Structural Evolution and Thermophysical Properties of $\text{Zr}_x\text{Ni}_{100-x}$ Metallic Liquids and Glasses

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Abstract

The results of high-energy X-ray scattering studies over a wide temperature range for equilibrium and supercooled $\text{Zr}_x\text{Ni}_{100-x}$ ($x = 36, 57, 76$) liquids and the corresponding glasses are presented. The results of liquid density and viscosity measurements are also shown. All of the liquid studies were made on containerlessly processed liquids using the technique of electrostatic levitation. The scattering data were used to determine the temperature-dependent total structure factor, $S(q)$, and pair-correlation function, $g(r)$. A discontinuity is observed between the magnitude of the first peak in $S(q)$ of the liquid when extrapolated to the glass transition temperature, T_g , and the value determined for the structurally relaxed glass at T_g . This indicates that the structural ordering in the liquid accelerates upon approaching T_g , consistent with the behavior expected for a fragile liquid. An asymmetry in the first peak in the pair correlation function develops with decreasing temperature for all alloy liquids and glasses, suggesting that chemical ordering accompanies the structural ordering.

Keywords: X-ray diffraction; liquid structure; metallic glass; fragility; chemical order

1. Introduction

Since the discovery of metallic glasses [1] considerable effort has gone into understanding the fundamental processes that govern why some metallic liquids can be cooled slowly into a glass, while others must be rapidly-quenched. The rapidly slowing liquid kinetics upon approaching the glass transition temperature, T_g , play a significant role in glass formation, which ultimately hinges on avoiding crystallization. Since the viscosity increases by nearly 15 orders of magnitude from the liquidus temperature to T_g , it is a particularly sensitive property, useful for characterizing liquids. As the temperature is decreased, the viscosity increases with an Arrhenius behavior for those liquids characterized as *strong*. In contrast, *fragile* liquids show highly non-Arrhenius behavior, with a rapid increase in the apparent activation energy upon approaching T_g [2]. Generally strong liquids have a higher glass forming ability (GFA) than fragile liquids [3-5], making a deeper understanding of fragility of both fundamental as well as practical interest. While fragility is typically defined in terms of the viscosity, it fundamentally reflects ordering in the liquid structure. Improvements in containerless processing and levitation techniques allow this ordering to now be investigated quantitatively. While some structural studies have been possible using containers, structural investigations of glass-forming liquids over a wide compositional range are lacking. The recent development of the Washington University Beamline Electrostatic Levitation facility (WU-BESL) [6, 7] has enabled such studies, allowing high-energy X-ray diffraction studies to be made of metallic liquids and glasses for a wide range of alloy families and compositions. These experiments have provided precise determinations of the X-ray static

structure factors, $S(q)$, and pair-correlation functions, $g(r)$ for many glass forming liquids. With this improved data quality, the link between structural ordering and fragility was recently demonstrated experimentally [8]. As explained later in this section, the Zr-Ni liquids provide an excellent system for exploring these points further and for developing possible correlations between GFA and structural and thermophysical properties.

Both X-ray and neutron scattering experiments have shown that with increased supercooling metallic liquids develop significant short-range and often medium-range order [9-13]. While the total structure factors and pair-correlation functions are qualitatively similar for almost all metallic liquids and glasses, it has been established recently that there are quantitative differences that may be correlated with GFA [8]. For Ni-Nb [14], Cu-Zr [15, 16], and other fragile metallic glass forming liquids, studies have shown that the ordering must accelerate as the temperature of the supercooled liquid approaches T_g . In several studies of fragile liquids, Reverse Monte Carlo (RMC) fits to experimental data [14] and molecular dynamics (MD) simulations [17] have demonstrated that the rapid ordering is due to a rapid increase in the number of particular local atomic clusters. Experimentally, the increased ordering is manifest as a deviation from an extrapolation of the first peak height in the total structure factor, $S(q_1)$, of the high temperature liquid to the glass at T_g , leading to the definition of a *structural fragility index* [8]

$$\gamma = 100 * \frac{S(q_1)_{glass} - S(q_1)_{liquid \text{ extrapolation}}}{S(q_1)_{glass}} \text{ at } T_g. \quad (1)$$

Like the kinetic fragility parameter, m , γ increases with increasing liquid fragility. The rapid increase in $S(q_1)$ near T_g for fragile liquids is in contrast to the behavior of $S(q_1)$ for stronger Zr- and Pd- based liquids [18]. There, the extrapolated high temperature liquid values for $S(q_1)$ are nearly the same as for the glass at T_g , indicating a more constant rate of structural ordering over the temperature range from near the liquidus temperature, T_L to T_g .

