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Correlations between the glass transition, crystallization, apparent activation energy and glass forming ability in Fe based amorphous alloys

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Abstract

The glass transition, crystallization, apparent activation energy and glass forming ability (GFA) of a metallic glass as well as their correlations were studied in amorphous alloys of composition $\text{Fe}_{91-x}\text{B}_x\text{Zr}_5\text{Nb}_4$ (FBZN, $5 \leq x \leq 30$ at.%) and $\text{Fe}_{61-x}\text{Co}_x\text{Zr}_5\text{B}_{30}\text{Nb}_4$ (FCZBN, $0 \leq x \leq 15$ at.%). It was found that the glass transition temperature T_g and the crystallization temperature T_x can be related by a formula, $T_x = \alpha T_g + \beta$, for each amorphous alloy in the two systems. α and β are constants for a given amorphous alloy, obtained by making measurements using non-isothermal scanning at various heating rates in a differential scanning calorimeter and then applying Lasocka's equation. The apparent activation energy of the glass transition E_g was observed to be directly proportional to α and have a correlation, $E_g = 3.527(T_x - \beta)/T_g + 1.09$, with T_x and T_g . The supercooled liquid region ΔT_x , which is used for characterization of the GFA, is related to E_g and T_g by the formula $\Delta T_x = (E_g/3.527 - 1.309)T_g + \beta$.

1. Introduction

Nonisothermal scanning in a differential scanning calorimeter (DSC) has been used widely in the investigation of the glass transition and crystallization kinetics of amorphous alloys [1–3]. Many important kinetic parameters, such as the glass transition temperature T_g , crystallization temperature T_x and apparent activation energy of the glass transition E_g , have been obtained by using the non-isothermal scanning technique together with the Kissinger method [4]. It is well known that T_g , T_x and E_g are important parameters for characterization of the thermal stability of amorphous alloys and they are considered to be related to the glass forming ability (GFA). So, it is necessary to study the dependence of T_g , T_x and E_g on the composition and also to search for correlations between the three parameters and the GFA in order to improve the thermal stability and GFA of amorphous alloys. Some efforts have been made to search for a

correlation between E_g and T_g [5, 6], or to characterize GFA using various parameters, which can be obtained by taking measurements using the non-isothermal scanning technique and then apply some suitable method or equation [7, 8]. However, a comprehensive understanding of the glass transition and the relationships between T_g , T_x , E_g and the GFA is still lacking. Therefore, the kinetics of the glass transition and the crystallization processes must be studied in more detail.

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 a distinct glass transition, a wide supercooled liquid region and high thermal stability and GFA. Extensive efforts have been made to improve T_g , T_x and the GFA by substitutions of elements. It was reported that T_g , T_x and the GFA showed considerable variation upon replacement of Fe by B and Co [11] in the Fe based metallic glass, resulting in many amorphous alloys with different T_g , T_x and GFA in the same system. The distinct glass transition, the wide supercooled liquid region and the plethora of T_g , T_x and GFA data in the metallic glass system allow us to measure the glass transition temperature accurately and to study the glass transition and crystallization kinetics systemically. The aim of this work is to investigate the effects of replacement of Fe by B or Co on the glass transition behaviour and crystallization kinetics in the Fe-Co-Zr-B-Nb amorphous system and to explore the correlations between T_g , T_x , E_g and the GFA.

2. Experimental procedures

Amorphous alloy ribbons of composition $\text{Fe}_{91-x}\text{B}_x\text{Zr}_5\text{Nb}_4$ (FBZN) with boron (B) content ranging from 5 to 30 at.% and $\text{Fe}_{61-x}\text{Co}_x\text{Zr}_5\text{B}_{30}\text{Nb}_4$ (FCZBN) with cobalt (Co) content between 0 and 15 at.% were prepared by the melt-spinning technique under an argon atmosphere. The as-spun ribbons were investigated by x-ray diffractometry (XRD) with Cu $K\alpha$ radiation and transmission electron microscopy, and found to contain no detectable crystallinity. The thermal stability and melting temperature of the ribbons were examined using a DSC and a differential temperature analyser (DTA) under a continuous argon flow at heating rates ϕ ranging from 2.5 to 40 K min^{-1} . T_g and T_x are defined as the temperature at the point of inflection of the glass transition endothermic curve and the peak temperature of the exothermic event in a DSC trace, respectively, in the present experiment.

