Effect of 5Gpa Pressure Treatment on the Phase Transformation of α+γ₂→ß in Cu-Al Alloy

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Abstract. The phase transformation temperature and time of α+γ₂→ß in Cu-Al alloy before and after 5Gpa pressure treatment were measured by differential scanning calorimeter, its activation energy and Avrami exponent were also calculated. The effect of 5Gpa pressure treatment on the phase transformation of α+γ₂→ß in the alloy was discussed based on the measurement, calculation and the observation of alloy's microstructure. The results show that 5Gpa pressure treatment can decrease the transformation temperature and transformation activation energy and shorten the transformation time, it is conducive to the phase transformation of α+γ₂→ß in the Cu-Al alloy, but has little effect on the phase transformation mechanism.

1. Introduction

Copper alloy has been widely applied in the fields of electricity, electrical and air due to its high electrical conductivity, thermal conductivity and good corrosion resistance. However, the obtaining of coarse grains of this material limits its further application[1]. It is well known that high pressure can promote nucleation, suppress atomic transport and inhibit grain growth, and thus efforts have been given to gain fine-grained alloy by means of high pressure treatment[2-4]. Therefore, a lot of attention has been paid on the effect of high pressure treatment on metal materials to ameliorate alloy microstructure[5-7].The recent study have founded that high pressure treatment is beneficial to obtain the refined microstructure of the Cu-Al alloy so as to enhance the strength of alloy[8]. Since the application part made of Cu-Al alloy, which is used at a certain temperature, would inevitably occur solid state phase transformation with the temperature increase. Therefore, the microstructure and properties have been badly influenced. However, the pressure effects on the solid state transformation of Cu-Al alloy in following heating process are still not clear. In this paper, the effect of high pressure treatment on solid state phase transformation of Cu-Al alloy during the following heating process has been studied and the results provide some reference to establish the hot working technology of the copper alloy after high pressure treatment and enrich the high-pressure research in the field of copper alloy.

2. Experimental

The materials to be test were Cu-Al alloys(88.24% Cu,11.76%Al and 0.63% other elements mass fraction, %).The specimen were first smelted into the vacuum intermediate frequency induction furnace at about 1150℃ and casted into cylindrical billets in graphite mold. High-pressure experiments were performed on the CS-IIB type six-anvil high-pressure equipment. The samples were pressurized to 5GPa and heated to 700℃ for 15 minutes. Then the pressure was released until the samples were cooled to room temperature. The Cu-Al alloy samples before and after high pressure treatment were then subjected to the differential scanning calorimeter (DSC) measurements (STA449C, Jupiter, Netzsch, Germany) with the heating temperature of 700℃ and the heating rate of   5℃·min⁻¹, 10℃·min⁻¹, and 20℃·min⁻¹ respectively. The phase transformation

activation energy (E_c) of the sample was calculated by the Kissinger equation[9]: $ln(B.T^{-2})=-Ec(R.T)^{-1}+c$. Where, B is the heating rate, T is the temperature, R is the gas constant, c is the constant. The phase transformation activation energy at certain stage (E_x) was calculated by the Doyle method[10]: $logB= logAE_x[RF(x)]^{-1}-2.315- 0.4567E_x (RT)^{-1}$. Where, B is the heating rate , R is the gas constant , T is the temperature , x is the phase transformation fraction , A is the frequency factor , and $F(x)$ is the phase transformation function. When x is a constant, $logAE_x[RF(x)]^{-1}$ is also a constant. Avrami exponent (n) can be obtained by n = $2.5T_p^2 (\Delta\tau_{FWTH}E_cR^{-1})^{-1}$[11] where: $\Delta\tau_{FWTH}$ is the full width at half maximum of the endothermic peak, T_p is the endothermic peak temperature, E is the phase transition activation energy, R is the gas constant. The samples were cut along the lengthwise through the sample, sanded, polished and etched in 1g $FeCl_3$+20mlHCl+100mlH_2O etching solution and microstructures of the samples were observed on the Axiovert 200MAT metalloscope and H-2010 transmission electron microscope (TEM).

