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# Effects of High Pressure Heat Treatment on Microstructure and Micro-Mechanical Properties of $Cu_{77.96}Al_{22.04}$ Alloy

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The hardness, elastic modulus, and friction coefficient of the $Cu_{77.96}Al_{22.04}$ alloy before and after treatment at 750°C and 5 GPa for 15 min were measured by nanoindenter. Effects of high pressure heat treatment on its micromechanical properties were discussed. The results show that high pressure heat treatment can refine the microstructures of the $Cu_{77.96}Al_{22.04}$ alloy, increase its hardness and elastic recovery rate, and decrease its friction coefficient. It also shows that high pressure treatment has little effect on the elastic modulus. As a result, the deformation resistance and the anti-indentation creep of the alloy are improved effectively. [doi:10.2320/matertrans.M2011296]

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***Keywords:*** *$Cu_{77.96}Al_{22.04}$ alloy, high pressure heat treatment, nanoindentation, microstructure, mechanical property*

## 1. Introduction

Cu–Al alloy has been widely used in shipping, machinery and aviation industries due to its high strength, good corrosion-resistance and excellent cold and hot workability. The main drawback of the traditional Cu–Al alloy is the coarse grains that lower its mechanical properties. Therefore, it is important to refine grains of the Cu–Al alloy. Recently, it has been found that high pressure has many advantages in facilitating nucleus formation, reducing atom diffusion coefficient, resulting in restraint in grain growth and in refinement of grain and crystal structure. Now high pressure has been attracting scientists' great attention because it can improve the microstructures of alloys.[1–3] Most work has been focused on the effects of high pressure on phase transformation during alloy solidification.[4–7] Recent work noticed that high pressure can also change the microstructures of Cu-based alloys,[8,9] providing an effective method to improve their mechanical properties. However, few reports about the mechanical properties of the high pressure treated Cu–Al alloy have been published.

Nanoindentation technique, a new effective method in studying mechanical properties of solid materials, has been developed in recent years.[10–13] Different from traditional micro-hardness testing, the hardness and elastic modulus of a micro-region can be determined according to the load-displacement curve obtained during nanoindentation test. And artificial errors from the observation of the indentation area and the values of diagonal can be avoided and the testing values are much more reliable. Therefore, the hardness, elastic modulus and friction coefficient of $Cu_{77.96}Al_{22.04}$ alloy were measured by nanoindentation, and the effects of high pressure heat treatment on microstructures and micromechanical properties were discussed.

## 2. Experimental

The as-cast $Cu_{77.96}Al_{22.04}$ (atomic fraction, %) alloy was prepared in the vacuum medium frequency induction furnace, and as-cast samples with the size of Φ6 mm × 10 mm were sealed into graphite heaters, and then were pressurized to 5 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. After that, the samples were cut into Φ6 mm × 5 mm size specimens, and then the micro-mechanical experiments were performed on a triboindenter nono-mechanical test instrument. Berkovich-type indenter with curvature radius of 150 nm was chosen to determine the hardness and elastic modulus. In which the maximum applied load was1000 μN and kept at this load for 10 s, using a loading and unloading rates of 100 $\mu N \cdot s^{-1}$. In addition, the changing values of the specimen's hardness and elastic modulus with indenting depth can be obtained by continuous loading on a certain area of the sample's surface. A Conical-type indenter with curvature radius of 2 μm was used for determining the fraction coefficient of the alloy, the applied load was 1000 μN, and the moving rate of indenter was 0.33 μm/s. The loading and displacement detectability of this testing system is 50 nN and 0.01 nm, respectively. In this experiment, the data is the mean value of three measured results. The microstructures of the $Cu_{77.96}Al_{22.04}$ alloy before and after high pressure heat treatment were observed by means of Axiovert200MAT optical microscope.

## 3. Results and Discussion

### 3.1 Microstructures

Figure 1 shows the microstructures of $Cu_{77.96}Al_{22.04}$ alloy before and after high pressure heat treatment. It can be seen that the grains are rather coarse before treatment, however, the grains become refined and more homogeneous after 5 GPa heat treatment.

