Synthesis and Mechanical Properties of Zr$_{55}$Al$_{10}$Ni$_{15}$Cu$_{30}$ Bulk Glass Composites Containing ZrC Particles Formed by the In-Situ Reaction

Tomoya Hirano*, Hidemi Kato, Atsushi Matsuo, Yoshihito Kawamura and Akihisa Inoue

Institute for Materials Research, Tohoku University, Sendai 980-8577 Japan

Bulk glassy Zr$_{55}$Al$_{10}$Ni$_{15}$Cu$_{30}$ composites containing ZrC particles up to 17.5 vol% were formed by the in-situ reaction between the Zr metal and graphite powder during melting-process. The glassy composites had a cylindrical form of 2 mm in diameter by a copper mold casting process. The in-situ reaction was effective for the homogeneous dispersion of ZrC particles and for the achievement of excellent wettability between pure glass and ZrC particles. Mechanical properties, particularly fracture strength and plastic elongation, were significantly improved in comparison with those of the pure glass as well as the similar bulk glassy composite formed by addition of ZrC particles. The present study has demonstrated that the in-situ reaction method is useful for the synthesis of the bulk glassy composites consisting of glassy matrix and dispersed reinforce particles with excellent mechanical properties.

(Received May 22, 2000; Accepted August 29, 2000)

Keywords: bulk metallic glassy composites, composites material, reinforcement, agglomeration, in-situ reaction, zirconium carbide, plastic elongation, dispersion strengthening

1. Introduction

Recently, the findings$^{1-3}$ of glassy alloys with a high glass-forming ability and a wide super-cooled liquid region have enabled us to use them for fundamental researches and practical applications. The multicomponent Zr–Al–TM (TM = transition metals)$^{4,5}$ system is known to be one of the best glass formers. The critical diameter reaching 30 mm has been achieved for the Zr$_{55}$Al$_{10}$Ni$_{15}$Cu$_{30}$ glassy alloy$^6$ prepared by the suction casting method and the temperature interval of the super-cooled liquid region $\Delta T_s$ ($=T_s - T_g$), is about 123 K.$^6$ Furthermore, the critical cooling rate of the Zr-based glassy alloy has been measured to be 1 to 3 K/s from the change in solidification temperature with cooling rate.

The glassy alloy deforms elastically and the consequent fracture, especially under uniaxial or compressive load, takes place along a localized shear plane without distinct plastic strain. In order to improve these mechanical properties, bulk metallic glassy composite materials reinforced by ceramics and ductile metals have been investigated up to date. In 1980, the first report$^7$ in this category has demonstrated an improvement of yield stress and a reduction in the degree of localization in the fracture mode. Later, it has been reported that the Ni–Si–B amorphous ribbons reinforced by WC particles have improved tensile strength.$^8$ Recently, the authors have found that bulk metallic glassy Zr–Al–Ni–Cu composite materials reinforced by ZrC particles exhibit higher fracture strength and larger plastic strain under a uniaxial compressive load as compared with the pure Zr–Al–Ni–Cu glass.$^9$ California institute of technology group has also reported that bulk metallic glassy Zr–Ti–Ni–Cu–Be alloys reinforced by ductile metal (W or steel) fiber have improved mechanical properties.$^{10}$ Moreover, it has been announced that bulk metallic glassy Zr–Nb–Al–Ni–Cu alloys reinforced by metals (W or Ta), steel fiber, ceramics such as (SiC, WC, or TiC) have improved mechanical properties.$^{11-14}$ When the second reinforced mediums are dispersed in the glassy matrix, there is a high risk of partial crystallization at the interface between the glassy and reinforced mediums. As the important factors for preparation of above-mentioned composite materials, one can list up a high glass-forming ability of the glassy matrix, low reactivity to the glassy phase, small difference in thermal expansion coefficient, and good wettability. If these factors are achieved and the second reinforced mediums are homogeneously dispersed without agglomerating or segregating in the glassy matrix, the second particles are likely to suppress the propagation of shear bands and might increase the toughness and fatigue resistance of the composite materials. The in-situ reaction between the glassy and dispersoid during preparation has been thought to be effective for good wettability and homogenization of the dispersoids because the in-situ reaction is likely to suppress the agglomeration among dispersoid particles. The first aim of this paper is to demonstrate the synthesis of bulk glassy Zr$_{55}$Al$_{10}$Ni$_{15}$Cu$_{30}$ composites containing ZrC particles formed by the in-situ reaction between Zr metal and graphite powder. The second is to investigate the effect of the in-situ reaction on the formation, thermal stability and mechanical properties of the composite materials.

