Effect of High Pressure Heat Treatment on Microstructure and Thermal Expansion Coefficients of Cu–Al Alloy

Ma Yu-quan

Mechanical and Electrical Engineering College, Hebei Normal University of Science and Technology, Qinhuangdao 066004, China

With different high pressure heat treatments on Cu–Al alloy, the effects on microstructure and thermal expansion coefficients of Cu–Al alloy are studied in the paper by optical microscopy, scanning electron microscopy, transmission electron microscopy and expansion instrument etc. The experimental results show that after heat treatment, the structure of Cu–Al alloy was refined obviously and the compactness increased. The grain refinement effect increases at first and then decreases when pressure is increased. When the pressure is 3 GPa, the most obvious is the thinning grain effect. In addition, the high pressure heat treatment can increase Cu–Al alloy thermal coefficient of expansion, when the Cu–Al alloy is treated by 3 GPa pressure and is at 596.37°C. Thermal expansion coefficient is the biggest, $3.1187 \times 10^{-5} \text{°C}^{-1}$, than that of the same temperature cast state samples increase 99.34%. [doi:10.2320/matertrans.M2012358]

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1. Introduction

Cu–Al alloy has been widely used in shipping, machinery, aviation and other related fields due to its high strength, corrosion resistance, excellent hot and cold processing performance. However, the coarse grains of this material restrict its further application.¹⁾ It is known that high pressure can promote the nucleation, but reduce the atomic diffusion coefficient and thus restrain the grain growth.^{2,3)} Therefore, the researches on the improvements of microstructure and properties of metal materials by means of high pressure heat treatment attracted considerable research interest.^{4,5)} High pressure treatment has been found to be effective in improving the microstructure and mechanical properties of Cu alloys.^{6–8)} However, studies on the effect of high pressure treatment on the thermal expansion property of Cu alloys have not been reported yet. Furthermore, the service condition for metal parts often involves the combination of thermal-dynamic coupling filed, and thus it is necessary to carry out study on the effect of high pressure heat treatment on the microstructure and thermal expansion of Cu–Al alloy. The results reported in this paper could provide basic reference for future application of high pressure heat treatment.

2. Experiment

The tested material was cast Cu–Al alloy whose chemical composition (mass fraction, %) is 84.67%Cu, 10.64%Al, 2.65%Fe, 1.58%Mn, 0.46% others. The samples were sealed in a graphite sleeve, and the sleeve has been embedded into the pyrophyllite mould which serves as the pressure transmitting medium. Consequently, the mould was placed into the high pressure cell of CS-IB type six-anvil high-pressure equipment as shown in Fig. 1. High pressure heat treatment involves three values: 1, 3 and 6 GPa. The samples were held at 750°C under pressure for 10 min and subsequently cooled to room temperature by cutting off the power supply with the holding pressure unchanged. Finally, the pressure was taken off. The samples before and after high pressure treatment

Fig. 1 Schematic map of pressure applying on sample.

were shaped into the size of $\phi 6 \text{ mm} \times 15 \text{ mm}$ by electronic spark cutting, and polished with 1200# sandpaper. The thermal expansion coefficient of sample in the temperature range of 25–650°C were measured using a DIL402C thermal expansion instrument (using Al_2O_3 as reference and the precision is 3%) with a heating rate of 5°C/min under protecting of argon atmosphere. The coefficient $\alpha = \Delta L / (L \cdot \Delta T)$, where α , L , ΔL and ΔT stands for linear expansion coefficient, sample length, linear expansion of the sample and the measured temperature range, respectively. To study the phase transformation of the Al–Cu alloy during the temperature range of 25–650°C, the thermal analyses were performed on a STA449C differential scanning calorimeter (DSC) for the samples (heated to 700°C with a heating rate of 5°C/min) before and after high pressure heat treatment. The microstructure of the samples was characterized by Axiovert 200MAT optical microscope, HATACHI S-3400N scanning electron microscope (SEM-BSE) and a JEOL-2010 transmission electron microscope (TEM).

3. Results and Discussion

3.1 Microstructure

Figure 2 shows the microstructure of Cu–Al alloy before and after high pressure treatment. It can be seen that the microstructure of as-cast Cu–Al alloy was coarse. The α

Fig. 2 Microstructure of Cu–Al alloy [(a) As-cast; (b) 1 GPa; (c) 3 GPa; (d) 6 GPa].

Fig. 3 TEM images of Cu–Al alloy before and after high pressure treatment. [(a) As-cast; (b) 3 GPa].

Fig. 4 SEM-BSE images of Cu–Al alloy [(a) As-cast; (b) 3 GPa].

phase exists in strip pattern. After high pressure heat treatment with 1–6 GPa, refine granular α phase begin to show up and the microstructure is refined significantly. Note is the thinning effects are the most obvious when the pressure is 3 GPa. TEM observation (Fig. 3) shows that the dislocation density in Cu–Al alloy organizations increases after pressure process. Figure 4 is Cu–Al alloy SEM backscatter images before and after high pressure. As can be seen, there are more microscopic holes in the less compact as-cast Cu–Al alloy matrix.

There is a significant reduce of the number of microscopic holes and holes size in the matrix after high pressure heat treatment, and compact level of the matrix increase.

Solid phase transformation involves nucleation and growth process of new phase which is controlled by atoms diffusion. Based on the diffusion theory, the grain size of the newly formed phase in Cu–Al alloy (d) can be described by following equation⁹⁾

$$d = \lambda \sqrt{Dt} \quad (1)$$

where λ is constant, D is atomic diffusion coefficient, and t is diffusion time.

