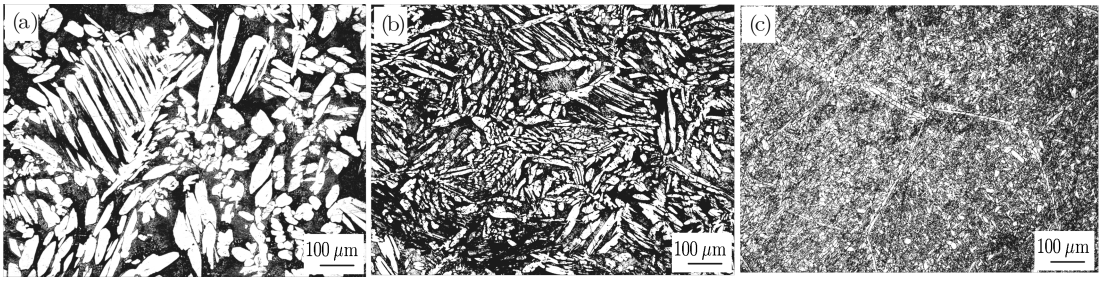


Fig. 1. Microstructures of $Cu_{61.13}Zn_{33.94}Al_{4.93}$ alloys: (a) as-cast alloy, (b) alloy after heat treatment at ambient pressure, and (c) alloy after heat treatment at 4 GPa.

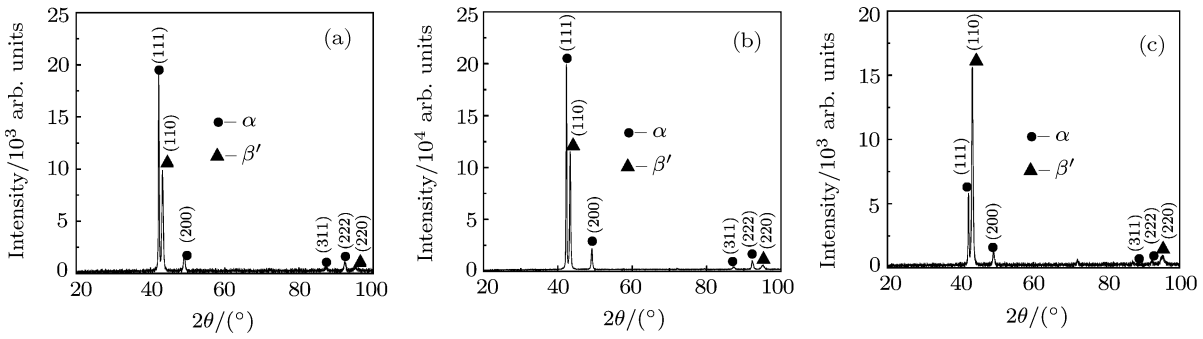


Fig. 2. XRD patterns of $Cu_{61.13}Zn_{33.94}Al_{4.93}$ alloys: (a) as-cast alloy, (b) alloy after heat treatment at ambient pressure, and (c) alloy after heat treatment at 4 GPa.

According to the classic nucleation theory,[12,13] the nucleation rate (I) can be expressed as: $I = I_0 \exp(-G/RT)$. Neglecting the influence of pressure on surface energy, the ratio of nucleation rate under high pressure to that at ambient pressure can be calculated according to Eq. (1), and the ratio of growth rate under high pressure and that at ambient pressure can be expressed as Eq. (2).

$$\frac{I_{\rm p}}{I_0} = \exp\left(\frac{G_0 - G_{\rm p}}{RT}\right), \quad (1)$$

$$\frac{\upsilon_{\rm p}}{\upsilon_0} = \frac{G'_0 - G'_{\rm p}}{RT}, \quad (2)$$

where $I_{\rm p}$, $G_{\rm p}$, $G'_{\rm p}$, and $\upsilon_{\rm p}$ are the nucleation rate, the nucleation activation energy, the growth activation energy, and the growth rate under high pressure; and I_0, G_0, G'_0, υ_0 are the nucleation rate, the nucleation activation energy, the growth activation energy, and the growth rate at ambient pressure respectively; T is the temperature, and R is the gas constant.

