

Study of glass transition of metallic glasses by temperature-modulated differential scanning calorimetry (MDSC)

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Received 15 September 1998; accepted 20 December 1999

Abstract

The glass transition behavior of several Zr- and Mg-based metallic glasses has been studied by temperature-modulated differential scanning calorimetry (MDSC). It is clearly demonstrated that the glass transition can be separated from crystallization for these glasses by MDSC. Some glass transitions that could not be observed by a conventional differential scanning calorimetry (DSC) have been detected. Furthermore, the complex change of the heat capacity of the samples during the glass transition and crystallization can now be determined for the first time in one single run. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Glass transition; MDSC; Metallic glass; DSC

1. Introduction

Glass transition and crystallization have been studied extensively by conventional differential scanning calorimetry (DSC). However, for many metallic glasses, the glass transitions are closely followed by crystallization and often the transitions are not observed by conventional DSC. Recently, an enhanced version of the DSC method, called temperature-modulated differential scanning calorimetry (MDSC), was introduced [1,2]. The benefits of the MDSC method have been documented in several recent publications [3–6] and a brief introduction of MDSC is given in our previous report [5]. The glass transition upon heating

is a reversing process in which heat is absorbed to accommodate the heat capacity increase during the transition, while crystallization is a non-reversing exothermic process which releases heats. One of advantages of the MDSC method is its ability to separate the reversing processes from the non-reversing process. This is accomplished by subtracting the reversing heat flow signal from the total heat flow signal to obtain the non-reversing heat flow signal. All heat flow associated with processes capable of following the temperature modulation is captured in the reversing heat flow signal. Any remaining heat flow attributable to processes not capable of following the temperature modulation is captured in the non-reversing heat flow signal. Several studies have been reported for glass transition and crystallization in polymeric materials and in chalcogenide glasses [4] by temperature-modulated DSC. Recently, we have

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reported the glass transition in a few metallic glasses by MDSC showing that the glass transitions can be separated from crystallization [6]. In this work, we present our latest results on a MDSC study of the glass transition for several Mg- and Zr-based metallic glasses.

2. Experimental

Alloy ingots of Zr-based alloys were first made by arc-melting under a Ti-gettered argon atmosphere, while the Mg-based alloys were induction-melted. The ingots were then melt-spun into ribbons by melt-spinning. The MDSC experiments were carried out on a temperature-modulated DSC (MDSC, TA Instruments, USA) using a refrigerated cooling system or an argon-gas cooling system with a nitrogen-gas DSC cell purge. The modulated DSC regime was utilized to measure the modulated heat flow under continuous heating rates of 1 or 5 K/min up to 880 K. The oscillation amplitudes and periods were determined so that at least four modulation cycles could be performed during the transition. Oscillation amplitudes of 0.6–1 K and a modulation period of 40 s were used with sample weights of 8–15 mg. The

experiments were repeated at least three times for each sample to eliminate other possible errors. All characteristic temperatures such as T_g and T_x are defined as the extrapolated onset temperature of the corresponding transition.

3. Results and discussion

Fig. 1 shows typical MDSC results for $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ metallic glass at an underlying heating rate of 5 K/min which illustrate total (HF), reversing (RHF) and non-reversing (NHF) heat flow curves. On the HF curve, the glass transition and crystallization are observed at temperature of 634 and 712 K, respectively, which are identical to the result obtained under a conventional DSC. On the RHF curve, there is a clear step change in the endotherm direction at an onset temperature of 645 K. In general, the glass transition only associated with a heat capacity change, and there is no heat involved. Since the reversing heat flow in MDSC is only related to the underlying heating rate and heat capacity, this step change clearly represents a glass transition in amorphous $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$. This glass transition temperature of 645 K on the reversing curve is about 11 K

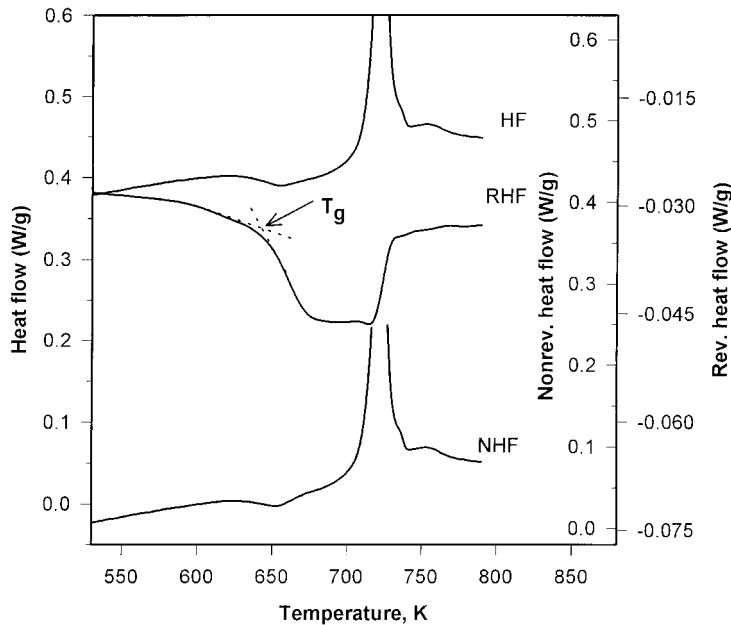


Fig. 1. MDSC results for $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ glass showing total (HF), reversing (RHF) and non-reversing (NHF) heat flow curves.

