Role of Ti in the formation of Zr–Ti–Cu–Ni–Al glasses

Department of Physics, Washington University, St. Louis, Missouri 63130

A. I. Goldman
Ames Laboratory USDOE and Iowa State University, Ames, Iowa 50011

R. W. Hyers
University of Massachusetts, Amherst, Massachusetts 01003

J. R. Rogers
NASA Marshall Space Flight Center, Huntsville, Alabama 35812

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It has been widely reported that glass formation improves in Zr$_{62}$Cu$_{20}$Ni$_8$Al$_{10}$ alloys when small amounts of Ti are substituted for Zr. Glasses containing greater than 3 at. % Ti crystallize to a metastable icosahedral phase, suggesting that Ti enhances icosahedral short-range order in the liquid/glass, making crystallization more difficult during cooling. However, based on containerless solidification and in situ high-energy synchrotron diffraction studies of electrostatically levitated supercooled liquids of these alloys, we demonstrate that Ti inhibits surface crystallization but neither increases the icosahedral short-range order nor improves glass formation. © 2005 American Institute of Physics. [DOI: 10.1063/1.2149368]

During the past decade, glass formation in a variety of multi-component Zr-based alloys has been reported. Of particular interest are the Zr-based bulk metallic glasses, which can be fabricated into intricate parts and may have important technical applications. It is well known that glass formation and stability in these alloys can be greatly influenced by the addition of small amounts of particular elements (microalloying), which also affects the crystallization products. Crystallization to the icosahedral quasicrystal phase, for example, is enhanced by the addition of O,6,7 products. Crystallization to the icosahedral quasicrystal phase, for example, is enhanced by the addition of O,6,7 metals such as Nb, Ta, and V.8 Many of these elements have strong heats of mixing with Zr,9 suggesting that they encourage the formation of strongly bound icosahedral clusters that give rise to icosahedral short-range order (ISRO) in the liquid/glass. A similar mechanism has been proposed for the improvement of glass formation due to Ti addition in Zr–Ti–Cu–Ni–Al alloys, presumably because of a higher nucleation barrier for competing crystal phases during cooling. Despite detailed investigations, however, the evidence for this enhanced ISRO remains unclear.

In this letter, we present the results from solidification and in situ high-energy synchrotron x-ray (125 keV) diffraction studies of supercooled Zr–Cu–Ni–Al alloys that were containerless processed using the electrostatic levitation (ESL) techniques. High-q diffraction studies of rapidly quenched amorphous ribbons are also presented. These data show strong ISRO in all liquids, independent of the Ti concentration. In contrast with previous reports the ESL studies demonstrate that the alloy made without Ti is a better glass former than those containing Ti. Scanning electron and optical microscopy studies show that surface crystallization is suppressed by the introduction of Ti into the alloy, making it appear that the amorphous samples containing no Ti were crystalline in previous low-energy Cu Kα x-ray diffraction studies.

Zr$_{62-x}$Ti$_x$Cu$_{20}$Ni$_8$Al$_{10}$ ingots (x=0, 3, 5) were prepared by arc-melting high purity elemental Zr (99.95%), Ti (99.999%), Cu (99.999%), Ni (99.995%), and Al (99.999%) on a water-cooled copper hearth in a high-purity Ar (99.999%) atmosphere. These ingots were subsequently crushed and portions were quenched in an Ar atmosphere onto a rotating copper wheel to produce amorphous ribbons of 30–50 μm thickness. Bulk samples were prepared by injecting the arc-melted ingots into a rectangular wedge-shaped copper mold that was approximately 3 mm in diameter at the top and 50 mm long (suction cast).

The undercooling and in situ liquid structure studies were made on small spheres (2.2–2.5 mm diameter) prepared by remelting portions of the arc-melted ingots, using the electrostatic levitation facility (ESL) located at NASA’s Marshall Space Flight Center and the Beamline ESL (BESL) at the Advanced Photon Source (APS, μ-CAT 6ID-D), as described elsewhere. Optical pyrometers (Mikron, Infrared, Inc.) with a 1.45–1.8 μm wavelength range were used to measure the sample temperature (relative accuracy of ±1 K) as a function of time during free radiative cooling. In addition, high-q (up to 20 Å$^{-1}$) x-ray diffraction studies were made on the quenched amorphous ribbons. The structure factors, S(q), were derived from the data, correcting for absorption, multiple scattering and Compton scattering contributions by using the PDFGetX2 analysis package. Structural and compositional information from all samples was obtained from transmission (JEOL 2000FX TEM) and scanning (Hitachi S-4500 SEM) electron microscopy. For the optical and SEM studies, the samples were sectioned, polished, and etched with a solution of 25 g CrO$_3$+40 ml HNO$_3$ +4 ml HF+70 ml H$_2$O.

