Structural relaxation in metallic glasses

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Abstract

Structural relaxation in several transition metal based metallic glasses has been studied using differential scanning calorimetry (DSC), X-ray diffraction (XRD), electrical resistivity, acoustic emission and Mossbauer spectroscopy techniques. Annealing of metallic glass below the crystallization temperature gives rise to discontinuous changes in electrical resistance. These changes are accompanied by acoustic emissions. The latter process provides an indication for the viscous flow in the matrix. In diverse alloy compositions, it has been observed that changes in electrical resistivity which begin instantly with the onset on isothermal annealing do not follow diffusion kinetics. Mossbauer experiments also show that neither long range diffusion nor the formation of a new phase occurs as a result of annealing. It is concluded that viscous flow is the mechanism for structural relaxation induced by isothermal annealing and short range ordering during this process is also a consequence of the viscous flow process. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Structural relaxation; Metallic glasses; Acoustic emission; Resistivity; Mössbauer spectroscopy

1. Introduction

Metastability is built into metallic glass systems through the method of preparation. As a result of the supercooling necessary for glass formation, a metallic glass is metastable with respect to the ideal glassy state below the glass formation temperature ($T_g$). During isothermal annealing below $T_g$, the glass tries to reach the ideal glassy state characteristic of the annealing temperature. This process is designated as structural relaxation [1,2]. Further annealing leads to crystallization of the glass. This latter process represents the tendency of the material to acquire its equilibrium crystalline structure. In the present paper, the mechanism of structural relaxation under isothermal annealing condition has been studied using electrical resistivity, acoustic emission measurements and Mossbauer spectroscopy. The studies have been carried out in the glassy phase below the crystallization temperature.

2. Experimental procedure

Differential scanning calorimetry (DSC) and X-ray diffraction (XRD) were employed to determine the crystallization temperature and to ascertain the amorphous structure of the matrix before and after annealing. The composition of metallic glasses used in the present experiments are given in Table 1. In metglass MG1, the electrical resistance measurements were performed manually, whereas for MG2, a microprocessor controlled experimental arrangement was employed. Isothermal annealing was carried out in a furnace maintained at preset temperature, the temperature control being within ±2 K. In both cases, four point probe measurements were carried out. The accuracy of the measured resistance is better than ±1 mΩ. The manual experiments were performed using a Kelvin double bridge having a sensitivity of $2 \times 10^{-8}$ Ω.

A microprocessor controlled two-channel acoustic emission set-up was used for monitoring and recording the acoustic emission generated with the onset of isothermal annealing. As stated earlier, annealing temperature was maintained below the crystallization temperature. Acoustic emission generated within the specimen were recorded with the help of two PZT sensors corresponding to the frequencies of 175 and 375 MHz. Each set of acoustic emission data was recorded for a period of 3840 s. Spurious signals were cut out with suitable band pass filters. Acoustic emission under load was recorded in a specially designed set-up. Microprocessor attached to the acoustic emission set-up was programmed to provide information regarding the
Table 1
Composition of metallic glasses

<table>
<thead>
<tr>
<th>No.</th>
<th>Code</th>
<th>Atomic composition</th>
<th>Experiments conducted(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MG1</td>
<td>Ni(<em>{45})Fe(</em>{20})Cr(<em>{10})Mo(</em>{4})B(_{16})</td>
<td>ER, AE, AE(L), MS</td>
</tr>
<tr>
<td>2</td>
<td>MG2</td>
<td>Fe(<em>{50})Ni(</em>{38})Mo(<em>{4})B(</em>{18})</td>
<td>ER, AE, AE(L)</td>
</tr>
<tr>
<td>3</td>
<td>MG3</td>
<td>Co(<em>{68})Mn(</em>{12})B(_{20})</td>
<td>AE</td>
</tr>
<tr>
<td>4</td>
<td>MG4</td>
<td>Fe(<em>{80})Si(</em>{6})B(<em>{13})C(</em>{1})</td>
<td>AE</td>
</tr>
<tr>
<td>5</td>
<td>MG5</td>
<td>Fe(<em>{40})Ni(</em>{40})B(<em>{13})Si(</em>{7})</td>
<td>AE</td>
</tr>
</tbody>
</table>

