

## Effects of cryogenic treatment on the thermal physical properties of $\text{Cu}_{76.12}\text{Al}_{23.88}$ alloy

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### Abstract

The thermal diffusion coefficient, heat capacity, thermal conductivity, and thermal expansion coefficient of  $\text{Cu}_{76.12}\text{Al}_{23.88}$  alloy before and after cryogenic treatment in the heating temperature range of 25°C to 600°C were measured by thermal constant tester and thermal expansion instrument. The effects of cryogenic treatment on the thermal physical properties of  $\text{Cu}_{76.12}\text{Al}_{23.88}$  alloy were investigated by comparing the variation of the thermal parameters before and after cryogenic treatment. The results show that the variation trend of the thermal diffusion coefficient, heat capacity, thermal conductivity, and thermal expansion coefficient of  $\text{Cu}_{76.12}\text{Al}_{23.88}$  alloy after cryogenic treatment was the same as before. The cryogenic treatment can increase the thermal diffusion coefficient, thermal conductivity, and thermal expansion coefficient of  $\text{Cu}_{76.12}\text{Al}_{23.88}$  alloy and decrease its heat capacity. The maximum difference in the thermal diffusion coefficient between the before and after cryogenic treatment appeared at 400°C. Similarly, thermal conductivity was observed at 200°C.

**Keywords:**  $\text{Cu}_{76.12}\text{Al}_{23.88}$  alloy; cryogenic treatment; thermal diffusion coefficient; thermal expansion coefficient

### 1. Introduction

Cu alloy is widely applied in instruments and machines due to its high strength, excellent properties of thermal conductivity, and low price [1-2]. With the rapid development of modern industry, people put forward higher demands for Cu alloy. Some references have shown that cryogenic treatment can play the effects of increasing mechanical properties, dimensional stability, and decreasing deformation of metal materials [3-6]. It is these effects of the cryogenic treatment that attract attention of some relative investigators. Some researching works about improving the structure and mechanical properties of Cu-alloy by the cryogenic treatment have been reported [7-11]. However, the reports about thermal physical properties of Cu-alloy after the cryogenic treatment are less. Furthermore, some mechanical components made of Cu alloy are serving at a certain temperature. For these reasons, in this study the thermal diffusion coefficient, heat capacity, thermal conductivity, and thermal expansion coefficient of  $\text{Cu}_{76.12}\text{Al}_{23.88}$  alloy before and after cryogenic treatment are measured at the temperature range of 25°C to 600°C. The effect of the cryogenic treatment on

the thermal physical properties of  $\text{Cu}_{76.12}\text{Al}_{23.88}$  alloy was also discussed. These results provide some reference data to the research and application of the cryogenic treatment to Cu alloy.

### 2. Experimental

The experimental material was as-cast  $\text{Cu}_{76.12}\text{Al}_{23.88}$  alloy (at.%). The samples were heated to 800°C in KLX-12B electric resistance furnace for 10 min, and then the samples were immersed in liquid nitrogen (-196°C) for 10 min. After that, the samples before and after cryogenic treatment were cut into  $\phi 10 \text{ mm} \times 1.75 \text{ mm}$  size specimens and then polished by 1200 # sandpaper. At 25°C, 100°C, 200°C, 300°C, 400°C, 500°C and 600°C, the thermal diffusion coefficient, heat capacity, and thermal conductivity were measured by a TC-7000 thermal constant measurement test instrument with precision of  $\pm 7\%$ . From 25°C to 600°C, the thermal expansion coefficient of the  $\text{Cu}_{76.12}\text{Al}_{23.88}$  was measured by DIL402C tester with precision of  $\pm 3\%$ , the specimen size was  $\phi 8 \text{ mm} \times 20 \text{ mm}$ , the heating rate was 5°C/min, and  $\text{Al}_2\text{O}_3$  was used as reference. To investigate

