Decomposition Mechanism in Supercooled Liquid Alloys

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Abstract:

We performed small-angle neutron scattering experiments on the bulk amorphous alloy $Zr_{41.2}Ti_{13.8}Cu_{12.3}Ni_{10}Be_{22.5}$ (Vit1®) and on further alloys, where the ZrTi and CuBe content have been changed, following the tie-line in the direction of $Zr_{46.8}Ti_{8.2}Cu_{7.3}Ni_{10}Be_{27.5}$ (Vit4®). The SANS data of the samples, preannealed at temperatures between 330°C and 390°C, show interference peaks giving evidence for spatially correlated arrangements of inhomogeneities. The $Q$ values of the interference peaks, $Q_{\text{max}}$, decrease with increasing annealing temperature $T_a$ and, at a given annealing temperature, with composition following the tie-line from Vit1 to Vit4. We find that, in two distinguished regimes, the data follow a relation $1/L^2 \propto T_a$ as predicted by Cahn’s theory ($L = 2\pi/Q_{\text{max}}$ is the wavelength of the decomposition), with a crossover at the glass transition temperature $T_g = 350°C$. We explain the crossover by different diffusion mechanisms below and above $T_g$. 
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I. Introduction

Since the first systematic studies on the crystallization behavior in supercooled liquids (Turnbull, 1950), many investigations have been devoted to the understanding of the thermodynamics and kinetics in various types of liquids (see, e.g., Herlach, 1994). Usually, such experiments are difficult to perform, since, in most alloys, the time scale for crystallization drops very rapidly with undercooling and is experimentally inaccessible at about 0.7 of the melting temperature.

Recently, new multicomponent glass forming systems with a high thermal stability and excellent glass forming ability were found [Drehman & Greer (1984); Inoue, Zhang & Masumoto (1990); Zhang, Inoue & Masumoto (1991); Peker & Johnson (1993)]. The critical cooling rate to bypass crystallization and to form a metallic glass is less than 100 K/s in these alloys. This value is several orders of magnitude smaller than the one of monatomic or binary metallic liquids, typically $10^7$ to $10^9$ K/s. Thus, new 'bulk amorphous alloys' can be produced with a diameter of 1 cm or more in its smallest dimension. Besides possible technical applications, the resistance of the undercooled melt to crystallization in these alloys has opened numerous opportunities to study the glass transition, thermophysical properties, and crystal nucleation kinetics in the undercooled liquids.

One of the best bulk metallic glass formers known so far, with a critical cooling rate of about 1 K/s, is the alloy Zr$_{41.2}$Ti$_{13.5}$Cu$_{12.5}$Ni$_{10}$Be$_{22.5}$ (Vit1) developed by Peker & Johnson (1993). The pathway of crystallization of this alloy has been investigated by small-angle neutron scattering after heating it into the supercooled liquid regime. A characteristic maximum of the scattering curves has been found, giving evidence for decomposition before (Schneider, Thiyagarajan & Johnson, 1996; Schneider, Thiyagarajan, Geyer & Johnson, 1998) or during (Hermann, Wiedenmann & Uebele, 1998) crystallization.

For a detailed understanding of the crystallization pathway in these Zr based bulk amorphous alloys, we have carried out further SANS studies on Vit1 as well as on the alloy Zr$_{46.8}$Ti$_{18.2}$Cu$_{7.3}$Ni$_{10}$Be$_{27.5}$ (Vit4), also developed by Peker & Johnson (1993). In
addition, we have investigated three further compositions which lie along the tie-line of Vit1 and Vit4 (replacing successively Ti by Zr and Cu by Be).

II. Experimental procedure

From all 5 compositions we have prepared 25 g ingots by arc melting a mixture of the pure elements (purity > 99.8%) in a vacuum of 10⁻³ mbar. The ingots were then remelted in a silica tube with an inner diameter of 10 mm and subsequently water quenched with a cooling rate of about 10 K/s. From these rods, we cut several disks of 1 mm thickness and annealed them for several hours at temperatures between 320°C and 410°C in a vacuum of 10⁻³ mbar (30 h at 320°C, 330°C; 15 h at 340°C, 350°C, 360°C, 370°C; 1 h at 390°C, 410°C).