Since metallic liquids with high GFA typically contain four or more components, the measured total structure factor is composed of many partial structure factors, making it extremely difficult to unravel the nature of the chemical and topological ordering. The simpler binary liquids and glasses are better suited for such studies, although they have a lower GFA. Zr-Ni is known to form a glass across a wide range of compositions, albeit only when rapidly-quenched at cooling rates of at 10^5 - 10^6 K/s [19]. These alloys also form the basis of more complex alloys with better GFA. Zr-Ni liquids and glasses have been extensively studied by X-ray [20-24] and neutron scattering [13, 22, 25-30], as well as through simulations [21, 31-33]. The results from these studies have attracted attention because of the evidence for significant chemical ordering in both the liquid and glass [21, 22, 31, 33]. However, to our knowledge, there has never been a comprehensive investigation of the ordering of Zr-Ni across a large compositional range. Furthermore, most structural studies have focused only on the liquid or the glass and not the relationship between the two.

In this work, results from a coordinated study of the structure and thermophysical properties are presented for three Zr-Ni alloys selected to represent a wide compositional range: $Zr_{36}Ni_{64}$, $Zr_{57}Ni_{43}$, and $Zr_{76}Ni_{24}$. Viscosity and density measurements were made over a wide temperature range for all liquids while processing in a containerless environment. Results from high-energy X-ray diffraction studies of the equilibrium and supercooled liquids and the corresponding glasses suggest that distinct asymmetric features in the total pair distribution function reflect chemical ordering in all three alloys,

starting in the high temperature liquid and increasing into the glass. Based on a quantitative analysis of the temperature dependence of the static structure factor, all three liquids are fragile.

2. Experimental procedure

Master ingots for all compositions were prepared by arc melting high purity Zr (99.95 at.%, including Hf nominal 3 at.%) and Ni (99.995 at.%) on a Cu hearth in a high purity (99.999 at.%) Ar atmosphere. A Ti-Zr getter located close to the sample was melted prior to arc melting to further reduce the oxygen concentration in the chamber. Each ingot was melted three times to ensure that the samples were homogeneous; each melt cycle lasted approximately 60 s. Sample mass loss during arc melting was negligible (less than 0.1%). The master ingots were subsequently crushed and portions were re-melted to obtain small spherical samples (~2.5 mm diameter) for *in situ* liquid structural studies at the Advanced Photon Source (APS) in sector 6-ID-D, using the Washington University Beamline Electrostatic Levitator (WU-BESL) [6, 7]. WU-BESL is optimized for X-ray diffraction studies of levitated, containerlessly processed liquids in a high vacuum environment ($\sim 10^{-7}$ Torr). Metallic glasses were prepared by RF induction, melting portions of the master ingot in a graphite crucible under a high purity (99.998%) Ar atmosphere and then rapidly quenching the liquid onto a copper wheel that was rotating at ~60 m/s. This produced continuous 3-10 cm ribbons with an average cross-section of 1-2 mm x 20-30 μm . Studies made using a Rigaku powder diffractometer (Cu K_α , $\lambda = 1.54 \text{ \AA}$) and high-energy X-ray diffraction studies made at the APS confirmed that the as-quenched ribbons were fully amorphous.

For the levitation experiments, the liquid samples were heated, melted, and subsequently thermally processed using a fiber-coupled diode laser (980 nm, 50 W continuous maximum power output). Crystallization of the supercooled liquid, marked by a sharp rise in temperature (recalescence), limited the lowest temperature for the X-ray diffraction studies to 230 °C below the liquidus temperature. Sample masses were measured before and after thermal processing to determine the mass loss during processing, which would indicate a change in composition due to Ni evaporation. Based on measurements of the partial pressure of oxygen in the levitation chamber, the mass change from oxygen absorption or oxidation is negligible. Our evaporation measurements indicate that the large negative heats of mixing between Ni and Zr decrease the evaporation rate significantly below a rule of mixtures estimate, leading to a maximum predicted composition shift of 0.1 at.% during the thermal cycling of these experiments. Care was taken to limit the time each sample was at extreme temperatures, and in all cases the mass loss was negligible.