Under high pressure, the atomic diffusion coefficient (D) can be expressed as follows¹⁰⁾

$$D = D_0 e^{-P\Delta V^*/RT} \quad (2)$$

where D_0 is constant, P is pressure, R is gas constant, T is temperature, ΔV^* is activation volume.

The following equation may be expressed from eqs. (1) and (2):

$$\ln d = -\frac{P\Delta V^*}{2RT} + \frac{1}{2} \ln t + \psi \quad (3)$$

where

$$\psi = \ln \lambda + \frac{1}{2} \ln D_0. \quad (4)$$

Due to $\Delta V^* > 0$, it can be seen from eq. (3), under the same conditions, the pressure can reduce the size of the new phase grain.

High degree of internal strain was introduced in the high pressure heat treated Cu–Al alloy, and the density of dislocation was increased by the consequently lattice distortion, providing more place that is available for the nucleation of newly formed phase and thus increasing the nucleation rate. However, the reverse effect of high pressure on the nuclear of newly formed phase begins to dominate when the pressure is higher than certain value, in which condition the atomic diffusion is prohibited. Therefore, it is reasonable to expect that there is one high pressure that can balance the increase of nucleation rate and the decrease of atomic diffusion. The resulting nucleation and growth of new phase could be promoted mostly. In this experiment, this pressure value is 3 GPa. Under this high pressure heat treatment, the nucleation rate is highest and microstructure is finest, also, the microscopic holes in the Cu–Al alloy matrix is closed and improve material compactness is improved by high pressure process.

3.2 DSC curves

Figure 5 shows DSC curves of Cu–Al alloy before and after high pressure treatment at the constant heating rate of 5°C/min. One endothermic peak at 569.11–572.34°C is observed on DSC curve for each heat treatment condition. Combined with Ref. 11), this endothermic peak results from the solid-state phase transformation: α (Cu) + γ_2 (Al₄Cu₉) $\rightarrow$ β (AlCu₃).

3.3 Thermal expansion coefficients

Figure 6 shows the relationship between the thermal expansion coefficients of Cu–Al alloy and temperature before and after high pressure heat treatment. It can be seen that thermal expansion coefficient of as-cast Cu–Al alloy increases with temperature from 25 to 650°C, but the changing trend is mild. When heat treated under high pressure, there is no change of the relationship between the thermal expansion coefficients and temperature, but in a more rapid rate. When the temperature increase to 570°C, the thermal expansion coefficients become greater increase with temperature increasing. There is a high peak for thermal

Fig. 5 DSC curves of Cu–Al alloy at different states.

Fig. 6 Relationship curves between the thermal expansion coefficients of Cu–Al alloy and temperature.

Table 1 The maximum thermal expansion coefficients and its corresponding temperatures of Cu–Al alloy after different high pressure treatment.

Pressure/GPa	1	3	6
Temperatures/°C	631.11	596.37	649.02
Thermal expansion coefficients/ $\times 10^{-5} \text{°C}^{-1}$	2.6950	3.1187	0.28888

expansion coefficient of Cu–Al alloy at temperature of 631.11 and 596.37°C after heat treatment at 1 and 3 GPa, respectively. Figure 5 also reveals that there is nearly no difference of thermal expansion coefficient between different high pressure when the temperature is below around 382°C. Above this temperature, the thermal expansion coefficient of sample after 3 GPa high pressure treatment is higher than that of sample treated under 1 and 6 GPa, and the difference peaks at the temperature where the highest thermal coefficient arrives. The maximum thermal expansion coefficients and its corresponding temperatures for each high pressure heat treatment have been tabulated in Table 1. Note that the thermal expansion coefficient the sample after high pressure treatment is remarkably higher than that of the as-cast sample. After 3 GPa treatment, the highest value of the thermal expansion coefficient arrives at 596.37°C with a value of $3.1187 \times 10^{-5} \text{°C}^{-1}$, which is about 99.34% higher than that value of the as-cast Cu–Al alloy at the same temperature.

Since the thermal expansion of the alloy is considered to be resulted by the increase of inter-atomic distance and the void in the material can be considered as a rigid phase with zero expansion coefficient¹²⁾ which shows no expansion when heated. Therefore, the voids can offset the expansion of matrix, resulting the increase of compactness of material, reduce of porosity, and finally the increase of the thermal expansion coefficient. High pressure treatment can also increase the compactness of Cu–Al alloy and decrease the residual porosity, and therefore can increase the thermal expansion coefficient. In principle, high pressure would lead to a higher compactness and lower porosity level, and thus a high thermal expansion rate. However, Fig. 5 shows the thermal expansion coefficient of Cu–Al alloy does not increase with the pressure in proportion, indicating that the thermal expansion coefficient is also related to the microstructure of materials (including morphology, size, content and distribution of phase).¹³⁾ Figure 5 also reveals that the maximum thermal expansion coefficient happens when the applied high pressure is 3 GPa. As for the reasons why the thermal expansion coefficient of samples after heat treatment under 3 GPa is higher than that of sample after other high pressure condition, and the appearance of the peak value at α -T curve, they need further investigation.

4. Conclusions

- (1) High pressure treatment can refine the grain of Cu–Al alloy, and the most optimizing effect happens at 3 GPa in the studied press range of 1 to 6 GPa.
- (2) High pressure treatment can obviously increase the thermal expansion coefficient of alloy in the temperature range of 25–650°C, but the thermal expansion coefficient doesn't increase as the pressure increases linearly.
- (3) Thermal expansion coefficient of Cu–Al alloy after 3 GPa treatment reaches its maximum value at 596.37°C with a value of $3.1187 \times 10^{-5} \text{C}^{-1}$, which is 99.34% higher than that of as-cast Cu–Al alloy at the same temperature.

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