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Journal of Non-Crystalline Solids 354 (2008) 970–974
JOURNAL OF NON-CRYSTALLINE SOLIDS
www.elsevier.com/locate/jnoncrysol

Correlations between apparent activation energy and thermostability and glass forming ability for Fe based metallic glasses

B. Yao [a,c,*], K. Zhang [a], H. Tan [b], Y. Li [b]

[a] Department of Physics, Jilin University, No. 2519, Jiefang Road, Changchun 130023, PR China
[b] Department of Material Science, National University of Singapore, 119260 Singapore, Singapore
[c] Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130021, PR China

Received 17 March 2007; received in revised form 10 July 2007
Available online 11 September 2007

Abstract

Apparent activation energies (E_g) of glass transition, glass transition temperature (T_g) and crystallization temperature (T_x) of amorphous alloys of composition $Fe_{91-x}B_xZr_5Nb_4$ (FBZN, $5 \leqslant x \leqslant 30$ at.%) and $Fe_{61-x}Co_xZr_5B_{30}Nb_4$ (FCZBN, $0 \leqslant x \leqslant 15$ at.%) were obtained by using differential scanning calorimeter (DSC) measurement and Kissinger equation, and correlations between E_g and T_g, T_x and glass-forming ability (GFA) were studied in the present work. It was found that the T_g and T_x are not independent each other for each glass composition in the two alloy systems, but related by a formula, $T_x = \alpha T_g + \beta$, where α and β are constants, and were measured by nonisothermally scanning in the DSC together with the Lasocka's equation. The E_g was found to be directly proportional to α and β, respectively, and had a correlation with T_x and T_g, $T_x = \frac{E_g - 1.09}{3.527} T_g - \frac{E_g - 4.86}{0.0041}$, indicating that E_g determines linear relationship between T_x and T_g. Supercooled liquid region ΔT_x is used as characterization of GFA of the Fe based metallic glasses and related to E_g and T_g by a formula: $\Delta T_x = E_g(\frac{T_g}{3.527} - 234.9) + 1185.37 - 1.309T_g$, indicating that E_g and T_g can characterize GFA of the Fe based metallic glass well.

PACS: 61.43.Dq; 71.23.Cq; 75.47.Np; 81.70.Pg

Keywords: Alloys; X-ray diffraction

1. Introduction

It is well known that theromstability and glass-forming ability (GFA) are two important features for amorphous alloys and have been investigated widely since amorphous alloy was produced. The thermostability is usually characterized by glass transition temperature (T_g) or crystallization temperature (T_x), which can be measured by nonisothermal scan in a differential scanning calorimeter (DSC) easily [1–3]. However, GFA measurement is complex and even difficult. Therefore, many scientists have tried to establish relations between GFA and some parameters measured in experiment, such as, T_g, T_x, and T_l etc., (T_l is liquidus temperature), to characterize GFA of alloys easily. In the past years, many criteria on GFA were put forward, such as T_g/T_l and $\Delta T_x = (T_x - T_g)$, etc., however, these criteria have been demonstrated to well characterize GFA of some alloys qualitatively, but not to be suitable to all alloys. So, it is necessary to establish correlations between some measurable parameters and GFA for preparation and research of amorphous alloys.

Apparent activation energy of glass transition (E_g) is an important kinetic parameter in crystallization kinetics research, which can be measured by using the nonisothermal sacnning technique together with the Kissinger method [4]. Its physical meaning and correlation with T_g, T_x and

* Corresponding author. Address: Department of Physics, Jilin University, No. 2519, Jiefang Road, Changchun 130023, PR China.
E-mail address: binyao@mail.jlu.edu.cn (B. Yao).

0022-3093/$ - see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.jnoncrysol.2007.08.021

GFA have been interesting subjects in amorphous alloy investigations. Some efforts have been made to set up a correlation between E_g and T_g [5,6], or characterize GFA by combining some parameters, which can be measured by the nonisothermal scanning technique together with some suitable method or equation [7,8]. However, it is still lacking in comprehensive understanding of E_g and relationships between T_g, T_x, E_g and GFA.

