Separation of glass transition and crystallization in metallic glasses by temperature-modulated differential scanning calorimetry

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Abstract
The glass transition behaviour of the four metallic glasses La$_{55}$Al$_{25}$Ni$_{30}$, Zn$_{65}$Mg$_{35}$, and Nd$_{60}$Fe$_{30}$Al$_{10}$ and Zr$_{30}$Y$_{30}$Al$_{15}$Ni$_{25}$ has been studied by temperature-modulated differential scanning calorimetry (MDSC). It is clearly demonstrated that the glass transition can be separated from crystallization by MDSC. Two glass transitions have been observed for Zn$_{65}$Mg$_{35}$, Nd$_{60}$Fe$_{30}$Al$_{10}$ and Zr$_{30}$Y$_{30}$Al$_{15}$Ni$_{25}$. Owing to the clearer observation of the glass transition, calculation of the reduced glass temperatures $T_{rg}$ (glass transition temperature divided by the melting point) can now be made with greater confidence.

§ 1. Introduction
The 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 (Reading 1993, Reading et al. 1993). The benefits of the MDSC method have been documented in several recent publications (Gill et al. 1993, Boller et al. 1995, Wagner and Kasap 1997) and a brief introduction to MDSC is given in one of our previous publications (Li et al. 1998). The glass transition upon heating is a reversible process in which heat is absorbed to accommodate the heat capacity increase during the transition, while crystallization is a non-reversible exothermic process which releases heat. One of the advantages of the MDSC method is its ability to separate these reversible and non-reversible processes by measuring the reverse heat flow and non-reverse heat flow in the total heat flow during a phase transition. Several studies have been reported for glass transitions and crystallization.
in polymeric materials and chalcogenide glasses (Boller et al. 1995, Wagner and Kasap 1997) by MDSC. To date, however, experimental results are yet to be reported for the glass transition in metallic glasses by MDSC. In this work, we present the first MDSC study on the glass transition for the four metallic glasses La$_{55}$Al$_{25}$Ni$_{20}$, Zn$_{65}$Mg$_{35}$, Nd$_{60}$Fe$_{30}$Al$_{10}$ and Zr$_{30}$Y$_{30}$Al$_{15}$Ni$_{25}$.

§ 2. EXPERIMENTAL DETAILS

Alloy ingots of La$_{55}$Al$_{25}$Ni$_{20}$, Nd$_{60}$Fe$_{30}$Al$_{10}$ and Zr$_{30}$Y$_{30}$Al$_{15}$Ni$_{25}$ were first made by arc melting 99.9% pure La, Y and Zr, 99.99% pure Ni and Fe, and 99.999% pure Al under a Ti-gettered Ar atmosphere, while the Mg-Zn alloy was obtained by induction melting of 99.99% pure Zn and Mg. The ingots were then melt spun into ribbons using a single-roller melt spinner under Ar. The MDSC experiments were carried out on a MDSC instrument (TA Instruments Inc. USA) using a refrigerated cooling system or an Ar-gas cooling system with a N$_2$-gas DSC cell purge. The MDSC regime was utilized to measure the modulated heat flow under continuous heating rates of 1 or 5 K min$^{-1}$ up to 880 K. In order to obtain accurate and reproducible results, three experimental parameters need to be controlled in MDSC measurements, namely the underlying heating rate, the temperature oscillation amplitude and the oscillation period. The oscillation amplitudes and periods were determined so that at least four modulation cycles could be performed during the transition. Oscillation amplitudes between 0.1 and 0.2 K and a modulation period of 60 s were used with sample masses of 8–15 mg. The experiments were repeated at least three times for each sample to eliminate other possible errors.

§ 3. RESULTS AND DISCUSSION

Figure 1 shows the results of conventional DSC for the four metallic glasses under a heating rate of 1 or 5 K min$^{-1}$. The results show that there is a clear glass transition at about 469 K and crystallization at 519 K for a La$_{55}$Al$_{25}$Ni$_{20}$ amorphous ribbon, while no glass transitions were observed for Mg$_{65}$Zn$_{35}$, Nd$_{60}$Fe$_{30}$Al$_{10}$ and Zr$_{30}$Y$_{30}$Al$_{15}$Ni$_{25}$ glasses although crystallization occurred at various temperatures. Table 1 summarizes the characteristic temperatures (the glass transition temperatures $T_g$, the crystallization onset temperatures $T_x$ and the peak temperatures $T_p$) for all four glasses.