Figure 1 shows the x-ray structure factors, S(q), for the rapidly quenched amorphous samples [Fig. 1(a)] and the levitated droplets at a supercooling of approximately 90 K.
The diffraction patterns from all of the supercooled liquid Zr–Ti–Cu–Ni–Al alloys also show this without crystallization. The presence of ISRO is insensitive to the Ti concentration below the liquidus temperature [Fig. 1(b)]. The rapidly quenched ribbons show a distinct shoulder on the high-\( q \) side of the second peak in \( S(q) \) [Fig. 1(a)] in agreement with previous experiments; this is generally taken to signal the presence of ISRO. The diffraction patterns from all of the supercooled liquid Zr–Ti–Cu–Ni–Al alloys also show this distinct shoulder [Fig. 1(b)], independent of the Ti concentration. These data indicate that there is no significant difference in the ISRO in the supercooled alloys as a function of Ti, hence it has no impact on glass formation, in conflict with earlier speculations. Further, primary crystallization to the icosahedral phase due to Ti addition is presumably because of a Ti-induced change in the relative free energy curves of the liquid/glass and potential crystallizing phases, and not due to enhanced ISRO as was previously speculated.

Figure 2 shows the free-radiation-cooling curves from far above the liquidus temperature (\( \approx 1100 \) K) for levitated liquid droplets of Zr\(_{57}\)Ti\(_5\)Cu\(_{20}\)Ni\(_8\)Al\(_{10}\) [Fig. 2(a)] and Zr\(_{62}\)Cu\(_{20}\)Ni\(_8\)Al\(_{10}\) [Fig. 2(b)]. To eliminate contaminants that limited the supercooling due to heterogeneous nucleation, the samples were first superheated and supercooled for several cycles (total mass loss: \( \approx 1\% \) for 10–15 cycles). A sharp rise in temperature due to the heat released during the crystallization of the liquid (recalescence) was observed in the Zr\(_{57}\)Ti\(_5\)Cu\(_{20}\)Ni\(_8\)Al\(_{10}\) alloy [Fig. 2(a)], while the Zr\(_{62}\)Cu\(_{20}\)Ni\(_8\)Al\(_{10}\) alloy was cooled to a solid glassy state without crystallization [Fig. 2(b)]. The higher vacuum and capability for containerless processing in ESL allow the critical quenching rate for glass formation to be better determined than by other techniques, in which heterogeneous nucleation on the sample holder can obscure the fundamental homogeneous-nucleation-based limit. Contrary to previous reports of improved glass formation with the addition of Ti in suction-cast alloys, for the slower cooling rates in the ESL (\( \approx 3–4 \) K/s near the nose of the time-temperature transformation curves) Zr\(_{62}\)Cu\(_{20}\)Ni\(_8\)Al\(_{10}\) forms a glass while Zr\(_{57}\)Ti\(_5\)Cu\(_{20}\)Ni\(_8\)Al\(_{10}\) does not.

This was confirmed by examining cross sections of the arc-melted and levitated samples by optical microscopy [Figs. 3(a)–3(d)] and the suction-cast samples by SEM [Figs. 3(e) and 3(f)]. A thick surface crystallization layer is observed in the arc-melted Zr\(_{62}\)Cu\(_{20}\)Ni\(_8\)Al\(_{10}\) ingots [Fig. 3(a)], with particularly severe crystallization for that portion of the sample in contact with the Cu hearth [Fig. 3(b)]. The interior of the sample is featureless, which x-ray diffraction studies confirmed as amorphous. Surface crystallization is much less severe in the Zr\(_{57}\)Ti\(_5\)Cu\(_{20}\)Ni\(_8\)Al\(_{10}\) ingot [Fig. 3(c)], demonstrating that it is suppressed by the addition of Ti. Heterogeneous nucleation on the Cu hearth is clearly a primary source of surface crystallization. The significant decrease in surface crystallization for the Zr\(_{62}\)Cu\(_{20}\)Ni\(_8\)Al\(_{10}\) sample that was pro-