According to the classic nucleation theory,[14] 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 with respect to that under ambient pressure can be calculated by eq. (1), and the ratio of growth rate under high pressure and that under ambient pressure can be expressed as eq. (2).

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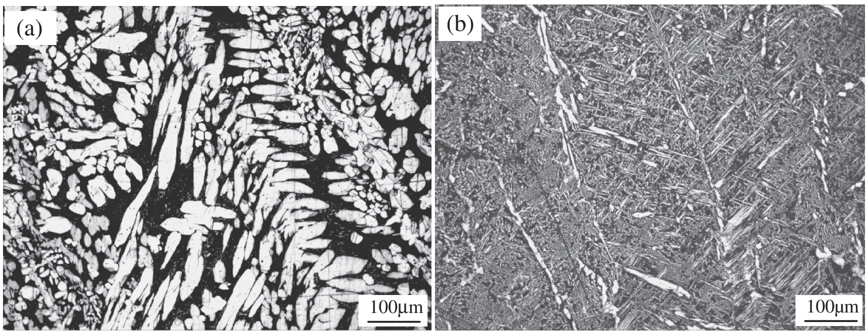


Fig. 1 Microstructures of the Cu–Al alloy [(a) cast; (b) 5 GPa].

$$\frac{I_p}{I_0} = \exp\frac{G_0 - G_p}{RT} \quad (1)$$

$$\frac{\upsilon_p}{\upsilon_0} = \frac{G_0' - G_p'}{RT} \quad (2)$$

where $I_p$, $G_p$, $G_p'$, $\upsilon_p$ is the nucleation rate, the nucleation activation energy, the growth activation energy, and the growth rate under high pressure, respectively; and $I_0$, $G_0$, $G_0'$, $\upsilon_0$ is 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 ($\Delta E$) and the free energy associated with the formation of a nucleus ($\Delta G$), and the $\Delta G$ can be expressed as:

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

Considering the influence of pressure on nucleation and given the surface energy $\sigma$ 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, $\sigma$ is the surface energy between two phases, $\Delta G_V$ is the Gibbs free energy difference per unit volume between the new phase and the original one; $\Delta V$ is the volume difference between the new phase and the original one. Because $\Delta G_v < 0$ 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 $Cu_{77.96}Al_{22.04}$ alloy is the nucleation and growth of new phase via atomic diffusion. The nucleus formation depends on its critical free energy, rather than the long range diffusion of Cu and Al atoms. Pressure can lower the critical free energy of nucleus formation, which decreases the nucleation activation energy ($G_p < G_0$) and increases the nucleation rate ($I_p > I_0$). High pressure increases the diffusion activation energy and then restrains the atom diffusion, thus pressure can increase the growth activation energy ($G_0' < G_p'$), therefore restrain the growth of nucleus and to lower the growth rate ($\upsilon_p < \upsilon_0$).

As a result, we proposed that high pressure can promote nucleation and restrain growth of nucleus, resulting in the fine grains of $Cu_{77.96}Al_{22.04}$ alloy after solid-state phase transformation under high pressure.

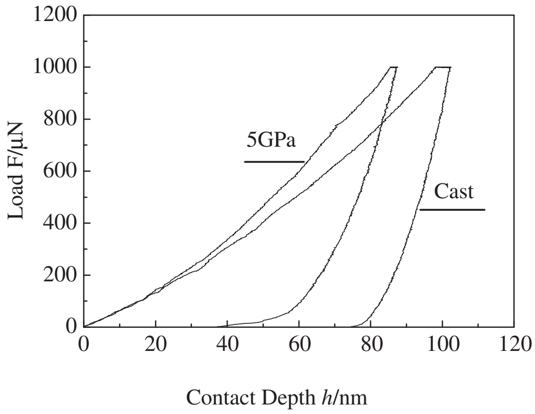


Fig. 2 Load-displacement curves for nano-indentation tests of the Cu–Al alloy.