Since nucleation activation energy G equals the sum of diffusion activation energy (ΔE) and the free energy associated with the formation of a nucleus (ΔG), and the ΔG can be expressed as:

$$\Delta G = \frac{16\pi}{3}\frac{\sigma^3}{\Delta G_V^2}. \quad (3)$$

Considering the influence of pressure on nucleation and supposing the surface energy σ is irrelevant to pressure, the following equation can be obtained from Eq. (3)

$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = -\frac{32\pi\sigma^3}{3}\cdot\frac{\Delta V}{\Delta G_V^3}, \quad (4)$$

where σ is the surface energy between two phases, ΔG_V is the Gibbs free energy difference per unit volume between the new phase and the original phase, ΔV is the volume difference between the new phase and the original phase. Due to $\Delta G_V < 0$ and $\Delta V < 0$, it can be deduced from Eq. (4) that high pressure can lower the critical free energy of nucleus formation.

The solid-state phase transformation of $Cu_{61.13}Zn_{33.94}Al_{4.93}$ alloy is the nucleation and growth process of new phase via atomic diffusion. The nucleus formation, which need not be the long range diffusion of Cu, Zn, and Al atoms, mainly depends on its critical free energy. Pressure can lower the critical free energy for nucleus formation, which decreases the nucleation activation energy ($G_{\rm p} < G_0$) and increases the nucleation rate ($I_{\rm p} > I_0$). High pressure restrains the atom diffusion and increases the diffusion activation energy, thus pressure can increase the growth activation energy ($G'_0 < G'_{\rm p}$), so as to restrain the growth of nucleus and to lower the growth rate ($\upsilon_{\rm p} < \upsilon_0$). As a result, we propose that high pressure can promote nucleation and restrain growth of nucleus, resulting in the fine grains of $Cu_{61.13}Zn_{33.94}Al_{4.93}$ alloy after solid-state phase transformation under high pressure.

3.2. Solid-state phase transformation

In Fig. 3, we show the DSC curves of the $Cu_{61.13}Zn_{33.94}Al_{4.93}$ alloys as-cast and after high-pressure heat treatment at a heating and cooling rate of 5 °C/min. It can be seen that heating DSC curves displays an endothermic peak and the cooling curves show an exothermic peak for both samples. It can be deduced from Ref. [14] that the endothermic peak is related to the solid-state phase transformation ($\beta' \rightarrow \beta$) and the exothermic peak is associated with the solid-state phase transformation ($\beta \rightarrow \beta'$). Both β phase and β' phase are electron compound CuZn-based solid solution with bcc lattice, while β phase is disordered solid solution and β' phase is ordered solid solution. The initial, the peak, and the ending temperatures, as well as the duration of the solid-state phase transformation, of the $Cu_{61.13}Zn_{33.94}Al_{4.93}$ alloys during the following heating and cooling process can be calculated from their DSC curves, as shown in Table 1 and Table 2.

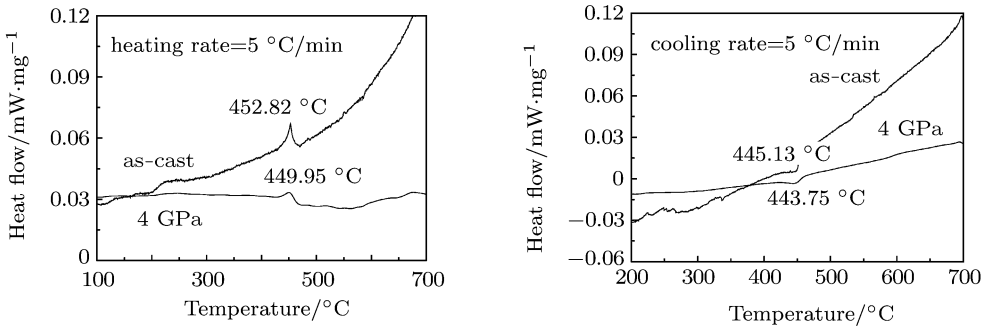


Fig. 3. DSC curves of the as-cast and the high pressure heat treated $Cu_{61.13}Zn_{33.94}Al_{4.93}$ alloys at heating and cooling rate.

