Structural Relaxation and Crystallization of a Zr$_{44}$Ti$_{11}$Cu$_{9.8}$Ni$_{10.2}$Be$_{25}$ Bulk Metallic Glass

Kwang Seok Lee$^{1,2,*}$, Hyun-Joon Jun$^{3}$, Dae Woo Kim$^{3}$, Jürgen Eckert$^{4}$ and Young Won Chang$^{2,3}$

$^1$IFW Dresden, Institute for Complex Materials, P.O. Box 270116, D-01171 Dresden, Germany
$^2$Center for Advanced Aerospace Materials, Pohang University of Science and Technology, Pohang 790-784, South Korea
$^3$Department of Materials Science and Engineering, Pohang University of Science and Technology, Pohang 790-784, South Korea

The influence of annealing on the structural changes and the room temperature mechanical properties of a Zr$_{44}$Ti$_{11}$Cu$_{9.8}$Ni$_{10.2}$Be$_{25}$ bulk metallic glass has been investigated. The structural evolution upon relaxation or crystallization after annealing at a temperature within the supercooled liquid region was studied by thermal analysis, x-ray diffraction, transmission electron microscopy, extended x-ray absorption fine structure and dilatometer measurements. The effects of structural relaxation and nanocrystallization on the mechanical properties were also examined by hardness and compression tests using specimens annealed for various times. The apparent disappearance of plastic strain was found to be due to embrittlement induced by considerable crystallization of the amorphous phase.

(Received November 24, 2006; Accepted April 2, 2007; Published June 25, 2007)

Keywords: bulk metallic glass, annealing, structural relaxation, crystallization, supercooled liquid region

1. Introduction

For more than a decade a lot of alloy systems showing excellent glass-forming ability with critical cooling rates less than 10 K·s$^{-1}$ have been developed. Among them, Zr-based bulk metallic glasses have especially attracted great interest due to their excellent mechanical properties in terms of strength, hardness, elastic response and fatigue at room temperature. In addition, these alloys also exhibit enhanced ductility and good formability during homogeneous viscous flow within the supercooled liquid state, enabling near-net-shape fabrication by conventional mold casting followed by warm deformation and possibly promising various applications as structural materials. These Zr-based metallic glasses show, however, an easy tendency to crystallize when annealed or deformed for considerable time in the supercooled liquid region even below the crystallization temperature, which affects many different physical properties of the material. It has also been reported recently that significant changes of physical properties occur in terms of flow behavior, magnetic and electrical properties and especially embrittlement characteristics due to structural relaxation followed by nanocrystallization, which can be viewed as a natural phenomenon exhibited in non-equilibrium amorphous alloys. It is, thus, indispensable to understand the relationship between the annealing treatment in the supercooled liquid region and the mechanical properties in order to provide feasible forming conditions in terms of processing temperature, strain rate and annealing time.

The major tools normally used to examine amorphous and nanocrystalline structures are thermal analysis for revealing the glass transition using differential scanning calorimetry (DSC) and direct structure observation by high-resolution electron microscopy (HREM). The glass transition endotherm observed via thermal analysis can provide valuable information about the concentration of free volume. Thermal analysis, however, has its own limitations with respect to structural relaxation because of many assumptions about the relation between the height of the endotherm and the free volume concentration. HREM has also some drawbacks in terms of sample preparation and structural analysis for an entire specimen. To circumvent or compensate these shortcomings, various analysis techniques have been introduced, such as positron annihilation spectroscopy, small-angle neutron scattering, high-energy x-ray diffraction, in-situ diffraction using synchrotron radiation, three-dimensional atom probe, nuclear magnetic resonance, and so on. Furthermore, the EXAFS technique and dilatometer measurements are believed to be useful tools for examining the change of the atomistic-scale structure. Even though the experimental information from the latter gives only the correlation between intrinsic materials properties and the atomistic-scale structural change, the former shows its ability to investigate a short-range order with a very small measurement range less than nm.

We have, therefore, attempted in this study to report on the effect of annealing on structural rearrangements and room temperature mechanical properties of a Zr$_{44}$Ti$_{11}$Cu$_{9.8}$Ni$_{10.2}$Be$_{25}$ bulk metallic glass because most of the structural engineering applications require materials with mechanically improved properties. Microstructural changes such as structural relaxation and crystallization were thoroughly characterized by differential scanning calorimetry (DSC), x-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), extended x-ray absorption fine structure (EXAFS) and dilatometric measurements. Maximum strength and hardness measurements as a function of annealing time were also evaluated. These results will be helpful to confirm the optimum pre-annealing time for structurally relaxed Zr$_{44}$Ti$_{11}$Cu$_{9.8}$Ni$_{10.2}$Be$_{25}$ bulk metallic glass specimens.

