Microstructural investigations of bulk metallic glass using small-angle neutron scattering techniques

Vasyl Ryukhtin[1], Sergiy Bakai[2], Tae-Gyu Shin[3], Baek Seok Seong[3], Vitaliy Pipich[4],

Artem Feoktystov[4], Nelia Wanderka[5], Oleksandr Bakai[2]

[1] Nuclear Physics Institute of the CAS v.v.i., Řež 130, 250 68 Řež, Czech Republic

[2] Institute of Physics and Technology of the UAS, Kharkiv, 1 Akademichna str., 61108, Ukraine

[3] Neutron Science Division, Korea Atomic Energy Research Institute, Daedok-daero 1045, Daejeon,305-353, Republic of Korea

[4] Jülich Centre for Neutron Science JCNS-FRM II, Lichtenbergstraße 1, Garching, 85747, Germany

[5] Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, 14109 Berlin, Germany

Abstract

Bulk metallic glasses (BMG) are very attractive materials exhibiting high specific strength, decent corrosion resistance and other benefiting features due to their amorphous microstructure. However, mechanisms of mechanical properties as an issue of structure-properties relation in BMG are not so well understood as for polycrystalline materials. For example, driving force of fatigue in crystalline materials is connected to grain boundary slip and formation of dislocations *i.e.* with those structural elements, which existence in BMG is still debatable. In order to find link between mechanical properties and microstructure in BMG, researchers investigate structural heterogeneities *i.e.* clusters. Size order of the clusters and intercluster boundaries is within the resolution of small-angle neutron scattering (SANS) techniques. Here we present results of SANS and very-small-angle neutron scattering (VSANS) studies of Vitreloy 4 (Vit.4) with a chemical composition of $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$. VSANS measurements revealed the creation and growth of large micropores induced by ultrasonic vibration (USV).

Introduction

$Zr_{46.75}Ti_{8.25}Ni_{10}Cu_{7.5}Be_{27.5}$ alloy commonly referred as Vit.4 invented first by Johnson et al. [1, 2] is one of the best bulk metallic glass (BMG) formers with a distinct stability of the supercooled melt above the glass transition temperature at 603 K [3-5]. Vit.4 is one of the first BMG materials which has found its commercial application, it is used for fabrication of golf club heads. The maximum of energy is transfering to the kinetic energy of the ball in a moment of collision with the golf head due to practical absence of plastic deformation in this BMG material. The first calorimetric crystallization temperature of this BMG is at 730 K. An exceptionally extended region of the supercooled liquid phase indicates a high resistance against crystallization. Many studies have been performed to investigate this pronounced stability. It has been found that crystallization depends on the preceding thermal treatment. The crystallization at different heat treatments follows different pathways. At the end different phases are crystallized. For instance, phase separation of amorphous $Zr_{41}Ti_{14}Ni_{10}Cu_{12.5}Be_{22.5}$ (Vit.1) glass in two supercooled liquids using field ion microscopy with atom probe (FIM/AP) has been reported after heat treatment at 643 K for 15 h [6]. The atom probe revealed composition fluctuations during the phase separation and showed anti-correlated fluctuations of Ti and Be. It was also found that Zr, Cu and Ni do not participate significantly in the decomposition [6]. Phase separation of the same glass at 623 K and 643 K was confirmed by in-situ SANS measurements [7]. Droplet-like nanosized amorphous particles develop in the amorphous matrix [7]. In contrast, the Vit.4 bulk glass shows the formation of quasicrystalline phase during isothermal

annealing at the same temperature of 643 K for 6 h [8]. A detailed study of the crystallization of the Vit.4 shows that during a heat treatment below the glass transition at 573 K, even after annealing periods of up to 128 d no crystalline or quasi-crystalline phases have been detected [9]. However, the subsequent heating of Vit.4 glass leads in particular to an increasing favor of the formation of a quasi-crystalline phase which is very much depleted in Be [9, 10].

How the bulk amorphous alloys behave under plastic deformation is little known. Deformation-induced crystallization of Al-rich amorphous alloys has been observed after cold rolling [11], nanoindentation [12], high pressure torsion (HPT) [13, 14].

To detect a rearrangement of elements within the nanometer sizes (atomic short range or long range order) after deformation is not trivial using available experimental methods.

Methods of experimental and theoretical investigations of the BMG are quite different of those for polycrystalline metals due to amorphous ("shape-less") microstructure. There are few theoretical approaches for description of the BMG. For example, for description of deformation one can consider BMG microstructure as density fluctuations regions – clusters surrounded by softer phase.

SANS is quite useful non-destructive method for studying of microstructure in nano- and mesoscopic size range. It does not sensitive to surface and usually does not require any sample preparation. Therefore, SANS data are not affected by a surface and describe bulk of studied material with excellent statistics. However, data interpretation might be distorted by simplification of a fitting model.