phase change of the Cu<sub>76.12</sub>Al<sub>23.88</sub> alloy in the range of 25°C to 600°C, the specimen of the Cu<sub>76.12</sub>Al<sub>23.88</sub> alloy before and after cryogenic treatment was investigated in a STA449C thermal analysis instrument at the heating rate of 20°C/min and heating temperature of 700°C. The microstructure of the Cu<sub>76.12</sub>Al<sub>23.88</sub> alloy before and after cryogenic treatment was analyzed by Axiovert200MAT optical microscope, H-800 transmission electron microscope (TEM), and D/MAX-rB type X-ray diffraction (XRD, with graphite monochromator, K<sub>α</sub> radiation).

### 3. Results and discussion

#### 3.1. Microstructure

Fig. 1 shows the microstructures of the Cu<sub>76.12</sub>Al<sub>23.88</sub> alloy

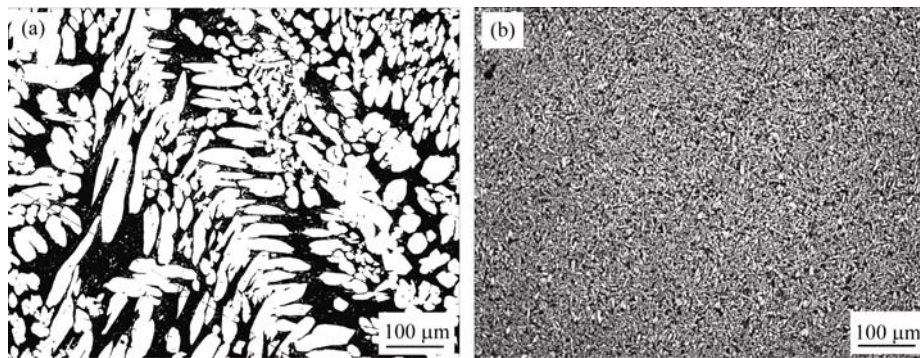


Fig. 1. Microstructures of the Cu<sub>76.12</sub>Al<sub>23.88</sub> alloy: (a) original; (b) cryogenic treatment.

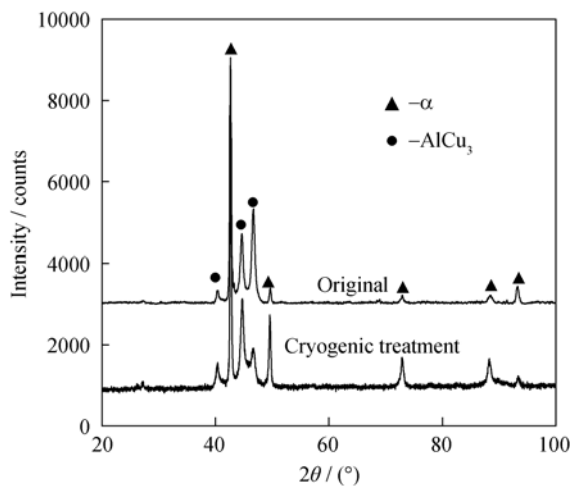


Fig. 2. XRD patterns of the Cu-Al alloy.

Fig. 4 shows differential scanning calorimetry (DSC) curves of the Cu<sub>76.12</sub>Al<sub>23.88</sub> alloy before and after cryogenic treatment heated at a constant rate. It can be seen in the DSC curves of the two states that, in the range of 560–590°C, both have an endothermic peak. According to Ref. [12], we know that the endothermic peak on the curve is due to  $\alpha(\text{Cu}) + \gamma_2(\text{Al}_4\text{Cu}_9) \rightarrow \beta(\text{AlCu}_3)$  occurring. By comparing the DSC