\(^a\) ER: electrical resistivity; AE: acoustic emission; AE(L): acoustic emission under load; MS: Mossbauer spectroscopy.

characteristic features of the signals. The important characteristic features of acoustic signals, ring down count (RDC), event duration (ED), event energy (EE) and the peak amplitude (PA) are shown in Fig. 1. An acoustic signal emitted by a solid is composite entity consisting of a number of individual waves. The number of such waves associated with each emission is RDC and the period over which the signal is given out is called ED. The amplitude of the most energetic component wave is a designated as PA and the energy associated with acoustic emission is called EE. Taken together, these parameters completely characterize the acoustic event and also constitute a signature of the process responsible for their emission.

\(^{57}\)Fe Mossbauer spectra were recorded at room temperature using a \(^{57}\)Co(Rh) source coupled to a constant acceleration drive and a conventional multichannel analyser. The spectra were analyzed to obtain the distribution of quadrupole splitting parameter (QS), which gives a measure of the short-range-order around the probe atom (Fe). The crystallization or a discrete emergence of a new phase can also be clearly seen through this method.

3. Results

Fig. 2(a) and (b) shows the variation of electrical resistance of two different metglass compositions. The results shown in Fig. 2(a) were manually recorded, whereas those in Fig. 2(b) were obtained using the microprocessor controlled set-up. In either case, the resistivity changes start almost instantaneously with the beginning of annealing and

![Fig. 1. A typical acoustic emission pattern indicating characteristic signal parameters: RDC, ED, PA.](image1)

![Fig. 2. (a) The variation of electrical resistance with time during isothermal annealing for metglass MG1 at various temperatures. Stepwise variation with time is observed at all temperatures. (b) Variation in electrical resistance with time for a Fe–Ni based metallic glass (MG2) during isothermal annealing.](image2)
the changes take place in a stepwise fashion. Typical acoustic emission results at two different temperatures are depicted in Fig. 3(a) and (b); the rate of emission being greater at the higher temperature. Application of load enhances the rate of acoustic emission and Fig. 3(c) shows one such result. The correspondence between the nature of variation in the electrical resistivity and acoustic emission is remarkable. In either case, the process begins with the start of annealing and occurs in a stepwise or discontinuous manner. Mossbauer spectrum of MG1 specimen annealed for 150 min at different temperature are shown in Fig. 4. The analysis of Mossbauer spectrum was performed using Fourier deconvolution method [3]. The results of this analysis are given in Fig. 5.

4. Discussion

4.1. Viscous flow vs. diffusion

An underlying assumption made by several authors [4–7] is that the crystallization kinetics of metallic glasses follows
diffusion kinetics, i.e., the process is mediated by random atomic jumps. The chief characteristics of a diffusion controlled process are that they exhibit an incubation time, take place in a continuous manner and the reaction kinetics follow either a sigmoidal behaviour or a C-type of curve [8]. It is obvious from Fig. 2 that the variation of electrical resistance during isothermal annealing does not conform to these characteristics. According to Christian [9], structural transformation in solids can be classified either as thermally activated diffusion process or movement of a glissile interface. The examples of latter process are grain boundary sliding, plastic deformation through slip and the transformation of austenite to martensite. These may be collectively designated as flow processes. The most important characteristics of the flow process is that they involve cooperative movement of a large number of atoms of the matrix, in contrast to the random movement of individual atoms in diffusion. Still another important characteristic of the flow process is that it is associated with emission of acoustic signals. Such signals constitute a signature of the microscopic unit process responsible for the flow process. Since the diffusion kinetics can be excluded for the structural changes responsible for the resistivity changes shown in Fig. 2(a) and (b), we are led to conclude that these are effected through a flow process. This interpretation is supported by experimental work, using mechanical testing [10] as well as computer simulation [11,12]. In metallic glasses, the operative flow process has been designated as viscous flow [8,13,14].