In recent years, a new class of Fe–(Co, Ni)–(Zr, Hf, Nb)–B bulk metallic glass with excellent soft magnetic properties prepared by different casting techniques has been intensively studied [9,10]. This bulk metallic glass shows distinct glass transition, wide supercooled liquid region, high thermal stability and GFA. Extensive efforts have been made to improve T_g, T_x and GFA by substitutions of elements. It was reported that T_g, T_x and GFA had considerable variation upon replacement of Fe by B and Co [11] in the Fe based metallic glass, resulting in that there are many amorphous alloys with different T_g, T_x and GFA in the same system. The distinct glass transition, wide supercooled liquid region and a lot of T_g, T_x and GFA data in the metallic glass system allow us to measure T_g, T_x and E_g accurately and study glass transition and crystallization kinetics systemically. The aim of the present work is to investigate effects of replacement of Fe by B or Co on glass transition behavior and crystallization kinetic of the Fe–Co–Zr–B–Nb amorphous system, establish correlations between E_g and T_g, T_x, and GFA, and explain physical meaning of E_g.

2. Experimental procedures

Amorphous alloy ribbons of composition $Fe_{91-x}B_xZr_5Nb_4$ (FBZN) with boron (B) content ranging from 5 to 30 at.% and $Fe_{61-x}Co_xZr_5B_{30}Nb_4$ (FCZBN) with cobalt (Co) content between 0 and 15 at.% were prepared by melt-spinning technique under an argon atmosphere. The as-spun ribbons were identified by X-ray diffractometry with Cu K_α radiation (XRD) and transmission electron microscopy to contain no detectable crystallinity. The thermal stability and melting temperature of the ribbons were measured by a differential scanning calorimeter (DSC) and a differential temperature analyzer (DTA) under a continuous argon flow at heating rates Φ ranging from 2.5 to 40 K/min. The T_g and T_x are defined as the temperature at the point of inflection of glass transition endothermic curve and peak temperature of exothermic event on a DSC trace, respectively, in the present experiment.

3. Experimental results and discussions

Fig. 1a–f shows typical DSC curves of the amorphous FBZN alloys with B contents of 8, 14, 20, 22.5 and 30 at.% and an amorphous FCZBN alloy with Co content of 7.5 at.% scanned at a heating rate of 10 K/min, respectively. The crystallization products of all the amorphous alloys heated in the DSC were examined by XRD and

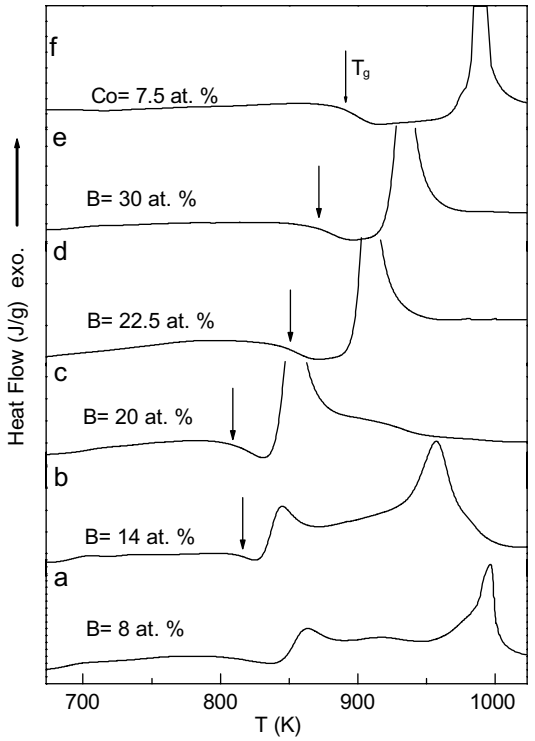

Fig. 1. DSC curves of amorphous FBZN with B contents of 8 (a), 14 (b), 20 (c), 22.5(d) and 30 at.% (e) and amorphous FCZBN with Co content of 7.5 at.% (f) scanned at a heating rate of 10 K/min.

TEM [11]. Based on DSC, XRD and TEM results, it was concluded that the amorphous FBZN alloys crystallized to α-Fe (Zr, B), Fe_2Nb (Zr) and ZrB_2 phases in two steps crystallization model in the B contents between 5 and 20 at.%, to a new metastable Fe–Zr–B–Nb cubic phase and α-Fe in an eutectic model in the range between 22.5 and 27.5 at.%, and to a single Fe–Zr–B–Nb cubic phase with a lattice constant of 1.0704 nm in a polymorphous model at B content of 30 at.% [11]. The T_g and T_x increase sharply when crystallization model changes from two steps model to eutectic one at B content above 20 at.%. While all amorphous FCZBN alloys crystallized to a metastable Fe–Co–Zr–B–Nb cubic phase in a polymorphous model, and its T_g and T_x varied with Co content and have maxima upon replacement of Fe by about 7.5 at.% Co. Glass transition was not observed in the amorphous FBZN alloys with B content below 8 at.%, but above 11 at.% and all amorphous FCZBN alloys, indicating that the former is an unstable amorphous alloy ($T_g > T_x$) and the latter is a stable one ($T_g < T_x$).