curves before and after cryogenic treatment. It is seen that the microstructure is coarser before cryogenic treatment and obviously refined after cryogenic treatment. XRD analysis results (see Fig. 2) show that the Cu<sub>76.12</sub>Al<sub>23.88</sub> alloy before and after cryogenic treatment is composed of  $\alpha$  phase (Cu solid solution) and AlCu<sub>3</sub> intermetallic compound. This indicates that the new phase cannot be generated by cryogenic treatment. The TEM analysis shows that the short rods-like structure in Cu<sub>76.12</sub>Al<sub>23.88</sub> alloy appeared after cryogenic treatment, as shown in Fig. 3(b). This is due to the volume contraction of the Cu<sub>76.12</sub>Al<sub>23.88</sub> alloy during cryogenic treatment process, inducing a greater internal stress in the material and a large number of dislocations that resulted in short rods-like structure.

curves of the specimens before and after cryogenic treatment, it can be seen that the DSC curve of the specimen after cryogenic treatment is volatile. This is due to cryogenic treatment that caused the microstructural differences of Cu<sub>76.12</sub>Al<sub>23.88</sub> alloy and made the material show the different thermal effect during the heating process.

#### 3.2. Thermal properties

Fig. 5 shows the changing curves of the thermal diffusivity, heat capacity, and thermal conductivity of the Cu<sub>76.12</sub>Al<sub>23.88</sub> alloy with temperature before and after cryogenic treatment. It can be seen that the thermal physical properties of the Cu<sub>76.12</sub>Al<sub>23.88</sub> alloy are changed by cryogenic treatment. It is reflected that, from 25°C to 600°C, the thermal diffusivity and thermal conductivity of Cu<sub>76.12</sub>Al<sub>23.88</sub> alloy are bigger after cryogenic treatment than without cryogenic treatment, and the heat capacity is less than that of without cryogenic treatment. At 400°C, the maximum values of thermal diffusion coefficient and thermal conductivity of the Cu<sub>76.12</sub>Al<sub>23.88</sub> alloy before and after cryogenic treatment appeared, the thermal diffusion coefficients are 0.2476 and 0.3113 cm<sup>2</sup>/s and the thermal conductivities are 0.8338 and 0.9223 W/(cm·K), respectively. Also, the heat capacity

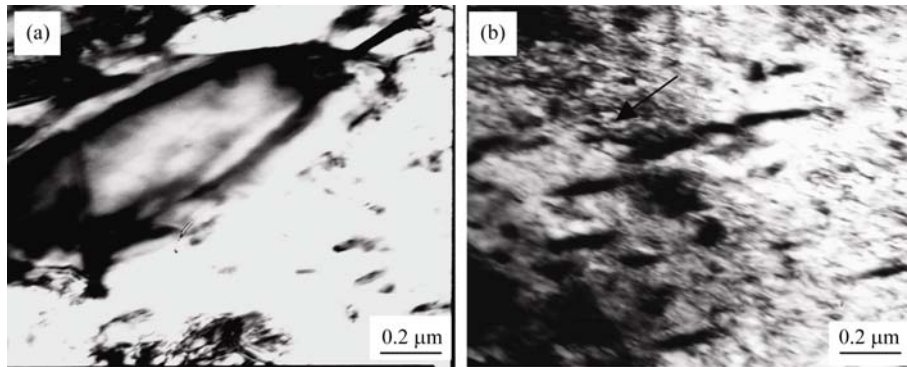


Fig. 3. TEM images of  $\text{Cu}_{76.12}\text{Al}_{23.88}$  alloy before and after cryogenic treatment: (a) original; (b) cryogenic treatment.