2. Experimental Procedures

Plate-shape ingots of Zr$_{44}$Ti$_{11}$Cu$_{9.8}$Ni$_{10.2}$Be$_{25}$ bulk me-
tallic glass with 2 mm thickness were supplied by Liquid-metal Technologies Inc. To obtain isothermal heat flow curves as a function of time, the as-received amorphous alloy was annealed using a TA Instruments 2920 differential scanning calorimeter (DSC) under purified argon atmosphere. The temperature was raised first to the pre-set temperature within the supercooled liquid region at a heating rate of 100 K min⁻¹ and then kept isothermally until exothermic peaks were observed, as shown in Fig. 1. To investigate the effect of annealing on structural relaxation as well as crystallization, the Zr₄₄Ti₁₁Cu₈Sn₁₀Ni₂Be₂₅ samples were isothermally annealed at 688 K for various times between 5 min and 120 min and then characterized by constant-rate heating DSC measurements employing a heating rate of 20 K min⁻¹ in an argon atmosphere and by XRD patterns obtained at the 10C1 beamline of the Pohang Accelerator Laboratory (PAL), respectively.

The microstructural changes resulting from the annealing treatments were also observed in detail using a Philips CM30 high resolution TEM (HRTEM) with an accelerating voltage of 300 kV. To obtain evidence of structural relaxation, extreme care has been taken to achieve an optimum uniform thickness of about 20 μm for extended x-ray absorption fine structure (EXAFS) measurements in transmission mode from the annealed specimens. Zr K-edge (17.998 keV) EXAFS spectroscopy was measured at the 7C beamline of the PAL where the beam intensities of both incident (I₀) and transmitted (I) beams were measured within an ionization chamber filled with a mixed gas of 50% N₂–50% Ar. The linear expansion due to structural rearrangement was also measured on rectangular samples with a dimension of 2 x 2 x 50 mm³ by using a Theta Dilatronic VIII dilatometer.

To investigate the effect of structural changes on the mechanical properties, a series of compression tests has been carried out using a computer controlled electro-mechanical testing machine (INSTRON 1361) with an initial strain rate of 1 x 10⁻³ s⁻¹. The samples for compressive deformation were prepared as rectangular-shape bars with a the cross section of 2 x 2 mm² and a height of 4 mm, which were electrically discharge machined and then carefully polished. Hardness measurements were also performed on the previously annealed specimens embedded in resin and polished.

Fig. 1 Isothermal DSC traces of the amorphous Zr₄₄Ti₁₁Cu₈Sn₁₀Ni₂Be₂₅ alloy measured at different temperatures within the supercooled liquid region.

3. Results and Discussion

An isothermal DSC trace recorded at 688 K is presented in Fig. 1. Two exothermic peaks indicate that two different events of structural changes occur during annealing. The onset times of the first and the second exothermic peaks were assumed to be the times for each step of the structural changes. Based on these isothermal DSC results, a number of samples were then prepared through various annealing treatments with subsequent quenching in brine, e.g. the samples were annealed prior to the first exothermic peak (less than 10 min annealing), prior to the second exothermic peak (between 15 min and 30 min of annealing), and the beyond the start of the second exothermic peak (more than 30 min annealing), respectively.

Figure 2 shows the XRD patterns of the samples annealed for various times at 688 K together with the pattern for the as-quenched bulk metallic glass. The XRD profiles for the specimens annealed for 15 min or less in Fig. 2(a) exhibit two broad diffraction maxima without sharp Bragg peaks, as it is typical for amorphous materials. The width of the first maximum of the annealed specimens can be, however, observed to become narrower by Δθ = 0.08° than that of the as-received sample, with θ representing the half value of the maximum peak width. This value of Δθ implies, in turn, a decrease of the free volume concentration due to structural relaxation. The XRD pattern of the specimen annealed for 45 min exhibits, on the other hand, two very small split peaks developed within the first broad diffraction maximum, as observed in Fig. 2(b). These peaks can be seen more clearly in the specimens annealed for more than 60 min, and were confirmed to represent an icosahedral phase. A similar result has already been reported for another Zr₄₄Ti₁₁Cu₈Sn₁₀Ni₂Be₂₅ BMG where an icosahedral phase forms from the amorphous matrix as an intermediate crystallization product between an amorphous single phase and a multiphase crystalline phase mixture containing nanocrystalline phases such as CuZr₂ and Be₂Zr.³⁵