3. Results and Discussions

3.1 Microstructure

Fig.1 shows the microstructure of Cu-Al alloy before and after 5GPa pressure treatment. The microstructures are composed of irregular white zone and black zone. The white zone belongs to α phase while β and γ_2 phase mainly exist in black zone. The metallographic images reveal that the grain size after 5GPa treatment is less than that before 5GPa treatment. It can be observed from TEM image(Fig.2) that the dislocation density increase obviously after high pressure treatment.
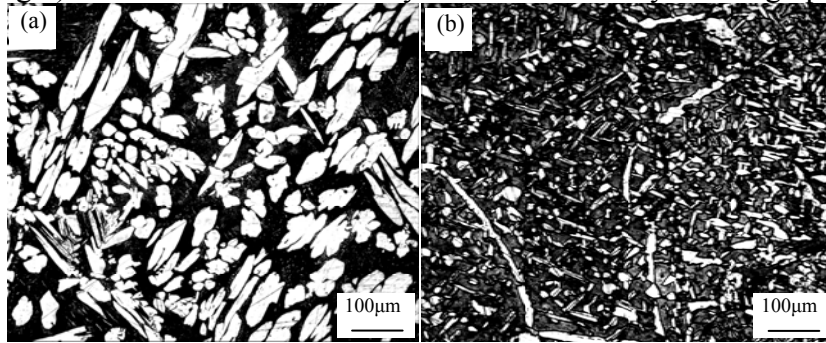

Fig.1 Microstructure of the Cu-Al alloys (a)As-cast;　(b) 5GPa pressure treatment
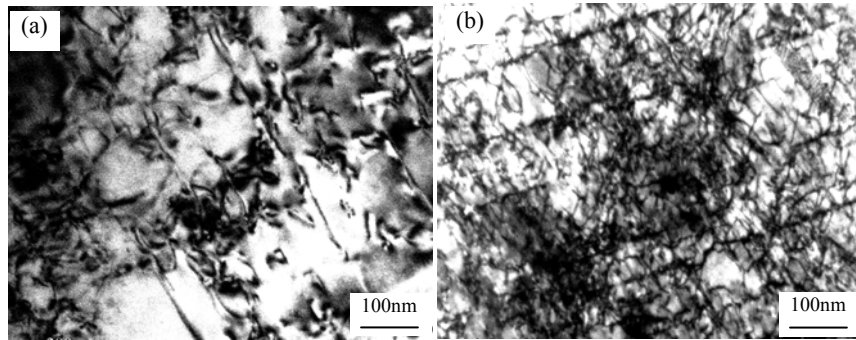

Fig.2 TEM images of the brass before and after high pressure treatment
(a) As-cast; (b) 5GPa pressure treatment

After high pressure treatment, high residual stress and strain remaining in the alloy causes lattice deformation, which results in plenty of dislocation in the alloy, the latter provides more favorable nucleation sites for α+γ_2→ß phase transformation. Meanwhile, high pressure can suppress atomic transport and the growth of crystal nucleus[6], Therefore, the refined grains of Cu-Al alloy can be obtained and higher dislocation density can be observed after high pressure treatment.

3.2 Phase transformation at constant heating rates

Fig.3 shows the DSC curves of Cu-Al alloy before and after high pressure treatment at constant heating rates at 5℃·min^{-1}, 10℃·min^{-1}, 20℃·min^{-1} respectively. One endothermic peak can be seen clearly on each DSC curve before and after high pressure treatment. Based on phase diagram of the