Single amorphous ribbons were mounted to a resistive heating apparatus in the WU-BESL and held in approximately the same location as the levitated samples. The ribbons were thermally cycled from room temperature to near T_g multiple times, while simultaneously acquiring diffraction images and temperature measurements. The cycling allowed the diffraction patterns to be monitored until they were completely reversible up to T_g , indicating complete structural relaxation before crystallization occurred. The relaxed glasses were then held isothermally for 60 s at a series of temperatures that increased towards T_g . They were then heated at a rate of 40 to 100 K/min through T_g until crystallization was observed. The resistive method used here allowed the samples to be heated quickly and their small size allowed them to cool quickly when the heating current was removed. It is more common to place samples in a quartz capillary, which is then heated with an external furnace. However, this suffers from slow heating and cooling rates. The lack of a capillary greatly reduced the background scattering, allowing the quantitative structural studies presented here.

The temperatures of the amorphous ribbons and levitated liquids were measured from 160 °C to 2300 °C using two infrared pyrometers with overlapping temperature ranges. A single color Process Sensors Metis MI18 MB8, operating at a 1.89 μm wavelength, was used for low temperature measurements (160-800 °C) of the liquids and glasses and a Process Sensors Metis MQ22 two-color ratio pyrometer, operating at 1.40 and 1.65 μm wavelengths, was used for high-temperature measurements (600-2300 °C) of the liquids. Ratio pyrometers provide more accurate measurements of the temperature because emissivity changes with temperature are normalized out [34], since relative changes in the emissivity at each of the two close wavelengths are expected to be small. A constant emissivity ratio was assumed for the entire temperature range over which structural data were acquired. For the liquids, the emissivity ratio was calibrated by matching the melt plateau in the temperature versus time curve measured on heating in the BESL to the largest endothermic signature measured in a differential thermal analyzer (DTA) (LabsysTM DTA/DSC, Setaram). In the ESL measurements, the plateau corresponds to the solidus temperature, T_s . For the amorphous ribbons, the low temperature pyrometer was calibrated by matching the onset temperature of the appearance of crystal peaks in the X-ray diffraction patterns with the onset temperature for the exothermic crystallization signature in a differential scanning calorimeter (DSC) (PerkinElmer DSC 7). The same heating rates were used for the X-ray and DSC studies.

For the liquid samples, the temperature was correlated with non-contact measurements of the volume. The projected area of the sample was obtained using the shadow method [35, 36] with a Pixelink PL-B74IG CMOS camera and a 455 nm collimated microscope LED, which has a total beam power of 240 mW and a beam diameter of 37 mm. The video data were taken at a frame rate of 20-25 fps. The pixel dimensions were calibrated before and after the set of measurements on each sample using 2.38125 ± 0.00076 mm diameter (grade 3) tungsten carbide standards. The volume was determined from the area data, assuming that the sample was symmetric about the vertical axis [37], and the density was calculated from the product of the inverse of the volume and the measured sample mass. The relative precision of the density data was $\sim 0.3\%$ over the temperature range studied, with an absolute accuracy of $\sim 0.5\%$; the measurement error is dominated by errors in the calibrations of the volume and mass. A more detailed discussion of the machine vision volume measurement algorithm can be found elsewhere [35]. The densities of the amorphous ribbons were determined at room temperature using Archimedes' method, with toluene as the working fluid. The total uncertainties in the values obtained were between 1% and 2%.

The liquid viscosity was measured as a function of temperature using the oscillating drop technique [38-40], where a perturbing voltage on the top and bottom electrodes caused sample oscillation. The viscosity is related to the decay time in the surface oscillation when the perturbation is removed. The surface oscillations were measured by a Pixelink PL-B74IG CMOS camera operating at a high frame rate (1500 fps). More detail is given elsewhere [40].

The diffraction studies of the liquids and glasses were made in a transmission geometry, using high-energy X-rays ($E = 132$ keV, $\lambda = 0.0940$ Å). Scattering data were obtained to a momentum transfer, q , of 20 Å^{-1} at a sampling rate of 1 Hz using a GE Revolution 41-RT amorphous Si flat-panel X-ray detector. The sample-to-detector distance, detector tilt, and detector center were calibrated by fitting the diffraction pattern of a levitated polycrystalline Si sample. These values were confirmed using a NIST Si standard in a capillary placed at the position of the levitated liquid sample. The scattering data obtained were processed by masking bad pixels, applying a pixel efficiency gain map, averaging the

images obtained during the isothermal hold, and subtracting the appropriate detector dark current and scattering background. Images were then corrected for oblique incidence, absorption, multiple scattering, fluorescence, polarization, sample geometry, and Compton scattering contributions using in-house analysis packages written in LabVIEWTM [41]. A series of measurements were made at each temperature step (15-20 s duration for liquids, up to 60 s for glasses) to obtain the total static structure factor using