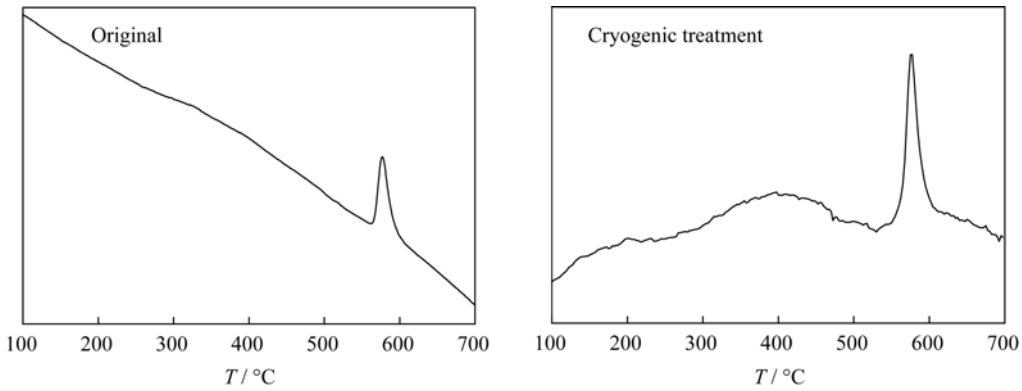


Fig. 4. DSC curves of the  $\text{Cu}_{76.12}\text{Al}_{23.88}$  alloy.