Cu-Al alloy[12], this peak corresponds to the solid state phase transformation α(Cu) + γ$_2$ (Al$_4$Cu$_9$) →ß(AlCu$_3$) in heating process. The initial temperature, the peak temperature, the ending temperature and the transformation duration of the phase transformation can be deduced from the DSC curves at different cooling rates, and listed in Table 1. It can be seen that the initial temperature, the peak temperature and the ending temperature of α+γ$_2$→ß phase transformation all increase with increasing heating rate and that the Cu-Al alloy after high pressure treatment shows lower phase transformation temperature and shorter phase transformation duration than that without high pressure treatment. Taking the heating rate of 10℃·min^{-1} for an example, the phase transformation peak temperature and the phase transformation duration of the Cu-Al alloy after high pressure treatment is decreased 7.23℃ and 33.48s respectively, which reveals that the α+γ$_2$→ß phase transformation is more prone to happen during the heating process after the high pressure treatment.
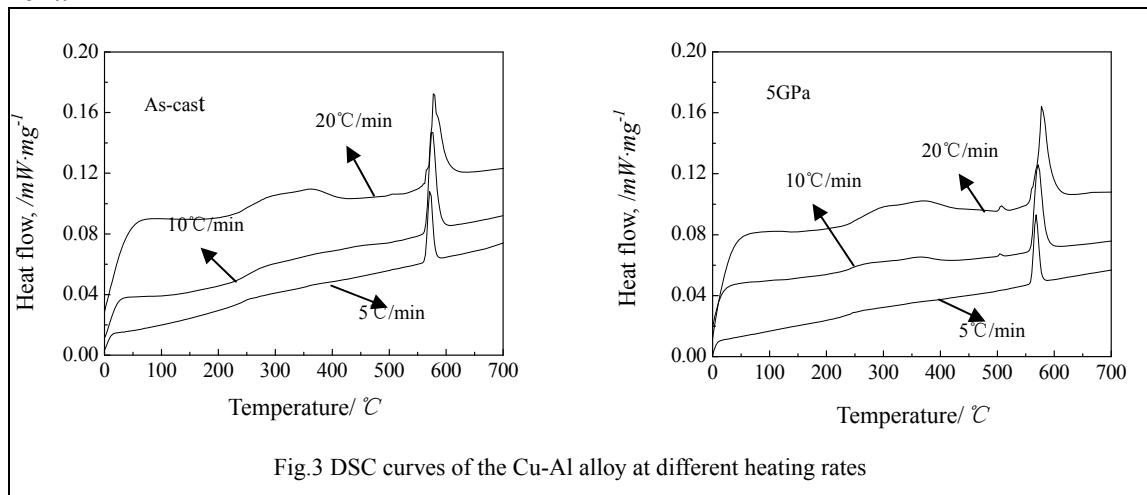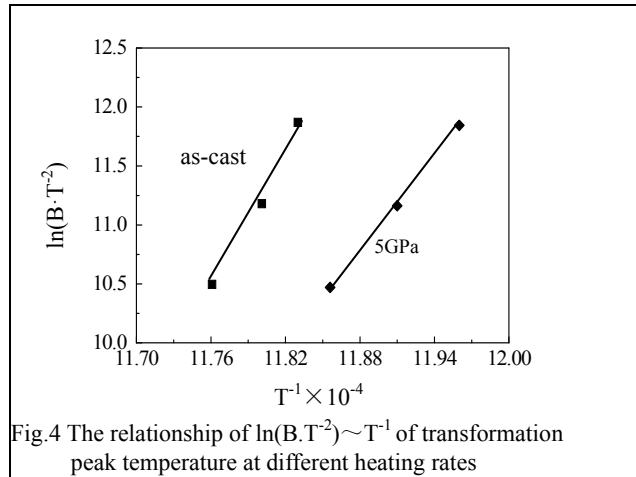

Fig.3 DSC curves of the Cu-Al alloy at different heating rates

Table1 Caption phase transformation temperature and time of α+γ$_2$→ß in Cu-Al alloy before and after high pressure treatment under different heating rates

Heating rate /℃.min^{-1}	Initial temperature/℃		Peak temperature/℃		Ending temperature/℃		Transformation duration/s	
	As-cast	5GPa	As-cast	5GPa	As-cast	5GPa	As-cast	5GPa
5	562.47		570.56		589.83		328.32	257.88
	559.59		564.11		580.68			
10	564.32		574.87		592.25		167.58	134.10
	560.02		567.64		582.37			
20	566.49		576.47		601.36		104..61	73.02
	561.07		571.52		585.41			

3.3 Phase transition activation energy

According to the phase transformation peak value at various heating rates shown in Table 1, linear relation of $ln(BT^{-2})$ and T^{-1} was obtained, as shown in Fig.4.