SANS instruments were successfully used for investigation of the Zn-Ti-Cu-Ni-Be BMG microstructure, *e.g.* spinodal decomposition in was observed during in-situ measurements at annealing temperatures close to glass transition temperature T_g [15-17]. Likewise, we applied SANS for BMG samples deformed in plastic mode in order to gain information about microstructural changes.

Samples description and deformation modes

BMG samples were cut from the rod with 3 mm diameter into 4 mm long parts. The deformation experiments are performed in air under compression stress with and without USV. The samples #01 and #03 were monotonically loaded at constant strain rates of ~10^{-4} s^{-1} at temperature close to the T_g. The samples #07 and #08 were deformed at constant loading (creep deformation) with F=750 kg (1061 MPa). The specimens #03 and #07 were deformed with ultrasound vibration (USV) of 20 kHz with amplitude of about 7 μm (see Table 1).

Table 1. Parameters of the sample treatments.

Sample	**Amplitude of USV**	**Temp., K**	$\dot{\varepsilon}$, s^{-1}	Time, s	Loading mode
#01	-	573	$7.5 \cdot 10^{-4}$	6000	constant length, the stress recorded
#03	7 μm	568	$2.5 \cdot 10^{-4}$	6000	constant length, the stress recorded
#07	7 μm	548	-	5600	constant loading at 850 kg (1061 MPa)
#08	-	548	-	6650	constant loading at 850 kg (1061 MPa)

The difference in shapes between samples treated with USV and without USV due to different fixing of the sides can be observed in Figure 1. Both edge surfaces of the specimen #08 were fixed due to large surface friction. As result, its shape after deformation is barrel-like. One edge surface of the specimen #07 was fixed while another one was free for sliding due to USV impact. Therefore, it has conical-like shape.

Specimen #07 Specimen #08

Fig. 1. Optical micrographs of $Zr_{46.75}Ti_{8.25}Ni_{10}Cu_{7.5}Be_{27.5}$ *samples #07 deformed under USV and specimen #08 deformed without USV at same temperature at T=543 K.*

SANS measurements and discussion

Pin-hole SANS measurements

The BMG samples were measured at 18 m SANS at HANARO (KAERI, Daejeon) and KWS-1 SANS [18] instruments. Deformation axis of the sample was parallel with respect to incident neutron beam. The scattering functions at low momentum transfer Q (Fig. 2) follow power-low dependences with non-integer exponent values close to -3 (Table 1). This may be evidence of fractal structure of density fluctuations in the measured size range [19].

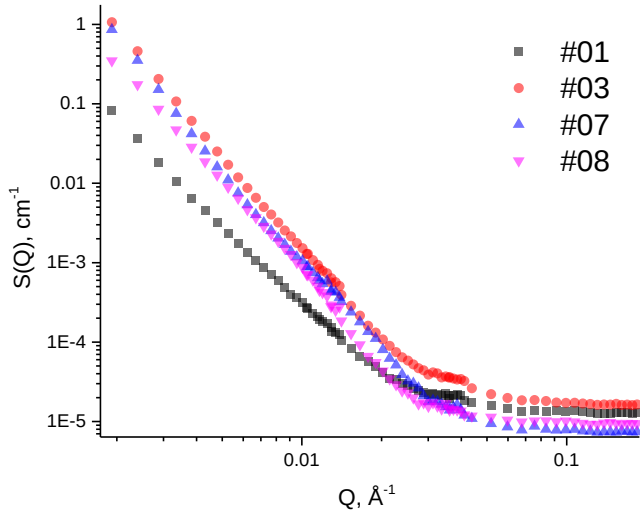

Fig. 2. Neutron scattering curves of $Zr_{46.75}Ti_{8.25}Ni_{10}Cu_{7.5}Be_{27.5}$ alloy after deformation with USV (samples #3 and #7) and without USV (samples #1 and #8).

The scattering curves in Fig. 2 of the samples (#07, #08) indicate the presence of the phase separation. The calculation shows the nanoscaled inhomogenities with radii 10 to 25 nm. The values of fitted maxima of log-normal distribution of spheres radii are summarized in Table 2.

Table 2. Fitted parameters of pin-hole SANS data.

Sample	Exponent D	R_{max}, nm	σ
#01	2.92	-	-
#03	3.01	-	-
#07	3.04	9.4	0.38
#08	2.97	24.3	0.1

VSANS measurements

Very small-angle neutron scattering (VSANS) measurements of the BMG specimens were conducted at KWS-3 instrument (JNSC, Garching) [20]. The data after treatment are shown at Fig. 3.