Figure 2(a) shows typical MDSC results for La$_{55}$Al$_{25}$Ni$_{20}$ glass at an underlying heating rate of 1 K min$^{-1}$ which illustrate the total, reversing and non-reversing heat flows. There are exothermic reactions at onset temperatures of 450 and 518 K on the total heat flow curve and at onset temperatures of 450 and 519 K on the non-reversing heat flow curve. The first exothermic reaction could be due to glass relaxation, which is still under investigation. The second exothermic reaction is obviously due to crystallization, which is identical with the result obtained under conventional DSC with crystallization at the same temperature of 519 K. There is a clear step change in the endotherm direction at an onset temperature of 481 K on the reversing heat flow curve. The glass transition is at best a second-order transition, only associated with a heat capacity change. Since the reversing heat flow in MDSC is only related to the heating rate and heat capacity, this step change clearly represents a glass transition in amorphous La$_{55}$Al$_{25}$Ni$_{20}$. This glass transition temperature of 481 K on the reversing curve is about 12 K higher than that obtained under conventional DSC for the same alloy. At the end of crystallization, the reversing heat flow curve turns upwards in a step change reaching the upper-scale limit, indicating that the heat capacity has
changed back to that of the crystalline state. The heat capacity of metallic glass materials using MDSC is under investigation. Figure 2(b) shows the MDSC results for Mg$_{65}$Zn$_{35}$ metallic glass obtained at an underlying heating rate of 5 K min$^{-1}$. The total and non-reversing heat flow curves closely resemble those obtained by conventional DSC. The onset crystallization temperatures of 379 and 470 K are also identical with those obtained by conventional DSC for the same alloy. On the reversing heat flow curve, it is evident that there is a clear step change in the endotherm direction associated with a glass transition at an onset temperature of 359 K, similar to that on the reversing heat flow curve in figure 2(a). At a higher temperature, there is a broad and shallow step change in the same direction 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 the crystallization onset temperatures of 379 K and 470 K respectively, as shown on the total heat flow curves for Mg$_{65}$Zn$_{35}$ alloy.

Table 1. Characteristic temperatures obtained from conventional DSC for four metallic glasses.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$T_g$</th>
<th>$T_{x1}$</th>
<th>$T_{x2}$</th>
<th>$T_{x3}$</th>
<th>$T_{p1}$</th>
<th>$T_{p2}$</th>
<th>$T_{p3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{55}$Al$</em>{25}$Ni$_{20}$</td>
<td>469</td>
<td>519</td>
<td>470</td>
<td>552</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg$<em>{65}$Zn$</em>{35}$</td>
<td></td>
<td>379</td>
<td>470</td>
<td>389</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd$<em>{60}$Fe$</em>{30}$Al$_{10}$</td>
<td>—</td>
<td>421</td>
<td>608</td>
<td>722</td>
<td>439</td>
<td>630</td>
<td>736</td>
</tr>
<tr>
<td>Zr$<em>{30}$Y$</em>{30}$Al$<em>{15}$Ni$</em>{25}$</td>
<td>—</td>
<td>646</td>
<td>801</td>
<td>663</td>
<td>805</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 2. MDSC results for (a) La$_{55}$Al$_{25}$Ni$_{20}$, (b) Mg$_{65}$Zn$_{35}$, (c) Nd$_{60}$Fe$_{30}$Al$_{10}$ and (d) Zr$_{30}$Y$_{30}$Al$_{15}$Ni$_{25}$ amorphous glasses showing total heat flows (curves HF), reversing heat flows (curves RHF) and non-reversing heat flows (curves NHF).
Figure 2. (Continued)
Figure 2(c) shows the MDSC results for Nd$_{60}$Fe$_{30}$Al$_{10}$ metallic glass obtained with an underlying heating rate of 5 K min$^{-1}$. There is weak crystallization with an onset temperature of about 596 K and strong crystallization with an onset temperature of about 722 K on the total and non-reversing heat flow curves respectively. There may be a third weak crystallization at the low temperature of 420 K. The MDSC results in figure 2(c) also show clearly that there is a step change in the endothermic direction with an onset temperature of 591 K associated with a glass transition on the reversing heat flow curve. The glass transition temperature is about 5 K below the corresponding crystallization temperature of 596 K on the total heat flow curve. There could be another step change which is very weak at a low temperature of around 408 K, presumably also associated with a glass transition. This weak glass transition could be related to the corresponding weak crystallization at 420 K. It is noted that clearly there is no further step change on the reversing heat flow curve near $T_{x3}$ ($=722$ K) corresponding to the main crystallization reaction, indicating that no glass transition occurs here.

Finally figure 2(d) shows the MDSC results for Zr$_{30}$Y$_{30}$Al$_{15}$Ni$_{25}$ glass obtained at an underlying heating rate of 5 K min$^{-1}$. There are three exotherms, two of which have onset temperatures of 644 and 792 K on the total heat flow curve. There are two step changes in the endothermic direction with onset temperatures of 629 and 723 K associated with two glass transitions. These two glass transition temperatures are also lower than those of the corresponding crystallizations on the total and non-reversing heat flow curves respectively. It is also noted that there is no further step change on the reversing heat flow curve near the temperature corresponding to the main crystallization reaction at $T_{x2}$ ($=792$ K), indicating that no glass transition occurs at this temperature. A summary of the characteristic temperatures for the glass transitions and the crystallizations obtained by MDSC for the four alloys is given in table 2.

