Kinetics of Glass Transition and Crystallization in Carbon Nanotube Reinforced Mg-Cu-Gd Bulk Metallic Glass

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Abstract: $Mg_{65}Cu_{25}Gd_{10}$ bulk metallic glass and its carbon nanotube reinforced composite were prepared. Differential scanning calorimeter (DSC) was used to investigate the kinetics of glass transition and crystallization processes. The influence of CNTs addition to the glass matrix on the glass transition and crystallization kinetics was studied. It is shown that the kinetic effect on glass transition and crystallization are preserved for both the monothetic glass and its glass composite. Adding CNTs in to the glass matrix reduces the influence of the heating rate on the crystallization process. In addition, the CNTs increase the energetic barrier for the glass transition. This results in the decrease of GFA. The mechanism of the GFA decrease was also discussed.

Key words: metallic glass; carbon nanotube; glass transition; crystallization; kinetic effect; composite glass; Gadolinium; rare earths

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Bulk metallic glasses (BMGs) have unique properties such as high strength, toughness and good corrosion resistance[1]. Among the BMGs developed so far, Mg-TM-RE (TM, transition metal; RE, rare earth metal) alloy system has gotten more and more attention for its excellent glass forming ability and high specific strength[2~5]. Recently, Kim[4] succeeded in manufacturing bulk $Mg_{65}Cu_{25}Gd_{10}$ glassy alloy with enhanced glass forming ability. Mg based BMGs are of interest as matrix of composite materials because of their low melting points and large undercooled liquid regions. Carbon nanotube, as the "ultimate" carbon fiber, is well known for its unique mechanical properties such as high modulus and toughness, so it can be introduced into other materials as a promising reinforcement. In recent years, many efforts have been dedicated to the study of CNTs reinforced polymer and metallic composites[6~10]. Wang et al.[11] studied the influences of CNTs on the ultrasonic properties of $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ BMG. However, the kinetic behavior of glass transition and crystallization of CNTs reinforced BMG composite was not concerned in their study. This paper is focused on the study of the glass transition and crystallization behavior of $Mg_{65}Cu_{25}Gd_{10}$ bulk metallic glass and its CNTs reinforced composite.

1 Experimental

Pure Cu and Gd elements (purity ~99.9%) were

arc-melted in Ti-gettered argon atmosphere to produce intermediate Cu-Gd alloys. Master alloys were prepared by induction-melting the intermediate Cu-Gd alloy together with Mg (purity 99.99%) in a quartz tube under vacuum. When the master alloys were homogeneously melted, they were cast into a copper mold to get a BMG cylinder with a length of 50 mm and diameter of 3 mm. In order to fabricate CNTs reinforced composites, the pre-alloyed Mg-Cu-Gd ingots were ground mechanically into fine powder. The CNT powder was cleaned in acetone and dehydrated at 473 K before mixing. The ingot powder was mixed homogenously with CNTs powder (3% (volume fraction)), and then the mixed powder was compressed into cylinders in steel dies (diameter = 5 mm). The cylinders were melted in a quartz tube rapidly by induction under a pure argon atmosphere and then cast into a copper mold to produce composite rods with a diameter of 3 mm.

The phase and atomic structure of the samples were investigated by X-ray diffraction (XRD) using a MAC M03 XHF diffractometer. The microstructure of the samples was analyzed using scanning electron microscopy (HITACHI S-570). The thermal stability was examined by differential scanning calorimeter (Netzsch DSC 404) at various heating rates of 5, 10, 20, and 40 K·min^{-1} under purified argon. At each heating rate, the calorimeter was adjusted using the purified In and Zn. The onset temperature of glass transition

T_g^{onset}, onset crystallization temperature T_x, and crystalline peak temperature T_p were determined by DSC traces with an accuracy of ± 1 K.