The glass transition and crystallization of the as-prepared alloys was studied with a Perkin-Elmer differential scanning calorimeter (DSC 7). The SANS measurements were performed on all as-prepared and annealed samples at the time-of-flight Small-Angle Diffractometer SAD (Thiyagarajan, Epperson, Crawford, Carpenter, Klippert & Wozniak, 1997) at the Intense Pulsed Neutron Source at Argonne National Laboratory. By using neutrons of wavelength 1 to 14 Å simultaneously by time-of-flight, this instrument produces SANS data in the Q region of 0.005 to 0.3Å⁻¹ in a single measurement.

III. Experimental results

Fig. 1 shows the DSC scans of the alloys Vit1 and Vit4, as well as of the three further alloys which lie along the tie-line, when replacing successively Ti by Zr and Cu by Be (further denoted as Vit1A, Vit1B and Vit1C). Within the error, all alloys have about the same glass transition temperature $T_g$ of around 363°C. However, the crystallization behavior of the alloys is quite different. In Vit1, four crystallization peaks are detected by DSC, with the first crystallization starting at 435°C. In Vit1A, the first crystallization event shifts up to 460°C. This trend is followed in Vit1B, where only one
crystallization, starting at 486°C, is detected. Vit1C and Vit4 show two crystallization events, starting at 473°C. Thus, the alloy Vit1B, showing the highest undercooling $\Delta T = T - T_x = 123°C$ and only one crystallization event, is the ideal composition to study the crystallization pathway of multicomponent bulk amorphous alloys.

Fig. 2 shows the SANS intensity data of Vit1, Vit1A and Vit1B annealed at different temperatures. In all three compositions, a clear interference maximum, indicating spatially correlated arrangements of inhomogeneities, is visible up to annealing temperatures of 390°C (Vit1), 370°C (Vit1A) and 360°C (Vit1B). Furthermore, for all three compositions, the SANS intensity peak shifts down to lower $Q$ values with increasing annealing temperature.

For a better comparison of the scattering intensity, Fig. 3 shows the SANS intensity data of all 5 compositions at certain annealing temperatures (330°C to 360°C). With decreasing Ti content, the interference peak shifts down to lower $Q$ values. Interestingly, after annealing at 330°C, the scattering contrast is the highest for Vit1, but after annealing at higher temperatures, the scattering contrast is higher for Vit1A ($T_a = 340°C$) and Vit1B ($T_a = 350°C, 360°C$).

IV. Discussion

In agreement with the results of Schneider, Thiyagarajan, Geyer & Johnson (1998), the SANS data of Vit1 show interference peaks when annealed between 330°C and 390°C (cf. Fig. 2a). These interference peaks shift down to lower $Q$ values with increasing annealing temperature $T_a$. The same trend is also visible in Vit1A and Vit1B (cf. Fig. 1b and c). However, at a given annealing temperature, when following the tie-line from Vit1 to Vit4, the interference peaks are shifted down to lower $Q$ values (cf. Fig. 3).

In general, the interference peaks give evidence for spatially correlated arrangements of inhomogeneities. Thus, during the annealing process, the supercooled liquid must have decomposed on a fixed length scale into regions with different compositions. At a given
annealing temperature, this fixed length scale is different for the different alloys and increases along the tie-line from Vit1 to Vit4.

The high stability against crystallization in these multicomponent alloys may be explained by this decomposition progress. With continuing decomposition the crystallization probability increases drastically, since the composition gets progressively closer to the one of the primarily solidified phase. In Cahn's theory (Huston, Cahn & Hilliard, 1966), the wavelength of decomposition, \( \lambda \), is proportional to the square root of the ratio of the gradient energy (with respect to composition change) and the curvature of the free energy (Cahn, 1961), which depends on the annealing temperature \( T_a \). The wavelength of decomposition, is then inversely proportional to the square root of the \( T_a \), i.e.

\[
\frac{1}{L^2} = \frac{Q_{\text{max}}^2}{4\pi^2} \propto T_a,
\]

with \( Q_{\text{max}} \) the scattering vector of the peak position.