Table 1 Nanoindentation results of the Cu–Al alloy.

| Samples | $H$/GPa | $Er$/GPa | $H$/Er | $h_{max}$/nm | $h_f$/nm | $R$/% |
|---|---|---|---|---|---|---|
| Cast | 3.50 | 112.47 | 0.031 | 102.56 | 76.84 | 33.47 |
| 5 GPa | 3.96 | 113.32 | 0.038 | 85.63 | 52.71 | 62.45 |

## 3.2 Micro-mechanical property

### 3.2.1 Nano-hardness and elastic modulus

Figure 2 shows the load-displacement curves of the $Cu_{77.96}Al_{22.04}$ alloy before and after high pressure heat treatment. Both the loading and unloading curves show no superposition, indicating that the elastic deformation takes place inside the alloy. To quantify the degree of the elastic deformation, elastic recovery rate ($R/\%$) is used to characterize elastic property of the alloy, $R = \frac{h_{max} - h_f}{h_f} \times 100\%$, wherein $h_{max}$ and $h_f$ is displacements at maximum load and after loading, respectively. Testing results are tabulated in Table 1. The nanoindentation hardness ($H$) is 3.50 and 3.96 GPa before and after high pressure heat treatment, and corresponding elastic modulus ($Er$) is 112.47 and 113.32 GPa, respectively. The hardness is increased by 13.14% while the elastic modulus does not change after the high pressure heat treatment. The reason for the increase of the nanohardness is that high pressure can not only refine the microstructure of $Cu_{77.96}Al_{22.04}$ alloy, but also reduce the holes in the alloy, therefore the density of the alloy increases. Besides, high pressure can cause large deformation of alloys and increase the strength of the alloy. Therefore, the hardness of the alloy increases after high pressure heat treatment.

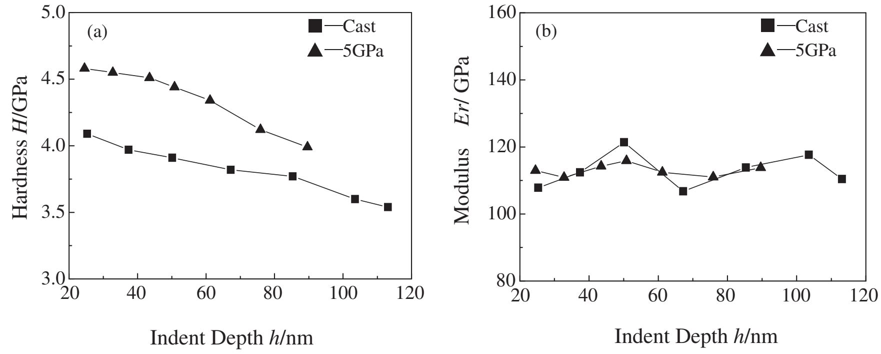


Fig. 3 Hardness, elastic modulus profile curves of the Cu–Al alloy along depth [(a) hardness-depth curves, (b) modulus-depth curves].