2. Experimental Procedure

A master ingot of Zr$_{55}$Al$_{10}$Ni$_{15}$Cu$_{30}$ alloy was prepared by arc-melting a mixture of pure Zr, Al, Ni and Cu metals in an argon atmosphere. Subsequently, a mixture of the pre-alloyed Zr$_{55}$Al$_{10}$Ni$_{15}$Cu$_{30}$, graphite powder (average particle diameter 10 $\mu$m and 99.99% purity) and extra Zr metal which is required to form ZrC were re-melted by arc-melting. As Zr metal has the highest reactivity with graphite and the resulting ZrC is the most stable among the all four elements, ZrC can be fabricated as the only reactant during melting. The composite ingot was melted in a quartz nozzle with a high-frequency furnace and cast into a copper mold. The copper mold had internal rod shaped cavities of 2 mm in diameter.

*Graduate Student, Tohoku University.
and 40 mm in length and dogbone-shaped cavities of 1 mm in thickness, 2.2 mm in width and 25 mm in length.

The structure of composites was examined by X-ray diffraction, optical microscopy (OM) and scanning electron microscopy (SEM). The glass transition and crystallization of composites were studied by differential scanning calorimeter (DSC) at a heating rate of 0.67 K/s. Mechanical properties, such as compressive and tensile strength, plastic elongation and Young's modulus, were measured by an Instron testing machine with a strain gauge meter. (Compression test samples were cut to an aspect ratio 2.)

3. Results

Figure 1 shows X-ray diffraction patterns of the Zr$_{55}$Al$_{10}$Ni$_{5}$Cu$_{30}$ glassy alloy and the cast composite bulk alloy of 2 mm in diameter containing 7.5, 12.5 and 17.5 vol%ZrC. It is confirmed that the composite material consists of the Zr-based glassy and fcc-ZrC phases and does not contain any other phases. In Fig. 2, DSC curves of the Zr$_{55}$Al$_{10}$Ni$_{5}$Cu$_{30}$ glassy alloy and the composite materials containing 7.5, 12.5 and 17.5 vol%ZrC are compared. The Zr-based glassy alloy has a high glass-forming ability enough to form an amorphous phase even in coexistence with ceramic dispersoids. Here $T_g$ is defined as the onset of the glass transition temperature and $T_x$ the crystallization event. It is observed that $T_g$ and $T_x$ between the Zr-based glassy alloy and the composite materials are coincident. This result indicates that the whole additional graphite reacted with Zr metal during the arc-melting, leading to the formation of ZrC particles. Figure 3 shows an optical micrograph of transverse cross-section of the composite material containing 15 vol%ZrC. It is seen that the ZrC particles with a particle size of about 10 μm are homogeneously dispersed in the glassy matrix phase. Furthermore, neither voids nor pores are seen over the whole micrograph. It is therefore concluded that the in-situ reaction does not affect the thermal stability of Zr-based glassy phase as well as the homogeneous dispersion state.

The homogeneously dispersed ZrC particles into the Zr-based glassy matrix are expected to improve mechanical properties. Figure 4 shows compressive stress-strain curves of the Zr-based glassy alloy and the composites. In general, the compressive fracture takes place along the maximum shear plane, which is inclined by about 45° to the direction of applied load. The pure Zr-Al-Ni-Cu glassy alloy does not exhibit inelastic deformation at all. On the other hand, the sam-
Fig. 4 Compressive stress-strain curves of the pure glassy Zr55Al10Ni3Cu30 alloy and the glassy composites containing 7.5, 12.5 and 17.5 vol% ZrC. The strain rate is \(5.0 \times 10^{-3}\) s\(^{-1}\).

Fig. 5 Change in the Young’s modulus with volume fraction of ZrC for the bulk glassy Zr55Al10Ni3Cu30 composites.

Fig. 6 Change in the compressive strength with volume fraction of ZrC for the bulk glassy Zr55Al10Ni3Cu30 composites.

Fig. 7 Change in the plastic elongation with volume fraction of ZrC for the bulk glassy Zr55Al10Ni3Cu30 composites.