The T_g and T_x of the amorphous FBZN and FCZBN alloys were measured with heating rates (Φ) of 2.5, 5, 10, 20 and 40 K/min, respectively. Fig. 2 shows typical plots of T_g and T_x versus $\ln\Phi$ for the amorphous FBZN alloy with 22.5 at.% B and amorphous FCZBN alloy with 7.5 at.% Co, indicating that both T_g and T_x increase with increasing heating rate. The dependences of T_g and T_x on the heating rate Φ follow the lasocka's relationship, respectively [12]

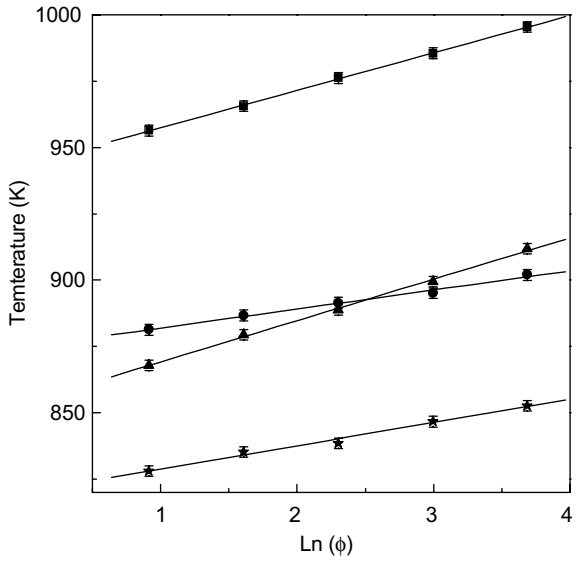

Fig. 2. Typical plots of T_g and T_x versus lnΦ for amorphous FBZN with 22.5 at.% B (✱,T_g,▲ T_x) and amorphous FCZBN with 7.5 at.% Co (● T_g, ■ T_x).

$$T_g = A_g \ln \phi + B_g \tag{1}$$

and

$$T_x = A_x \ln \phi + B_x \tag{2}$$

where the A_g, B_g, A_x and B_x are constants for a given glass composition. Combining Eq. (1) with (2), a linear correlation between T_g and T_x is obtained.

$$T_x = \alpha T_g + \beta \tag{3}$$

where α and β are constants for a given amorphous alloy, and can be calculated using A_x/A_g and $(B_xA_g - B_gA_x)/A_g$, respectively. Table 1 lists the calculated α and β for each composition of the amorphous FBZN and FCZBN systems.

The apparent activation energy of glass transition E_g for the amorphous FBZN and FCZBN alloys were calculated by Kissinger's equation [4,7]:

$$\ln \frac{\phi}{T_g^2} = -\frac{E_g}{RT_g} - \ln \frac{E_g}{RK_0} \tag{4}$$

where R is the gas constant, and K_0 frequency factor in Arrehenius law of reaction rate constant K, $K = K_0\exp(-E_g/RT)$. Plotting $\ln\Phi/T_g^2$ versus $1/T_g$ enables calculation of E_g from the slop of this plot, $-E_g/R$, and the frequency factor K_0 can be determined from the intercept of this line, $\ln RK_0/E_g$. The calculated E_g in unit of eV, denoted as $E_g$exp, are listed in Table 1 for the amorphous FBZN and FCZBN alloys. By using the $E_g$exp and α data, the E_g versus α plot for the amorphous FBZN, FCZBN and both FZBN and FCZBN alloys is given in Fig. 3a, b and c, respectively. All the three plots show a well linear relationship between the E_g and α. Fitting linearly relating the data points in the three plots, respectively, the E_g can be written as a function of α, $E_g = A\alpha + B$, where A and B are fitting parameters. The A and B for the three plots are listed in Table 2. Obviously, the A (or B) values of the three plots are very close, so the A (or B) in the three plots can be considered as the same within errors approximately. Furthermore, based on errors of A and B in Table 2, it is also concluded that there is a better linear relationship between the E_g and α in Fig. 3c, though the data points belong to different compositions. Above facts imply that all the data points of the amorphous FZBN and FCZBN can be well related by a single line, as shown in Fig. 3c, and that the linear correlation between E_g and α is not related to compositions in the Fe based amorphous alloy. The same conclusion was obtained for the E_g and β, as shown in Fig. 4. Therefore, the E_g can be expressed as a linear function of α and β, respectively, for both amorphous FBZN and FCZBN alloys:

$$E_g = 3.527\alpha + 1.09 \tag{5}$$

$$E_g = -0.0041\beta + 4.86 \tag{6}$$

Combining Eq. (3) with (5) and (6), a correlation between E_g, T_g and T_x was obtained:

$$E_g = 3.527\frac{T_x - 919.52}{T_g - 860.24} + 1.09 \tag{7}$$

or

$$T_x = \frac{E_g - 1.09}{3.527} \quad T_g - \frac{E_g - 4.86}{0.0041} \tag{8}$$

Table 1
α, β, apparent activation energies of glass transition measured $E_g$exp and calculated $E_g$cal for each composition in the amorphous FBZN and FCZBN