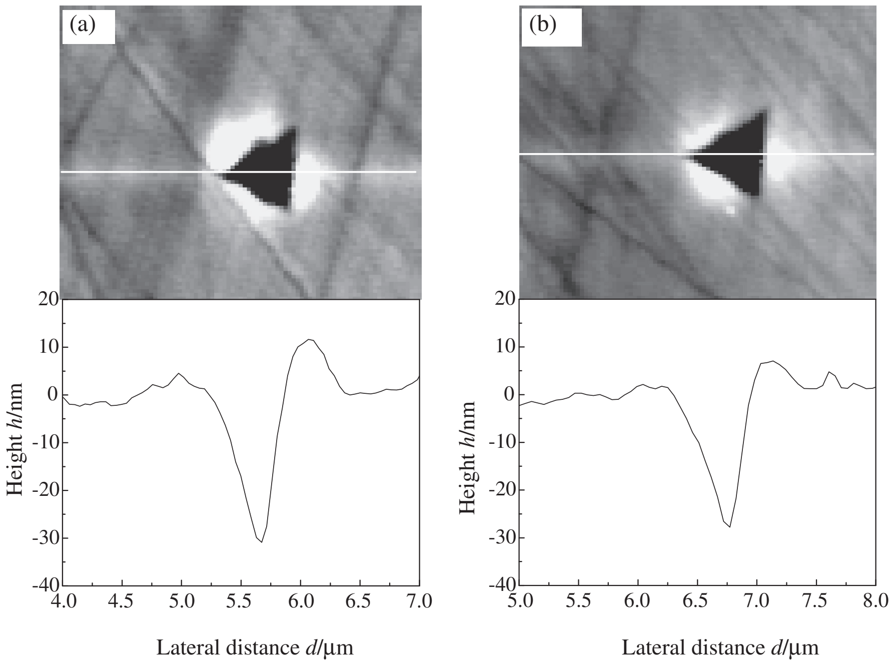


Fig. 4 Morphology around indentation and sectional analysis of $Cu_{77.96}Al_{22.04}$ alloy after keeping the load of 1000 μN for 10 s.

It can be seen from Fig. 3 that the dependences of nanohardness and elastic modulus on the indent depth are different. The nanohardness decreases gradually with the indent depth, which indicates that the size effect phenomenon exists in the case of the nanohardness measurement. However, the elastic modulus exhibits fluctuant trend with increasing depth, which indicates that the size effect phenomenon does not exist in the elastic modulus measurement. This phenomenon may be caused by the following reasons. With the increase of the indent depth, the width of indenter that dents into the alloy increases, resulting in the decrease of the nucleation rate of the dislocations under the indenter and then lower the density of dislocation. Therefore, hardening effect of the alloy decreases. Since the nanohardness characterizes material's resistance of deformation,[15)] the improved nanohardness means that high pressure increases the deformation resistance of the alloy. The fluctuant elastic modulus is caused by the micropores and inhomogeneity of phase distribution in the alloy. As shown in Fig. 3, the elastic modulus fluctuation decreases after high pressure heat treatment, therefore, it can be concluded that micropores decreases and the phase distribution becomes more homogeneous after high pressure heat treatment.

Table 1 shows that the elastic recovery rate of the alloy before and after high pressure heat treatment is 33.47 and 62.45%, respectively, and the elastic recovery rate shows an increase of 86.58% after high pressure heat treatment. In addition, it can be seen from Fig. 2 that there is a plateau on the curve. The length of the plateau before and after high pressure heat treatment is 4.21 and 1.63 nm, respectively, indicating that the two alloys produce creep. The creep amount of the $Cu_{77.96}Al_{22.04}$ alloy before high pressure heat treatment is bigger than that of the $Cu_{77.96}Al_{22.04}$ alloy after high pressure heat treatment. Figure 4 shows the morphology around indentation and sectional analysis of the $Cu_{77.96}Al_{22.04}$ alloy after keeping the load of 1000 μN for 10 s. It can be seen that pile up around indentation of the $Cu_{77.96}Al_{22.04}$ alloy before and after high pressure heat treatment is 11.64 and 7.06 nm, and both indentation depth is 30.89 and 27.78 nm, respectively. That means the pile up of the $Cu_{77.96}Al_{22.04}$ alloy after high pressure heat treatment is less than that of the $Cu_{77.96}Al_{22.04}$ alloy before high pressure heat treatment, and so the indentation depth. In general, the more the depth of indentation is, the worse the ability to anti-indentation creep. Thus it can be concluded that the high pressure heat treatment can enhances the ability to anti-indentation creep.

