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HIGH STRENGTH AND GOOD DUCTILITY OF $Zr_{55}Al_{10}Ni_5Cu_{30}$ BULK GLASS CONTAINING ZRC PARTICLES

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Introduction

The recent developments [1–3] of glassy alloys that have high glass-forming ability and high thermal stability against crystallization allow us to use them for fundamental investigations and practical uses. The multicomponent Zr-Al-TM (TM = transition metals) [4,5] alloy system is known to be one of the best glass formers. The critical diameter reaching 30 mm has been achieved for $Zr_{55}Al_{10}Ni_5Cu_{30}$ alloy [6] prepared by a suction casting method. In the temperature range well below glass transition temperature ($T_g \sim 680$ K), the glassy alloy deforms elastically and the subsequent fracture, in particular under a uniaxial or compressive load, takes place along a localized shear plane without distinct plastic elongation, as is case for other amorphous alloys [7]. With the aim of improving the mechanical properties without macroscopic elongation, amorphous composite materials containing second phases (ceramics, ductile metals and so on) have been investigated up to date. In 1980, the first report [8] in this category has indicated an increase of yield stress and a reduction in the degree of localization in the deformation mode. That is, melt-spun $Ni_{78}Si_{10}B_{12}$ amorphous ribbons containing μm-sized WC particles have improved tensile strength [9]. Recently, we have found that bulk glassy Zr-Al-Ni-Cu composite materials containing ZrC particles exhibit higher fracture strength and larger plastic strain as compared with the Zr-Al-Ni-Cu single phase [10]. Caltech group has also reported that bulk glassy Zr-Ti-Ni-Cu-Be alloys containing ductile metal (W or steel) fiber have improved mechanical properties [11]. The similar data have been obtained by changing the volume fraction of W, steel fiber or some ceramic particles [12–14]. As the important factors for the preparation of the above-described composite glassy alloys, one can list up limited reactivity, good wettability, and coincidence of thermal expansion coefficient and specific density. Great efforts have been devoted to control these factors. The in-situ reaction between dispersoid and matrix phase during preparation has been thought to be effective for good wettability and homogenization of the filler dispersoids because the in-situ reaction can suppress the agglomeration among dispersoid particles. This paper is intended to demonstrate the effectiveness of the in-situ reaction between Zr metal and graphite to form ZrC particles that are dispersed homogeneously in a bulk glassy $Zr_{55}Al_{10}Ni_5Cu_{30}$ alloy and to present significantly improved mechanical properties, especially of compression tests, in the dispersion state.

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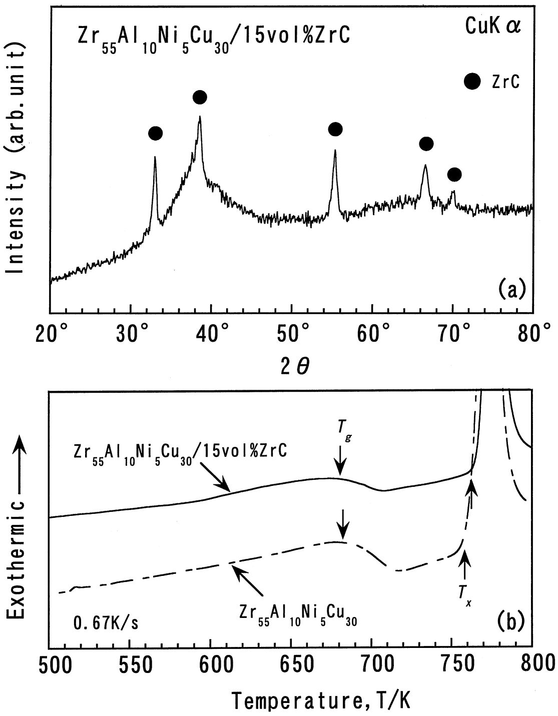

Figure 1. X-ray diffraction pattern (a) and differential scanning calorimetric curve (b) of a cast glassy $Zr_{55}Al_{10}Ni_5Cu_{30}$ composite material containing 15 vol.% ZrC. The data of a $Zr_{55}Al_{10}Ni_5Cu_{30}$ glassy single-phase alloy are also shown for comparison.