2 Results and Discussion

2.1 Experimental results

Figs. 1 (a), (b) show DSC curves obtained from BMG and CNTs composite at different heating rates. Fig. 1(a) illustrates that T_g, T_x and T_p of BMG move to higher temperature with increasing of heating rate. Not only crystallization but also glass transition shows a strong dependence on the heating rate during continuous heating, indicating that both the glass transition and crystallization processes have significant kinetic effects. This phenomenon is also reported for Zr-based BMGs by Wang et al[12]. Fig. 1(b) shows that similar trend exists in CNTs composite, which implies that CNTs addition cannot change the kinetic effects of glass transition and crystallization. Values of T_g, T_x, T_p and SLR, ΔT ($= T_x - T_g$) for both monothetic BMG and CNTs composite at a heating rate of 20 K·min^{-1} are listed in Table 1. With CNTs addition, T_x, T_p and ΔT of BMG decrease about 20 K, indicating that GFA and thermal stability of BMG are reduced, but the dependence of glass transition and crystallization behavior on heating rate is retained.
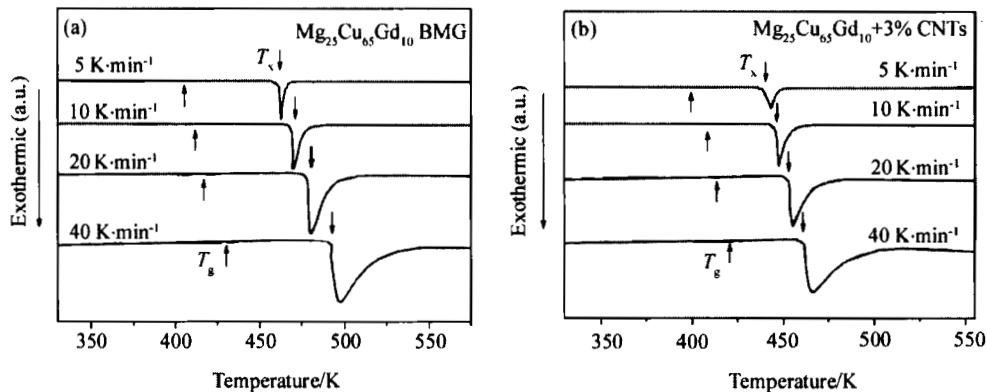

Fig. 1　DSC curves of Mg-Cu-Gd BMG and its CNTs composite at different heating rates
(a) Mg$_{65}$Cu$_{25}$Gd$_{10}$ bulk metallic glass; (b) CNTs-BMG composite

Table 1　T_g, T_x, T_p and ΔT of Mg-Cu-Gd BMG and its CNTs composite at different heating rates

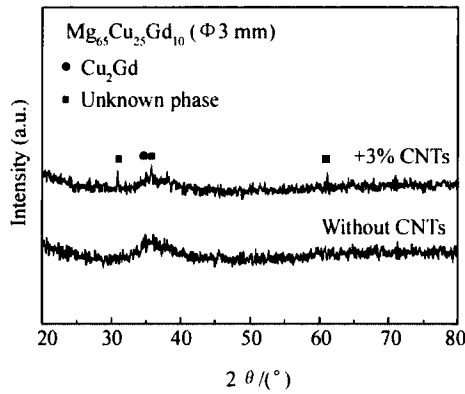| Samples	Heating rates/(K·min^{-1})	T_g/K	T_x/K	T_p/K	$\Delta T(T_x - T_g)$/K
Mg$_{65}$Cu$_{25}$Gd$_{10}$ BMG	5	405.3	461.6	462.4	56.3
	10	409	469.1	470.6	60.1
	20	415	478.3	480.6	63.3
	40	425.8	491.6	497.2	65.8
CNTs-BMG composite	5	400.4	439.6	443.4	39.2
	10	408.2	446.4	447.6	38.2
	20	413.3	453.2	455.4	39.9
	40	420.3	461.6	466.2	41.3

Fig.2   XRD patterns of Mg-Cu-Gd BMG and its CNTs composite

X-ray diffraction patterns of undoped BMG and 3% CNT-reinforced BMG composite are shown in Fig.2. The curve of the composite exhibits a superimposition of broad maximum from amorphous phase and several sharp peaks indicating the existence of crystalline phase. The crystalline peaks are identified as Cu_2Gd phase and an unknown phase. SEM images of the BMG and its composite are shown in Fig.3. The precipitated phase can be well identified.

2.2   Kinetic effects of glass transition and crystallization

The above-obtained results show that T_g, T_x, T_p and ΔT are closely dependent on heating rate and shift to higher temperatures with an increasing heating rate Φ for BMG, as well as CNTs composite. Fig.4 shows the variation of T_g, T_x as a function of $\ln\Phi$. It has good linearity that can be expressed as:

$$\theta = A + B\ln\Phi \tag{1}$$

where A and B are constants. The formula is referred to as Lasoka equation[13]. The values of B indicate the pertinency of T_g on heating rate Φ. On the basis of the results of Fig.4, it could be known that the variation of heating rate has more influence on crystallization process than glass transition. In another aspect, CNTs addition made a big change of B value, as shown in the $T_x - \ln\Phi$ curve. This demonstrates that CNTs addition lowers kinetic effect in crystallization process.

