ELSEVIER Science Press

Available online at www.sciencedirect.com

ScienceDirect

Trans. Nonferrous Met. Soc. China 21(2011) 2205−2209

Transactions of
Nonferrous Metals
Society of China

www.tnmsc.cn

Microstructure evolution and thermal expansion of Cu-Zn alloy after high pressure heat treatment

CHEN Yan[1, 2], LIU Lin[3], WANG Yue-hui[4], LIU Jian-hua[1], ZHANG Rui-jun[1]

1. State Key Laboratory of Metastable Materials Science and Technology,
Yanshan University, Qinhuangdao 066004, China;
2. Department of Environmental and Chemical Engineering, Yanshan University, Qinhuangdao 066004, China;
3. Department of Basic Medical, Tangshan Vocational Technology College, Tangshan 063000, China;
4. College of Physics and Chemistry, Hebei Normal University of Science and Technology,
Qinhuangdao 066004, China

Received 30 September 2010; accepted 18 February 2011

Abstract: The thermal expansion coefficients of Cu-Zn alloy before and after high pressure treatment were measured by thermal expansion instrument in the temperature range of 25−700 °C, and the microstructure and phase transformation of the alloy were examined by optical microscope, X-ray diffractometer (XRD) and differential scanning calorimeter (DSC). Based on the experimental results, the effects of high pressure treatment on the microstructure and thermal expansion of Cu-Zn alloy were investigated. The results show that the high pressure treatment can refine the grain and increase the thermal expansion coefficient of the Cu-Zn alloy, resulting in that the thermal expansion coefficient exhibits a high peak value on the $\alpha-T$ curve, and the peak value decreases with increasing the pressure.

Key words: Cu-Zn alloy; high pressure heat treatment; microstructure; thermal expansion coefficient

---

1 Introduction

Cu-Zn alloys have been widely applied in many areas due to their high strength, good plasticity and excellent corrosion resistance. However, the coarse grains of the materials limit their further application [1]. So it is very important to refine grain of Cu alloys [2−3]. It is known that high pressure can promote nucleation, and restrain the grain growth [4−6]. Thus the research on grain refinement by means of high pressure treatment has been getting more and more attention [7−8]. At present, the investigations of pressure effects on metals are mainly focused on solidification process under high pressure [9−10]. As is known, microstructures of many kinds of alloys depend on solid-state phase transformation, and high pressure heat treatments have some other advantages, such as relatively low temperature and simple operations. It can be predicted that high pressure heat treatment may be an effective way to change the microstructures of alloys and to improve their overall properties. Recently, some results about the microstructure of Cu alloys improved by high pressure treatment have been reported [11−12], but few reports were about the property of Cu alloys after high pressure heat treatment. In practice application, especially under the temperature conditions, good mechanical properties and dimensional stability of Cu-Zn alloy were required. Therefore, in this study, high pressure heat treatment was applied to Cu-Zn alloy during solid-state phase transformation process, and the microstructure and thermal expansion of Cu-Zn alloy after high pressure heat treatment were investigated.

2 Experimental

The tested material was an annealed Cu-Zn alloy, its chemical composition (mass fraction, %) is 63.72 Cu, 36.12 Zn, and 0.16 others. The samples were sealed in a graphite pipe, sending pressure with the medium of pyrophyllite. The high pressure experiment was carried out on a CS-IIB tester with the pressures of 1, 3 and

---

Foundation item: Project (11541012) supported by the Scientific Research Foundation of Heilongjiang Provincial Education Department, China

Corresponding author: ZHANG Rui-jun; Tel: +86-13833596156; E-mail: Zhangrj@ysu.edu.cn

DOI: 10.1016/S1003-6326(11)60996-5

5 GPa, respectively, in which the sample was heated up to 750 °C for 15 min, then the electricity (kept pressure) was shut off and the sample was cooled to room temperature (about 25 °C). The samples before and after high pressure treatment were shaped into the dimensions of *d*6 mm×10 mm, and polished with 1 $200^{\#}$ metallic sand papers, then their thermal expansion coefficients in the temperature range of 25−700 °C were measured using a DIL402C thermal expansion instrument. The heating rate was 5 °C/min, precision was 3%, and Al_2O_3 was used as reference in argon protecting. The $\alpha-T$ curve was spontaneously calculated. To investigate the phase transformation of the Cu-Zn alloy during the heating process, the thermal analyses were performed using a STA449C differential scanning calorimeter(DSC), in which the sample was heated to 700 °C and with a heating rate of 5 °C/min. The microstructure and phase composition of the samples were analyzed by Neophot21 optical microscope and D/MAX-rB diffractometer (XRD) (with a graphite monochromator, and K_α radiation).