Figure 3 shows the continuous heating DSC curves (heating rate 20 K min⁻¹) of the annealed specimens and the results obtained from these DSC curves are summarized in Table 1. The as-received monolithic Zr₄₄Ti₁₁Cu₈Sn₁₀Ni₂Be₂₅ BMG exhibits a wide supercooled liquid region (ΔT = Tₐ - Tₐ) of 129 K between the glass transition onset temperature (Tₐ) of 628 K and the crystallization onset temperature (Tₐ) of 757 K. The crystallized volume fraction Vf is associated with the area of the exothermic peaks for the annealed specimens and can be determined by the following equation:

\[ V_f = \frac{\Delta H_{\text{ex}} - \Delta H_{\text{sp}}}{\Delta H_{\text{exm}}} \times 100 \% , \]

with \( \Delta H_{\text{ex}} \) and \( \Delta H_{\text{sp}} \) representing the enthalpies for the as-received and pre-annealed specimens, respectively. The enthalpies for the first exothermic peak are observed to decrease continuously as the annealing time increases, caused by an increase in the volume fraction of crystals during this period.⁴² It is interesting to note that increasing isothermal annealing time not only results in the decrease in the area of first exothermic peak, but also induces a
significant decrease in the crystallization onset temperature ($T_{x,\text{onset}}$). As described in Table 1, $T_g$ only weakly increases upon annealing, while $T_{x,\text{onset}}$ of the first exothermic peak is drastically shifted from 757 K for the as-received specimen to 724 K for the 120-min annealed counterpart. The second exothermic peak, generally observed at temperatures above 773 K, is still present for the specimens annealed for 45 min or longer, which may have a certain relation to the appearance of the two split peaks in the XRD patterns. These observations suggest that the precipitation of the metastable icosahedral phase probably occurs upon annealing for more than 45 min.

Figure 4 shows HRTEM images and diffraction patterns obtained after annealing for 30 and 60 min at 688 K. As shown in Fig. 4(a), the specimen annealed for 30 min at 688 K exhibits a typical amorphous structure without any sign of lattice fringes. The halo rings from the Fourier transform in the inset of Fig. 4(a) also clarify that this annealed specimen is amorphous without any indication for crystallization. This suggests that the first exothermic peak of the isothermal DSC trace at 688 K is not associated with nanocrystallization but may be caused by structural relaxation or phase separation. This interpretation is also consistent with the absence of sharp Bragg peaks in the XRD pattern after 30 min annealing (Fig. 2). Some crystalline phases are observed in the HRTEM images of the sample annealed for 60 min at 688 K (Fig. 4(b)). The Fourier transform of the sample annealed for 60 min is composed of typical 5-fold points implying the appearance of a quasicrystalline icosahedral phase in the amorphous matrix. This observation as well as the appearance of sharp Bragg peaks in the XRD pattern for the 60 min annealed specimen gives evidence for nanocrystallization of an icosahedral phase, which corresponds to the second exothermic peak of the isothermal DSC trace recorded at 688 K.