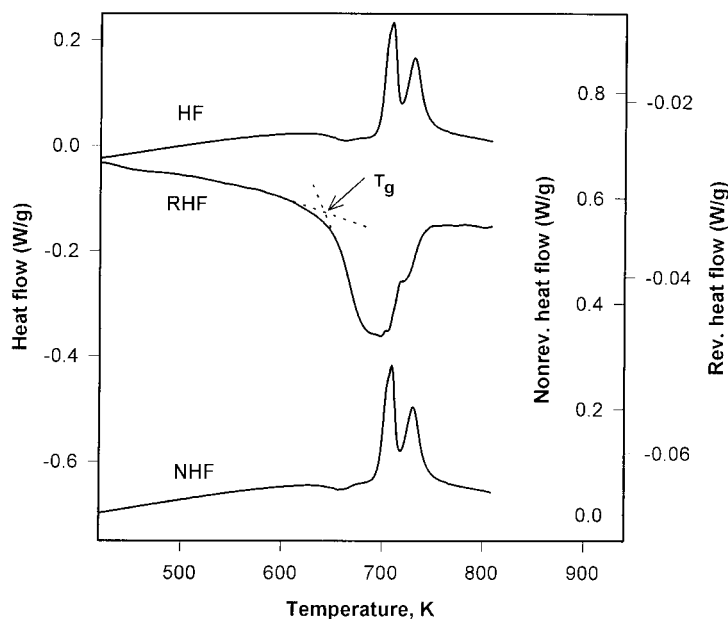


Fig. 2. MDSC results for $Zr_{65}Al_{7.5}Cu_{7.5}Ni_{20}$ glass showing total (HF), reversing (RHF) and non-reversing (NHF) heat flow curves.

higher than that obtained under a conventional DSC for the same alloy. The reversing heat flow curve turns upward sharply in a step change reaching the baseline at the temperature of about 727 K, which corresponds to the end of crystallization shown on the HF curve. This implies that the heat capacity changed back to that of the crystalline state. Furthermore, when there are two major crystallization transitions as shown in Fig. 2 for $Zr_{65}Al_{7.5}Cu_{7.5}Ni_{20}$ amorphous, the RHF curve turns up in two separated steps associated with the two ends of crystallization of the glass.

Fig. 3 shows the MDSC results for $Mg_{65}Zn_{35}$ metallic glass obtained at an underlying heating rate of 5 K/min. The total and non-reversing heat flow curves resemble closely that obtained by the conventional DSC. The onset crystallization temperatures at 379 and 470 K are also the same as those for crystallization from the conventional DSC for the same alloy. On the reversing curve, it is shown that there is a clear endothermic reaction associated with glass transition at an onset temperature of 359 K. Further, at higher temperature, there is a broad and shallow endothermic reaction with a possible glass transition at about 450 K on the same curve. These two glass transition temperatures are about 20 K below those of crystallization onset temperatures of 379 and 470 K, respectively,

shown on the total heat flow curve for $Mg_{65}Zn_{35}$ alloy. Fig. 4 shows the MDSC results for $Mg_{77}Nd_5Ni_{18}$ metallic glass obtained with an underlying heating rate of 1 K/min. On the HF curve, the identification of glass transition is not very obvious. However, the glass

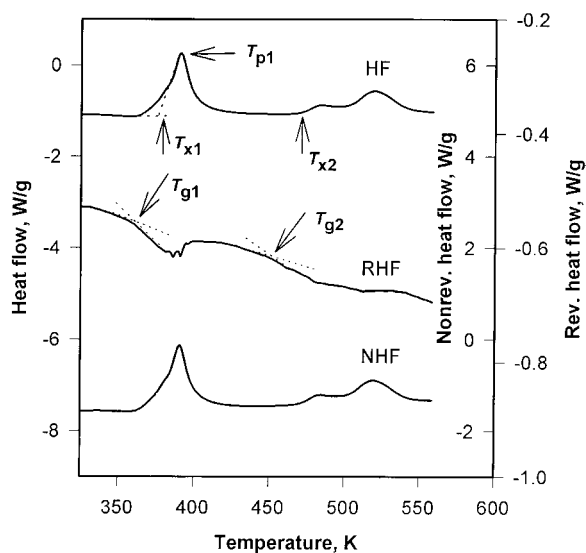


Fig. 3. MDSC results for $Mg_{65}Zn_{35}$ glass showing total (HF), reversing (RHF) and non-reversing (NHF) heat flow curves.

