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Study of kinetics of glass transition of metallic glasses

Ashmi T. Patel · Arun Pratap

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Abstract In this study, the kinetics of glass transitions of $Ti_{50}Cu_{20}Ni_{30}$ and $Fe_{67}Co_{18}B_{14}Si_1$ metallic glasses are studied using thermal analysis technique, i.e., differential scanning calorimetry, by means of continuous heating of the sample at various heating rates. In the present study, based on the heating rate dependence of glass transition temperature (T_g), the activation energy (E) of the glass transition region is determined by two most frequently used approaches, i.e., Moynihan's method and Kissinger's equation. The fragility index, m, is also calculated using T_g, which is a measure of glass-forming ability of the given system. The result shows that the fragility index, m, of the given systems is <16. This indicates that the given systems are strong liquids with excellent glass-forming ability.

Keywords Glass transition · Metallic glass · Activation energy · Fragility index

Introduction

Metallic glass has a combination of amorphous structure and metallic bond. Metallic glasses have been regarded as potential structural and functional materials with unique disordered atomic configuration [1, 2]. They are used in sky equipment, cell phone casings, in USB Memory Stick, baseball bats, golf sticks, as well as in jewelry making.

Titanium-based alloys are lighter and less expensive, yet maintaining their toughness and ductility. Owing to the absence of crystallinity, they have high tensile strength, high hardness, and excellent wear properties. They exhibit good corrosion resistance because they lack crystal structure. They are much more ductile than conventional glasses and have high fatigue resistance. They have high electrical resistivity than crystalline alloys of same composition.

Fe-based metallic glasses have been recognized to possess two important properties, i.e., slender magnetization loop and high resistivity. Also, Fe-based metallic glasses have attracted much attention as they possess soft ferromagnetic properties which make them widely applicable in different devices, including transformers, sensors, magnetic tapes, and heads of recorder [3].

Understanding the glass transition kinetics of metallic alloys is of great importance to know its thermal stability, and finally to determine the useful range of operating temperatures for a specific technological application before the crystallization takes place [4]. In the present study, kinetics of glass transitions of $Ti_{50}Cu_{20}Ni_{30}$ and $Fe_{67}Co_{18}B_{14}Si_1$ metallic glasses are studied using differential scanning calorimetry (DSC) for four different heating rates and activation energies are calculated.

Experimental methods

The amorphous ribbons of $Ti_{50}Cu_{20}Ni_{30}$ alloy were prepared by a single roller melt-spinning technique in an argon atmosphere at the institute of materials research, Tohoku university, Sendai (Japan). The amorphicity of these ribbons were examined using X-ray diffractometry (XRD) and transmission electron microscopy (TEM).

Specimens of amorphous $Fe_{67}Co_{18}B_{14}Si_1$ (2605CO) ribbons were procured from Allied Corporation, USA prepared by single roller melt-spinning technique. The

A. T. Patel · A. Pratap (✉)
Condensed Matter Physics Laboratory, Applied Physics Department, Faculty of Technology & Engineering, The M. S. University of Baroda, Vadodara 390 001, India
e-mail: apratapmsu@yahoo.com

amorphous nature of ribbons was confirmed by XRD and TEM.

The DSC has become a convenient and widely used tool not only for studying the thermal stability of amorphous phase but also for investigating the kinetics of phase transformations. The samples of $Ti_{50}Cu_{20}Ni_{30}$ and $Fe_{67}Co_{18}B_{14}Si_1$ are heated in DSC (Shimadzu, DSC-50) at four different heating rates (2, 4, 8, and 16 °C min^{-1} for $Ti_{50}Cu_{20}Ni_{30}$ and 5, 10, 15, and 20 °C min^{-1} for $Fe_{67}Co_{18}B_{14}Si_1$) with temperatures ranging from room temperature to 560 °C. The DSC scans are recorded by Thermal Analyzer (TA-50, WSI, Shimadzu, Japan) interfaced to computer. The curves of heat flux versus temperature are shown in Figs. 1 and 2 for $Ti_{50}Cu_{20}Ni_{30}$ and $Fe_{67}Co_{18}B_{14}Si_1$ metallic systems, respectively.