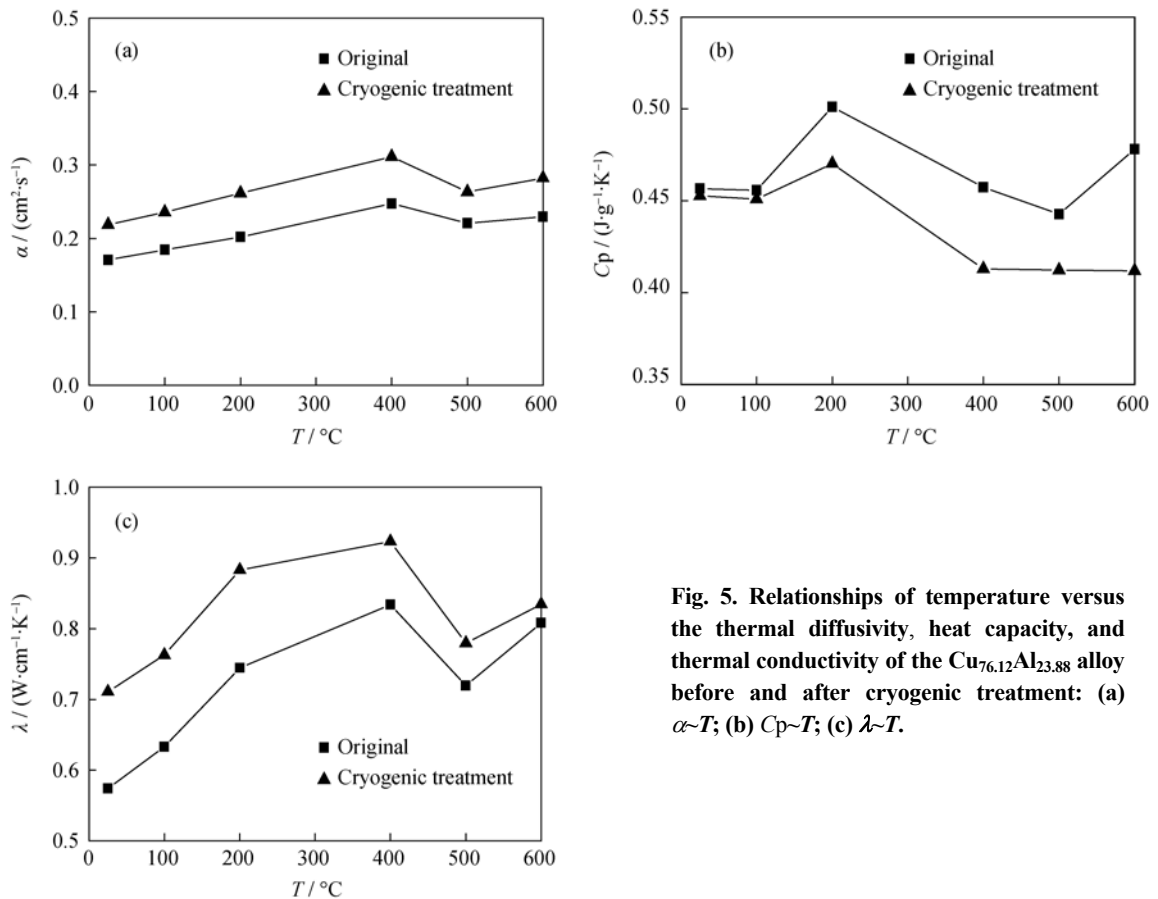


Fig. 5. Relationships of temperature versus the thermal diffusivity, heat capacity, and thermal conductivity of the  $\text{Cu}_{76.12}\text{Al}_{23.88}$  alloy before and after cryogenic treatment: (a)  $\alpha \sim T$ ; (b)  $C_p \sim T$ ; (c)  $\lambda \sim T$ .

of the two states Cu<sub>76.12</sub>Al<sub>23.88</sub> alloy reaches its maximum at 200°C, and its values are 0.5011 and 0.4752 J/(g·K), respectively. However, it is easily found that the variation of the thermal diffusivity, heat capacity, and thermal conductivity of Cu<sub>76.12</sub>Al<sub>23.88</sub> alloy before and after cryogenic treatment with temperature is similar.

Fig. 6 shows the difference curves of the thermal diffusivity, heat capacity, and thermal conductivity of Cu<sub>76.12</sub>Al<sub>23.88</sub> alloy before and after cryogenic treatment with temperature. From Fig. 5, it can be seen that the differences

in the thermal diffusion coefficient, heat capacity, and thermal conductivity change with temperature. When the temperature is 400°C and 200°C, the maximum value of differences in the thermal diffusion coefficient and the thermal conductivity before and after cryogenic treatment are 0.0637 cm<sup>2</sup>/s and 0.1386 W/(cm·K), respectively. When the temperature is 600°C, the maximum value of the heat capacity difference before and after cryogenic treatment is 0.0662 J/(g·K).