Fig.4 The relationship of ln(B.T^{-2})～T^{-1} of transformation
peak temperature at different heating rates

By calculating its slope according to the Kissinger equation using the least square method, (E_c/R) is achieved, thus the phase transformation activation energy of α+γ$_2$→ß of the Cu-Al alloy before and after high pressure treatment is obtained, *i.e.*,1290.22.58kJ·mol^{-1} and 1084.44kJ·mol^{-1}, respectively. The high pressure treatment can reduce the α +γ$_2$→ ß phase transition activation energy. It can be concluded that high pressure treatment can decrease the α+γ$_2$→ ß phase transition consumption barrier in the subsequent heating process, leads to the α + γ$_2$→ ß phase transition easier.The relation of the phase transformation volume fraction (x_i) and the corresponding temperature (T) of the samples with and without high pressure treatment can be obtained from the DSC curves, as shown in Fig.5. According to Fig.5, the α+γ$_2$→ ß phase transformation activation energy at various stages can be calculated by the Doyle equation and is plotted in Fig.6. It indicated that the phase transformation activation energy is relatively higher at initial stage, and then decreases with increasing volume fraction. Thus, high pressure treatment can reduce theα+γ$_2$→ß phase transformation activation energy.

Fig.5 Relationship between the transformation volume fraction and temperature at different heating rates

Fig.6 Relationship between the phase transformation activation energy
and the phase transformation volume fraction
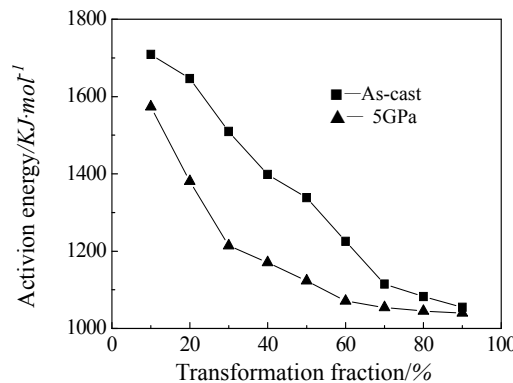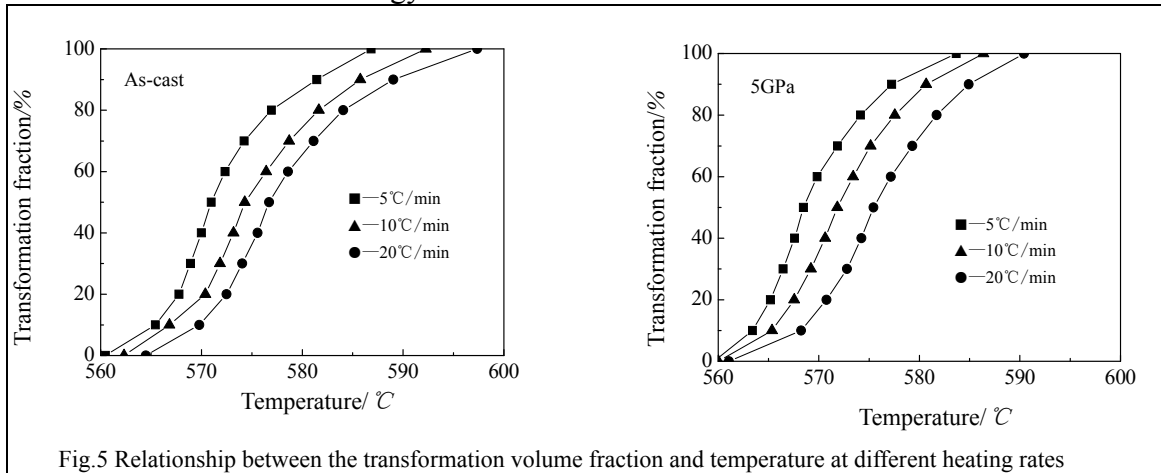
3.4 Avrami exponent