To identify the atomic-scale structural redistribution of these BMG specimens upon annealing qualitatively, EXAFS measurements have been performed. The EXAFS signals were processed by a cubic spline method originally developed by the FEFF research group at the University of Washington\(^4\) to obtain normalization and background removal. The extracted EXAFS oscillation functions, $C_3 \frac{\zeta(k)}{k^2}$, were then transformed with the weighting factor 2, $\frac{\zeta(k)}{k^2}$, to emphasize the information in the high energy region. Figure 5 can eventually be extracted by the Fourier transforms (FTs) from $\frac{\zeta(k)}{k^2}$ with a Hanning window in the range between 0.195 and 1.03 nm to reduce the effect of truncation. The $R_p$ values of the main peak for each FT curve are positioned between 0.279 and 0.288 nm providing the phase-shifted distances of the first shells between Zr atoms. The Fourier transformed plot of the as-quenched amorphous sample shows partial overlap between the main peak around 0.288 nm and the right-nearest radial distribution peak around 0.350 nm, which is envisaged as wide distribution of the distances among the constitutive elements. As the annealing time at 688 K increases to 15 min, the $R_p$ value obviously decreases from 0.288 to 0.279 nm caused by the effect of free volume redistribution\(^4\) even though the overlap between the above-mentioned two peaks is still
Ausanio et al. proposed that this free volume redistribution leads to an optimized homogeneity of the sample, which directly means concurrent structural relaxation of the bulk metallic glass after the early stage of annealing at the mid-temperature within the supercooled liquid region. Such a slight decrease of the interatomic distances between the main constituent atoms during structural relaxation has also been reported for another alloy system. The \( R_p \) values for the main peak saturate at 0.279 nm after 15 min annealing implying a saturation of structural relaxation after 15 min of annealing at 688 K. On the other hand, both the continuous increase of main radial distribution peak height with increasing annealing time and the separation of the overlap between the main and the right-nearest peaks for the specimen annealed for 45 min at 688 K could give evidence for a distinct modification of the local environment around the Zr absorption atom, which can be attributed to structural reordering or crystallization of the metallic glass after annealing.

The change of the free volume concentration was confirmed by dilatometric measurements conducted with a heating rate of 10 K/min, as exemplified in Fig. 6. Below 573 K, the rate of change in linear expansion continuously increases with increasing temperature. However, the change in linear expansion fluctuates between 573 and 623 K and then decreases drastically between the glass transition temperature \( T_g \) and a mid-temperature of about 700 K within the supercooled liquid region. A similar result has also been reported by Shek et al. even though the temperature for the sudden drop of \( \Delta \lambda \) is higher in their report due to the higher heating rate (16 K/min) used for the measurement. These fluctuations and the sudden decrease of the length change are clearly attributed to the structural relaxation indicating a significant decrease in free volume concentration within the aforementioned temperature span including the pre-annealing temperature (688 K) applied in this study.

To estimate the average nearest-neighbor distance \( r_0 \), the measurement of the length change can be applied into a classical solid state theory. The relation between thermal expansion coefficient \( \alpha \), Young’s modulus \( E \), and \( r_0 \) can be expressed by the following equation:

\[
 r_0 = \left( \frac{m+n+3}{12E\alpha} \right)^{1/3},
\]

where \( k \) is Boltzmann’s constant and the constants \( m \) and \( n \) are typical parameters for a Lennard-Jones potential. From the experimental result obtained by dilatometry, the average thermal expansion coefficient \( \alpha \), was determined to be \( 8.5 \times 10^{-6} \text{ K}^{-1} \) between room temperature (300 K) and the glass transition temperature (628 K). The parameters \( m \) and \( n \) are assumed as 7 and 14 for a typical metallic glass, respectively. The average nearest-neighbor separation \( r_0 \) was then obtained as 0.32 nm when inserting these constants into

| as-received | 628 | 757 | 763 | 102.0 | — |
| 688 K - 5 min | 629 | 753 | 759 | 99.4 | 2.5 |
| 688 K - 10 min | 630 | 750 | 756 | 93.7 | 8.1 |
| 688 K - 15 min | 629 | 749 | 755 | 91.3 | 10.5 |
| 688 K - 30 min | 632 | 742 | 748 | 75.7 | 25.8 |
| 688 K - 45 min | 629 | 732 | 738 | 60.0 | 41.2 |
| 688 K - 60 min | 635 | 730 | 737 | 48.8 | 52.2 |
| 688 K - 120 min | 633 | 724 | 733 | 47.4 | 53.5 |
eqn. (2). It should be noted here that the $R_p$ value obtained by EXAFS has its own limitations to analyze the distance between atoms quantitatively because the peaks are shifted to lower radial distance values. However, it is difficult to correct the phase-shifted $R_p$ values because it is impossible to construct a proper model for this quinary BMG system composed of five elements for extracting the first shell information by the inverse Fourier transformation. It is also impossible to distinguish the role of each possible atom pair combination on the determination of $r_0$ indicating just a macroscopically averaged quantity. 47) Regardless of the above-mentioned limitations, the phase-shifted distance of the first shells between the Zr atoms ($R_p$) derived from EXAFS analysis corresponds well with the average nearest-neighbor separation ($r_0$) deduced from dilatometry considering the ‘phase-shift’ to lower R-distances. This may lead to a realization that EXAFS is an attractive route to investigate the atomistic-scale structural rearrangements, being especially capable of quantitative characterization for simple binary and ternary BMG systems.