These indicate that high-pressure heat treatment can lower the β phase transformation temperature and

shorten the $\beta' \rightarrow \beta$ and $\beta \rightarrow \beta'$ phase transformation duration of the $Cu_{61.13}Zn_{33.94}Al_{4.93}$ alloy during the following heating and cooling process. For instance, at the heating rate of 5 °C/min, the $\beta' \rightarrow \beta$ phase transformation peak temperature and duration of the high-pressure heat treated alloy are decreased by 2.87 °C and 16.2 s respectively, and at the cooling rate of 5 °C/min, its peak temperature and duration are decreased by 1.38 °C and 12.48 s, as compared with that of the as-cast alloy.

Table 1. $\beta' \rightarrow \beta$ phase transformation peak temperature and duration of $Cu_{61.13}Zn_{33.94}Al_{4.93}$ alloys at various heating rates.

heating rate/(°C/min)	beginning temperature/°C		peak temperature/°C		ending temperature/°C		time/s	
	as-cast	4 GPa	as-cast	4 GPa	as-cast	4 GPa	as-cast	4 GPa
5	437.71	435.69	452.82	449.95	464.39	461.02	320.16	303.96
10	440.93	438.12	455.26	453.45	473.12	467.72	193.14	177.60
20	444.85	442.18	458.27	457.06	478.64	472.73	101.37	91.65

Table 2. $\beta \rightarrow \beta'$ phase transformation peak temperature and duration of $Cu_{61.13}Zn_{33.94}Al_{4.93}$ alloys at various cooling rates.

cooling rate/(°C/min)	beginning temperature/°C		peak temperature/°C		ending temperature/°C		time/s	
	as-cast	4 GPa	as-cast	4 GPa	as-cast	4 GPa	as-cast	4 GPa
5	455.16	453.03	445.13	443.75	428.58	427.49	318.96	306.48
10	453.67	451.42	441.58	439.66	424.38	423.93	175.74	164.94
20	452.87	450.18	438.02	436.04	419.01	418.42	101.58	95.28

The phase transformation peak value curves $\ln(BT^{-2}) - T^{-1}$ at various heating and cooling rates can be obtained from Table 1 and Table 2, as shown in Fig. 4. It can be seen that $\ln(BT^{-2})$ varies almost linearly with T^{-1}. The β solid phase transformation activation energy of the as-cast and the high pressure heat treated $Cu_{61.13}Zn_{33.94}Al_{4.93}$ alloy during the following heating and cooling processes can be obtained from the slope of the line (E_c/R), which can be calculated by the least square method according to the Kissinger equation (shown in Table 3). It indicates that high pressure heat treatment can reduce the solid phase transformation activation energy of the $Cu_{61.13}Zn_{33.94}Al_{4.93}$ alloy during the following heating and cooling processes. The reason may be that high-pressure heat treatment increases the defect density of phase β, which creates favourable conditions for the solid phase transformation, shown as the lower phase transformation temperature, lower phase transformation activation energy and shorter phase transformation duration.