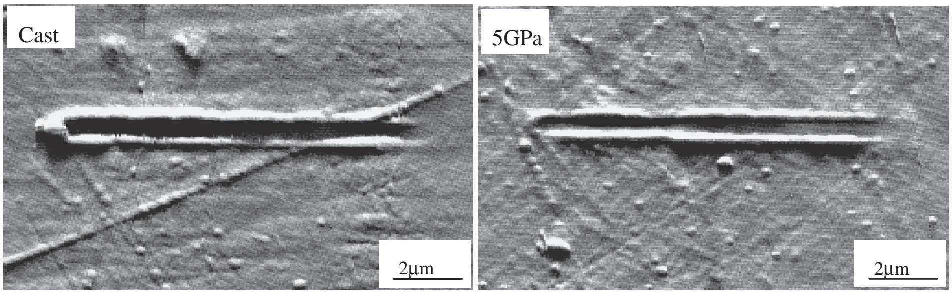


Fig. 5 Micrograph of scratches of the $Cu_{77.96}Al_{22.04}$ alloy.

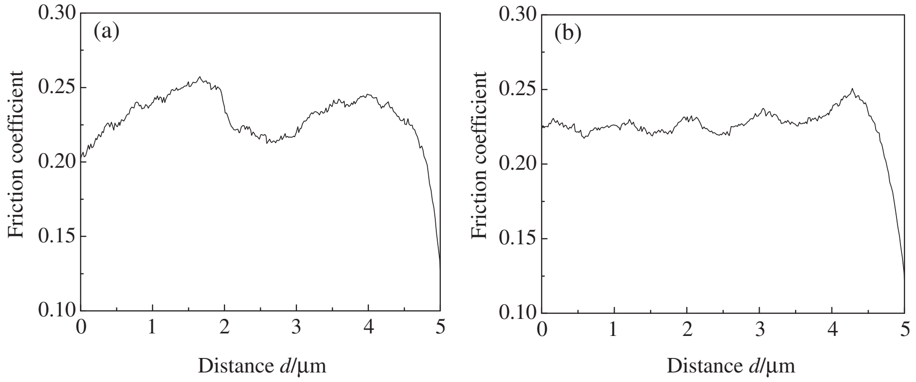


Fig. 6 The friction coefficient of the Cu–Al alloy [(a) cast; (b) 5 GPa].

### 3.2.2 Friction coefficient

Figure 5 shows the scratch morphologies of the $Cu_{77.96}Al_{22.04}$ alloy. The friction coefficient distribution is shown in Fig. 6. It is shown that the average friction coefficient before and after high pressure heat treatment is 0.234 and 0.226, respectively. Furthermore, the fluctuation phenomenon exists in both friction coefficient curves. And less fluctuation can be obtained in the friction coefficient after high pressure treatment. Meanwhile, the absolute value of friction coefficient is also small comparing with that before high pressure heat treatment. The changes of friction coefficient reflect the inhomogeneity in holes and defects in alloys. High pressure heat treatment reduces the value and fluctuating degree of friction coefficient, indicating that high pressure heat treatment can reduce hole and gap defects and make the microstructure more homogenous. In addition, the ratio of hardness to modulus ($H/E$) influence the wear resistance of the materials.[16] Larger $H/E$ increases is, higher the wear resistance is. High pressure heat treatment can increase $H/E$ (as shown in Table 1) and reduce friction coefficient, thus which is helpful to improve the wear resistance of the $Cu_{77.96}Al_{22.04}$ alloy.

## 4. Conclusions

(1) High pressure treatment at 750°C under 5 GPa for 15 min refines the microstructure and enhances the homogenous distribution of the $Cu_{77.96}Al_{22.04}$ alloy, therefore improves the resistance of deformation and anti-indentation creep, indicating high pressure treatment may be a novel method to improve the mechanical property of the $Cu_{77.96}Al_{22.04}$ alloy.

(2) The nanoindentation hardness and the elastic recovery rate of $Cu_{77.96}Al_{22.04}$ alloy after high pressure treatment is increased by 13.14 and 71.84%, respectively. But the friction coefficient has a slight decrease and elastic modulus change a little.

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