3. Experimental results and discussions

Figures 1(a)–(f) show typical DSC curves for the amorphous FBZN alloys with B contents of 8, 14, 20, 22.5 and 30 at.% and an amorphous FCZBN alloy with the Co content of 7.5 at.%, scanned at a heating rate of 10 K min^{-1} , respectively. The crystallization products of all the amorphous alloys heated in the DSC were examined by XRD and 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 a two step crystallization model for B contents between 5 and 20 at.%, to a new metastable Fe-Zr-B-Nb cubic phase and α -Fe in a 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 a B content of 30 at.% [11]. T_g and T_x increase sharply when the crystallization model changes from the two step model to the eutectic one at a B content above 20 at.%. However, all amorphous FCZBN alloys crystallized to a metastable Fe-Co-Zr-B-Nb cubic phase in a polymorphous model, and T_g and T_x varied with the Co content and had maxima upon replacement of Fe by about 7.5 at.% Co. No glass

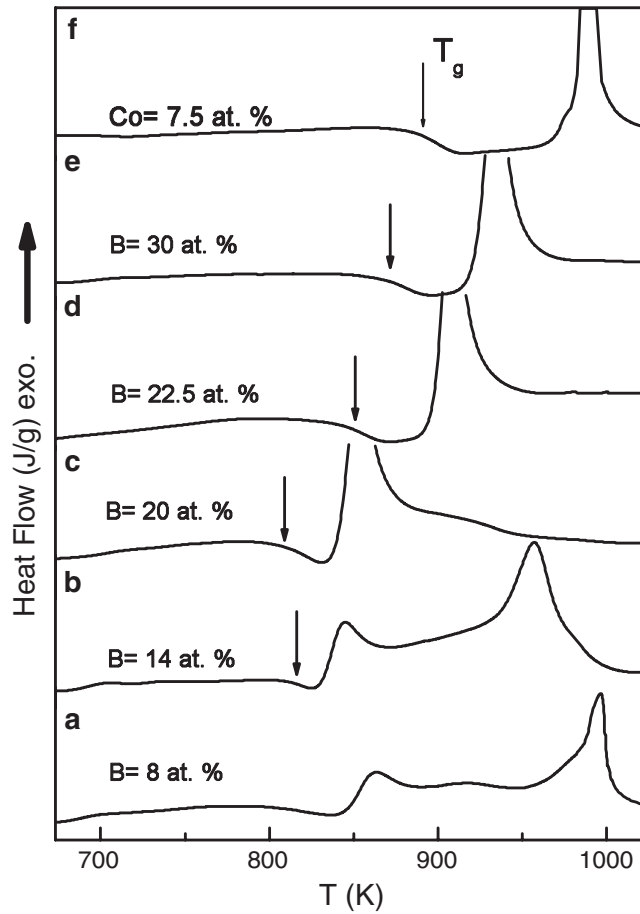


Figure 1. DSC curves for amorphous FBZN with B contents of 8 (a), 14 (b), 20 (c), 22.5 (d) and 30 at.% (e) and amorphous FCZBN with a Co content of 7.5 at.% (f) scanned at a heating rate of 10 K min^{-1} .

transition was observed in the amorphous FBZN alloys with B contents below 8 at.%, but one was observed in the amorphous FBZN alloys with B contents above 11 at.% and in all amorphous FCZBN alloys, indicating that the former is an unstable amorphous alloy ($T_g > T_x$) and the latter is a stable one ($T_g < T_x$).