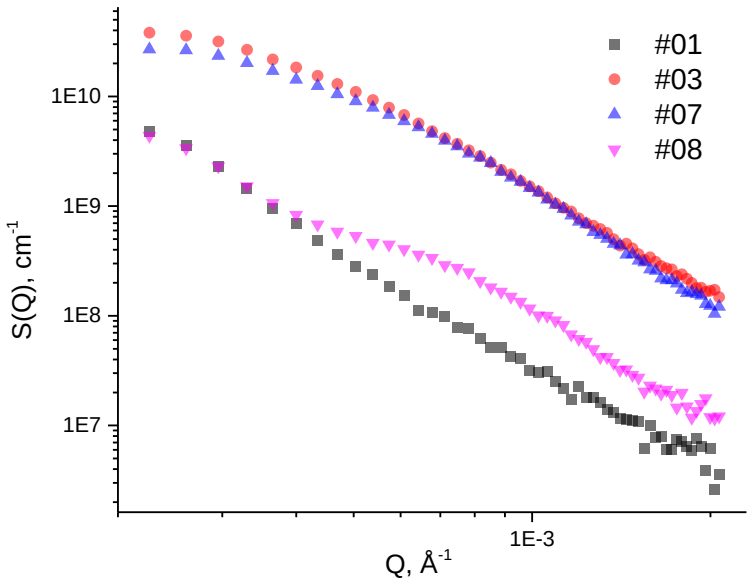

Fig. 3. Neutron scattering curves of $Zr_{46.75}Ti_{8.25}Ni_{10}Cu_{7.5}Be_{27.5}$ alloy after deformation with USV (samples #03 and #07) and without USV (samples #01 and #08) as measured by VSANS *at KWS-3.*

VSANS scattering intensities from reference sample (#01) and sample deformed without high-frequency cycling stress #08 are sufficiently much lower than from the samples (#03, #07) mechanically tested in presence of USV. Most likely this difference is given by presence of large (about few *μm*) cracks in these samples. Such cracks were described in similar material deformed with high-frequency (20 kHz) USV as coalescence of nano-crackes initiated from slip at intercluster boundaries [21]. Furthermore, the samples #08 has scattering evidence of smaller heterogeneities.
SASfit software [22] was exploited for fitting of the data using log-normal distributions of simple spheres. The example of the data fitting for sample #08 is demonstrated in Fig. 4.

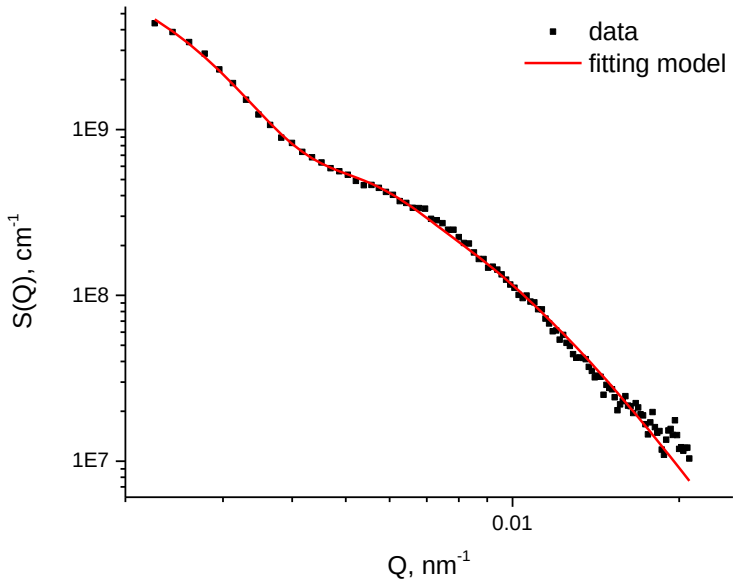

Fig. 4. VSANS data of sample #08 (squares) with fitted model of log-normally distributed of spherical particles (line).

The maximum of the obtained size distributions and width parameters are summarized in Table 3.

Table 3. Fitted parameters of the VSANS data.

Sample	**R_{max}, nm**	**σ**
#07	94	0.38
#08	103.9	0.49

VSANS scattering for two samples (#07 and #08) show on presence of about 100 nm inhomogenities (see Table 3). Usually, SANS signal is stronger in case of scattering from pores or cracks than from precipitates or density fluctuations due to higher scattering contrast. This point let us suggest that strong signal for samples treated using USV comes from the coalesced cracks. The scattering effect from smaller inhomogenities is well observable for the sample #07, but not for the samples #03, although, tales in the scattering functions from the microcracks sufficiently shadow in smaller Q region (around 10^{-3} $Å^{-1}$). These inhomogenities are supposed to be similar to those described earlier in [15-17] as the spinodal decomposition, however, in our case the inhomogenities were induced by the plastic deformation not by annealing. However, more investigations with complementary methods are necessary to find out the nature of the microstructure.