An abrupt change of specific heat of BMGs was observed during the transition from glass states into supercooled liquid region. The changes of specific heat are 0.477 and 0.606 $J\cdot g^{-1}\cdot K^{-1}$ for monothetic Mg-
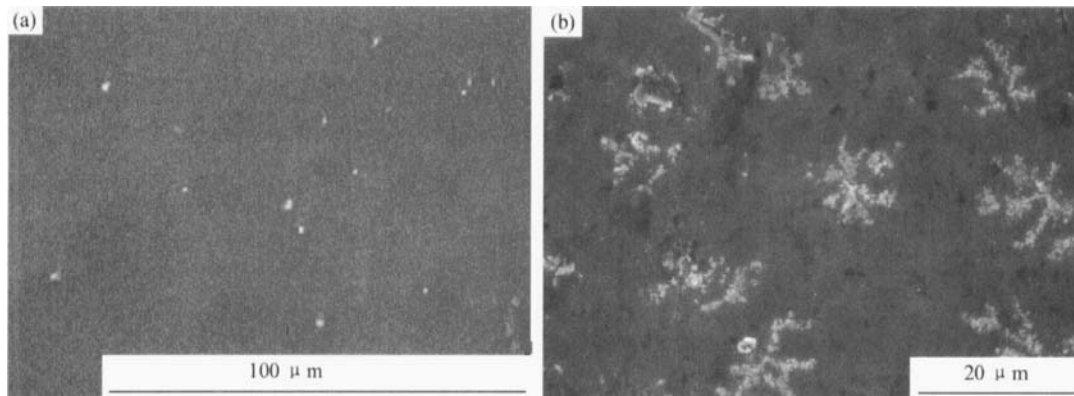

Fig.3   SEM images taken from cross-sectional surface of as-cast rods
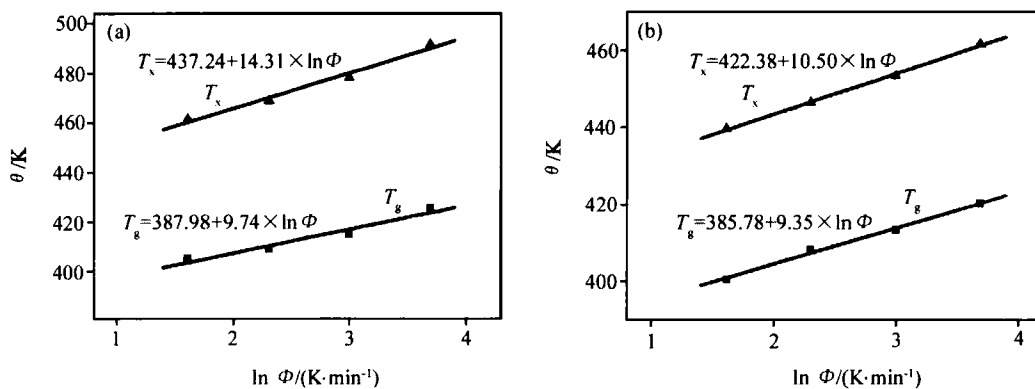(a) Mg-Cu-Gd BMG;   (b) CNTs-BMG composite

Fig.4   Plots of T_g, T_x vs. $\ln\Phi$ for Mg-Cu-Gd BMG (a) and CNTs-BMG composite (b)

Cu-Gd BMG and its CNTs composite, respectively, under a heating rate of 5 K·min^{-1}. It indicates the occurrence of second-order phase transition from glass state to supercooled liquid state, which has been discussed in Ref.[14].

2.3 GFA and crystallization kinetics

During crystallization process, atoms participating in crystallization reaction should acquire additional energy to form nuclei of crystallization. The activation energy can be interpreted as the additional energy acquired by an atom before it becomes a part of the nuclei. Kissinger method is widely used in calculating the activation energy in BMG[15].

Kissinger equation can be described as follows:

$$\ln \frac{\theta^2}{\Phi} = \frac{E}{k_B \theta} + \ln \frac{E}{k_B \nu_0} \qquad (2)$$

where θ stands for T_g or T_x, Φ is the heating rate represents Boltzmann constant. k_B is the value of crystallization constant. The value of crystallization activation energy E can be calculated from the slope. Fig.5 shows the Kissinger plots of glass transition and crystallization for monothetic BMG and its CNTs composite. There exists a strong linear relation between $\ln(\theta^2/\Phi)$ and $1/T$ in spite of CNTs addition. The apparent activation energy of glass transition increases af-

ter the addition of CNTs, implying that the addition of CNTs degrades glass-forming ability of BMG matrix.

