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Calorimetric study of β-relaxation in an amorphous alloy: An experimental technique for measuring the activation energy for shear transformation

Jae-Chul Lee*

Department of Materials Science and Engineering, Korea University, Seoul 136-701, Republic of Korea

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When loaded at cryogenic temperature under stresses below the global yield, an amorphous alloy revealed two clearly distinguishable exothermic events during heating in calorimetric experiments. These exotherms, commonly known as the α- and β-relaxations, were attributed to the annealing out of two different local structures with different structural stability, presumably free volume and shear transformation zone (STZ). In this study, we introduced a simple and reliable experimental technique, which enables the evaluation of the activation energy corresponding to the β-relaxation, E_β. Based on experimental evidence and comparison with earlier studies, it is presumed that E_β is directly related to the potential energy barrier to shear transformation.

1. Introduction

The concept of the flow defect exists even in amorphous alloys to an extent similar to that of crystalline alloys. Free volume and shear transformation zone (STZ) are the typical examples. Considerable efforts have been devoted to establishing theories on the creation of free volume and STZ associated with deformation; the movements of ‘individual’ atoms by shear stress are responsible for the creation of free volume [1], while STZs are created by the ‘cooperative/collective’ motion of atomic clusters which contain tens or hundreds of atoms [2]. Although tangible evidence confirming the existence of free volume and STZ is yet to be found, recent atomic simulations [3–5] suggest that both the individual movements and cooperative movements of atoms are feasible in an amorphous solid, supporting the earlier theories on the formation of free volume and STZ. Considering that free volume and STZ are feasible sites for the nucleation of local deformation, understanding the characteristics of such defects, especially measuring their activation energy, is important for exploring the nature of the plastic behavior of amorphous alloys. Since an STZ is a medium-range structure consisting of hundreds of atoms, a mathematical description of the cooperative motion is too difficult to obtain, and thus, a simple but reliable technique to monitor and measure the shear transformation behavior is necessary.

In contrast to the plastic deformation of crystalline alloys, irreversible transformation of atomic groups occurs in amorphous alloys, even by the application of stresses below the global yield [5–9].This shear transformation occurs initially at local regions with loose atomic packing. As the deformation proceeds, structural disordering has to take place to supply additional STZs required to sustain the plastic flow at the imposed strain rate. STZs, which are the medium-range structures characterized by a lower density of atomic packing, can be regarded as local regions with large free volume sites and thus, a higher energy state than that of the surrounding structure [10]. Therefore, during heating at temperatures below T_g, these structures relax toward equilibrium, or toward a more stable state through structural ordering. This behavior is called structural relaxation and in general, is accompanied by the release of a measurable amount of enthalpy. As such, measuring the relaxation behaviors below T_g can not only quantify the degree of structural disorder [9,11,12], but also allow the structures of the deformed sample to be deduced [8,13].

Studies on relaxation dynamics have been conducted extensively on various glassy materials, including amorphous polymers, network glasses, and amorphous alloys. In the case of amorphous alloys, most studies on relaxation behaviors focused on the α-relaxation (also called the primary relaxation or glass transition) occurring near T_g. In contrast, the relaxation behavior at

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* Tel.: +82 2 3290 3283.
E-mail address: jclee001@korea.ac.kr.

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temperatures far below T_g, which is commonly referred to as the β-relaxation (or secondary relaxation), has attracted little research attention. In previous studies, the β-relaxation of amorphous alloys was attributed to a small positional change, typically less than one atomic distance, associated with the atomic rearrangement of short- to medium-range structures [14]. This concept of the β-relaxation viewed in amorphous alloys is analogous to that of amorphous polymers, in that it was known to be associated with reorientational motions of a small number of molecules or molecular groups confined to certain sites of loose packing [15]. Although the materials dealt with in these studies are different, the common feature drawn from the results is that the β-relaxation is related to the annihilation of disorder, which was created either during quenching or subsequent deformation, and thus, provides a suitable means that enables a glassy structure with different distributions of disorder to be deduced. The present study is an attempt to create such a technique, and the results can be viewed as a stepping stone in the ongoing search for an efficient method that can correlate the β-relaxation with the plastic behavior of amorphous alloys.

In this study, using calorimetric experiments, we obtain comparative information on the two different types of relaxation behaviors associated with the annihilation of created disorder in an amorphous alloy. We also seek a simple and reliable method to estimate the effective activation energy of the β-relaxation, which presumably is related to the energy necessary to activate the shear transformation in the glassy structure.