3 Results and discussion

3.1 Microstructure

Figure 1 shows the microstructures of Cu-Zn alloys before and after high pressure treatment. It can be seen that the microstructure of original Cu-Zn alloy is coarse. After the high pressure heat treatment, fine needle-like grain with random distribution has been formed in the alloy, and the number of the fine needle-like grain increases and then decreases with increasing pressure. When the pressure is 3 GPa, the maximum fine needle-like grain with a width range of 3−6 μm exists in the microstructure, and its volume fraction is around 78.68%, indicating that the high pressure treatment can refine grain; when the pressure is 3 GPa, it exhibits better effect of grain refinement. XRD analysis (Fig. 2) shows that the Cu-Zn alloy before and after high pressure treatment is composed of α phase (Cu solid solution) and minor β phase (Cu-Zn solid solution), and there are changes in the intensity of α phase and minor β phase diffraction peaks. This means that the shape, content, size, and distribution of the phases can be changed by the high pressure, but no new phase has been introduced. Based on the theory of classical crystal nucleation [13−14], the crystal nucleation rate may be described as follows:

$$I = I_0 \exp(-\frac{G}{RT}) = I_0 \exp(-\frac{\Delta G + \Delta E}{RT}) \tag{1}$$

$$G=\Delta G + \Delta E \tag{2}$$

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

Considering the effect of pressure on crystal nucleation, the following equation may be expressed from Eqs. (2) and (3):

$$(\frac{\partial G}{\partial p})_T = -\frac{32\pi\sigma^3}{3\Delta G_V^3}\Delta V + (\frac{\partial \Delta E}{\partial p})_T \tag{4}$$

where G is the nucleation activation energy; ΔG is the critical Gibbs free energy; ΔE is the diffusion activation energy; 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.

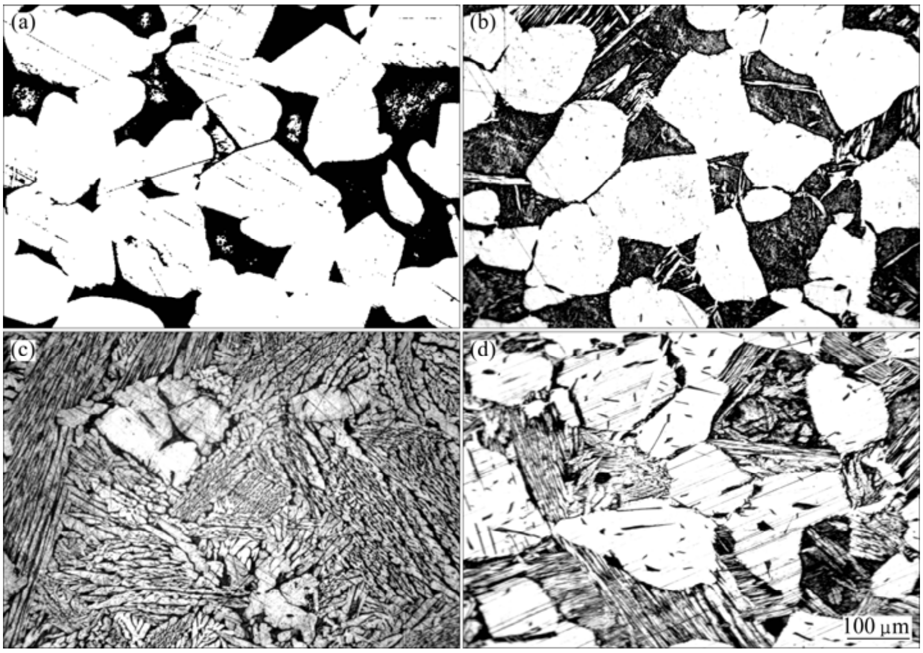

Fig. 1 Microstructures of Cu-Zn alloys after different pressure treatments: (a) Original alloy; (b) 1 GPa; (c) 3 GPa; (d) 5 GPa