An in situ experiment, which we performed for 15h on the alloy Vit1A at a temperature of 348°C showed a small shift in \( Q_{\text{max}} \) from 0.036 Å\(^{-1}\) (after 200 min, where the maximum developed) to 0.026 Å\(^{-1}\) (after 15 h). Thus, during the long annealing times some nucleation and growth events occur, which of course are mediated by the decomposition. However, the sample did not show any crystallization peak after the 15 hours of annealing, as detected by x-ray diffraction.

Thus, although we observe a small shift in \( Q_{\text{max}} \) by the in situ experiment, for an attempt to quantify our experimental results, we plotted the value of \( 1/L^2 \) vs. \( T_a \) for all our samples investigated. This is shown in Fig. 4. The data follow Eq. (1) down to an annealing temperature of 350°C and show a change in slope for lower annealing temperatures, giving evidence for a change of decomposition in this lower temperature regime. Fig. 4 shows the fits of straight line, according to Eq. (1), for the experimental data in both regimes. The extrapolation of the fits down to \( 1/L^2 = 0 \), i.e. \( L \to \infty \), gives (in the high temperature regime) values of \( T_a = 397°C, 376°C \) and \( 369°C \) for the alloys Vit1, Vit1A and Vit1B. In Vit1C, an interference maximum developed only at 350°C and no
maximum was detected in Vit4. Presumably, Vit4 also decomposes, but on a length scale which cannot be resolved any more by SANS. However, we also performed Auger scanning microscopy experiments on the Vit4 sample, annealed at 350°C, and could not resolve any decomposition down to 1 μm.

The very interesting result, which deserves a further discussion, is the crossover in the $I/L^2$ vs. $T_a$ plot at 350°C. First of all, one should note that the glass transition temperature $T_g$ depends on the heating rate, and is thus lower for the preannealed samples compared to those measured by DSC with a heating rate of 10 K/min. Thus, the temperature $T_a$ of 350°C in the SANS experiment compares to the glass transition temperature $T_g$. Second, investigations have shown that the self-diffusivity of Be in Vitl changes at 350°C (Geyer, Schneider, Johnson, Qiu, Tombrello & Macht, 1995). Furthermore, recent viscosity measurements on Vitl show that at the transition from the amorphous into the supercooled liquid regime the time scales for the diffusion of small and medium sized atoms decouple from the internal relaxation time probed by the viscosity measurements (Masuh, Waniuk, Busch, & Johnson, 1999). Thus, we conclude that at temperatures below $T_g = 350°C$, the decomposition mechanism is mediated by a single atomic jump behavior of the small and medium sized atoms (like Be, Ni and Cu). Above 350°C, the diffusion process is mediated by a cooperative motion involving a cluster of neighboring atoms. Thus, since the diffusion mechanism changes at the glass transition temperature, the mechanism of decomposition, which is influenced by the driving force and the diffusion mechanism, also has to change.

Fig. 5 gives a schematic illustration of the situation, showing a quasiternary phase diagram combining the elements Ni, Cu and Be at the right corner of the phase diagram. The miscibility gap will be surely anisotropic in this quasiternary system. At low temperatures, where the decomposition is mediated by small and medium sized atoms like Be, Cu and Ni (but not by Zr and Ti), the wavelength of decomposition may be determined by the opening of the miscibility gap directing in the Ni, Cu, Be corner of the phase diagram (dotted line in Fig. 5). Above the glass transition temperature, where the diffusion mechanism is mediated by a cooperative motion (involving also Zr and Ti), the direction of the decomposition in the quasiternary diagram has to change. Thus, a new decomposition mechanism becomes effective at the glass transition temperature $T_g$. 
V. Summary and Conclusion

We have presented DSC and SANS measurements on the bulk amorphous alloys Zr$_{41.2}$Ti$_{13.8}$Cu$_{12.5}$Ni$_{10}$Be$_{22.5}$ (Vit1) and Zr$_{46.8}$Ti$_{8.2}$Cu$_{7.5}$Ni$_{10}$Be$_{27.5}$ (Vit4) as well as on three further alloys along the tie-line, varying the ZrTi and CuBe concentration. At a heating rate of 10 K/min, we measured a glass transition temperature of around 363°C for all alloys. The crystallization behavior, however, changed significantly for the different compositions, with the highest undercooling, $T_{x1} - T_g$, for the alloy Vit1B.