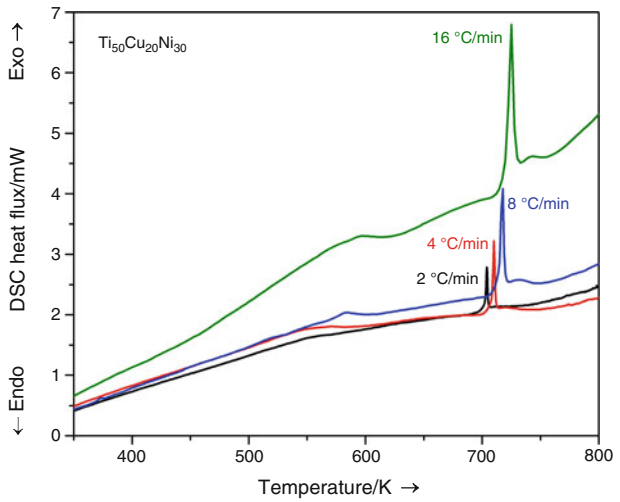

Fig. 1 DSC thermograms of the metallic glass $Ti_{50}Cu_{20}Ni_{30}$ at four different heating rates

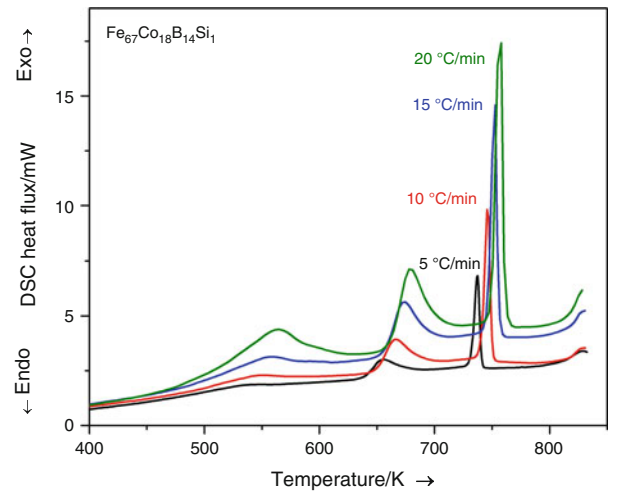

Fig. 2 DSC thermograms of the metallic glass $Fe_{67}Co_{18}B_{14}Si_1$ at four different heating rates

In the present study, the kinetics of glass transition for a metallic glass $Ti_{50}Cu_{20}Ni_{30}$, which is a shape memory alloy, and for $Fe_{67}Co_{18}B_{14}Si_1$, commercial name of which is 2605CO, are studied. Using glass transition temperature (T_g), the activation energy (E), and fragility index (m) are determined.

The DSC defines the glass transition as a change in the heat capacity as the amorphous matrix goes from the glassy state to the rubber state. This is a second-order endothermic transition (requires heat to go through the transition). Hence, in the DSC, the transition appears as a step transition.

Results and discussion

One of the most interesting problems in the area of glasses is the understanding of glass transition kinetics which can be studied in terms of glass transition temperature (T_g) and activation energy of thermal relaxation (E). The T_g of an amorphous material is the critical temperature at which the material changes its behavior from being "glassy" to being "rubbery". For the systems taken up in the present study, the values of glass transition temperature were found to increase with the increasing heating rates (Table 1). This may be attributed to the fact that when heating rate is high, the system does not get sufficient time for nucleation and crystallization. As heating rate increases, relaxation time, τ decreases. As relaxation time decreases, T_g increases because the product of relaxation time and glass transition temperature is constant.

$$\tau T_g = Const.$$

Hence, T_g shifts to higher values with increasing heating rates.

The activation energy, E, is determined using the following glass transition methods [4].

(1) Moynihan's method; and
(2) Kissinger's method

The evaluation of E using the theory of glass transition kinetics and structural relaxation as developed by

Table 1 Glass transition temperatures for $Ti_{50}Cu_{20}Ni_{30}$ and $Fe_{67}Co_{18}B_{14}Si_1$ metallic glasses

$Ti_{50}Cu_{20}Ni_{30}$		$Fe_{67}Co_{18}B_{14}Si_1$	
Heating rate, β/deg min^{-1}	Glass transition Temp., T_g/K	Heating rate, β/deg min^{-1}	Glass transition Temp., T_g/K
2	554	5	539
4	568	10	547
8	583	15	560
16	596	20	566.5

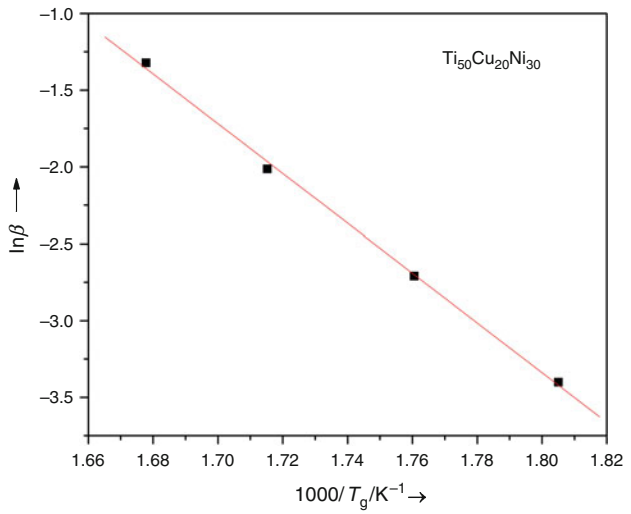

Fig. 3 A plot of ln β versus $1/T_g$ for Moynihan's method for $Ti_{50}Cu_{20}Ni_{30}$ metallic glass