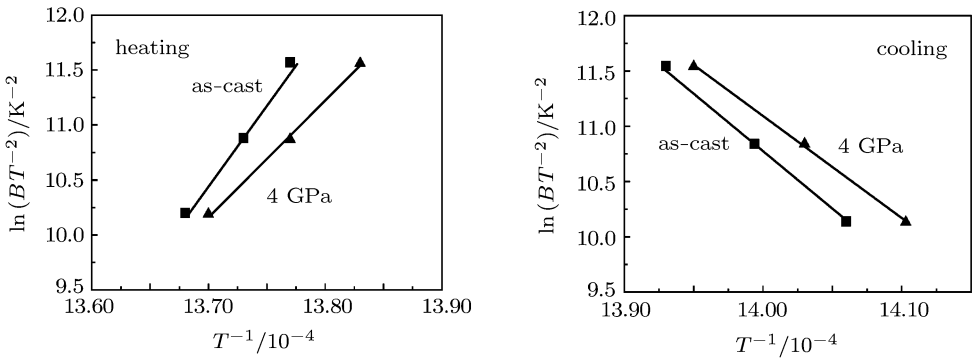


Fig. 4. Relationship between $\ln(BT^{-2})$ and T^{-1} at DSC peak values under various conditions.

Table 3. Solid phase transformation activation energy of $Cu_{61.13}Zn_{33.94}Al_{4.93}$ alloy under various conditions.

conditions	activation energy/KJ/mol	
	as-cast	4 GPa
heating ($\beta' \rightarrow \beta$)	1106.03	843.07
cooling ($\beta \rightarrow \beta'$)	839.18	770.42

The microstructures of the as-cast and the high-pressure heat treated $Cu_{61.13}Zn_{33.94}Al_{4.93}$ alloys after DSC measurements are shown in Fig. 5. It can be seen from Fig. 5 that the α phase in the as-cast $Cu_{61.13}Zn_{33.94}Al_{4.93}$ alloy after annealing for 1 min at 700 °C and then cooling down to room temperature at 5–20 °C/min shows granular grains and the size of the grains decreases with the increasing cooling rate. However, the α phase in the high-pressure heat treated alloy demonstrates a fine needle-like and granular shape at the same temperature scale, and the number of the fine needle-like grains increases with increasing cooling rate. Moreover, the high-pressure treated sample shows finer grains than the as-cast one, which can be evidenced by the fact that, at the cooling rate of 5 °C/min the grain size of granular α phase of the sample without high-pressure treatment is around 35.47–44.56 μm, while the grain size of the sample with high-pressure treatment is around 21.64–34.39 μm. The reason may be that high-pressure heat treatment produces high density defects in the alloys, such as dislocations and grain boundaries, which provides preferential nucleation sites for the solid-state phase transformation, resulting in increasing nucleus amount and decreasing grain size. We note that more high-pressure heat treatments are not beneficial for grain refinement through our SEM results, as shown in Fig. 1(c) and Figs. 5(d)–5(f).