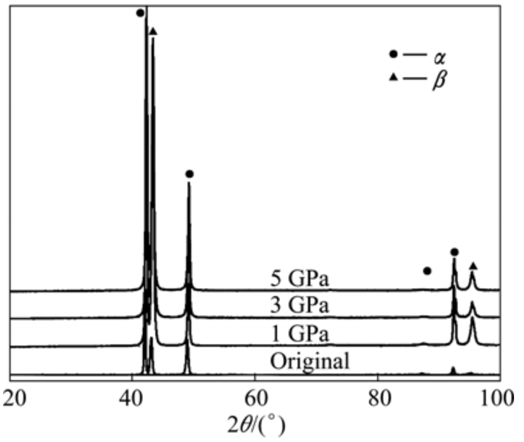

Fig. 2 XRD patterns of Cu-Zn alloys after different pressure treatments

Since solid-state phase transformation of Cu-Zn alloy is the nucleation and growth process of new phase, it is determined by the atomic diffusion process. From Eq. (4), it can be concluded that if high pressure causes ΔG to decrease, it benefits to the nucleation of new phases; on the other hand, if high pressure makes the ΔE increase, it will prevent forming the crystal cores. Only when the first term value is greater than the second term value in Eq. (4), that is when $(\partial G/\partial P)_T<0$, high pressure can increase the nucleation rate of new phases; on the contrary, high pressure can decrease the nucleation rate. Therefore, the nucleation rate of new phase will decrease at higher pressure or lower pressure, and there is a propriety pressure for the nucleation rate of new phase achieves a maximum value, resulting in that the formative grain size is the smallest. In our experiment, when pressure is 3 GPa, the effect of grain refinement is obvious.

3.2 DSC curves

Figure 3 shows the DSC curves of Cu-Zn alloy before and after high pressure treatment at heating rate of 5 ℃/min. One endothermic peak at 442−460 °C is observed on each DSC curve, and the endothermic peaks of the samples after 1 GPa and 3 GPa pressure treatments are higher. It can be concluded from Ref. [15] that the endothermic peak corresponds to the solid-state phase transformation ($\beta'\rightarrow\beta$). It is also seen from Fig. 3 that there is difference on each DSC curve. Comparatively, the feature of DSC curve of Cu-Zn alloy after 1 GPa treatment is similar to that of Cu-Zn alloy after 3 GPa treatment.