The Avrami exponent (*n*) is an important kinetics parameter characterizing the phase transformation behavior such as nucleation and growth. The average Avrami exponent (*n*) of the Cu-Al alloy before and after high pressure treatment can be obtained by above equation according to the DSC data, as shown in Fig.7. It shows that high pressure treatment can increase Avrami exponent (*n*), but the Avrami exponents (*n*) in both cases are less than 2. According to the Avrami exponent (*n*) $(1<n<2)$[13-14] , the $\alpha+\gamma_2\rightarrow \text{ß}$ phase transformation of the Cu-Al alloy both with and without high pressure treatment obeys the one-dimensional growth mode characterized by gradually decreasing nucleation rate and diffusion-controlled crystal growth process. High pressure treatment has no obvious effect on the $\alpha+\gamma_2\rightarrow \text{ß}$ phase transformation mechanism. The $\alpha+\gamma_2\rightarrow \text{ß}$ phase transformation process includes the formation and growth of crystal nucleus. The whole process is performed through the diffusion of atoms. The more the grain boundary, vacancies and dislocation in microstructure of Cu-Al alloy exist, the more tunnels for the diffusion of Cu and Al atoms are, as a result, the easier the phase transformation goes. The fine grain microstructures obtained after high pressure treatment is mainly to the increment of the density of interface and the interfacial deficiency.Meanwhile, a lot of internal stress remaining in the alloy during heating process causes plenty of lattice distortion and dislocations in the interior of grain, the latter provides more favorable channel for the diffusion of copper and aluminum atoms, resulting in the atoms rearrange easily achieved in the subsequent heating process and reduce the phase transition activation energy and phase transition time, which is attributed to the $\alpha+\gamma_2\rightarrow \text{ß}$ phase transition.
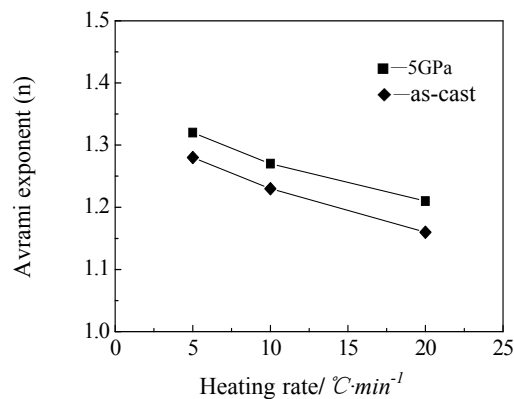

Fig.7 Relationship between the heating rate and Avrami exponent

4. Conclusions

(1) High pressure treatment can decrease the $\alpha+\gamma_2\rightarrow \text{ß}$ phase transformation temperature and shorten phase transformation duration, which is favorable to the $\alpha+\gamma_2\rightarrow \text{ß}$ solid state phase transformation. Compared with no pressure treatment, the phase transformation peak temperature and the phase transformation duration of the Cu-Al alloy after high pressure treatment is decreased 7.23℃ and 33.48s respectively after the Cu-Al alloy was processed by 5Gpa and succedent heating at the rate of 10°C·min^{-1}.

(2) High pressure treatment can reduce the activation energy of the $\alpha+\gamma_2\rightarrow \text{ß}$ solid phase transformation and elevate Avrami exponent during heating process, but has no obvious effect on the growth mode of the solid phase transformation.

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