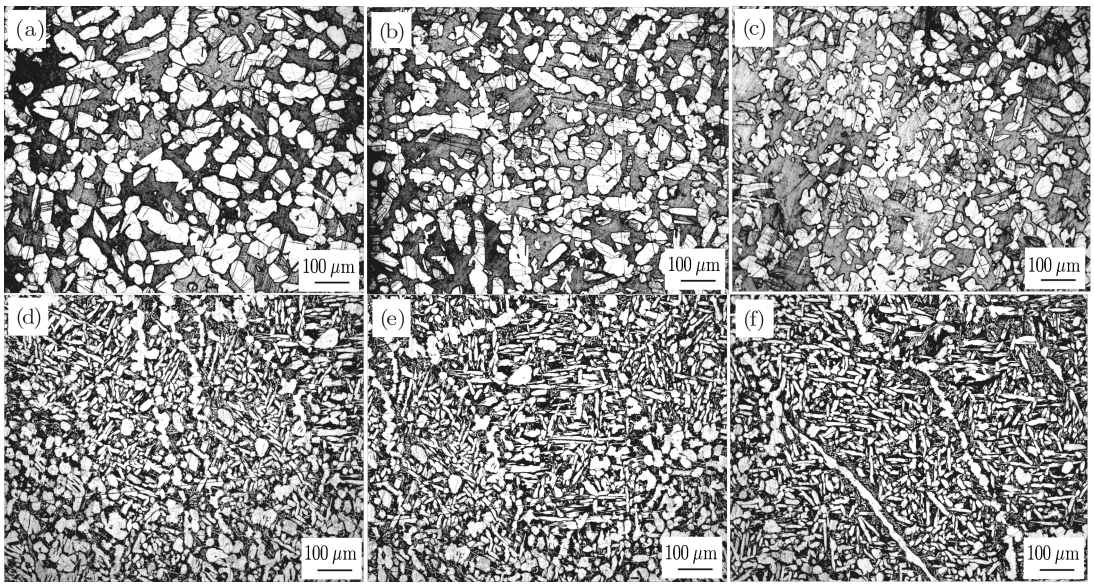


Fig. 5. Microstructures of the as-cast and the high-pressure treated alloys after DSC measurements: (a) as-cast, 5 °C/min; (b) as-cast, 10 °C/min; (c) as-cast, 20 °C/min; (d) 4 GPa, 5 °C/min; (e) 4 GPa, 10 °C/min; (f) 4 GPa, 20 °C/min.

4. Conclusions

(i) High-pressure heat treatment can refine the grains of $Cu_{61.13}Zn_{33.94}Al_{4.93}$ alloy, change the preferred orientation of α phase from (111) to (200) and increase the relative XRD peak intensity of β phase.

(ii) High-pressure heat treatment decreases the $\beta' \rightarrow \beta$ and $\beta \rightarrow \beta'$ phase transformation temperature and activation energy, and shortens the phase transformation duration during the heating and cooling process.

(iii) The number of the needle-like α phase in the high-pressure heat treated $Cu_{61.13}Zn_{33.94}Al_{4.93}$ alloy after annealing for 1 min at 700 ° and then cooling at the rate of 5–20 °C/min increases with increasing cooling rates. More high-pressure heat treatments make against grain refinement.

References

[1] Yang G S, Lee J K and Jang W Y 2009 *Transactions of Nonferrous Metals Society of China* **19** 979

[2] Peng K P, Su L F, Shaw L L and Qian K W 2007 *Scripta Materialia* **56** 987

[3] Oishi K C, Sasaki I and Otani J C 2003 *Mater. Lett.* **57** 2280

[4] Chen D N, Fan C L, Hu J W, Wu S X, Wang H R and Tan H 2009 *Acta Phys. Sin.* **58** 2612 (in Chinese)

[5] Wang H Y, Cui H B, Li C Y, Li X S and Wang K F 2009 *Acta Phys. Sin.* **58** 5598 (in Chinese)

[6] Lü M Y, Chen Z W, Li L X, Liu R P and Wang W K 2006 *Acta Phys. Sin.* **55** 3576 (in Chinese)

[7] Straumal B B, Baretzky B, Mazilkin A A, Phillipp F, Kogtenkova O A, Volkov M N and Valiev R Z 2004 *Acta Materialia* **52** 4469

[8] Degtyareva V F, Chipenko G V and Belash I T 1985 *Phys. Stat. Sol.* (a) **89** 127

[9] Xu R, Zhao H, Li J, Liu R P and Wang W K 2006 *Mater. Lett.* **60** 783

[10] Min T K and One Y O 2009 *J. Alloys Compd.* **477** 224

[11] Kissinger H E 1975 2009 *Anal. Chen.* **29** 1702

[12] Zhou Y H, Hu Z Q and Jie W Q 1998 *Solidification Technology* (Beijing: Machinery Industry Publisher) p467 (in Chinese)

[13] Sun S H, Li J, Xu R, Zhao H L and Liu R P 2008 *Chinese Journal of High Pressure Physics* **22** 434 (in Chinese)

[14] Wang Z T 2002 *Cu Alloys and Its Working Handbook* (Changsha: Central South University Press) p28 (in Chinese)