

Irreversible Structural Change Induced by Elastostatic Stress imposed on an Amorphous Alloy and Its Influence on the Mechanical Properties

Seung-Jae Lee¹, Byung-Gil Yoo², Jae-II Jang², and Jae-Chul Lee^{1,*}

¹ Department of Materials Science and Engineering, Korea University,
1, Anam-dong 5-ga, Seongbuk-gu, Seoul 136-701, Korea

² Division of Materials Science and Engineering, Hanyang University,
17, Haengdang-dong, Seongdong-gu, Seoul 133-791, Korea

The elastic deformation behaviors of bulk amorphous alloys during elastostatic compression were examined. Depending on the alloy deformation characteristics, the elasticity of amorphous alloys consists of strain components characterized by ideal elasticity, anelasticity, and viscoelasticity. The strain component associated with viscoelasticity is irreversible and causes the generation of excess free volume, which in turn alters the mechanical properties. This article discusses how the properties of amorphous alloys can be altered by the application of elastostatic compression.

Keywords: amorphous alloy, elastostatic compression, elastic shear stress, free volume, plasticity

1. INTRODUCTION

In general, the stress-strain response of crystalline materials is linear in an elastic regime and most often fully reversible and instantaneous upon the removal of applied stress. In contrast to these well-defined elastic behaviors of crystalline materials, many of the elastic responses of amorphous alloys are still unclear.

By conducting tensile creep tests of an amorphous wire at an elevated temperature, Taub and Spaepen found that the elastic behaviors of amorphous alloys consist of strain components characterized by the ideal-elasticity, anelasticity and viscoelasticity^a [1]. On the basis of their theoretical modeling and computations, Argon and Kuo claimed that amorphous alloys subjected to an external stress lose the memory of their initial structures when the applied stress is removed [2]. These earlier studies implicitly suggested that, unlike crystalline materials, amorphous alloys may exhibit permanent deformation associated with structural changes, even at a stress level well below the yield strength.

Several theoretical reports have explained how these structural changes can be caused by the application of elastic stress. Argon suggested that some atomistic-scale deformation induced by shear stress can occur in local regions of amorphous alloys [3]. Wakeda *et al.* [4] and Ogata *et al.* [5],

using definitive three-dimensional molecular dynamics simulations, demonstrated that structural change occurs irreversibly under elastic shear stress, resulting in the formation of an excess free volume. In another study, Spaepen suggested that the generation rate of excess free volume becomes larger as the magnitude of the shear stress increases [6]. All of these theories implicitly suggest that irreversible (or non-recoverable) structural changes take place in amorphous alloys even under the application of elastic shear stress, which not only causes permanent deformation, but also generates excess free volume.

We discuss two fundamental questions: firstly, whether permanent deformation occurs even at a stress level below the yield strength, thereby resulting in the creation of excess free volume; and, secondly, whether the created free volume is maintained even after the removal of the applied stress. Using the simple binary amorphous alloy Cu₆₅Zr₃₅ as a representative alloy, we examined elastic deformation behaviors during elastostatic compression and the effect of those behaviors on the mechanical properties during subsequent compression tests. In addition, we demonstrated that the application of elastic stress does indeed cause irreversible structural changes in amorphous alloys. Moreover, we addressed some likely problems that may be encountered when amorphous alloys are used as structural members.

2. EXPERIMENTAL PROCEDURES

To demonstrate the structural changes of an amorphous

*Corresponding author: jcleee001@korea.ac.kr

^aAnelastic strain is recoverable and time-dependent, while viscoelastic strain is permanent and time-dependent.