Conclusions

Pin-hole SANS and focused VSANS techniques were applied for characterization of Vit4 BMG microstructure. The observed appropriate increasing of VSANS intensity in the samples deformed with USV are proposed to be originated with presence of the merged cracks developed from intercluster boundaries. Since the structural changes are similar at the quasistatic (sample #3) and at constant loading (sample #8) we conclude that time of the USV treatment plays the decisive role in the structure rearrangements. The smaller submicrometers inhomogenities observed in the deformed BMG samples are subjected to thermally activated phase separation at deformation and obviously not depended considerably on USV treatment. Pin-hole SANS curves of the specimens has fractal region with exponent close to -3 from cluster self-similar short-range order.

Acknowledgements
The SANS results work is based upon experiments performed at the KWS-1 and KWS-3 instruments operated by JCNS at MLZ and 18 m SANS instrument at HANARO (KAERI, Daejeon).

References
[1] W.L. Johnson: Mater. Sci. Forum **225–227** (1996) 35–50, DOI:10.4028/www.scientific.net/MSF.225-227.35
[2] W.L. Johnson: MRS Bulletin **24** (1999) 2–56.
[3] T. Waniuk, J. Schroers, and W.L. Johnson, *Applied Physics Letters*, **78** (2001) 1213.
[4] T. Waniuk, J. Schroers, and W.L. Johnson, *Phys. Rev. B*, **15(8)** (2003) 1729-1734.
[5] Th. Zumkly, V. Naundorf, M.-P. Macht, Z. Metallkd **91** (2001) 901.
[6] M.-P. Macht, N. Wanderka, A. Wiedenmann, H. Wollenberger, Q. Wei, H. Fecht and S. G. Klose, Mat. Science Forum **225-227** (1996) 65-70.
[7] A. Wiedenmann, J.-M. Liu, Solid State Comm. **100** (1996) 331-335.
[8] N. Wanderka, M.-P. Macht, M. Seidel, S. Mechler, K. Stahl, J.Z. Jiang, APL **77** (2000) 3935-3937.
[9] S. Mechler, PhD Thesis, Berlin Institute of Technology, Berlin, Germany (2007).
[10] S. Mechler, N.Wanderka, M.-P. Macht, Int. J. Mat. Res. **101** (2010) 601-610.
[11] J.H. Perepezko, R.J. Hebert, R.I. Wu, Mater. Sci. Forum **386-388** (2002) 11-20.
[12] J.-J. Kim, Y. Choi, S. Suresh, A.S. Argon, Science **295** (2002) 654-657.
[13] N. Boucharat, R. Hebert, H. Rösner, R. Valiev, G. Wilde, Scripta Mater. **53** (2005) 823-827.
[14] Zs. Kovács, P. Henits, A.P. Zhilyaev, A. Révész, Scripta Mater. **54** (2006) 1733-1737.
[15] J.-M. Liu, A. Wiedenmann, U. Gerold, U. Keiderling and H Wollenberger, *J. Phys.: Condens. Matter* **9** (1997) 2731–2738.
[16] S. Schneider, P. Thiyagarajan, & W.L Johnson,. (1996). *Appl. Phys Letters* **68**, 493-495.
[17] E. Pekarskaya, J.F. Loffler, W.L. Johnson, *Acta Materialia* 51 (2003) 4045–4057.
[18] A. V. Feoktystov, et at KWS-1 high-resolution small-angle neutron scattering instrument at JCNS: current state *J. Appl. Cryst.* (2015). **48**, 61-70.
[19] E.W. Fischer, A. Bakai, A. Patkowski, W. Steffen, L. Reinhardt, Heterophase fluctuations in supercooled liquids and polymers (2002) *Journal of Non-Crystalline Solids* **307–310** (2002) 584–601.
[20] Heinz Maier-Leibnitz Zentrum et al. (2015). KWS-3: Very small angle scattering diffractometer with focusing mirror. *Journal of large-scale research facilities*, **1**, A31. http://dx.doi.org/10.17815/jlsrf-1-28.
[21] Yu. Petrusenko, A. Bakai, I. Neklyudov, S. Bakai, V. Borysenko, G. Wang, P.K. Liaw, T. Zhang, Low- and high-frequency fatique of bulk metal glasses (2011) *Journal of Alloys and Compounds* 5095, 5123-5123.
[22] I. Breßler, J. Kohlbrecher and A. F. Thünemann, *J. Appl. Cryst.* (2015). **48**, 1587-159.