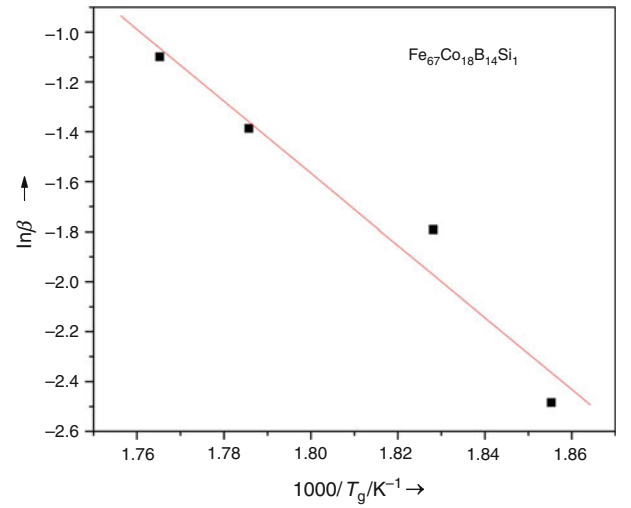

Fig. 4 A plot of ln β versus $1/T_g$ for Moynihan's method for $Fe_{67}Co_{18}B_{14}Si_1$ metallic glass

Moynihan and other workers [5–7], based on the heating rate dependence of glass transition temperature, is widely discussed in the literature [8]. The most frequently used approach to evaluate the activation energy of glass transition is the Moynihan's method [9].

$$\frac{d\ln\beta}{d(1/T_g)} = -\frac{E}{R} \quad (1)$$

where, β is the heating rate, and R is the gas constant. The plot of ln β versus 1,000/T_g gives straight line (Fig. 3 and Fig. 4), and the activation energies, E, of glass transition are calculated using the slope for both Ti- and Fe-based metallic glasses (Table 2).

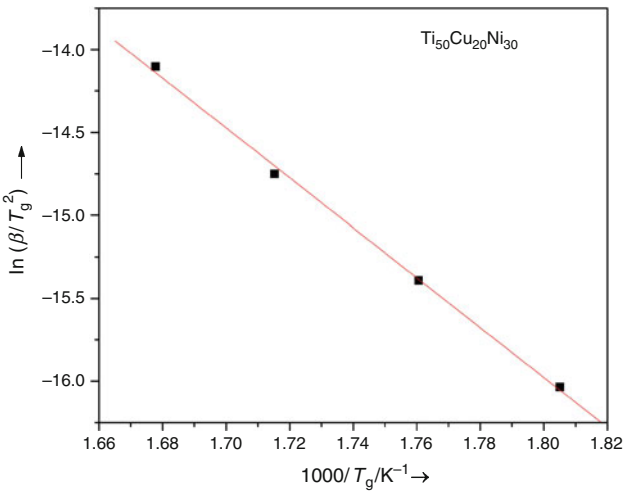

Fig. 5 A plot of ln (β/T_g^2) versus $1/T_g$ for Kissinger's equation for $Ti_{50}Cu_{20}Ni_{30}$ metallic glass

Table 2 Activation energy for $Ti_{50}Cu_{20}Ni_{30}$ and $Fe_{67}Co_{18}B_{14}Si_1$ metallic glass

$Ti_{50}Cu_{20}Ni_{30}$		$Fe_{67}Co_{18}B_{14}Si_1$	
Method	Activation energy, E/kJ mol^{-1}	Method	Activation energy, E/kJ mol^{-1}
Moynihan's method	134.74	Moynihan's method	120.01
Kissinger's equation	125.20	Kissinger's equation	110.82

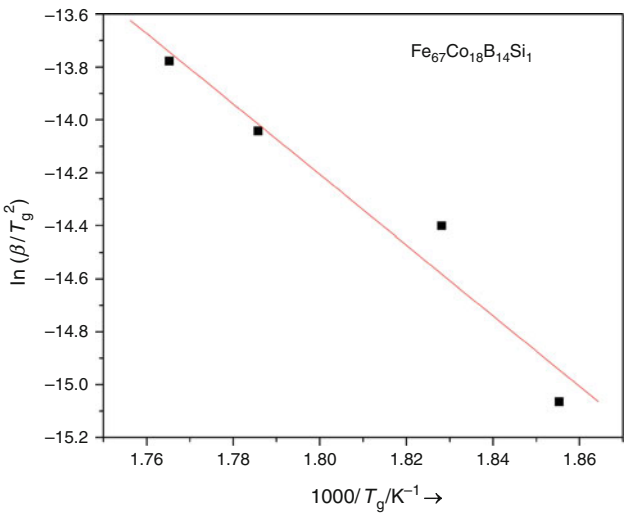

Fig. 6 A plot of ln (β/T_g^2) versus $1/T_g$ for Kissinger's equation for $Fe_{67}Co_{18}B_{14}Si_1$ metallic glass