alloy during ‘*elastostatic compression*’^b and to discuss their influence on the mechanical properties, we selected a model alloy on the basis of several criteria. First, the model alloy must be a simple alloy system so that the structural changes can be analyzed during the elastostatic compression. Furthermore, the changes in the properties should be readily traceable as a function of the conditions of the elastostatic compression. Thus, an alloy that has no plasticity (or minimal initial free volume) in its as-cast condition is considered to be appropriate. From this perspective, we selected the model alloy from the Cu-Zr alloy system because it has a simple binary system and can be synthesized in a $\Phi 1$ mm diameter bulk form over a wide compositional range (Cu at.% = 50 % to 66 %, [7]). Of these compositions, nine different bulk samples ($\Phi 1$ mm \times $h 30$ mm) were synthesized so that we could select the most appropriate model alloy that did not exhibit plasticity in its as-cast conditions. To measure the mechanical properties of the Cu-Zr binary alloys, we used compression tests. Room temperature uniaxial compression tests were carried out on cylindrical cast rods ($\Phi 1$ mm \times $h 2$ mm) at a strain rate of approximately 10^{-4} s⁻¹. We also made nanoindentations (MTS nanoindenter XP) on the samples at a constant loading rate (1 mN s⁻¹) to measure their Young’s moduli.

3. RESULTS AND DISCUSSION

3.1. Selection of the model alloy

Figure 1 shows the variations in the atomic packing density, yield strength and plastic strain of the Cu-Zr binary alloys measured as a function of their composition [8]. As shown in Fig. 1(a), when we increased the Cu content, the atomic packing density increased to a maximum value at Cu₆₅Zr₃₅ and then decreased. Interestingly, the tendency observed in the packing density versus composition relation is very similar to that of the properties versus composition relation in Fig. 1(b). In the compositional range of interest, Cu₆₅Zr₃₅, which has the highest atomic packing density, exhibited the lowest plastic strain (0 %) [8]. Hence, we considered Cu₆₅Zr₃₅ to be the most appropriate model alloy for validating our main postulation: namely, that the structures of amorphous alloys can be altered even by the application of elastic stress for a prolonged period of time, and that the altered structures can in turn lead to changes in their properties.

3.2. Changes of mechanical properties and excess free volume

Before the compression tests, the Cu₆₅Zr₃₅ rod samples were elastostatically compressed at room temperature for 12 h

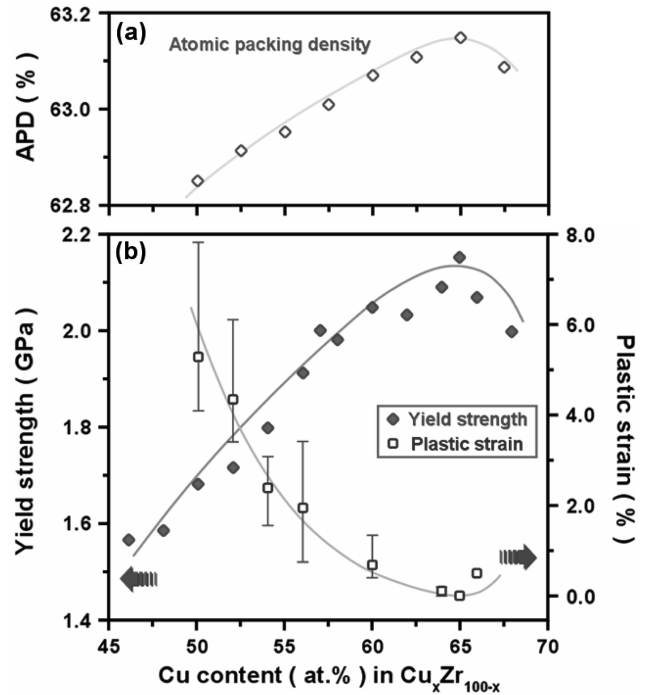


Fig. 1. Variations in (a) the atomic packing density and (b) the yield strength and the plastic strain as a function of the composition of Cu_xZr_{100-x}. Note that at the maximum packing density, which was attained for Cu₆₅Zr₃₅, the strength was minimal and the plasticity was maximal.