T_g and T_x for the amorphous FBZN and FCZBN alloys were measured with heating rates (ϕ) of 2.5, 5, 10, 20 and 40 K min^{-1} . Figure 2 shows typical plots of T_g and T_x versus $\ln \phi$ for the amorphous FBZN alloy with 22.5 at.% B and the 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 Lasocka's relationship [12]:

$$T_g = A_g \ln \phi + B_g \quad (1)$$

and

$$T_x = A_x \ln \phi + B_x \quad (2)$$

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

$$T_x = \alpha T_g + \beta \quad (3)$$

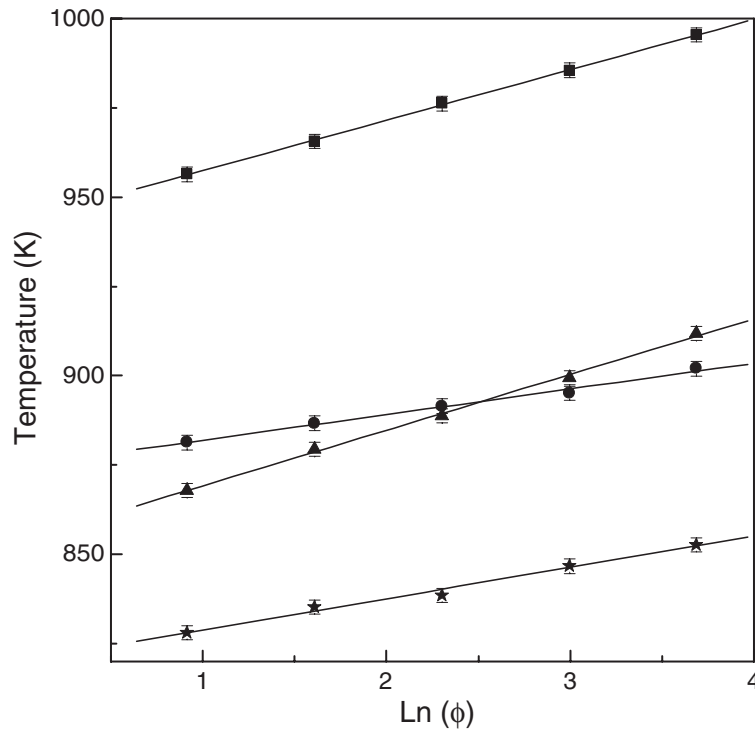


Figure 2. Typical plots of T_g and T_x versus $\ln \phi$ for amorphous FBZN with 22.5 at.% B (★: T_g ; ▲: T_x) and amorphous FCZBN with 7.5 at.% Co (●: T_g ; ■: T_x).

Table 1. α , β , and apparent activation energies of the glass transition (measured $E_g(\text{exp})$ and calculated $E_g(\text{calc})$) for each composition in the amorphous FBZN and FCZBN systems.

Fe _{91-x} B _x Zr ₅ Nb ₄						Fe _{61-x} Co _x Zr ₅ B ₃₀ Nb ₄					
B (at.%)	α	β	$E_g(\text{exp})$ (eV)	$\Delta E_g(\text{exp})$	$E_g(\text{calc})$ (eV)	Co (at.%)	α	β	$E_g(\text{exp})$ (eV)	$\Delta E_g(\text{exp})$	$E_g(\text{calc})$ (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

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

The apparent activation energies of the glass transition E_g for the amorphous FBZN and FCZBN alloys were calculated using Kissinger's equation [2]:

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

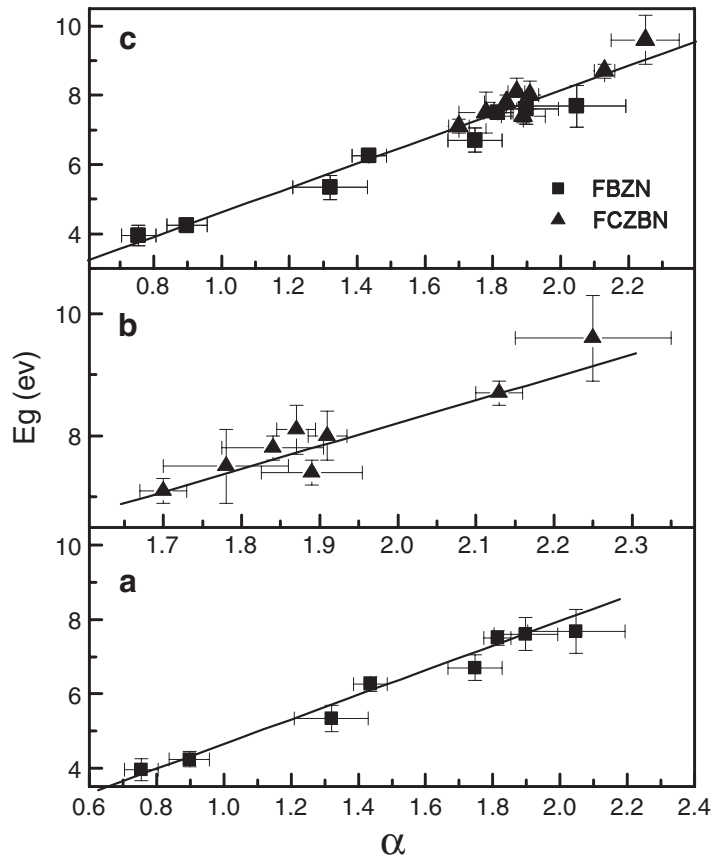


Figure 3. E_g versus α plots for amorphous FZBN (a), FCZBN (b) and both FZBN and FCZBN (c).

where R is the gas constant and K_0 is the frequency factor in the Arrhenius law for the 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 slope 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 values of E_g , in units of eV, denoted as $E_g(\text{exp})$, are listed in table 1 for the amorphous FBZN and FCZBN alloys. By using the $E_g(\text{exp})$ and α data, the E_g versus α plots for the amorphous FBZN, FCZBN and both FZBN and FCZBN alloys were obtained, and these are given in figures 3(a)–(c), respectively. All three plots show a good linear relationship between E_g and α . Fitting linearly relations to the data points in the three plots, E_g can be written as a function of α : $E_g = A\alpha + B$, where A and B are fitting parameters. A and B for the three plots are listed in table 2, together with their goodness-of-fit R . Obviously, the A (or B) values of the three plots are very close, so A (or B) for the three plots can be considered as the same within errors, approximately. Furthermore, on the basis of the errors of A and B as well as R in table 2, it is also concluded that there is a better linear relationship between the E_g and α in figure 3(c), though the data points belong to different compositions. The above facts imply that all the data points for amorphous FZBN and FCZBN can be related well by a single line, as shown in figure 3(c), and that the linear correlation between E_g and α is not related to the composition in the Fe based amorphous alloy. Therefore, E_g can be expressed as a linear function of α for both amorphous FBZN and

Table 2. Fitting parameters (A and B) and their errors, as well as the goodness-of-fit (R), for the E_g versus α plots for amorphous FZBN, FCZBN and both FZBN and FCZBN.

	A	A errors	B	B errors	R
FZBN	3.316	0.232	1.327	0.334	0.989
FCZBN	3.740	0.608	0.725	1.155	0.926
FZBN + FCZBN	3.527	0.166	1.09	0.28	0.986

FCZBN alloys:

$$E_g = 3.527\alpha + 1.09. \quad (5)$$

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

$$E_g = 3.527 \frac{T_x - \beta}{T_g} + 1.09 \quad (6)$$

or

$$T_x = \frac{E_g - 1.09}{3.527} T_g + \beta. \quad (7)$$

Using equation (6) as well as T_g and T_x measured in the present experiment, E_g was calculated for each composition in the amorphous FBZN and FCZBN systems; the results are listed in the column headed $E_g(\text{calc})$ of table 1. $E_g(\text{calc})$ is close to the value of $E_g(\text{exp})$ obtained by Kissinger's method; the difference between them is within experimental error. Equation (6) indicates that the apparent activation energy of the glass transition is directly proportional to the crystallization temperature, but inversely proportional to the glass transition temperature for the present Fe based amorphous alloys. This is very different from previously reported results [5, 6], in which the apparent activation energy of the glass transition was deduced from the structural relaxation model to be approximately directly proportional to the glass transition temperature. In order to confirm the correlation between E_g and T_g for Fe based amorphous alloy, E_g as a function of T_g is plotted in figures 4(a) and (b), respectively, for the amorphous FCZBN and FBZN alloys. Obviously, E_g does not vary linearly with T_g in either amorphous system and the dependences of E_g on T_g are different in the two systems. Therefore, the conclusion that E_g is directly proportional to T_g is not a law common to all amorphous alloys; it may be related to composition.

