# EXAFS AND DILATOMETRIC ANALYSIS OF STRUCTURAL REARRANGEMENT AFTER ANNEALING IN A Zr-BASED BULK METALLIC GLASS

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**Abstract.** The atomic-scale structural rearrangement of a $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk metallic glass has been investigated in relation to the duration of annealing time at 430 °C by applying both dilatometric measurements and extended X-ray absorption fine structure (EXAFS) spectroscopy. The phase-shifted distance between first shells of Zr atoms ($R_p$) was 2.95 Å by EXAFS and the average nearest-neighbor distance $r_0$ calculated from dilatometry was 3.2 Å. From the results, the progress of structural relaxation caused by the annihilation of free volume could be revealed as the annealing time increases.

## 1. INTRODUCTION

There has been increasing interest in bulk metallic glasses (BMGs) since these alloys show unique mechanical properties such as ultra-high strength and a large elastic limit, which are quite desirable for application as structural materials [1]. BMGs exhibit also enhanced ductility and good formability within the supercooled liquid state [2,3]. However, Zr-based metallic glasses show a tendency to structural relaxation and/or crystallization when they are exposed for considerable time in the supercooled liquid region, even below the crystallization temperature. This leads to changes of the original properties of monolithic BMGs [4,5]. Therefore, it is important to understand the effect of annealing within the supercooled liquid region on the structural rearrangement of BMGs. In this regard, the structural rearrangement of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ (Vit-1) has been investigated using extended X-ray absorption fine structure (EXAFS) analysis and dilatometry.

## 2. EXPERIMENTAL PROCEDURES

Bulk amorphous alloys, originally developed at the Caltech and supplied by Liquidmetal Technologies Inc., were prepared by casting as ingot with the nominal composition of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$. Three pre-annealing times, i.e. 8, 13, and 18 min at 430 °C were determined based on the isothermal DSC result reported elsewhere [6] to investigate the effect of annealing time on structural changes. EXAFS data utilizing the synchrotron radiation of the Pohang Light Source (PLS) were obtained to investigate structural changes after annealing. The Zr K-edge (17.998 keV) EXAFS spectroscopy was carried out at the 7C beamline at the Pohang Accelerator Laboratory (PAL). The incident ($I_0$) and transmitted ($I_t$) beam intensities were measured within an ionization chamber filled with a mixed gas of 50% $N_2$ – 50% Ar for EXAFS experiments. The linear expansion was also measured by dilatometry using as-received Vit-1 BMG specimen with rectangular shape cross-section
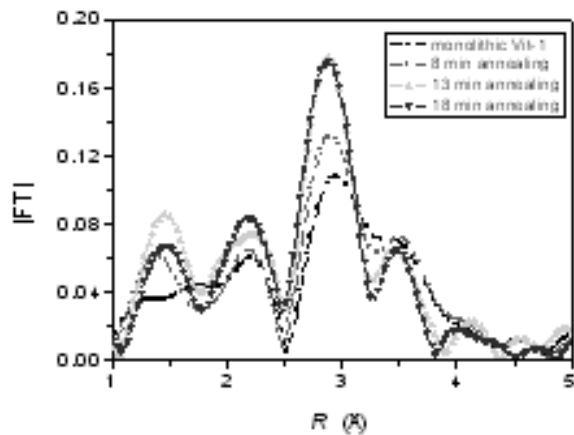
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**Fig. 1.** Fourier transformed plots of the EXAFS oscillation of Vit-1.



**Fig. 2.** The $R_p$ values and |FT| are plotted in terms of annealing times.
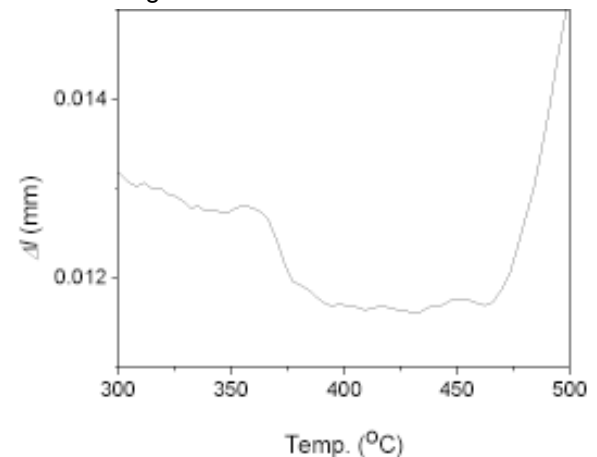


**Fig. 3.** The dilatation curve for Vit-1 by continuous heating.

(3×3 mm) and 50 mm in length machined by an electrical discharge machine (EDM).