at various loading levels in the range of 50 % to 90 % of the yield strength (σ_y , approximately 2.2 GPa) of the as-cast Cu₆₅Zr₃₅ alloy. Observations on the surfaces of the preloaded samples subjected to different loading levels showed no evidence of the formation of shear bands. These samples were then tested under compression. Figure 2(a) shows their engineering stress-strain curves along with that of the as-cast alloy. The results indicate that, with an increasing preloading level, the yield strength of the samples decreased from 2.2 GPa to 1.6 GPa, whereas the plastic strain increased from 0 % to 5.2 %. Figure 2(b) shows the variations in the Young’s moduli of the preloaded samples, revealing that the modulus decreased linearly as the preloading level increased. It is clear from Fig. 2 that preloading via elastostatic compression alters the properties of amorphous alloys. In addition, the extent of the property changes depends strongly on the preloading level, thereby providing clear evidence that elastostatic compression induces irreversible structural changes.

It is widely accepted that the mechanical properties of amorphous alloys are closely related to the amount of excess free volume within them [9-15]. Thus, by measuring these mechanical properties, we can gain information on the way they vary as a result of elastostatic compression. Various techniques can be used to evaluate the relative amount of free volume. Of these techniques, differential scanning calorimetry (DSC) is a practical method that considers how

^bIt is referred to as preloading with a compressive stress smaller than the yield strength of the amorphous alloy.

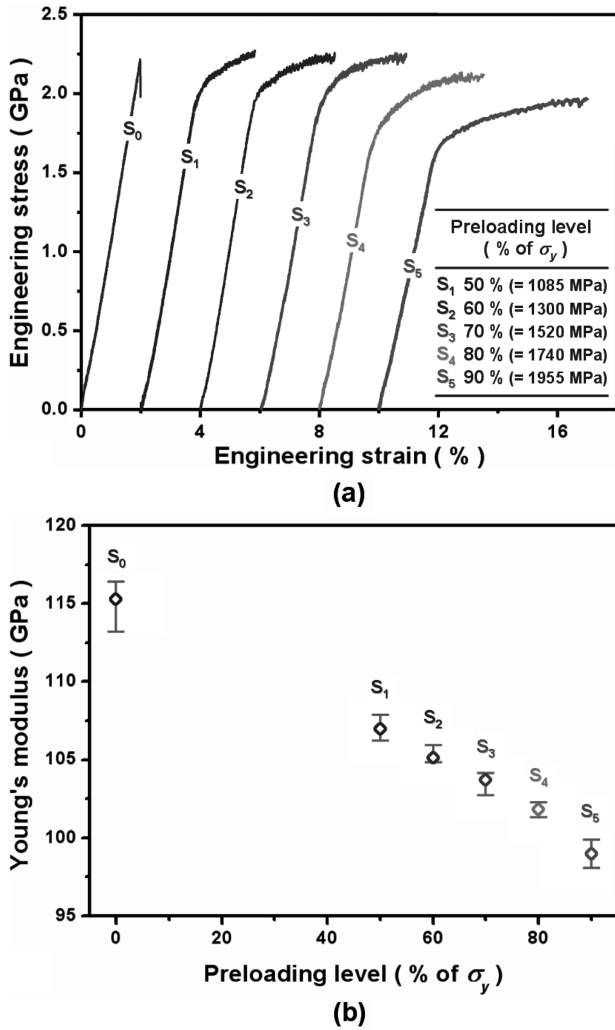


Fig. 2. Variations in (a) the flow curve and (b) Young's modulus of the as-cast and preloaded $\text{Cu}_{65}\text{Zr}_{35}$ amorphous alloys held at various preloading levels at room temperature for 12 h.

much excess free volume exists in proportion to the energy release associated with structural relaxation (or the annihilation of excess free volume) during the heating process at temperatures lower than the glass transition temperature, T_g [16-19]. Figure 3(a) shows the DSC (Perkin-Elmer DSC 7) thermograms recorded from the as-cast and preloaded samples. The rectangular region of Fig. 3(b), which shows a magnified view of the thermograms below T_g , reveals that the amount of exothermic heat associated with the annihilation of excess free volume increases as the preloading level increases. This experimental observation provides direct evidence that the application of elastic stress does indeed create an excess free volume, the amount of which is proportional to the loading level. To understand how elastostatic compression can generate excess free volume, we monitored the detailed strain stages of the amorphous sample as a function of time during the loading-unloading experiments.