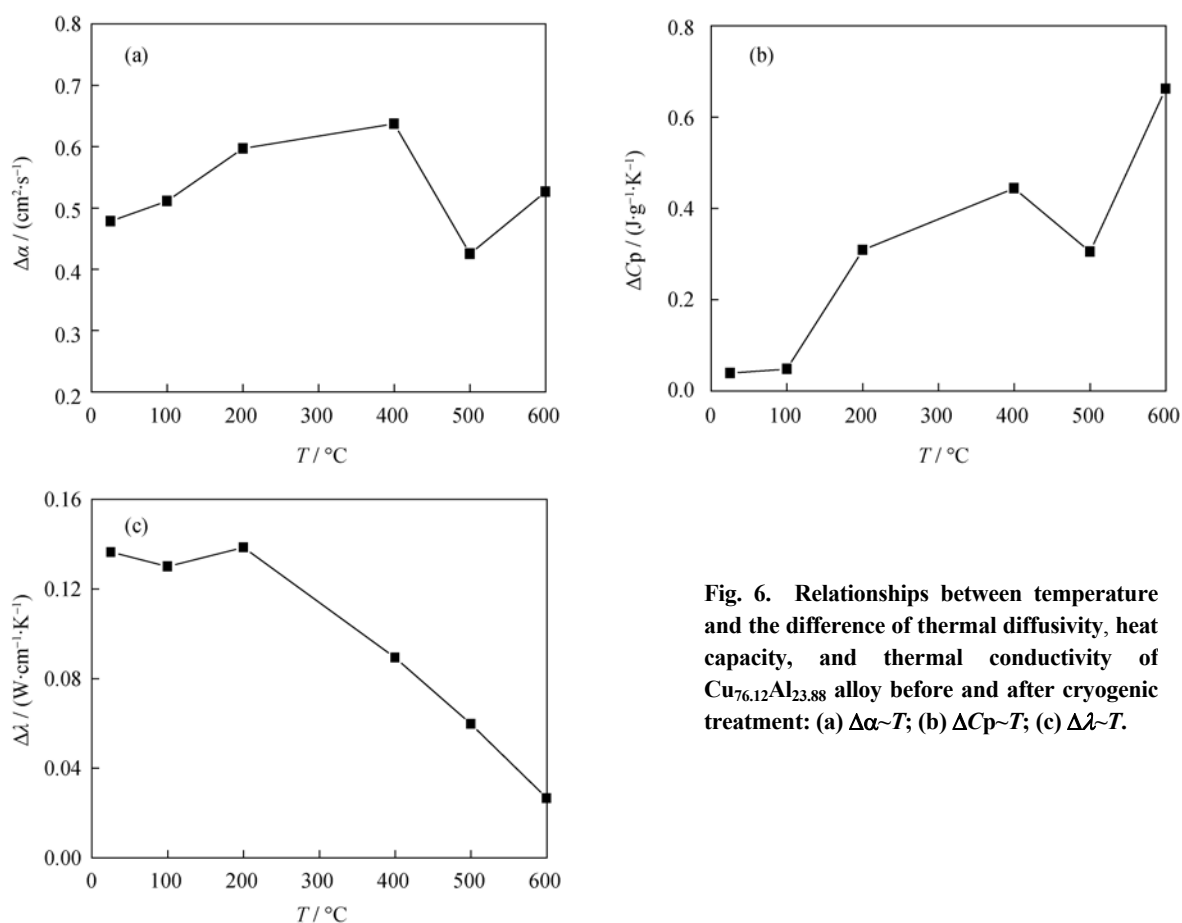


Fig. 6. Relationships between temperature and the difference of thermal diffusivity, heat capacity, and thermal conductivity of Cu<sub>76.12</sub>Al<sub>23.88</sub> alloy before and after cryogenic treatment: (a)  $\Delta\alpha$ ~T; (b)  $\Delta C_p$ ~T; (c)  $\Delta\lambda$ ~T.

In general, in a heat transfer process, the free electrons and photons collide with atoms or molecules; meanwhile, due to the obstruction of the interface and various defects, the scattering of the free electrons and photons increases; all these lead to the formation of the thermal resistance [13]. Therefore, the more complete the metal crystals are, the less the grain boundary defects such as dislocations and others are; the more easily the electrons get through, the better the thermal conductivity of the metal is [14-15]. The heat transfer of the Cu<sub>76.12</sub>Al<sub>23.88</sub> alloy consisted of two parts: one is the heat transfer of  $\alpha$  phase and the other is AlCu<sub>3</sub> intermetallic compound. Cryogenic treatment did not change the phase composition of the Cu<sub>76.12</sub>Al<sub>23.88</sub> but refined the mi-

crostructure. This led to an increase in the volume fraction of grain boundaries. Furthermore, there are some kinds of defects due to the volume shrinkage of the Cu<sub>76.12</sub>Al<sub>23.88</sub> alloy during cryogenic treatment processing, such as lattice distortion and dislocation produced in the structure of the alloy. On the one hand, these interfaces and defects make the electronic scattering strong, reducing the thermal conductivity and thermal diffusivity; on the other hand, the volume shrinkage of the Cu<sub>76.12</sub>Al<sub>23.88</sub> alloy during cryogenic processing deduces some pores close and results in low pore content in the materials. These also are helpful to electron thermal diffusion [16], leading to the thermal diffusion coefficient increase [17]. Comparing the two effects

above, the latter plays a leading role. Thus, the thermal diffusion coefficient and heat conductivity of the  $\text{Cu}_{76.12}\text{Al}_{23.88}$  alloy after cryogenic treatment have been increased.