4. Discussion

It was shown in Figs. 1 to 3 that Zr-metal and C powder completely reacted during arc-melting, resulting in the formation of the composite structure consisting of homogeneously dispersed ZrC particles in the glassy matrix. It was further clarified that the composite materials containing ZrC particles consisted of the Zr55Al10Ni3Cu30 glassy alloy and ZrC particles formed by the \textit{in-situ} reaction. The synthesis of the glassy
Zr₅₅Al₁₀Ni₅Cu₃₀ composite materials containing ZrC particles has previously been reported. The previous composites were prepared from the mixture of the master ingot of the four metals and ZrC particles. In that way, the partly agglomeration of ZrC particles was confirmed. In this case, however, the in-situ reaction between the Zr metal and graphite powder enabled the homogeneous dispersion of ZrC particles.

As shown in Fig. 4, the compressive ductility of the bulk glassy alloy was significantly enhanced for the composites containing ZrC formed by the in-situ reaction. Figure 9 shows SEM micrographs of the side and the fracture surface of the composite and the Zr-based glassy alloy. As shown in (a) and (c), the fracture takes place at the initial shear plane. The fracture surface consists of smooth and typical vein pattern regions. On the other hand, in (b) and (d), the fracture surface is rough and ZrC particles are recognized. The micrographs clearly indicate that the ZrC particles suppress the propagation of shear band. Figure 10 reveals that multiple shear bands generate in the composite. This suggests that the deformation mechanism in the composites changes from that of the Zr-based glassy alloy. Evidently, the constrain leads to the generation of the multiple shear bands parallel to the initial band. As a result of the generation of the multiple shear bands.
bands, it is reasonable to suppose that the $\varepsilon_p$ is significantly enhanced as compared with the Zr-based glassy alloy. The improvement of compressive stress $\sigma_f$ is due to the restraint of slipping on each shear plane by ZrC particles. This behavior also causes an enhancement of fracture toughness of the glassy alloy. Figure 11 shows an external appearance of the composite containing 10 vol% ZrC subjected to final fracture. It is clear that the significant plastic deformation for the composite enables a plastic buckling deformation that has not been observed in deformation behavior of the glassy alloy.

As mentioned above, the shear bands that generated and propagated in a matrix are suppressed by the ZrC particles. In other words, the place where ZrC particles exist in composites is the generating site of the shear bands. Here, let us consider the relation between the density of the shear bands and the compressive stress (or the plastic elongation) of the composites. As the ZrC particles increase by 10 ~ 12.5 vol% ZrC, both the $\sigma_f$ and $\varepsilon_p$ increase. The ZrC particles are the generating site of the shear band and restrict the propagation of the slip band. Over 12.5 vol% ZrC, however, the $\sigma_f$ increases linearly, which the $\varepsilon_p$ decreases. The reason for the improvement of the compressive stress is that a number of shear bands generate in the glassy matrix and then are suppressed around ZrC particles, leading to the strengthening of the bonding between the matrix and ZrC particles. In the larger plastic elongation region where a number of shear bands generated, it is supposed that the shear bands correlates and interferes with each other, resulting in a significant decrease in $\varepsilon_p$.

5. Summary

We examined the possibility of fabricating bulk glassy Zr$_{55}$Al$_{10}$Ni$_5$Cu$_{30}$ composites containing ZrC particles by the

in-situ reaction between Zr metal and graphite powder during arc-melting. The results obtained are summarized as follows.

1. Cylindrical bulk glassy composites containing up to 17.5 vol% ZrC were prepared through the in-situ reaction. Neither appreciable agglomeration nor segregation for ZrC particles is observed. The in-situ reaction is effective for the suppression of the agglomeration and segregation among dispersed particles.

2. No other crystalline phase is observed at the interface between the glassy and ZrC phases. The interface has a rugged morphology on a nanometer scale and does not have any facet plane on the ZrC phase.

3. The $E$ and $\sigma_f$ under compression increase almost linearly from 100 GPa and 1821 MPa, respectively, for the 0 vol% ZrC composite to 118 GPa and 2265 MPa, respectively, for the 15 to 17.5 vol% ZrC composites. This improvement is realized by the dispersion strengthening of ZrC particles as well as by the strong bonding nature between the glassy matrix and ZrC particles. In addition, the $\varepsilon_p$ significantly increases from ~0% for the 0 vol% ZrC composite to 7.65% for the 10 vol% ZrC composite. The improvement of the plastic elongation is attributed to the increase in the density of the shear bands before adiabatic final fracture resulting from the increase in fracture strength.

Acknowledgement

This work was performed under the auspices of the Research Fellowship Division, Japan Society for the Promotion of Science (JSPS).

REFERENCES