Experiments

A master alloy ingot of $Zr_{55}Al_{10}Ni_5Cu_{30}$ (at. %) without graphite particles was first prepared by arc-melting the mixture of pure Zr, Al, Ni and Cu metals in an argon atmosphere. Then it was re-melted by arc-melting with graphite powders (particle diameter under 10 μm and 99.99% purity) and extra Zr metal which is required to form ZrC. As Zr metal has the highest reactivity with graphite and the resulting ZrC is the most stable among the four constituent elements, ZrC can be produced as the only reactant phase during melting. The composite ingot was melted in a quartz nozzle and cast into a copper mold. The composite structure was examined by X-ray diffraction, optical microscopy (OM) and scanning electron microscopy (SEM). Thermal properties associated with glass transition and crystallization temperature were evaluated by differential scanning calorimetery (DSC) at a heating rate of 0.67 K/s. Mechanical properties, such as Young's modulus, tensile strength and elongation, were measured by an Instron testing machine with a strain gauge meter.

Results and Discussion

Figure 1 shows X-ray diffraction pattern (a) and DSC curve (b) of the cast composite bulk glass of 2 mm in diameter containing 15 vol.% ZrC, together with the date of $Zr_{55}Al_{10}Ni_5Cu_{30}$ glassy alloy. It is confirmed in Fig. 1(a) that the composite material consists of Zr-based glassy and fcc-ZrC phases and does not contain any other phase. The Zr-based multicomponent alloy has a high glass-forming ability enough to form an amorphous phase even in coexistence with ceramic dispersoids. The coincidence of

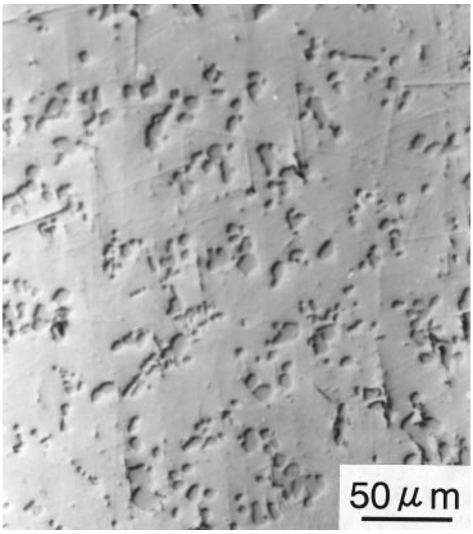

Figure 2. Optical micrograph of transverse cross-section of the cast glassy $Zr_{55}Al_{10}Ni_5Cu_{30}$ composite material containing 15 vol.% ZrC.

glass transition (T_g) and crystallization (T_x) temperatures between the composite material and the $Zr_{55}Al_{10}Ni_5Cu_{30}$ glassy alloy (see Fig. 1(b)) indicates that the whole additional graphite was combined with Zr metal during arc-melting to form the ZrC phase. Fig. 2 shows an optical micrograph of transverse cress-section of the cast composite bulk containing 15 vol.% ZrC. The ZrC particles of ~10 μm size are homogeneously dispersed and neither pores nor voids are seen. Although the arc-melting is a convenient mixing method, it also has a risk of inhomogeneous dispersion of the filler. It is presumed that the high reactivity stimulates the wettability and bonding between the glassy and the ZrC phases, and enables the homogenized dispersion of ZrC in the glassy phase because the reaction can remove agglomeration of graphite particles themselves.

The homogeneous dispersion of ZrC particles into the Zr-based glassy phase is expected to enhance mechanical properties. Fig. 3 shows compressive stress-strain (S-S) curves of the composite bulk alloys containing of 7.5 vol.% and 15 vol.% ZrC, together with the data of the $Zr_{55}Al_{10}Ni_5Cu_{30}$ bulk glassy single phase alloy. As seen in the S-S curve of the $Zr_{55}A_{10}Ni_5Cu_{30}$ glassy alloy, the amorphous alloy deforms elastically and fractures on a maximum shear plane without distinct plasticity [7]. On the other hand, the composite glassy alloys have enhanced values of Young's modulus, fracture strength and plastic elongation after yielding. The Young's modulus E increases with increasing volume fraction V_f of ZrC, i.e., 101 GPa at 0%V_f, 109 GPa at 7.5%V_f and 121 GPa at 15%V_f. The fracture strength σ_f and plastic strain ϵ_p also increase with an increase of V_f, e.g., 1836 MPa and ~0% at 0%V_f, 1996 MPa and 1.4% at 7.5%V_f, and 2060 MPa and 4.5% at 15%V_f. It is noted that the ϵ_p is remarkably improved. After yielding, the composite alloy still endures and deforms at a nearly constant flow stress, accompanying with the generation of a number of slip steps. Fig. 4 shows an optical micrograph of the alloy containing 15 vol.% ZrC subjected to plastic deformation up to 4.5%. A number of slip steps and their crossing are seen only for the composite alloy. The improvement of mechanical properties is due to the restraint of slipping on one maximum shear plane by ZrC particles. Fig. 5 shows an external appearance of the sample containing 15 vol.% ZrC subjected to final fracture. It is clearly seen that the significant large plastic deformation for the composite glassy alloy enables a plastic buckling deformation that has not been observed in deformation behaviors of amorphous alloys.