For the  $\text{Cu}_{76.12}\text{Al}_{23.88}$  alloy, the reasons of heat capacity reducing after cryogenic treatment may be due to the existence of the higher density of lattice distortion and dislocation in  $\alpha$  phase, causing a higher storage capacity in the system, and the energy needed to result in the temperature of the  $\text{Cu}_{76.12}\text{Al}_{23.88}$  alloy increasing 1 K decreased. It remains to be further explored.

### 3.3. Thermal expansion coefficient

Fig. 7 shows the relationship curves between the thermal expansion coefficients of the  $\text{Cu}_{76.12}\text{Al}_{23.88}$  alloy before and after cryogenic treatment with heating temperature. It can be seen that, in the range of 25°C to 600°C, the thermal expansion coefficient of the  $\text{Cu}_{76.12}\text{Al}_{23.88}$  alloy before and after cryogenic treatment increased with increasing temperature. The variation trends of the thermal expansion coefficient of the two kinds of states are the same. Cryogenic treatment can increase the thermal expansion coefficients of the  $\text{Cu}_{76.12}\text{Al}_{23.88}$  alloy. In the range of 280°C to 400°C, the difference value of the thermal expansion coefficient of the two kinds of states is lesser, about  $3.16 \times 10^{-7} \text{ K}^{-1}$ . The thermal expansion of material is due to the average distance among particles in lattice structure increasing with increasing temperature. The internal voids of material can be considered as a zero-phase expansion where there is no expansion during heating process [18]. The volume of the  $\text{Cu}_{76.12}\text{Al}_{23.88}$  alloy shrinks during cryogenic treatment, deducing some pores close and reducing pore content in the materials. Thus, the coefficients of thermal expansion of the  $\text{Cu}_{76.12}\text{Al}_{23.88}$  alloy after cryogenic treatment can be increased.

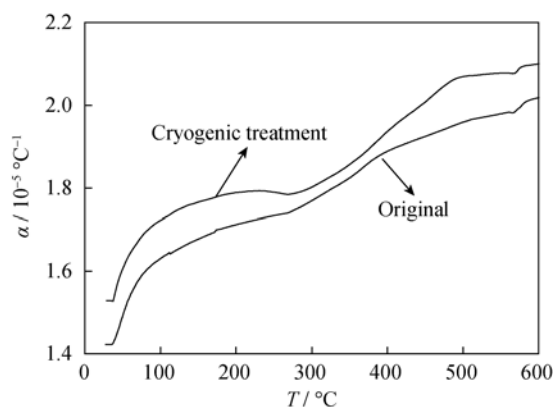


Fig. 7. Relationship curves between the coefficients of thermal expansion of the  $\text{Cu}_{76.12}\text{Al}_{23.88}$  alloy and temperature.

## 4. Conclusions

(1) In the range of 25°C to 600°C, the thermal diffusion

coefficient, thermal conductivity, and thermal expansion coefficient of the  $\text{Cu}_{76.12}\text{Al}_{23.88}$  alloy can be increased and the heat capacity can be reduced by cryogenic treatment. However, their variation trends with temperature cannot be changed.

(2) The maximum value of the thermal diffusion coefficient and thermal conductivity of the  $\text{Cu}_{76.12}\text{Al}_{23.88}$  alloy appears at 400°C and that of the heat capacity appears at 200°C before and after cryogenic treatment. The thermal expansion coefficients of the samples before and after cryogenic treatment increase largely with increasing the temperature.

(3) When the temperature is 400 and 200°C, the maximum value of the differences in the thermal diffusion coefficient and thermal conductivity before and after cryogenic treatment are  $0.0637 \text{ cm}^2/\text{s}$  and  $0.1386 \text{ W}/(\text{cm}\cdot\text{K})$ , respectively. When the temperature is 600°C, the maximum value of the heat capacity difference before and after cryogenic treatment is  $0.0662 \text{ J}/(\text{g}\cdot\text{K})$ . In the range of 280°C to 400°C, the difference value of the thermal expansion coefficient of the two kinds of states is not obvious.

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