## 3. RESULTS AND DISCUSSION

The main focus of the EXAFS measurements for multiphase BMG is qualitative evaluation of the atomic-scale structural rearrangement of the specimens upon annealing. The $\chi$ data, defined as the EXAFS oscillations, were extracted from the EXAFS result by a cubic spline method originally developed by the FEFF research group at the University of Washington [7]. The EXAFS oscillation functions with the weighting factor 2, $k^2\chi$, were then chosen to emphasize the information in the high energy region. As shown in Fig. 1, radial distribution function (RDF) can then be extracted by the Fourier transforms (FTs) from $k^2\chi$ for the specimens annealed at 430 °C with a Hanning window in the range between 3.4 and 11.6 Å$^{-1}$ to reduce the effect of truncation. The $R_p$ values of the main peak for each FT curve are positioned between 2.89 and 2.95 Å providing the phase-shifted distances of first shells between Zr atoms. The Fourier transformed plot taken from the as-quenched amorphous sample shows a typical disordered structure with many ambiguous radial distribution peaks as well as the main peak around 2.95 Å. It is worth noting here that the $R_p$ value is directly related to the free volume concentration [8]. As the annealing time at 430 °C increases to 13 min, the $R_p$ value decreases from 2.95 to 2.89 Å. This is
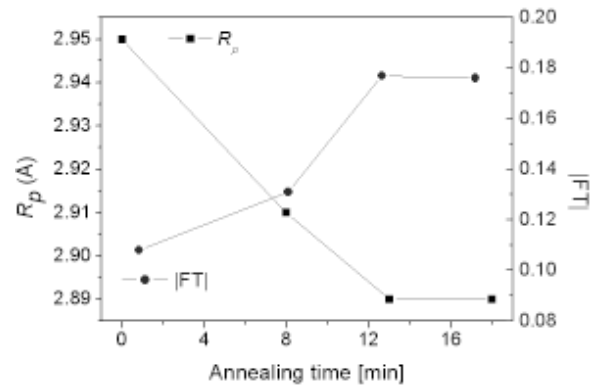
caused by structural relaxation in the form of short-range ordering and concurrent decrease in free volume concentration with several obvious distances between nearest neighbor atoms and the absorbing Zr atom. The $R_p$ value saturates after 13 min annealing implying a saturation of the structural relaxation. It is interesting to note here that the amplitude of main peaks (|FT|s) in the specimens annealed for 13 min and more are considerably increased when compared to the as-received counterpart. Another significant difference in RDF between as-received and annealed samples is the gradual development of the peaks at around ~3.5 Å upon increasing annealing time. These seem to be general trends for the crystallization of amorphous alloys after proper annealing [9]. The authors recently reported actual occurrence of complex crystallizations indexed as $Zr_2Cu$, $Be_2Zr$, and unlabelled diffraction peaks in the specimens an-

nealed for 13 min and more by X-ray diffraction elsewhere [10]. Fig. 2 illustrates the variation of the $R_p$ value of the main peak related to the distance between the first shells of Zr atoms and |FT| of the main peak for the specimens annealed at 430 °C.

The concentration change of free volume was also confirmed by dilatometric measurements. Fig. 3 shows the total length change of a monolithic Vit-1 BMG specimen plotted as a function of temperature with a heating rate of 10 °C/min. The linear expansion ($\Delta l$) drastically decreases in the temperature range from 350 to 380 °C during continuous dilatometric analysis. This clearly indicates the structural relaxation around the glass transition temperature ($T_g$). This drastic change is closely related to the annihilation of excess free volume in the sample, which mainly results in the appearance of atomic-scale short-range order [11].