$Fe_{91-x}B_xZr_5Nb_4$						$Fe_{61-x}Co_xZr_5B_{30}Nb_4$					
B (at.%)	α	β	$E_g$exp (eV)	ΔE_gexp	$E_g$cal (eV)	Co (at.%)	α	β	$E_g$exp (eV)	ΔE_gexp	$E_g$cal (eV)
11	0.88	125	4.24	0.2	4.21	2	1.7	−556	7.07	0.38	7.10
14	0.76	227	3.95	0.3	3.75	3	1.87	−701	8.13	0.31	7.69
17	1.29	−212	5.34	0.35	5.65	4	1.84	−677	7.83	0.24	7.58
20	1.42	−317	6.26	0.1	6.13	5	2.13	−931	8.66	0.29	8.61
22.5	1.75	−581	6.71	0.35	7.26	7.5	2.25	−1036	9.64	0.7	9.02
25	2.05	−840	7.68	0.6	8.33	10	1.91	−724	8.00	0.41	7.81
27.5	1.9	−724	7.61	0.45	7.81	12.5	1.78	−620	7.45	0.55	7.37
30	1.81	−655	7.5	0.15	7.48	15	1.89	−710	7.38	0.26	7.76

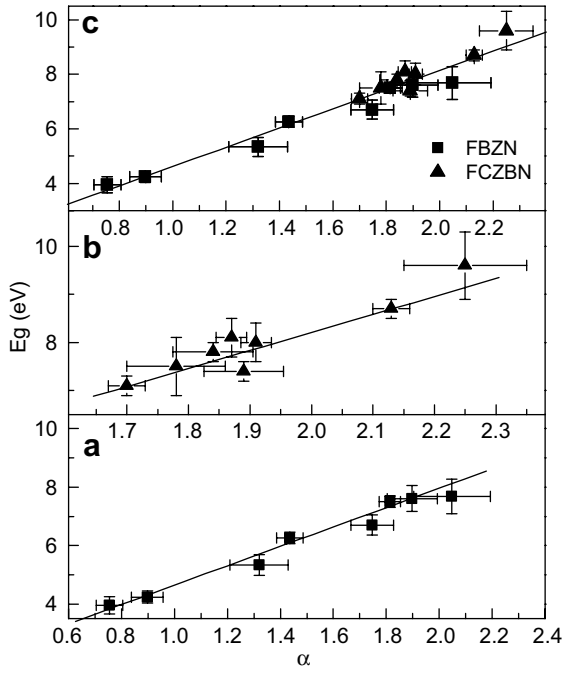

Fig. 3. E_g versus α plots for amorphous FZBN (a), FCZBN (b) and both FZBN and FCZBN (c).

Table 2
Fitting parameters (A and B) and their errors (ΔA and ΔB) of the E_g versus α plots for the amorphous FZBN, FCZBN and both FZBN and FCZBN

	A	ΔA	B	ΔB
FZBN	3.316	0.232	1.327	0.334
FCZBN	3.740	0.608	0.725	0.155
FZBN + FCZBN	3.527	0.166	1.09	0.28

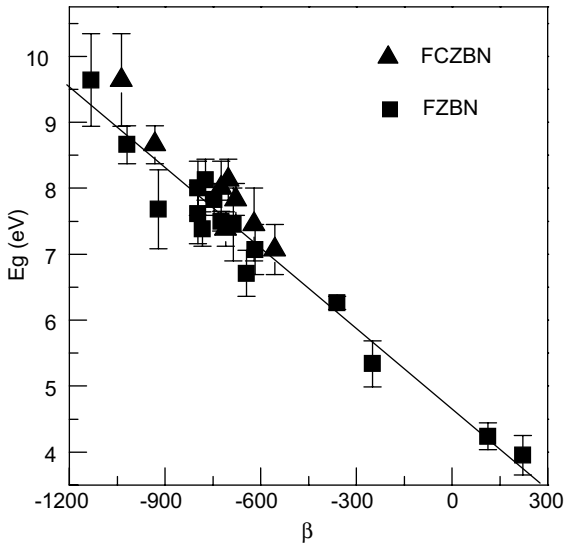

Fig. 4. E_g versus β plot for amorphous both FZBN and FCZBN.