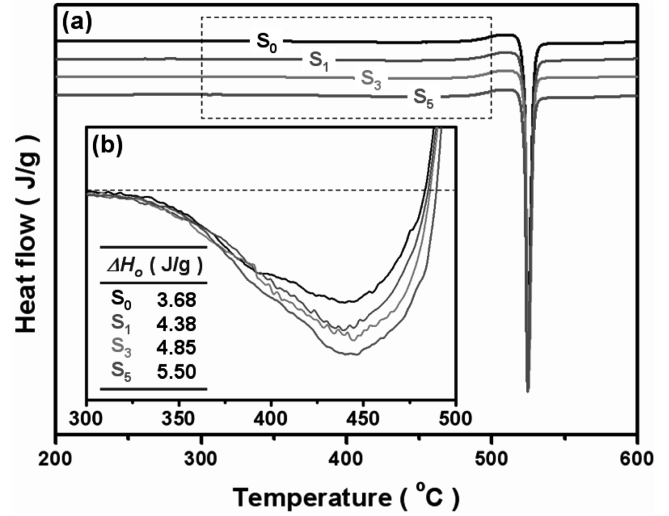


Fig. 3. (a) DSC thermograms recorded from the as-cast and preloaded samples at a heating rate of 40 K/min. (b) Magnified view of the rectangular region of (a), showing the amount of the exothermic heat associated with the annihilation of the excess free volume.

3.3. Elastostatically driven irreversible structural changes

Figure 4 shows a typical strain versus time response of the as-cast sample during a loading-unloading cycle at the level of 90 % of its yield strength. The result clearly demonstrates that the total strain caused by the elastostatic compression consists of strain components corresponding to the ideal elasticity (ϵ_E), anelasticity (ϵ_A), and viscoelasticity (ϵ_V). This strain response of the bulk amorphous sample subjected to compression at room temperature is nearly identical to those reported for wire [1] or ribbon [2] samples subjected to tension at an elevated temperature. Of the strain components in

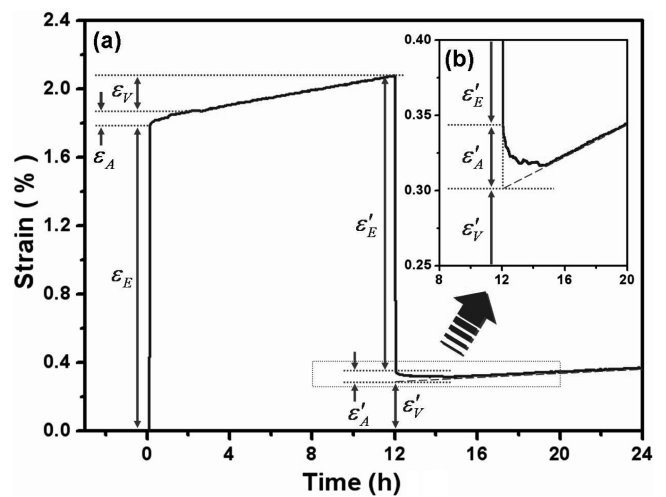


Fig. 4. Strain response measured during loading at 90 % of the yield strength of the $\text{Cu}_{65}\text{Zr}_{35}$ alloy and unloading by the removal of the applied stress. Note that the total strain consists of strain components corresponding to ideal elasticity (ϵ_E), anelasticity (ϵ_A), and viscoelasticity (ϵ_V).

