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Pressure Effects on Solid State Phase Transformation of Aluminium Bronze in Cooling Process *

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Effects of high pressure (6 GPa) on the solid state phase transformation kinetic parameters of aluminum bronze during the cooling process are investigated, based on the measurement and calculation of its solid state phase transformation temperature, duration and activation energy and the observation of its microstructures. The results show that high pressure treatment can reduce the solid phase transformation temperature and activation energy in the cooling process and can shorten the phase transformation duration, which is favorable when forming fine-grained aluminum bronze.

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Aluminum bronze has been widely applied in shipping, machinery and aviation industries owing to its high strength, good corrosion-resistance and excellent hot and cold workability. However, the coarse grains of this material limit its further application.[1] It is known that high pressure can promote nucleation and suppress atomic transport, and thus efforts have been given to gain fine-grained Cu-based alloy by means of a high pressure treatment.[2,3] So far, the investigations of pressure effects on metals are mainly focused on solidification fields,[4−7] while refinement of grains by means of solidification under high pressure is difficult to operate. As we know, microstructures of metals are determined not only by the liquid-solid transformation near its melting point, but also by the solid-solid transformation phase in the cooling process. However, the pressure effects on the solid state transformation of metals during the cooling process are still unclear. In this Letter, we investigate the changes of the solid state phase transformation of aluminum bronze during the cooling process after a high pressure treatment (6 GPa).

High-pressure experiments were performed on a CS-ⅡB type six-anvil high-pressure apparatus. Pyrophyllite was used as the pressure-transmitting medium. The Cu-11.71Al (wt%) alloy samples were first sealed into graphite heaters, and were then pressurized to 6 GPa and heated to 750°C for 15 min. After the samples were cooled to room temperature, we released the pressure. The aluminium bronze samples before and after high pressure treatment were then subjected to the differential scanning calorimetry (DSC) measurements (STA449C, Jupiter, Netzsch, Germany) with the initial temperature of 700°C and the cooling rate of 5°C/min, 10°C/min, and 20°C/min, respectively.

The temperature and the duration of the solid state phase transformation were measured according to the DSC curves. The phase transformation activation energy E_c of the sample was calculated by the Kissinger equation[8] $\ln(BT^{-2}) = -E_c(RT)^{-1}+\text{const}$. The phase transformation activation energy E_x at a certain stage was calculated by the Doyle method[9] $\log B = \log AE[RF(x)]^{-1} - 2.315 - 0.4567E_x(RT)^{-1}$, 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, $\log AE[RF(x)]^{-1}$ is also a constant. Here x is calculated by the equation $x_i = S_i/S$, where S_i is the area of the exothermic peaks on the DSC curves from the initial stage to a certain temperature of the phase transformation, S is the total area of the exothermic peaks from the initial stage to the end of the phase transformation. Microstructures of the samples were observed on the NEOPHOT21-type optical microscope.

Figure 1 shows the DSC curves of the aluminum bronze with and without high pressure treatment at constant cooling rates. One exothermic peak can be seen clearly on each DSC curve. It can be concluded that this peak corresponds to the solid state phase transformation $\beta \rightarrow \alpha + \gamma_2$ during the cooling process.[10] 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, as listed in Table 1. It can be seen from Table 1 that

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the initial temperature, the peak temperature, and the ending temperature of $\beta \rightarrow \alpha + \gamma_2$ phase transformation all decrease with an increasing cooling rate and that the aluminum bronze after high pressure treatment shows a lower phase transformation temperature and shorter phase transformation duration than that without high pressure treatment. Taking the cooling rate of 10°C min for example, the phase transformation peak temperature and the phase transformation duration of the aluminum bronze after high pressure treatment is decreased by 5.75°C and 10.98 s respectively, compared with that without high pressure treatment.

Table 1. Phase transformation temperature and duration at different cooling rates.