In the process of preparing BMG and its CNTs composite, cooling rate during quenching and sample size are kept as the same. The rate constant of crystalline reaction reflects GFA to some extent[16]. The relation between rate constant of crystalline reaction ane the temperature obeys Arrehenius law:

$$\nu_T = \nu_0 \exp(-E/k_B T) \qquad (3)$$

where ν_0 is frequency factor. According to Kissinger Eq.(2), ν_0 can be obtained from the slope and intercept of Kissinger plots. The calculated ν_T of BMG and its composite at crystallization peak are 0.333 and 0.522 s^{-1}, respectively. The addition of CNTs increases the rate constant of crystalline reaction, and subsequently decreases GFA of BMG matrix. The same phenomena were also reported for Zr-based CNTs-BMG composite[11]. It is argued that the formation of ZrC at the interface between amorphous matrix and CNTs leads to the decrease of GFA. However, there is no element, which can react with the added CNTs for Mg-based BMGs. In order to reveal the mechanism of this GFA decrease for Mg-based CNTs reinforced composite, EDX analysis of the matrix is carried out which is shown in Fig.6 . EDX results
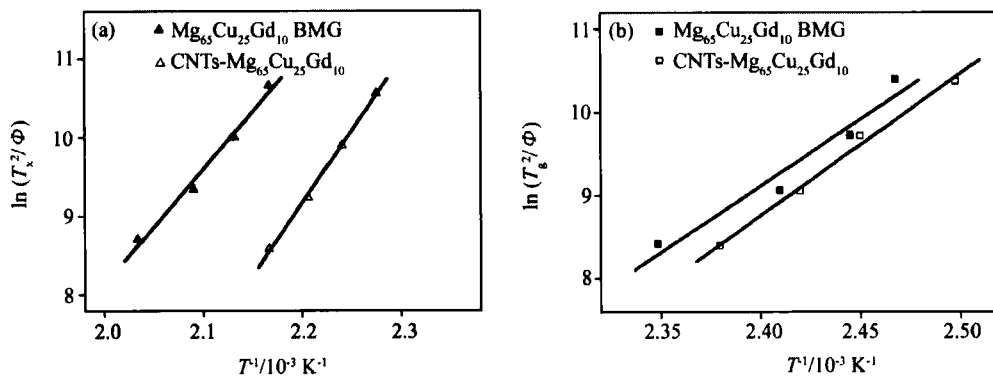

Fig.5   Kissinger plots of crystallization temperature (a) and glass transition (b) for Mg-Cu-Gd BMG and its CNTs composite
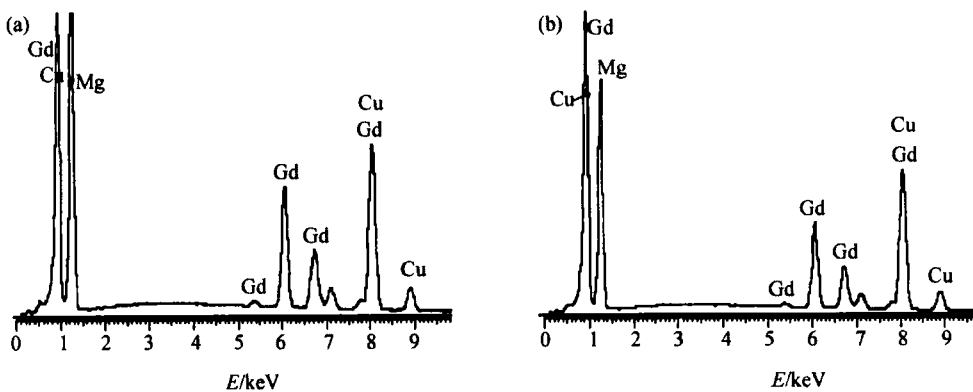

Fig.6   EDX spectra of Mg-Cu-Gd BMG and its CNTs composite
(a) Mg-Cu-Gd BMG; (b) CNTs-BMG composite

show that the compositions of undoped BMG and CNTs-BMG composite are $Mg_{63.28}Cu_{26.88}Gd_{9.83}$ and $Mg_{67.5}Cu_{25.1}Gd_{7.4}$, respectively. Considering the loss of Gd element is the same at the same cast condition, the relatively low Gd content in BMG composite should be induced by CNTs addition. Xi et al.[17] studied the properties of Mg-Cu-RE (RE, rare earth metal) BMG. They found that GFA of BMG is very sensitive to Gd content, when the Gd atomic suffix is not equal to 10, GFA of BMG decreases obviously and crystallization temperature shifts to lower temperature, which is very similar with our experimental results. Therefore, the decrease of GFA might be attributable to the change of Gd content in the matrix by CNTs addition.