Using Eq. (7) as well as T_g and T_x measured in the present experiment, the E_g was calculated for each composition in the amorphous FBZN and FCZBN systems, as listed in column $E_g$cal of Table 1. The $E_g$cal is close to the value of $E_g$exp obtained by Kissinger's method, the difference between them is within experimental errors. Eq. (7) indicates that the apparent activation energy of glass transition is directly proportional to crystallization temperature, but inversely to glass transition temperature in the present Fe based amorphous alloys, It is very different from previously reported results [5,6], in which apparent activation energy of glass transition was deduced from structural relaxation model to be approximately directly proportional to glass transition temperature. In order to confirm correlation between E_g and T_g in the Fe based amorphous alloy, the E_g as a function of T_g for the amorphous FCZBN and FBZN alloys is plotted on Fig. 5a and b, respectively. Obviously, the E_g is not linear with T_g in the both amorphous systems, and dependence of the E_g on T_g is different in the two systems. Therefore, the conclusion that E_g is directly proportional to T_g is not a common law for amorphous alloys, it may be related to compositions.

Eqs. (3) and (8) show that crystallization and glass transition temperatures are not independent each other for a given amorphous alloy, but has linear relationship. The crystallization temperature increases with increasing glass transitions temperature, and increasing rate is determined by the apparent activation energy of glass transition.

Many literatures have reported that supercooled liquid region of an amorphous alloy, $\Delta T_x = T_x - T_g$, can well characterize glass-forming ability of Fe based and other amorphous alloy systems [13,14]. The larger ΔT_x is, the stronger GFA. In order to confirm if this criterion is suitable to the amorphous FBZN and FCZBN alloys, reduced glass transition temperature T_{rg} ($=T_g/T_l$, T_l is a liquidus temperature), one of criteria widely used for characterization of GFA, was measured for each composition of the two systems. It was found that the ΔT_x has similar composition dependence to T_{rg}, indicating ΔT_x is good GFA criterion for the Fe based amorphous alloy used in

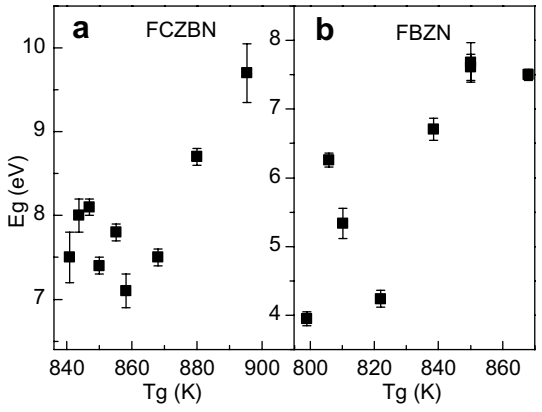

Fig. 5. Plots of E_g as a function of T_g for amorphous FCZBN (a) and FBZN (b).

the present experiment. From Eq. (8), the ΔT_x can be deduced:

$$\Delta T_x = \left(\frac{E_g}{3.527} - 1.309\right) T_g - \frac{E_g - 4.86}{0.0041} = E_g\left(\frac{T_g}{3.527} - 234.9\right) + 1185.37 - 1.309 T_g \quad (9)$$

Eq. (9) gives a correlation between GFA, E_g and T_g, indicating that the GFA is related to the apparent activation energy and glass transition temperature.

4. Conclusions

Correlations between E_g and T_g, T_x and GFA are studied for the amorphous FBZN and FCZBN systems. The T_g and T_x are not independence each other, but can be related by a formula, $T_x = \frac{E_g - 1.09}{3.527} T_g - \frac{E_g - 4.86}{0.0041}$, indicating that T_x increases with increasing T_g and the increasing rate is determined by E_g GFA can be characterized by supercooled liquid range ΔT_x in the present amorphous systems, and is related to E_g and T_g by a formula: $\Delta T_x = E_g(\frac{T_g}{3.527} - 234.9) + 1185.37 - 1.309 T_g$, indicating that the GFA of the Fe based metallic glasses can be characterized by E_g and T_g.

Acknowledgements

This work is supported by the National Natural Science Foundation (grant no. 50472003), Doctoral Foundation of Education Ministry of China (grant no. 20040183063) and Creative Fund of Jilin University.

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