Cooling rate	Initial temperature (°C)		Peak temperature (°C)		Ending temperature (°C)		Duration (s)	
(°C/min)	0 GPa	6 GPa	0 GPa	6 GPa	0 GPa	6 GPa	0 GPa	6 GPa
5	535.18	532.28	523.85	520.59	506.30	506.21	346.56	312.84
10	530.61	527.36	517.51	511.76	494.13	492.71	218.88	207.90
20	526.14	518.81	511.43	504.87	482.29	478.11	131.55	122.10

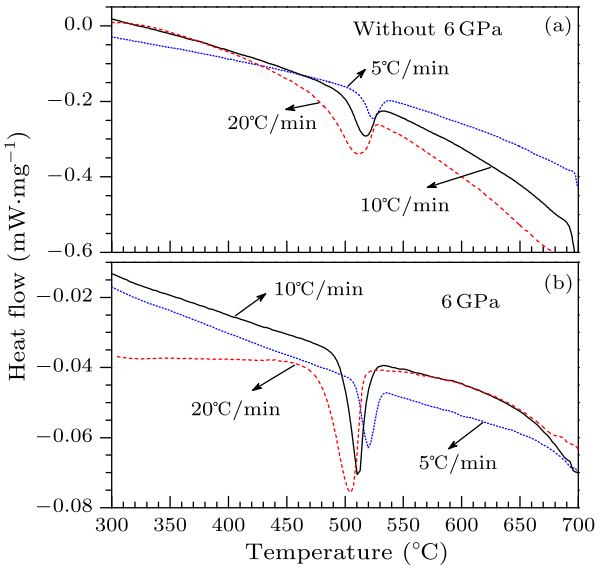


Fig. 1. DSC curves of the aluminum bronze under various conditions.

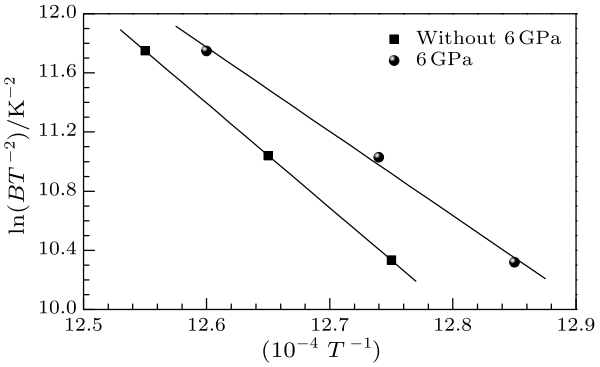


Fig. 2. Plot of $\ln(BT^{-2}) \sim T^{-1}$ at DSC peak value at different heating rates.

According to the phase transformation peak value at various cooling rates shown in Table 1, a linear relation of $\ln(BT^{-2})$ and T^{-1} was obtained, as shown in Fig. 2. By calculating its slope according to the Kissinger equation by the least square method, (E_c/R) is achieved, thus the phase transformation activation energy of $\beta \rightarrow \alpha + \gamma_2$ with and without high pressure is obtained, i.e., 428.34 kJ/mol and 592.89 kJ/mol, respectively.

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. 3. According to Fig. 3, the $\beta \rightarrow \alpha + \gamma_2$ phase transformation activation energy can be calculated at various stages by the Doyle equation and is plotted in Fig. 4, which shows that the phase transformation activation energy is relatively higher at the initial stage, and then decreases with the increasing volume fraction. Figure 4 also shows that high pressure treatment can reduce the $\beta \rightarrow \alpha + \gamma_2$ phase transformation activation energy.

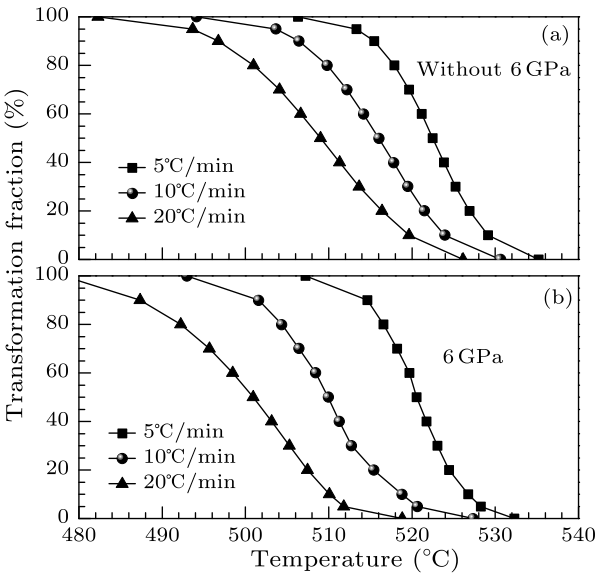


Fig. 3. Relation between the phase transformation volume fraction and the temperature at different cooling rates.