We found that the SANS data show interference peaks, when the alloys were preannealed between 330°C and 390°C, giving evidence for spatially correlated arrangements of inhomogeneities. The wavelength of these correlations, $L$, increased with increasing annealing temperature and, at a given annealing temperature, with composition following the tie-line from Vit1 to Vit4. The wavelength followed in two distinguished regimes a relation $1/L^2 \propto T_x$ as predicted by Cahn's theory, with a crossover in slope at the glass transition temperature $T_g = 350°C$; ($T_g$ depends on the heating rate and is thus lower for the preannealed samples compared to the one measured by DSC). This gives evidence that the mechanism of decomposition changes at the glass transition temperature, which we can explain by a change of the diffusion mechanism at $T_g$. The interference maxima in the different compositions occur up to annealing temperatures $T_a = 397°C$ (in Vit1), 376°C (Vit1A), 369°C (Vit1B) and 350°C (Vit1C). No interference maximum was detected for the alloy Vit4.

Acknowledgements

We acknowledge the assistance of Ed Lang while running the SANS experiment. This work was supported by the U.S. Department of Energy (Grant No. DEFG-03-86ER45242) and benefited from the use of the Intense Pulsed Neutron Source, funded by the U.S. Department of Energy, Office of Basic Energy Sciences under contract W-31-109-ENG-38 to the University of Chicago. Partial support for J. Löffler was provided by the Alexander von Humboldt Foundation via the Feodor Lynen Program.
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Fig. 1. DSC scans of $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ (Vit1), $\text{Zr}_{42.6}\text{Ti}_{12.4}\text{Cu}_{11.25}\text{Ni}_{10}\text{Be}_{23.75}$ (Vit1A), $\text{Zr}_{44.7}\text{Ti}_{11.0}\text{Cu}_{10.0}\text{Ni}_{10}\text{Be}_{25}$ (Vit1B), $\text{Zr}_{45.4}\text{Ti}_{9.6}\text{Cu}_{8.75}\text{Ni}_{10}\text{Be}_{26.25}$ (Vit1C) and
Zr_{46.8}Ti_{8.2}Cu_{7.5}Ni_{10}Be_{27.5} (Vit4), performed at a heating rate of 10 K/min ($t_c =$ endothermic heat flow).
Fig. 2. SANS intensity data of Vit1 (a), Vit1A (b) and Vit1B (c) annealed at different temperatures, as indicated in the figure. For a better comparison, the intensity of some samples is reduced by the scaling factor S, given in parentheses.

Fig. 3. SANS intensity data of all 5 compositions (Vit1, Vit1A to C and Vit4), annealed at 330°C (a), 340°C (b), 350°C (c) and 360°C (d). The SANS intensity of Vit1C in Fig. 3d is reduced by a factor 2 (S = 2).
Fig. 4. $1/L^2$ vs. $T_a$ plot for the alloys Vit1 and Vit1A to C.
Fig. 5. Quasiternary phase diagram combining the elements Ni, Cu and Be at the right corner. The arrows in the anisotropic miscibility gap indicate the direction of decomposition below and above the glass transition temperature of 350°C.
Figure caption

Fig. 1. DSC scans of Zr_{41.3}Ti_{13.8}Cu_{13.5}Ni_{10}Be_{22.5} (Vit1), Zr_{42.6}Ti_{12.4}Cu_{11.25}Ni_{10}Be_{23.75} (Vit1A), Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{2.5} (Vit1B), Zr_{45.5}Ti_{9.8}Cu_{8.75}Ni_{10}Be_{2.25} (Vit1C) and Zr_{16.8}Ti_{8.2}Cu_{7.5}Ni_{10}Be_{27.5} (Vit4), performed at a heating rate of 10 K/min (\(j_e\) = endothermic heat flow).

Fig. 2. SANS intensity data of Vit1 (a), Vit1A (b) and Vit1B (c) annealed at different temperatures, as indicated in the figure. For a better comparison, the intensity of some samples is reduced by the scaling factor S, given in parentheses.

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Fig. 5. Quasitermary phase diagram combining the elements Ni, Cu and Be at the right corner. The arrows in the anisotropic miscibility gap indicate the direction of decomposition below and above the glass transition temperature of 350°C.