Fig. 4, the elastic and anelastic strains are linear and fully recoverable, though their strain response differs in terms of their instant recoverability upon the removal of the applied load. In contrast, the viscoelastic strain is not recoverable even if the load is removed; thus, as shown in Fig. 4, the viscoelastic strain produces a permanent deformation characterized by a constant strain rate ($d\varepsilon/dt$). Our observation confirms that the magnitude of the permanent deformation caused by the viscoelasticity (ε_V) varies linearly with the loading level, resulting in the formation of excess free volume.

Inhomogeneous deformation of amorphous alloys is known to occur at room temperature and is characterized by the formation of localized shear bands, leading to permanent deformation [6]. In contrast, homogeneous deformation of amorphous alloys is known to occur at low stress and a high temperature (approximately $0.7 T_g$ [3]): that is, each volume element undergoes the same strain and no macroscopic shear localization is observed [6]. Interestingly, however, amorphous alloys can undergo permanent deformation even at room temperature under elastostatic compression without forming shear bands. At high temperatures, homogeneous deformation is strongly influenced by structural relaxation, resulting in the annihilation of free volume during deformation. On the other hand, at room temperature the structural relaxation is negligible; moreover, the disordering of amorphous alloys occurs as a result of the generation of excess free volume [20,21]. Thus, these experimental results agree well with the prediction that the generation rate of excess free volume increases in proportion to the magnitude of the shear stress [6].

3.4. Influence of irreversible structural changes on mechanical properties

Many earlier studies implicitly suggested that various mechanical and physical properties of amorphous alloys are closely related to the structural stability of the alloys [22-24]; the studies also suggested that structural stability can be determined in terms of the packing density of the alloys [8,25,26] as characterized by the short-range ordered atomic clusters. Park *et al.* used a combination of experiment and simulation to show that amorphous alloys with higher atomic packing densities exhibit higher strength and lower plasticity [8]. They also demonstrated that the atomic packing density of amorphous alloys is inversely proportional to the free volume. As such, the mechanical properties of amorphous alloys are closely related to the amount of excess free volume. From this perspective, as confirmed in the study of Huang *et al.* [27], we can deduce state that, due to its lower free volume, an alloy with a higher atomic packing density has a higher yield strength and lower plasticity. In addition, we observed that the amount of free volume increases as the level of elastostatic compression increases. As such, we assume that the variations shown in Fig. 2 with regard to the yield strength,

Young's modulus, and plasticity originate from the change in the free volume that was created during the viscoelastic deformation associated with the elastostatic compression.

Free volume is one of the heterogeneities that act as preferential sites for the initiation of shear bands [6,28,29]. Thus, the enhancement of the plasticity is thought to be due to the excess free volume created by the elastostatic compression. In addition, the increased free volume in an amorphous alloy causes an increase in the average interatomic spacing, resulting in a lowering of the atomic bonding force. As a result, we consider the reduced yield strength, Young's modulus, and the hardness of the elastostatically compressed samples to be due to the increased interatomic spacing associated with the creation of the excess free volume. Our findings suggest that amorphous alloys may not be suitable for some structural applications that are exposed to severe elastostatic stress or fatigue for a prolonged period, such as high-precision springs and high-strength bolts.

4. CONCLUSION

In summary, we found that the elastostatic compression of amorphous alloys for a prolonged period results in the formation of viscoelastic strain, which is characterized by permanent deformation caused by irreversible structural changes. Unlike plastic behaviors of amorphous alloys during inhomogeneous deformation at low temperature, the permanent deformation induced by elastostatic compression occurs homogeneously at room temperature without the formation of shear bands. During the irreversible structural changes, excess free volume is created and its amounts were proportional to the level of the elastostatic compression. As the level of elastostatic compression increases, the plasticity of the amorphous alloys increases but the yield strength decreases. This phenomenon can be explained in terms of the relative amount of free volume created during elastostatic compression. Nonetheless, better structural models are needed to elucidate the underlying mechanism of the detailed structural changes that are responsible for the formation of free volume.

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