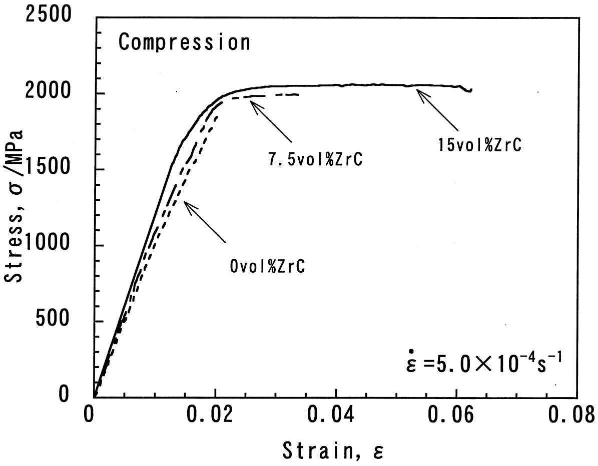

Figure 3. Compressive stress-strain curves of the cast glassy $Zr_{55}Al_{10}Ni_5Cu_{30}$ composite materials containing various volume fractions of ZrC at a strain rate of 5.0×10^{-4} s^{-1}: 0 vol.%(- - - - -), 7.5 vol.%(– – – – –) and 15 vol.%(——).

The synthesis of the glassy $Zr_{55}Al_{10}Ni_5Cu_{30}$ composite materials containing ZrC particles has previously been reported [10]. The previous composites were prepared from the mixture of the master ingot of the four metals and ZrC particles. And the improvement of mechanical properties was also recognized, though the degree of the increases in strength and ductility are much lower than those of the present material. That is the compressive plastic elongation of the previous alloy was about 0.5%, being much lower than 4.5% for the present alloy. The improvement may be due to the more homogenized dispersion of the ZrC dispersoids and the increase of mechanical/chemical bonding between the matrix and the ZrC by use of the in-situ reaction between Zr metal and graphite. The

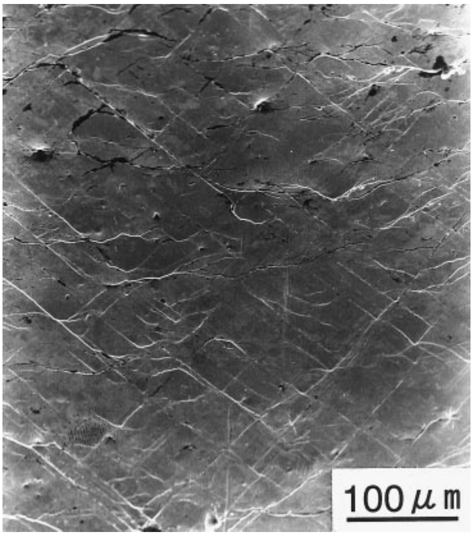

Figure 4. Scanning electron micrograph of outer lateral surface of the cast glassy $Zr_{55}Al_{10}Ni_5Cu_{30}$ composite material containing 15 vol.% ZrC subjected to 4.5% plastic elongation. A number of shear bands occur crosswise and interfere with each other.

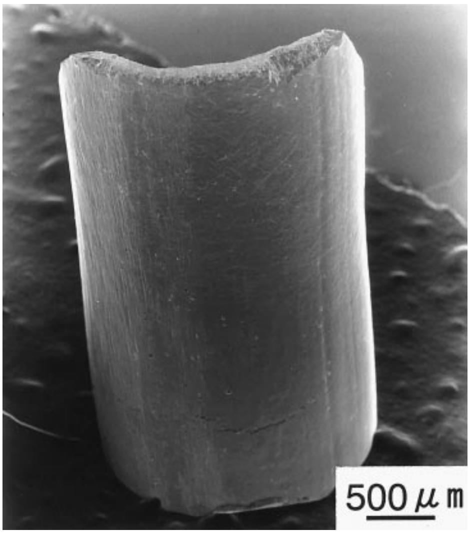

Figure 5. Scanning electron micrograph of the external appearance of the cast glassy $Zr_{55}Al_{10}Ni_5Cu_{30}$ composite material containing 15 vol.% ZrC subjected to 4.5% plastic elongation. The ZrC particles contribute to the large plastic elongation which causes a buckling deformation (see the curved outline).

present results indicate that the synthesis of composite glassy alloys by using the in-situ reaction can be developed as a production process of bulk glassy alloys with high strength and good ductility.

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