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**FIG. 1.** (a) Structure factor, \( S(q) \), for Zr\(_{62-x}\)Ti\(_x\)Cu\(_{20}\)Ni\(_8\)Al\(_{10}\) (\( x = 0, 3, 5 \)) (a) rapidly quenched amorphous ribbons and (b) supercooled liquids at 973±5 K. Note that the shoulder on the high-\( q \) side of the second peak (near 5 Å\(^{-1}\)), which is indicative of ISRO, is insensitive to the Ti concentration.

**FIG. 2.** The free radiation cooling curves for electrostatically levitated (a) Zr\(_{57}\)Ti\(_5\)Cu\(_{20}\)Ni\(_8\)Al\(_{10}\) and (b) Zr\(_{62}\)Cu\(_{20}\)Ni\(_8\)Al\(_{10}\) alloys from the liquid to the solid phase. (b) Does not show a recalescence, signaling glass formation, while (a) shows a recalescence near 790 K, indicating crystallization.

**FIG. 3.** Optical micrographs of sample sections showing the (a) side and (b) bottom portions of an arc-melted Zr\(_{62}\)Cu\(_{20}\)Ni\(_8\)Al\(_{10}\) ingot; (c) side of an arc-melted Zr\(_{57}\)Ti\(_5\)Cu\(_{20}\)Ni\(_8\)Al\(_{10}\) ingot; (d) surface of an ESL processed Zr\(_{62}\)Cu\(_{20}\)Ni\(_8\)Al\(_{10}\) drop. SEM micrographs of sample sections close to the Cu mold for suction-cast samples of (e) Zr\(_{62}\)Cu\(_{20}\)Ni\(_8\)Al\(_{10}\) and (f) Zr\(_{57}\)Ti\(_5\)Cu\(_{20}\)Ni\(_8\)Al\(_{10}\).
cessed in the ESL [Fig. 3(d)] from that present in the portions of the arc-melted sample that were not in contact with the hearth [Fig. 3(a)] indicates that surface crystallization is also likely related to the oxygen of the processing atmosphere. No evidence of surface crystallization was observed in the Zr_{62}Cu_{20}Ni_{8}Al_{10} samples processed in the ESL (not shown). Significant surface crystallization is observed in SEM images of sections taken from the thickest portions (3 mm × 3 mm) of the suction-cast Zr_{62}Cu_{20}Ni_{8}Al_{10} sample [Fig. 3(e)], while no evidence of surface crystallization is observed in the suction-cast Zr_{57}Ti_{5}Cu_{20}Ni_{8}Al_{10} alloy. Due to the higher cooling rates, however, the interiors of both samples were amorphous. These observations explain why earlier studies of suction-cast samples using conventional low-energy x-ray methods indicated that glass formation improved with the addition of Ti. The amorphous interiors of the as-cast Zr_{62}Cu_{20}Ni_{8}Al_{10} samples in those studies were obscured by the surface crystallization layer.

The mechanism by which Ti suppresses surface crystallization is unclear at present. Based on TEM and SEM energy dispersive x-ray studies, the chemical concentration is spatially uniform in all glasses; there is no measurable segregation of Ti to the surface in the alloys made with Ti. Further, if the function of Ti is primarily to remove oxygen, it is difficult to understand how Ti could be a more effective getter than Zr.

In summary, based on containerless solidification and in situ x-ray diffraction studies of electrostatically levitated supercooled liquids of Zr_{62−x}Ti_{x}Cu_{20}Ni_{8}Al_{10} and its amorphous solids, we find that (1) Ti plays no significant role in improved glass formation by enhancing the ISRO in the liquid and (2) alloys made without Ti have a lower critical cooling rate for glass formation, in contradiction with previous reports. This difference can be explained in the light of the present observation of a significant suppression of surface heterogeneous nucleation in these alloys with the addition of Ti.

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