The $\beta \rightarrow \alpha + \gamma_2$ phase transformation, including the nucleation and the crystal growth processes, is determined by the atomic diffusion process. The more defects, such as grain boundaries, vacancies, and dislocations exist, the more new nucleation sites and atom diffusion paths may generate, thus the easier the phase

transformation process goes. High pressure treatment may cause high strain, so as to increase the dislocation density and the interfacial deficiency and meanwhile reduce the critical free energy of nucleation.[11] Therefore, high pressure treatment is favorable for the $\beta \rightarrow \alpha + \gamma_2$ solid state phase transformation of aluminium bronze during the cooling process, leading to lower activation energy and a shorter phase transformation duration.

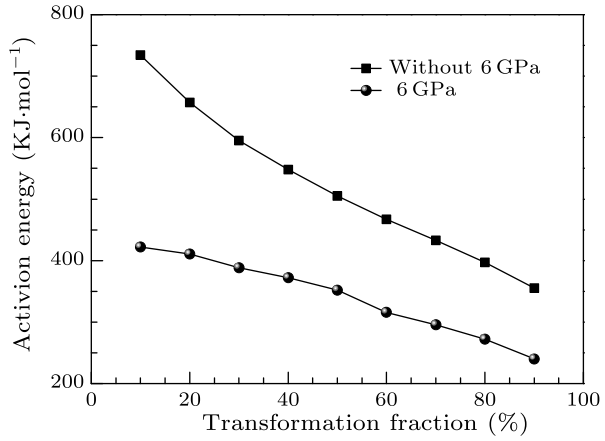


Fig. 4. Relation between the phase transformation activation energy and the phase transformation volume fraction.

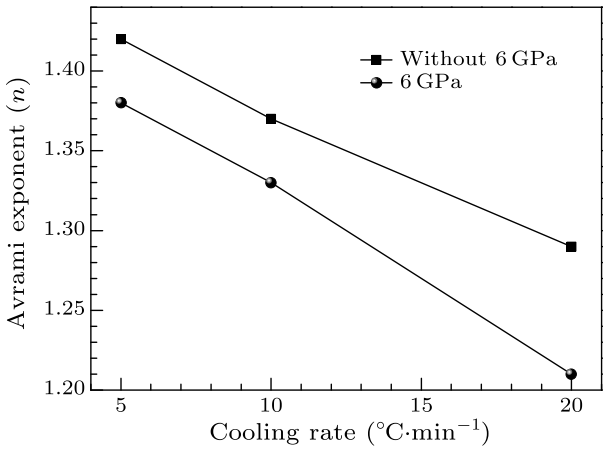


Fig. 5. Relation between the cooling rate and the Avrami exponent.

The Avrami exponent n is a phase transformation exponent, which is an important kinetics parameter in characterizing the phase transformation behavior, such as nucleation and crystal growth. The Avrami exponent n can be calculated by the following equation[12] $n = 2.5T_p^2(\Delta\tau_{\mathrm{FWTH}}ER^{-1})^{-1}$, wherein $\Delta\tau_{\mathrm{FWTH}}$ is the half band width of the exothermic peak, T_p is the exothermic peak temperature, E is the phase transformation activation energy, and R is the gas constant. The average Avrami exponent n of the aluminum bronze before and after high pressure treatment can be obtained by the above equation according to the DSC data, as shown in Fig. 5. It shows that the Avrami exponents n in both the cases are less than 2, indicating that high pressure treatment has little effect on the Avrami exponent, as far as our experimental conditions are concerned. It can be concluded from the Avrami exponent n shown in Fig. 5 that[13,14] the $\beta \rightarrow \alpha + \gamma_2$ phase transformation of the aluminum bronze both with and without high pressure treatment obeys the one-dimensional growth mode characterized by a gradually decreasing nucleation rate and diffusion-controlled crystal growth process. Our experimental results indicate that high pressure treatment has little effect on the $\beta \rightarrow \alpha+\gamma_2$ phase transformation mechanism.