The average nearest-neighbor distance $r_0$ can be described by the following equation:

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

where $E$ is Young's modulus, $k$ is Boltzmann's constant, $\alpha$ is the average thermal expansion coefficient determined as $8.5 \cdot 10^{-6}$ /K between room temperature and $T_g$, and the constants $m$ and $n$ for a Lennard-Jones potential are taken as 7 and 14, typical for metallic glasses [12,13]. When inserting these constants into Eq. (1), the calculated average nearest-neighbor separation $r_0$ is 3.2 Å.

It should be noted here that the obtained $R_p$ values by EXAFS in this study are phase-shifted toward lower than actual interatomic distance since it is difficult to correct phase-shifted $R_p$ values by means of inverse Fourier transformation of RDF in Fig. 1. This is due to the fact that there are too many interatomic combinations in this quinary BMG system, which hampers proper local atomic structure modeling. The $r_0$ calculated by classical solid state theory also has a limitation because $r_0$ is just an 'averaged mean' value which reckons without the role of each possible atom pair combination [13]. Considering the 'phase-shift' to lower $R$-distances, however, the phase-shifted distance of the first shells between Zr atoms ($R_p$) from EXAFS analysis corresponds reasonably well with the average nearest-neighbor separation, $r_0$. Therefore EXAFS technique can be considered as a useful tool for statistical averaging of the atomic-scale structural rearrangements.

## 4. SUMMARY

The influence of annealing at 430 °C on the atomic-scale structural rearrangement of a $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk metallic glass was investigated. Thermally induced structural relaxation was observed in the annealed specimens due to the annihilation of free volume concentration. Formation of the annealing-induced crystalline phases is also supposed by both the increase of amplitude in the main peak of RDF and the distinct development of another peak at around ~ 3.5 Å upon increasing annealing time. The phase-shifted distance of the first shells between Zr atoms ($R_p$) determined by EXAFS and the average nearest-neighbor distance $r_0$ obtained by using the results from dilatometry were determined as 2.95 Å and 3.2 Å, respectively. We can conclude that both EXAFS and dilatometry are useful tools to reveal atomic-scale structural rearrangements considering the 'phase-shift' toward the direction of decreasing interatomic distance.

## ACKNOWLEDGEMENTS

## REFERENCES

[1] H. A. Bruck, T. Christian, A. J. Rosakis and W. L. Johnson // *Scripta Metall. Mater.* **30** (1994) 429.

[2] Y. Kawamura, T. Shibata, A. Inoue and T. Masumoto // *Acta Mater.* **46** (1998) 253.

[3] K. S. Lee and Y. W. Chang // *Mater. Sci. Eng. A* **399** (2005) 238.

[4] J. Schroers, R. Busch, S. Bossuyt and W. L. Johnson // *Mater. Sci. Eng. A* **304-306** (2001) 287.

[5] R. C. Y. Tam and C. H. Shek // *Mater. Sci. Eng. A* **364** (2004) 198.

[6] K. S. Lee and Y. W. Chang // *Met. Mater. Int.* **11** (2005) 53.

[7] A. L. Ankudinov, B. Ravel, J. J. Rehr and S. D. Conradson // *Phys. Rev. B* **58** (1998) 7565.

[8] G. Ausanio, V. Iannotti, F. M. Granozio, C. Meneghini, M. Minicucci, F. Ricci and L. Lanotte // *J. Magn. Magn. Mater.* **242-245** (2002) 904.

[9] S. U. Kim, K. H. Kim and Y. M. Koo // *J. Alloys Compd.* **368** (2004) 357.

[10] K. S. Lee, J. Eckert, H-J. Jun and Y. W. Chang // *J. Mater. Res.*, in press.

[11] D. V. Louzguine, A. R. Yavari, K. Ota, G. Vaughan and A. Inoue // *J. Non-cryst. Solids* **351** (2005) 1639.

[12] B. Porscha and H. Neuhäuser // *Phys. Status Solidi (b)* **186** (1994) 119.

[13] C. H. Shek and G. M. Min // *Materials Letters* **57** (2003) 1229.