In our experiments, evidence for the viscous flow mechanism is provided by the acoustic emission shown in Fig. 3(a) and (b) for MG3 at two different temperatures. Two significant aspects are: (1) the acoustic emission start almost immediately with the onset of isothermal annealing, and (2) the annealing temperatures, being well below the crystallization temperatures, can be expected to promote structural relaxation in the amorphous phase without leading to crystallization. Higher temperature is expected to enhance the rate of structural relaxation and it is also found to increase the rate of acoustic emissions. It is, therefore, logical to infer that the changes in electrical resistivity as well as the acoustic emission are a manifestation of the structural relaxation of the amorphous matrix. In order to further corroborate our ideas on the unit process responsible for structural relaxation in amorphous phase, the monitoring of acoustic signals under load was also carried out. The application of the load enhances the flow rate in crystalline as well as in amorphous solids and the analysis of acoustic signals emitted with and without load can give significant clues regarding mechanism of structural relaxation during isothermal annealing in the absence of the load. The effect of the load on acoustic emission is shown in Fig. 3(c). The rate of emission as well as the total number of events rises after the load is applied. The characteristics of acoustic emission for MG1 metallic glass with and without application of load are shown in Table 2. It can be seen that the nature of acoustic emission in the amorphous matrix with and without load application is nearly same. For majority of signals, RDC and ED lie between 1 and 6, and 0 and 100 μs, respectively. Similar behaviour in respect of PA and EE is observed for other metglass composition also (Table 3). The identical nature of acoustic signals with and without application of load shows that the unit flow processes in either conditions are identical. Hence main physical process occurring during isothermal annealing is the viscous flow.

4.2. Short range order during structural relaxation

Mossbauer spectra shown in Fig. 4 were recorded at room temperature and correspond to MG1 sample subjected to annealing treatment at various temperatures mentioned there. The annealing time of 150 min is considered adequate for the amorphous matrix to acquire the structure characteristics of the given temperatures. The crystallization temperature of this material is ~700 K. Hence 770 K spectrum is for the crystallized matrix. All other spectra shown are for the amorphous state. The amorphous nature of the specimens was verified through XRD pattern taken before and after the annealing treatment. A model independent analysis using Fourier deconvolution method [14] was performed to obtain the distribution of QS from these spectra. In this method of analysis, the even part of Fourier deconvoluted spectrum gives the even part of dominant hyperfine interaction, which is QS in this case. The odd part of the deconvoluted spectrum determines the correlation of QS with the chemical isomeric shift (IS). The results of such an analysis are shown in Fig. 5. QS is found to be more sensitive to the structural arrangements than IS within the amorphous system. According to Czjzek et al. [15], the probability of QS distribution, P(QS), gives an indication of the randomness in the atomic distribution among the nearest neighbour sites of iron atoms. P(QS) value close to zero, suggests nearly complete randomness and a value close to unity.

<table>
<thead>
<tr>
<th>Serial No.</th>
<th>Stress (N/m²) × 10³</th>
<th>Total events</th>
<th>RDC (events)</th>
<th>ED (μs)</th>
<th>PA (dB)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1–6 76</td>
<td>1–100 7100</td>
<td>30–40 40–50 50–60</td>
</tr>
<tr>
<td>1</td>
<td>Nil</td>
<td>47</td>
<td>46 1</td>
<td>46 1</td>
<td>10 35 2</td>
</tr>
<tr>
<td>2</td>
<td>2.15</td>
<td>65</td>
<td>63 2</td>
<td>64 1</td>
<td>14 47 4</td>
</tr>
<tr>
<td>3</td>
<td>4.31</td>
<td>81</td>
<td>73 8</td>
<td>74 7</td>
<td>17 55 9</td>
</tr>
</tbody>
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Table 3
Characterization of acoustic events on the basis of PA and EE