The separation of glass transition from relaxation and crystallization in polymeric materials, which may occur simultaneously, has been reported by Gill et al. (1993). For example, for a bilayer film containing polycarbonate (PC) and amorphous poly(ethylene terephthalate) (PET), the total heat flow curve exhibits a transition between 403 K and 423 K, which is difficult to interpret. However, the MDSC results showed unambiguously on the reversing and non-reversing curves that the event represents the overlap of the PC glass transition and the PET crystallization exotherm respectively (Gill et al. 1993). Our present results clearly demonstrate that the MDSC can also be used to separate the glass transition from transitions such as crystallization and relaxation, a separation usually unobtainable by conventional DSC for metallic glasses. Although La$_{55}$Al$_{25}$Ni$_{20}$ glass shows a clear separation of glass transition and crystallization by conventional DSC, the glass transition temperature obtained in MDSC is higher than that obtained by DSC. Our present MDSC results clearly show that the discrepancy arises because there is an overlapping of relaxation and glass transition on the total heat flow. The relaxation process in this metallic glass is under further investigation by MDSC. For Mg$_{65}$Zn$_{35}$ and Nd$_{60}$Fe$_{30}$Al$_{10}$ glasses, the glass transition was not observed using conventional DSC (figure 1). From the MDSC results (figures 2(b) and (c), it can be seen clearly that the glass transition in these two metallic glasses occurred first and was closely followed by the crystallization and is thus hidden under the crystallization in the total heat flow curve. This is consistent with the fact that the crystallization usually follows closely on the glass transition for most metallic glasses (Cahn
### Table 2. Characteristic temperatures for four metallic glasses obtained by MDSC from the reversing, total and non-reversing heat flow curves

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Reversing heat flow</th>
<th>Total heat flow</th>
<th>Non-reversing heat flow</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{gl}$ (K)</td>
<td>$T_{g2}$ (K)</td>
<td>$T_{x1}$ (K)</td>
</tr>
<tr>
<td>Nd$<em>{60}$Fe$</em>{30}$Al$_{10}$</td>
<td>481</td>
<td>—</td>
<td>518</td>
</tr>
<tr>
<td>Mg$<em>{65}$Zn$</em>{35}$</td>
<td>359</td>
<td>450</td>
<td>379</td>
</tr>
<tr>
<td>Nd$<em>{60}$Fe$</em>{30}$Al$_{10}$</td>
<td>408</td>
<td>591</td>
<td>420</td>
</tr>
<tr>
<td>Zr$<em>{30}$Y$</em>{30}$Al$<em>{15}$Ni$</em>{55}$</td>
<td>629</td>
<td>723</td>
<td>644</td>
</tr>
</tbody>
</table>
and Haasen 1983). Our MDSC results also revealed that there could be more than one glass transition in these glasses, which has not been reported before for these alloys. Our observation of two glass transitions in amorphous Zr$_{30}$Y$_{30}$Al$_{15}$Ni$_{25}$ has confirmed the previous report of two glass transitions in the same alloy (Inoue et al. 1994). It is also revealed that the glass transition starts much earlier and may not be associated with the main crystallization process for some metallic glasses (figures 2(c) and (d)).

The ratio of the glass transition temperature to the melting point is termed the reduced glass transition temperature $T_{rg}$. It is generally regarded as an indicator for glass-forming ability; the larger $T_{rg}$, the better is the glass-forming ability (Li et al. 1997). However, previous calculations of $T_{rg}$ for those metallic glasses with no obvious glass transition were carried out using the ratio of crystallization temperature to the melting point, assuming that the glass transition occurred simultaneously with crystallization. With clear separation of glass transition and crystallization, the reduced glass transition temperature $T_{rg}$ can now be calculated more precisely and with more confidence. The values of $T_{rg}$ for the four glasses in the present study are given in table 2. We would like to point out that the value of 0.68 for Nd$_{60}$Fe$_{30}$Al$_{10}$ glass is inconsistent with the previous report of 0.89 for $T_x/T_m$ for the same alloy (Inoue et al. 1997). This certainly shows that the MDSC is helpful in the investigation of glass transition and other related transitions in metallic glasses.

§ 4. CONCLUSIONS

The separation of glass transition and crystallization in four metallic glasses has been successfully achieved using MDSC. More than two glass transitions were observed in Zn$_{65}$Mg$_{35}$, Nd$_{60}$Fe$_{30}$Al$_{10}$ and Zr$_{30}$Y$_{30}$Al$_{15}$Ni$_{25}$ metallic glasses. Even for the La$_{55}$Al$_{25}$Ni$_{20}$ glass with a clear separation of glass transition and crystallization, MDSC can be used to separate the glass transition from relaxation and leads to a clearer observation of the glass transition.

REFERENCES


"Glass transition and crystallization in metallic glass"