A series of compression tests with an initial strain rate of $1 \times 10^{-3}$ s$^{-1}$ was performed in order to examine the effects of structural rearrangement and nanocrystallization on the mechanical properties at room temperature. The results are given in Fig. 7 where the curves are shifted consecutively along the strain axis by an increment of 0.005 for clarity. It is clear that the deformation behavior of the annealed samples can be divided into two different modes by means of the existence of plastic strain after linear stress-strain relationship. The samples annealed for not more than 15 min generally promote several % of plastic strain. The as-received BMG exhibits a high tensile strength of more than 1900 MPa with more than 6% total engineering strain. The deformation behavior appears to be still similar to that of the as-received BMG with nearly the same total engineering strain for annealing times up to 10 min, although the maximum strength slightly decreases. The maximum engineering strain of 8.4% was achieved in this study for the specimen annealed for 15 min at 688 K. It is interesting to note here that considerable plastic strain is maintained after structural relaxation by annealing for less than 30 min in the present study, which is contradictory to the well-known concept that embrittlement is generally observed as an effect of annealing-induced free volume annihilation during structural relaxation. 23,48) This result is in line with the negligible effect of structural relaxation caused by short-time annealing on the amount of plastic deformation as long as a critical minimum concentration of free volume still exists in the relaxed metallic glass, as it was already reported by other researchers. 49,50) The deformation mode is noted to become brittle without any microplasticity for the specimens annealed for 30 min or more implying a detrimental effect of annealing-induced nanocrystallization on the room temper-

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**Fig. 5** The modulus of the FT transformed from EXAFS spectra for both as-received and several annealed specimens subjected to different annealing times at 688 K.

**Fig. 6** The change of $\Delta l$ measured by dilatometry with a continuous heating rate of 10 K·min$^{-1}$.

**Fig. 7** Compressive engineering stress-strain curves of the samples annealed for various times at 688 K.

**Fig. 8** Changes in the maximum stress and Vickers hardness as a function of annealing time at 688 K.
ature plasticity of the Zr$_{44}$Ti$_{11}$Cu$_{9.8}$Ni$_{10.2}$Be$_{25}$ bulk metallic glass. Specifically, the specimen annealed for 60 min shows a drastic decrease of its maximum strength down to 1327 MPa implying an annealing-induced embrittlement due to a long exposure time in the supercooled liquid region, during which the two onset exothermic events were passed through in the isothermal DSC curve shown in Fig. 1.

The variations of Vickers hardness and the maximum stress are plotted in Fig. 8 for different annealing times and the results are summarized in Table 2. It can be clearly observed that the hardness of the structurally relaxed samples reaches a first plateau around 570 HV before reaching the first exothermic event. The presence or increase in the fraction of nanocrystalline precipitates after structural relaxation and crystallization, on the other hand, appears to raise the hardness after annealing for more than 45 min. The hardness of structurally relaxed samples has recently been reported to increase, because the excess free volume in the glass is annealed out, which enhances the atomic bonding strength after annealing. The hardness of the structurally relaxed samples shows, however, a relatively weak dependence on the short-term annealing at 688 K when compared to that of partially nanocrystallized specimens obtained after long-term annealing, indicating that a dispersion of nanocrystalline phases in the amorphous matrix plays a major role in the increase of the hardness.

It is well known that highly localized deformation within few shear bands is responsible for the limited plasticity of these BMGs, which prevents them to be utilized in the fields of industrial application. To enhance the room temperature plasticity of the BMGs while maintaining their high maximum strengths of around 2000 MPa, fabricating BMG composites with a second phase is mostly accepted as an effective method to circumvent catastrophic fracture without any plastic strain. Furthermore, the hardness was found to increase with increasing annealing time, which in turn indicates that nanocrystals embedded in the amorphous matrix may play a primary role for increasing the hardness.

### Acknowledgements

This work was partly supported by both the 2005 National Research Laboratory (NRL) Program of the Korea Ministry of Science and Technology and the Korea Research Foundation Grant funded by the Korean Government (KRF-2006-214-D00204). The experiments at PLS were also supported in part by MOST and POSTECH. One of the authors (K. S. Lee) would also like to thank Dr. C. P. Kim of Liquidmetal Technologies, Inc. for supplying the BMG samples used in this study.

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