3 Conclusions

1. Both the glass transition and crystallization process of Mg-based BMG and CNTs composite have kinetic effect. CNTs addition cannot change this feature. The relation between T_g, T_x and heating rate can be well described by Lasoka equation. CNTs addition weakens the dependence of crystallization on heating rates.

2. The activation energy of glass transition of BMG as well as its CNTs composite was calculated by Kissinger equation. The activation energy increases after the addition of CNTs, indicating the decrease of glass-forming ability.

3. CNTs addition increases the rate constant of crystalline reaction, hence decreases GFA.

4. GFA decrease in CNTs composite is possibly attributable to the change of Gd content in the matrix induced by CNTs addition.

References:

[1] Inoue A. Stabilization of metallic supercooled liquid and bulk amorphous alloys [J]. Acta Mater, 2000, 48 (1): 279.

[2] Amiya K, Inoue A. Thermal stability and mechanical properties of Mg-Y-Cu-M (M = Ag, Pd) bulk amorphous alloys [J]. Mater. Trans. JIM, 2000, 41(11): 1460.

[3] Yuan G, Zhang T, Inoue A. Thermal stability, glass-forming ability and mechanical properties of Mg-Y-Zn-Cu glassy alloys [J]. Mater. Trans., 2003, 44 (11): 2271.

[4] Men H, Kim D H J. Fabrication of ternary Mg-Cu-Gd bulk metallic glass with high glass-forming ability under air atmosphere [J]. Mater. Res., 2003, 18(7): 1502.

[5] Han S M, Liu B Z, Zhang Z, et al. Phase structure and electrochemical properties of RE-Mg based composite hydrogen storage alloys [J]. Journal of Rare Earths, 2004, 22(6): 878.

[6] Carneiro O, Covas J, Bernardo C, et al. Production and assessment of polycarbonate composites reinforced with vapour grown carbon fibres [J]. Comp. Sci. Technol., 1998, 58(3): 401.

[7] Thostenson E T, Li W Z, Wang D Z, et al. Carbon nanotube/carbon fiber hybrid multiscale composites [J]. J. Appl. Phys., 2002, 91(9): 6034.

[8] Lau K T, Hui D. The revolutionary creation of new advanced materials-carbon nanotube composites [J]. Composites Part B-Engineering, 2002, 33(4): 263.

[9] Thostenson E T, Ren Z F, Chou T W. Advances in the science and technology of carbon nanotubes and their composites: a review [J]. Composites Science and Technology, 2001, 61(13): 1899.

[10] Harris P J F. Carbon nanotube composites [J]. International Materials Reviews, 2004, 49(1): 31.

[11] Bian Z, Wang R J, Wang W H, et al. Carbon-nanotube-reinforced Zr-based bulk metallic glass composites and their properties [J]. Adv. Fuct. Mater., 2004, 14 (1): 55.

[12] Zhuang Y, Zhao D, Zhang Y, et al. Kinetics of glass transition and crystallization in multicomponent bulk amorphous alloys [J]. Science in China (Series A), 2000, 43(3): 1195.

[13] Lasocka M. The effect of scanning rate on glass transition temperature of splat-cooled $Te_{85}Ge_{15}$ [J]. Mater. Sci. Eng., 1976, 23(1): 173.

[14] Zhuang Yuanxin, Zhao Deqian, Zhang Yong, et al. Kinetics of glass transition and crystallization in multicomponent bulk amorphous alloys [J]. Science in China (Series A), 2000, 43(11): 1195.

[15] Kissinger H E. Variation of peak temperature with heating rate in differential thermal analysis [J]. J. Res. Nat. Bur. St., 1956, 57(1): 217.

[16] Xu H, Tan X H, Dong Y D. Crystalline behavior and magnetic properties of $Nd_{60}Fe_{30-x}Al_{10}Co_x$ ($x = 0$, 5, 10) bulk amorphous alloys [J]. Journal of Rare Earths, 2003, 21(5): 552.

[17] Xi X K, Wang R J, Zhao D Q, et al. Glass-forming Mg-Cu-RE (RE = Gd, Pr, Nd, Tb, Y, and Dy) alloys with strong oxygen resistance in manufacturability [J]. J. Non-Crystalline Solids, 2004, 344(1): 105.