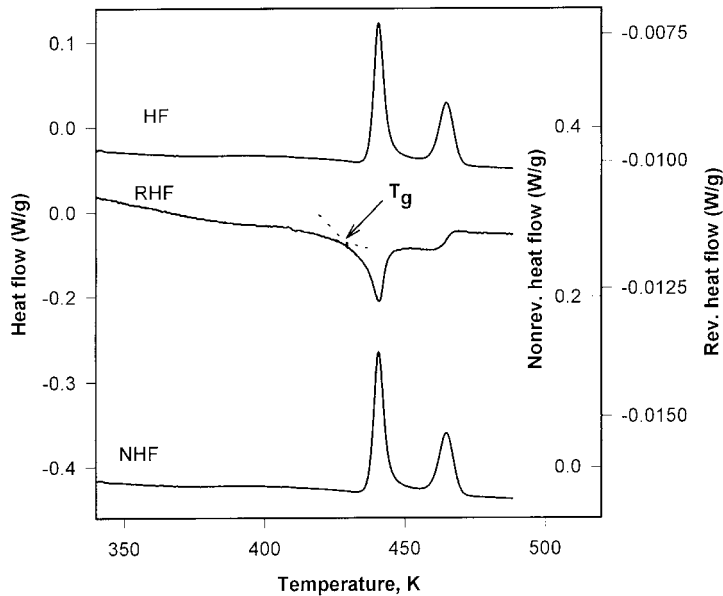


Fig. 4. MDSC results for $\text{Mg}_{77}\text{Nd}_5\text{Ni}_{18}$ glass showing total (HF), reversing (RHF) and non-reversing (NHF) heat flow curves.

transition at round 429 K is clearly observed on RHF curve, which is ahead of crystallization. Furthermore, corresponding to the end of first crystallization, the RHF curve turned upward in two clear steps corresponding to two crystallization transitions. Table 1 summarizes the temperatures for glass transition and crystallization.

Similar downward turn in the endotherm direction on the RHF curve, representing the glass transition has also been reported for polymers [1,2]. However, our present results of RHF curves turning back to the baseline after crystallization appear to be different from the results of crystallization for polymers studied by MDSC [1,2]. This is mainly attributed to the incomplete development of crystallinity in polymers. As we know, there is such a large non-reversing heat

flow associated with crystal perfection processes, this effect is lost in the reversing signal baseline. Nevertheless, this does not take away from the magnitude of the heat capacity recovery shown here since the heat capacity of the crystal-solid and the glass is more comparable.

Since the RHF is associated with underline heating rate and heat capacity of the sample, it is obvious that the upward turns in the RHF curve when the crystallization is finishing in our samples are related to the heat capacity changes. The heat capacity of the crystallized sample is always smaller than that of undercooled liquid [7]. Furthermore, the two turns of RHF in some of our samples show clearly that when the material is partially crystallized, the heat capacity changes to that of the mixture of crystalline and

Table 1

Characteristic temperatures (K) obtained from an MDSC for $\text{Zr}_{65}\text{Al}_{7.5}\text{Cu}_{17.5}\text{Ni}_{10}$, $\text{Zr}_{65}\text{Al}_{7.5}\text{Cu}_{7.5}\text{Ni}_{20}$, $\text{Mg}_{65}\text{Zn}_{35}$ and $\text{Mg}_{77}\text{Nd}_5\text{Ni}_{18}$ glasses

Alloy	RHF (K)		HF (K)		NHF (K)		T_m (K)	T_{rg} (K)
	T_{g1}	T_{g2}	T_{x1}	T_{x2}	T_{x1}	T_{x2}		
$\text{Zr}_{65}\text{Al}_{7.5}\text{Cu}_{17.5}\text{Ni}_{10}$	645	–	712	–	712	–	1072	0.60
$\text{Zr}_{65}\text{Al}_{7.5}\text{Cu}_{7.5}\text{Ni}_{20}$	647	–	697	–	696	–	1111	0.58
$\text{Mg}_{65}\text{Zn}_{35}$	359	450	379	470	378	470	616	0.58
$\text{Mg}_{77}\text{Nd}_5\text{Ni}_{18}$	429	–	437	460	437	451	717	0.60

amorphous. The ability of MDSC to measure the heat capacity of the fully amorphous or partially amorphous samples in one single run can give us more detailed knowledge on the glass transition and crystallization. Detailed study of heat capacity of metallic glasses in the region of the glass transition and crystallization upon heating or cooling is under investigation.

4. Conclusion

Glass transitions in Zr- and Mg-based metallic glasses have been observed by MDSC. Our results show that glass transition hidden under crystallization in some of the glasses can be observed now. Furthermore, the complex change of the heat capacity of the samples during the glass transition and crystallization

can be now determined for the first time in one single run.

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