<table>
<thead>
<tr>
<th>Serial No.</th>
<th>Metallic glass</th>
<th>Temperature (K)</th>
<th>Stress (N/m²)</th>
<th>Time (min)</th>
<th>Total event</th>
<th>PA (dB) 30–40</th>
<th>40–50</th>
<th>50–60</th>
<th>EE 30–40</th>
<th>40–50</th>
<th>50–60</th>
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<tbody>
<tr>
<td>1</td>
<td>Ni₄₅Fe₅Co₂₀Cr₁₀Mo₄B₁₆ (MG1)</td>
<td>548</td>
<td>–</td>
<td>120</td>
<td>47</td>
<td>10</td>
<td>35</td>
<td>2</td>
<td>10</td>
<td>35</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>548</td>
<td>2.15</td>
<td>120</td>
<td>65</td>
<td>14</td>
<td>47</td>
<td>4</td>
<td>14</td>
<td>47</td>
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<td>4.31</td>
<td>120</td>
<td>81</td>
<td>17</td>
<td>55</td>
<td>9</td>
<td>17</td>
<td>50</td>
<td>14</td>
</tr>
<tr>
<td>2</td>
<td>Fe₄₀Ni₃₀Mo₂₀B₁₈ (MG2)</td>
<td>598</td>
<td>–</td>
<td>120</td>
<td>54</td>
<td>9</td>
<td>42</td>
<td>3</td>
<td>9</td>
<td>40</td>
<td>5</td>
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<tr>
<td></td>
<td></td>
<td>548</td>
<td>–</td>
<td>90</td>
<td>65</td>
<td>12</td>
<td>48</td>
<td>5</td>
<td>2</td>
<td>57</td>
<td>6</td>
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<tr>
<td>3</td>
<td>Co₆₈Mn₁₂B₂₀ (MG3)</td>
<td>598</td>
<td>–</td>
<td>90</td>
<td>128</td>
<td>4</td>
<td>99</td>
<td>25</td>
<td>4</td>
<td>93</td>
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<td>17</td>
<td>1</td>
<td>7</td>
<td>16</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>Fe₄₀Si₆B₁₃C₁ (MG4)</td>
<td>598</td>
<td>–</td>
<td>90</td>
<td>30</td>
<td>6</td>
<td>21</td>
<td>3</td>
<td>7</td>
<td>19</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>Fe₄₀Ni₄₀B₁₃Si₁ (MG5)</td>
<td>598</td>
<td>–</td>
<td>90</td>
<td>29</td>
<td>9</td>
<td>17</td>
<td>3</td>
<td>9</td>
<td>15</td>
<td>5</td>
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</tbody>
</table>

represents strong tendency for clustering. Thus values of $P(QS)$ in Fig. 5 imply a definite deviation from complete randomness, i.e., QS-distribution analysis shows small but definite changes in SRO around atoms. The randomness is maximum at 297 K (i.e. without annealing) and 521 K. Minimum randomness is seen after annealing at 478 K. From these Mossbauer studies, it is inferred that there is no evidence of gross compositional change or formation of a new phase up to 638 K. Thus, these results also do not support any significant role for diffusion kinetics during structural relaxation in the amorphous state.

4.3. Mechanism of structural relaxation

Based on the experimental evidence presented above, it is possible to arrive at the mechanism of structural relaxations in the metallic glass. The main inference from the acoustic emission data presented here is that the progress of amorphous phase towards the ideal glassy state is mediated through the viscous flow. It appears that the so-called “topological ordering” [16] is in fact a viscous flow phenomenon taking place in the matrix. The driving force for the viscous flow is the tendency of participating flow units to acquire a configuration characteristic of the annealing temperature. This tendency of the various flow units to reach a stable configuration from the original metastable state induces viscous flow. From the mathematical treatment of Van Den Beukel et al. [2,16] and other authors [4,5], it is apparent that topological ordering is envisaged to be a thermally activated diffusion controlled process. However, the experimental evidence presented in this paper points to an athermal viscous flow mechanism. According to simulation experiments of Argon and Kho [17], microscopic shear regions in glass have a dimension of 4–5 atoms across. It is believed that the viscous flow unit responsible for structural relaxation have nearly same dimension. Further, the property changes during structural relaxation of metallic glasses are given an effect only through the viscous flow process in the matrix.

So far, we have brought out that the long range diffusion does not play a major role during isothermal annealing of metallic glass in the amorphous temperature range. However, small changes in short range order do take place as shown by Mossbauer studies. A plausible explanation is as follows. The viscous flow within the matrix may result in interlocking of the flow units. Such configuration locks [18] entrap higher local volume and are associated with high energy. Hence, diffusion in and around such areas may occur till the large local volume is annihilated by further viscous flow.

5. Conclusions

1. Structural relaxation in metallic glasses during isothermal annealing in the amorphous region takes place through the process of viscous flow within the matrix.
2. The viscous flow is also responsible for property changes during structural relaxation.
3. There is no evidence of long range diffusion or formation of a new phase during the structural relaxation of the matrix.

References