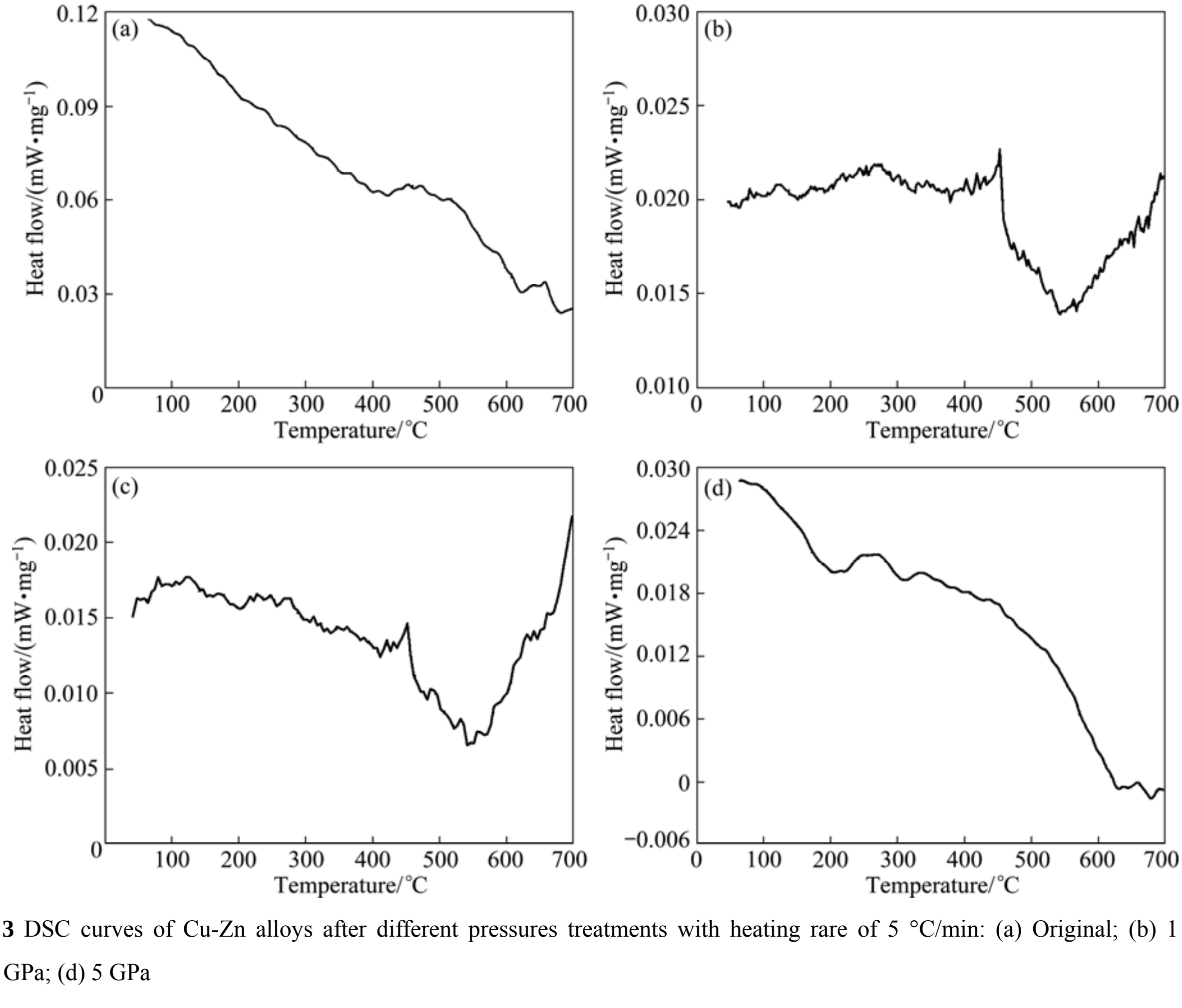

Fig. 3 DSC curves of Cu-Zn alloys after different pressures treatments with heating rare of 5 °C/min: (a) Original; (b) 1 GPa; (c) 3 GPa; (d) 5 GPa

3.3 Thermal expansion coefficients

Figure 4 shows the relationship between the thermal expansion coefficients of Cu-Zn alloy before and after pressure treatments and temperature. It can be known that thermal expansion coefficient of original Cu-Zn alloy increases with increasing the temperature in the range of 25−700 °C, whereas the change of thermal expansion coefficient is flat when temperature above about 241℃. After high pressure treatment, the thermal expansion coefficient increases and then decreases with increasing the heating temperature. When the temperature increases to a certain value, the thermal expansion coefficient exhibits a high peak value, and the peak value decreases with increasing the pressure, as shown in Table 1. The Cu-Zn alloys after 1 GPa and 3 GPa treatments exhibit a similar thermal expansion behavior, and the feature of $\alpha-T$ curve of the Cu-Zn alloy after 5 GPa treatment is close to that of the original alloy.

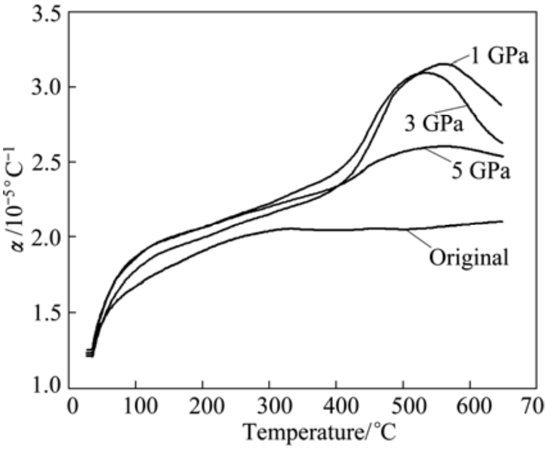

Fig. 4 Relationship between thermal expansion coefficient of Cu-Zn alloy and treatment temperature

Table 1 Peak value and corresponding temperature of thermal expansion coefficients of Cu-Zn alloy with different pressure treatments