2. Experimental procedures

$Cu_{57}Zr_{43}$ was selected as the model alloy of the study. The ingots, which had a chemical composition of $Cu_{57}Zr_{43}$, were prepared by arc-melting high-purity elemental Cu (99.99%) and Zr (99.7%) under Ar flow. An appropriate amount of ingots was remelted several times in order to ensure microstructural homogeneity while preventing oxidation. The ingots were cast into a copper mold to produce 30-mm-long cylindrical rods with 1-mm diameter. The samples were machined into cylindrical rods with dimensions of 1-mm diameter and 2-mm length. Structural disorder was induced by applying a compressive stress to the level of 85% (=1.7 GPa) of the global yield strength (σ_y, ~2.0 GPa) at room (25 °C) and cryogenic (−196 °C, liquid nitrogen temperature) temperatures for extended periods. This loading scheme (previously, termed 'elastostatic compression' [16]) not only facilitates the induction of structural anisotropy [17,18], but is also effective for intentionally promoting the formation of the two clearly different types of defect structures with a measurable amount in a controlled manner [9].

The relaxation behaviors of the disordered amorphous alloy were evaluated by measuring the exothermic heat (or enthalpy) using differential scanning calorimetry (DSC, Perkin-Elmer DSC7, USA). This method is based on the fact that the amount of exothermic heat associated with the β-relaxation allows for the quantification of the relative change in the structure of amorphous alloys [13,19]. Prior to measurements, the calorimeter cell was calibrated by recording the melting temperatures of pure In, Zn, and Al. Since the changes in the exothermic heat associated with the β-relaxation are usually very small and subtle, the exothermic heat was measured by subtracting the DSC baseline from each sample's thermograms. For this purpose, the sample was placed in a platinum crucible, held at an initial temperature of 150 °C for 10 min, heated to 600 °C at a rate of 40 °C/min, cooled back to 150 °C at the same rate, and then naturally cooled to room temperature. The second scan to obtain the baseline was performed on the same sample using the same procedure as that used for the first scan.

3. Results and discussion

Fig. 1(a) shows the representative thermograms obtained from the first and second scans of the as-cast sample. The shaded area in Fig. 1(b) is the difference in the thermograms between the two scans, which corresponds to the relative change of the amorphous and crystalline structural states of the sample.[1] This exothermic event, commonly known as the α-relaxation, is known to arise from the annihilation of various short-range orders with loose atomic packing [9], excess free volume [9,14,20], or residual stress release [17,20,21]. The exothermic event occurring below T_g quantifies the net structural change in the amorphous sample and reflects the structural state of the amorphous alloy prior to relaxation.

In the past, structural relaxation was not considered to take place at ambient or room-temperature due to the low atomic mobility and thus, was usually ignored. Despite this common belief, the recent theories [22], atomic simulations [6,23], and various experiments [24,25] suggest that relaxation can take place even at ambient temperatures, although its rate is sensitive to the exposure temperature. The feasibility of the ambient-temperature relaxation of amorphous alloys is quite natural, considering the characteristics of the structural changes in terms of the magnitude of atomic displacement. In crystalline alloys, the structural changes associated with deformation are accompanied by long-range atomic displacement, mostly greater than one atomic distance (~3 Å). However, structural changes in amorphous alloys, as characterized by disordering and ordering, are associated with a very small positional change, usually much smaller than one atomic distance (~0.3 Å) (see Fig. 9 of Ref. [26]). This characteristic of the structural changes in amorphous alloys makes it feasible to relax to a more ordered state even by the application of small thermal energy corresponding to ambient/room temperature. Therefore, if elastostatic compression as a means of promoting structural disorder is conducted at ambient temperature, structural disordering and thermal relaxation take place simultaneously. However, elastostatic compression of amorphous alloys performed at cryogenic temperature would eliminate or minimize the thermally activated relaxation process that otherwise can take place at ambient temperatures.

Fig. 2 shows the changes in enthalpy reflecting the change in the glassy structure of the samples subjected to elastostatic compression at 25 and −196 °C for various durations. The results suggest that the degree of disorder created by elastostatic compression was measurably larger in the samples compressed at −196 °C than in those at 25 °C. At the same time, upon comparing the two curves, it is evident that the ordering associated with thermal relaxation did take place even at ambient temperatures and its magnitude is significant and thus, cannot be ignored. This ambient temperature relaxation seems to be universal in most glassy materials, including amorphous polymers [27] and amorphous alloys [24,25]. Overall, the structural changes induced by the elastostatic compression at −196 °C can eliminate or minimize the effect of ambient-

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[1] The relaxation curve is conventionally obtained by first heating the as-cast sample to a temperature slightly above T_g. After cooling the sample, the second scan is conducted on the same sample by heating it to the same temperature. The relaxation curve is then obtained by subtracting the thermogram of the second scan from that obtained from the first scan. However, in this study, we performed the first scan by heating the sample to a temperature above the crystallization temperature. The relaxation curve was obtained by subtracting the second scan as the background of DSC from the first scan. This operation makes the relaxation enthalpy corresponding to the area of the relaxation curve larger than that obtained using the conventional method. However, it does not alter the peak positions of the exotherms. These characteristics help to reveal the individual relaxation events clearly, which facilitates the evaluation of the activation energy for the α- and β-relaxations.