Figure 6 shows the microstructures of the aluminum bronze under various conditions. All the microstructures consist of irregular white and black areas, in which the white are α phase and the black are β' and γ_2 phases. It can be seen in Fig. 6 that the grain sizes of the aluminum bronze after high pressure treatment are smaller than that without high pressure treatment, whether the samples undergo DSC measurements or not.

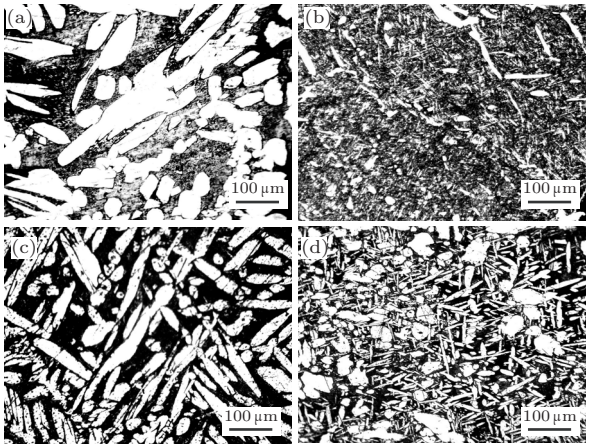


Fig. 6. Microstructures of the specimens after different treatments (cooling rate of DSC measurement 5°C/min): (a) original state, (b) after 6GPa treatment, (c) after DSC measurement of the original state specimen, (d) after DSC measurement of the 6 GPa pressurized specimen.

The fine grain microstructures obtained after high temperature treatment are mainly attributed to the increment of the defects, such as the grain boundaries and the dislocations, which provides more favorable nucleation sites, resulting in a larger nucleation rate. Meanwhile, the $\beta \rightarrow \alpha+\gamma_2$ phase transformation temperature of the sample drops after high pressure treatment, which depresses the atomic diffusion rate. In addition, the high pressure condition shortens the phase transformation duration, i.e., the growth process of the new nucleus is shortened. As a result, fine grains are formed after high pressure treatment.

In conclusion, the effects of high pressure on the solid phase transformation kinetic parameters of aluminium bronze during the cooling process have been investigated quantificationally via the differen-

tial scanning calorimetry method. The results show that high pressure treatment can reduce the temperature and the activation energy and can shorten the duration of the $\beta \rightarrow \alpha + \gamma_2$ solid phase transformation, which is favorable when forming fine-grained aluminum bronze. High pressure treatment (6 GPa) does not change the growth mode of the $\beta \rightarrow \alpha + \gamma_2$ solid phase transformation.

References

[1] Li W et al 2009 *Transactions of Nonferrous Metals Society of China* **19** 311
[2] Zhao J et al 2008 *Rare Metals* **27** 541
[3] Zhao J et al 2009 *Rare Metal Mater. Engin.* **38** 601
[4] Li G, et al 2007 *Chin. Phys. Lett.* **24** 2323
[5] Qi L et al 2008 *Comput. Mater. Sci.* **43** 732
[6] Xu R et al 2006 *Mater. Lett.* **60** 783
[7] Kim M T et al 2009 *J. Alloys Compd.* **477** 224
[8] Liu J H et al 2002 *Trans. Nonferrous Met. Soc. China* **12** 466
[9] Han Z L 2007*J. Mater. Sci. Engin.* **1** 61
[10] M. R. F. Hurtado, et al 1998 *J. Alloys Compd.* **280** 188
[11] Wang W K et al 1992 *Sci. Chin.* A **35** 1017
[12] Harnisch K et al 1982 *J. Non-Cryst. Solids* **53** 235
[13] I. Sinha et al 2005 *J. Non-Crystal. Solids* **355** 361
[14] Branden B et al 2003 *J. Non-Crystal. Solids* **317** 106