The Kissinger's equation [10] is another approach which is extensively used to determine the glass transition activation energy [11, 12] and is given by

Table 3 Fragility Index, m, for $Ti_{50}Cu_{20}Ni_{30}$ metallic glass

Heating Rate, β/deg min^{-1}	Glass Transition Temp., T_g/K	Fragility Index, m by Moynihan's method	Fragility Index, m by Kissinger's equation
2	554	12.70	11.80
4	568	12.39	11.51
8	583	12.07	11.22
16	596	11.81	10.97

Table 4 Fragility Index, m, for $Fe_{67}Co_{18}B_{14}Si_1$ metallic glass

Heating Rate, β/deg min^{-1}	Glass Transition Temp., T_g/K	Fragility Index, m by Moynihan's method	Fragility Index, m by Kissinger's equation
5	539	11.63	10.74
10	547	11.46	10.58
15	560	11.49	10.34
20	566.5	11.06	10.22

$$\frac{d\ln\left(\beta/T_g^2\right)}{d\left(1/T_g\right)} = -\frac{E}{R} \tag{2}$$

The plot of ln (β/T_g^2) versus 1,000/T_g is linear (Figs. 5 and 6) in nature and obtains the value of E from the slope. The glass transition activation energies are calculated using Kissinger's equation for both the systems taken up in the present study (Table 2). The glass transition activation energy is the amount of energy which is absorbed by a group of atoms in the glassy region to jump from one metastable state to another [13]. Around the T_g, the structure undergoes relaxation, and rearrangement of the atoms starts.

Fragility is defined as the increasing rate of viscosity of a supercooled liquid at a glass transition temperature in the cooling process. Glass-forming liquids can be classified into strong liquids and fragile liquids, depending on their fragility [14–16]. The fragility of a given glass can be quantified by the fragility index, m, which is a measure of the rate at which the relaxation time decreases with increasing temperature around T_g and is given by [17]

$$m = \frac{E}{RT_g \ln 10} \tag{3}$$

where, E is the glass transition activation energy.

If the fragility index, m, is below 16, then the system falls in the category of "strong" glass former. On the contrary, for the other class termed as "fragile," this index lies between 16 and 200. The fragility indices, m, are calculated for both the metallic glasses using activation energies obtained by Moynihan's method and Kissinger's method and listed in Table 3 and Table 4. It is clear that these values of m for $Ti_{50}Cu_{20}Ni_{30}$ and $Fe_{67}Co_{18}B_{14}Si_1$ metallic alloys are below 16, and hence they fall in the category of strong glass-forming systems.

Conclusions

The Kinetics of the glass transition of two types of metallic glasses, namely, $Ti_{50}Cu_{20}Ni_{30}$ and $Fe_{67}Co_{18}B_{14}Si_1$ are studied using DSC with continuous heating of the sample at various heating rates. The glass transition activation energy is a good indicator of thermal stability. The glass transition activation energy is involved in the molecular motions and rearrangement of the atoms around the glass transition temperature.

The main advantage of using kinetics of glass transition is that one can determine activation energy at glass transition temperature which is lower than the crystallization peak temperature. By employing different models, the activation energy of the glass transition was determined. It is clear from the values of activation energy that despite different theoretical basis of the two methods, Moynihan and Kissinger's equations lead to similar values for the activation energies.

The Moynihan and Kissinger's equations are based on different theoretical methods. The activation energy determined by Moynihan's method depends substantially on the thermal history because of the dependence of relaxation time on temperature as well as structure. Hence, activation energy determined from this relation must be taken as apparent activation energy.

On the contrary, activation energy evaluated from Kissinger's method has less dependence on thermal history. This method is most commonly used in analyzing crystallization data in DSC. Although originally derived for the crystallization process, which is a phase transformation from amorphous phase to crystalline phase, it may be valid for glass-to-amorphous transformation process also. Kissinger's method was originally used for peak crystallization temperatures. When applied for glass transition process, the glass transition temperature, T_g, is obtained by the intersection of the onset and the endset of endothermic shift of base line.

The fragility Index of a given system is determined using the activation energy, E, and the glass transition temperature, T_g. The result shows that the fragility index, m. of the given systems is <16. This indicates that the given systems are strong liquids with excellent glass-forming ability.

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