Pressure/GPa	Temperature/°C	Thermal expansion coefficient/10^{-5} °C^{-1}
1	560.81	3.1556
3	535.14	3.0948
5	560.69	2.6038

Figure 4 also indicates that high pressure treatment can increase thermal expansion coefficient, and it is more obvious when the temperature is above about 432 °C. There is no larger difference between the thermal expansion coefficient of the Cu-Zn alloys after 1 GPa and 3 GPa treatments, but both are larger than that of the alloy after 5 GPa treatment, and the maximum difference appears at the peak value of the thermal expansion coefficient. After 1 GPa treatment, the highest value of the thermal expansion coefficient can be obtained at 560.81 °C, its value is 3.155 6×10^{-5} °C^{-1}, about 52.41% higher than that of the original Cu-Zn alloy at the same temperature.

Since thermal expansion of the alloy is the result of inter-atomic distance increase, the void in the material can be considered a rigid phase with zero expansion [16], there is no expansion when it is heated, and the void can hold part of the inter-atomic distance increase caused by heating. Thus, reducing the void in the material can elevate the thermal expansion coefficient. Since high pressure treatment can increase the density of Cu-Zn alloy and decrease its residue void, the thermal expansion coefficient of Cu-Zn alloy increases after high pressure heat treatment. In general, the void in the material decreases with increasing pressure. However, Fig. 4 shows that the thermal expansion coefficient of Cu-Zn alloy does not linearly increase with increasing pressure, and high pressure treatment can change the microstructure of Cu-Zn alloy, indicating that the thermal expansion coefficient relates to the microstructure (including the number, size, shape and distribution of the phase composition). It can be concluded that the thermal expansion is co-regulated by many factors including internal void, internal stress, phase transition and microstructure [17−18]. The effects of thermal expansion coefficient are complex and the affecting degrees are different. The experimental results show that larger thermal expansion coefficient of the Cu-Zn alloy after 1 GPa pressure treatment can be obtained and high pressure treatment can make thermal expansion coefficient of Cu-Zn alloy exhibit peak value on the $\alpha-T$ curve.

4 Conclusions

1) High pressure treatment can refine the grain of Cu-Zn alloy, the refinement effect increases and then decreases with increasing pressure. When the pressure reaches 3 GPa, the refinement is the most remarkable.

2) High pressure treatment can obviously increase the thermal expansion of Cu-Zn alloy, and also lead to the thermal expansion coefficient exhibiting peak value on the $\alpha-T$ curve, the peak value decreases with increasing the pressure in the range of 1−5 GPa.

3) Thermal expansion coefficient of the Cu-Zn alloy after 1 GPa treatment reaches a maximum value (3.155 6×10^{-5} °C^{-1}) at 560.81 °C, which increases by 52.41% in comparison with original Cu-Zn alloy at the same temperature.

References

[1] PENG K P, SU L F, SHAW L L, QIAN K W. Grain refinement and crack prevention in constrained groove pressing of two-phase Cu-Zn alloys [J]. Scripta Materialia, 2007, 56(11): 987−990.

[2] YANG G S, LEE J K, JANG W Y. Effect of grain refinement on phase transformation behavior and mechanical properties of Cu-based alloy [J]. Transactions of Nonferrous Metals Society of China, 2009, 19(4): 979−983.

[3] OISHI K, SASAKI I, OTANI J. Effect of silicon addition on grain refinement of copper alloys [J]. Materials Letters, 2003, 57(15): 2280−2286.

[4] QI L, DONG L F, ZHANG S L. Cluster evolution in the rapid cooling process of Cu-Ag melts under high pressure: Molecular-dynamics simulation [J]. Computational Materials Science, 2008, 43(4): 732−735.

[5] LI G, DONG Y G, HUANG L, HE G W, LIU R P, WANG W K. High-pressure annealing effect on glass transformation temperature of Zr41Ti14Cu12.5Ni10Be22.5 bulk metallic glass [J]. Chinese Physics Letters, 2009, 26(8): 086102-1−086102-4.