Equations (3) and (7) show that the crystallization and glass transition temperatures are not independent of each other for a given amorphous alloy, but have a linear relationship. The crystallization temperature increases with increasing glass transitions temperature and, more interestingly, the rate of increase α is directly proportional to the apparent activation energy of the glass transition.

Many studies in the literature have reported that the supercooled liquid region of an amorphous alloy, $\Delta T_x = T_x - T_g$, can characterize the GFA of Fe based and other amorphous alloy systems well [13, 14]. The larger ΔT_x is, the stronger the GFA. In order to confirm whether this criterion applies to amorphous FBZN and FCZBN alloys, the reduced glass transition temperature T_{rg} ($=T_g/T_1$, where T_1 is the liquidus temperature), one of criteria widely used for characterization of GFA, was measured for each composition of the two systems. It was found that ΔT_x has a similar composition dependence to T_{rg} , indicating that ΔT_x is a good criterion for characterization of GFA for the Fe based amorphous alloy used in the present experiment. From equation (7), ΔT_x can be deduced:

$$\Delta T_x = \left(\frac{E_g}{3.527} - 1.309 \right) T_g + \beta. \quad (8)$$

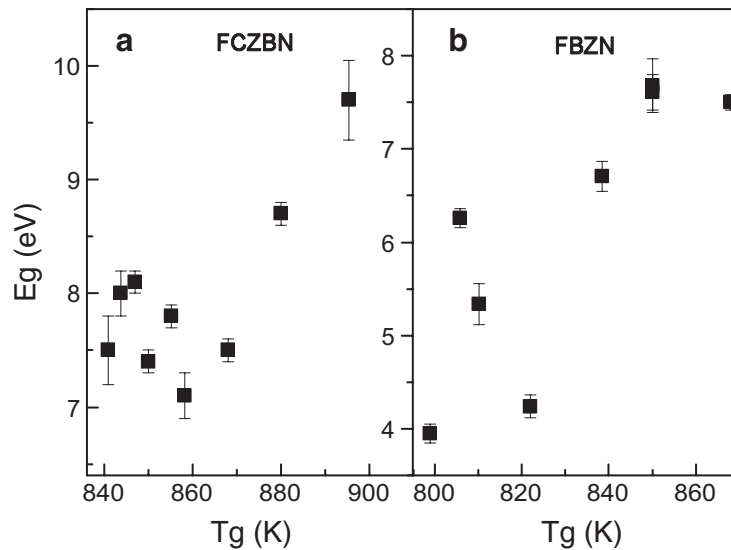


Figure 4. Plots of E_g as a function of T_g for amorphous FCZBN (a) and FBZN (b).

Equation (8) gives a correlation between the GFA, E_g and T_g , indicating that the GFA is determined by the apparent activation energy and the temperature of the glass transition. The GFA increases with increasing E_g and T_g .

4. Conclusions

Correlations between T_g , T_x , E_g and GFA are studied for the amorphous FBZN and FCZBN systems. T_g and T_x are not independent of each other, but can be related by a formula: $T_x = \alpha T_g + \beta$. α and β are constants for a given amorphous alloy and can be obtained by taking measurements using non-isothermal scanning at different heating rates in a DSC and then applying Lasocka's equation. The correlation between T_g , T_x and E_g can be expressed as $E_g = 3.527(T_x - \beta)/T_g + 1.09$. The GFA can be characterized by the supercooled liquid region ΔT_x in the present amorphous systems; this has the relationship $\Delta T_x = (E_g/3.527 - 1.309)T_g + \beta$ with E_g and T_g .

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