[6] LI Rong-de, CAO Xiu-sheng, QU Ying-dong. Effect of super high pressure on crystal structure and microstructure of ZA27 alloy [J]. The Chinese Journal of Nonferrous Metals, 2009, 19(9): 1570−1574. (in Chinese)

[7] LI Run-xia, LI Rong-de, BAI Yan-hua. Effect of specific pressure on microstructure and mechanical properties of squeeze casting ZA27 alloy [J]. Transactions of Nonferrous Metals Society of China, 2010, 20(1): 59−63.

[8] WANG Z X, LI F Y, PAN M X. Effects of high pressure on the nucleation of Cu60Zr 20Hf10Ti10 bulk metallic glass [J]. Journal of Alloys and Compounds, 2005, 388(2): 262−265.

[9] STRAUMAL B B, BARETZKY B, MAZILKIN A A, PHILLIPP F, KOGTENKOYA O A, VOLKOY M N, VALIEY R Z. Formation of nanograined structure and decomposition of supersaturated solid solution during high pressure torsion of Al-Zn and Al-Mg alloys [J]. Acta Materialia, 2004, 52(15): 4469−4478.

[10] XU R, ZHAO H, LI J. Microstructures of the eutectic and hypereutectic Al-Ge alloys solidified under different pressures [J]. Materials Letters, 2006, 60(6): 783−785.

[11] WANG Hai-yan, LIU Jian-hua, PENG Gui-rong, WANG Wen-kui. 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 [J]. Chinese Physics B, 2010, 19(9): 096203-1−096203-6.

[12] LU Jin-quan, DENG Chun-yan, XU Tao, PENG Gui-rong, LIU Jian-hua, ZHANG Rui-jun. Effect of heat treatment on microstructure of Cu-Al alloys under 1 GPa [J]. Journal of Materials Science and Engineering, 2010, 4(5): 58−60.

[13] ZHOU Yao-he, HU Zhuang-qi, JIE Wan-qi. Solidification technology [M]. Beijing: China Machine Press, 1998: 467−479. (in Chinese)

[14] SUN Shu-hua, LI Jie, XU Rui, ZHAO Hai-li, LIU Ri-ping. Microstructural characteristics in Al-based alloys solidified under high pressure [J]. Chinese Journal of High Pressure Physics, 2008, 22(4): 434−438. (in Chinese)

[15] WANG Zhu-tang. Cu Alloys and it’s working handbook [M]. Changsha: Central South University Press, 2002: 5. (in Chinese)

[16] YANG Fu-liang, YI Dan-qing. Effect of milling pretreatment to powders on microstructure and physical properties of Al-Si alloy materials [J]. Journal of Mechanical Engineering, 2009, 45(1): 253−257. (in Chinese)

[17] BYUNG G K, DONG S L, PARK S D. Effects of thermal processing on thermal expansion coefficient of a 50 vol % SiCp/Al composite [J]. Mater Chem Phys, 2001, 72: 42−46.

[18] YANG Fu-liang, GAN Wei-ping, CHEN Zhao-ke. Effect of particle size on microstructure and property of high-silicon aluminum alloy [J]. Materials Science & Technology, 2006, 14(3): 268−271. (in Chinese)

Cu-Zn 合金高压热处理后的组织演化及热膨胀性能

谌岩[1,2]，刘琳[3]，王月辉[4]，刘建华[1]，张瑞军[1]

1. 燕山大学 亚稳材料制备技术与科学国家重点实验室，秦皇岛 066004；
2. 燕山大学 环境与化学工程学院，秦皇岛 066004；
3. 唐山职业技术学院 医学基础部，唐山 063000；
4. 河北科技师范学院 理化学院，秦皇岛 066004

摘 要：利用膨胀仪测试了 Cu-Zn 合金高压热处理前、后在 25~700 °C 的热膨胀系数；采用金相显微镜、X 射线衍射仪及差示扫描量热分析仪对 Cu-Zn 合金高压热处理前、后的组织进行研究；探讨高压热处理对 Cu-Zn 合金的组织及热膨胀性能的影响。结果表明：高压热处理能细化 Cu-Zn 合金的组织，增大 Cu-Zn 合金的热膨胀系数，同时，也能使 Cu-Zn 合金的热膨胀系数在 $\alpha-T$ 曲线上出现高峰值，且压力越大，热膨胀系数峰值越小。

关键词：Cu-Zn 合金；高压热处理；组织；热膨胀系数

(Edited by YANG Hua)