$$S(q) = \frac{I(q) - \sum_{i=1}^n c_i |f_i(q)|^2}{\left| \sum_{i=1}^n c_i f_i(q) \right|^2} + 1, \quad (2)$$

where $I(q)$ is the measured diffraction intensity, c_i is the atomic fraction of each elemental species, and $f_i(q)$ is the q -dependent atomic form factor for each species. The sums were taken over all species and an isotropic and statistically homogeneous atomic distribution was assumed. The total pair correlation function, $g(r)$, was computed from a Fourier transform of the structure factor,

$$g(r) - 1 = \frac{1}{4\pi\rho_0} \frac{2}{\pi} \int (S(q) - 1) \frac{\sin(qr)}{qr} q^2 dq, \quad (3)$$

where ρ_0 is the average number density.

The positions and magnitudes of the first peaks in $S(q)$ were refined by fitting a cubic spline to the peak. The total measurement uncertainties were estimated by considering perturbations from independent sources of error (including statistical uncertainties) following the method described by Hammersley [42], and from the confidence intervals of fitted correction factors (e.g. intensity normalization). Based on this the precision of the peak heights in $S(q)$ was 0.4-1.7% for both liquids and glasses. However, because the scattering from the single-ribbon glasses was weak, the accuracy of the calculated peak heights in $S(q)$ is estimated, at ~6%. The accuracy in the calculated peak heights in $S(q)$ for the liquids is much better, ~1%, due to the high signal-to-noise in the scattering data.

3. Results and Discussion

For each composition, a single melt plateau at the solidus temperature, T_s , was observed upon heating. These temperatures were calibrated using DTA measurements of T_s , which gave 1070 ± 5 °C for $\text{Zr}_{36}\text{Ni}_{64}$, 1025 ± 5 °C for $\text{Zr}_{57}\text{Ni}_{43}$, and 980 ± 5 °C for $\text{Zr}_{76}\text{Ni}_{24}$. Representative temperature-time curves for each composition are shown in Fig. 1. An inflection was observed during the heating of $\text{Zr}_{57}\text{Ni}_{43}$ at constant laser intensity (Fig. 1b), indicating a two-phase solid-liquid region that extended to a liquidus temperature, T_L , of 1180 ± 5 °C. These temperatures are in reasonable agreement with the best available phase diagram for these alloys [43]. The accessible temperature range for the liquid studies was limited by the evaporation rate of Ni at high temperatures and the maximum supercooling temperature, which varied with composition.

Figure 1 near here, high-resolution figure in attached files

Figure 1 – Representative temperature-time curves for a typical heating and free-cooling cycle for the three compositions studied: (a) $\text{Zr}_{36}\text{Ni}_{64}$, (b) $\text{Zr}_{57}\text{Ni}_{43}$ and (c) $\text{Zr}_{76}\text{Ni}_{24}$. The solidus temperature, T_s , in each cycle corresponds to the temperature plateau upon heating. An inflection at higher temperature in (b) corresponds to the liquidus temperature, T_L . The absence of an inflection in either Fig. 1a or 1c indicates that these are eutectic alloys.

The sample volume was measured as a function of temperature for multiple radiative free-cooling cycles and combined with the mass to compute the liquid density. Over the measured temperature range (~400 °C) the density and volume scale linearly with temperature for all liquid compositions. The density is described by

$$\rho(T) = \rho_s + \frac{d\rho}{dT}(T - T_s), \quad (4)$$

where ρ_s is the liquid density at the solidus temperature, T_s . The average density increases with increasing Ni concentration, consistent with the higher density of Ni relative to Zr, and agrees with measurements made in other Zr-Ni glasses [30]. The coefficient of thermal expansion at the solidus temperature, α_s , was calculated for all liquids from a linear fit of the volume as a function of temperature using

$$\alpha_s = \left(\frac{1}{V} \frac{\partial V}{\partial T} \right)_{P, T=T_s}. \quad (5)$$

The fitting parameters are listed in Table 1.

Table 1
Fitting Parameters for the Density and Volume for each Liquid Composition^a

Composition	T_s (°C)	Liquid ρ_s (g cm ⁻³)	Liquid $d\rho/dT$ (g cm ⁻³ C ⁻¹)	α_s (C ⁻¹)	Glass ρ (g cm ⁻³)
$\text{Zr}_{36}\text{Ni}_{64}$	1070 ± 5	7.50 ± 0.01	-5.09 ± 0.02 E-4	6.87 ± 0.03 E-5	7.87 ± 0.10
$\text{Zr}_{57}\text{Ni}_{43}$	1025 ± 5	7.02 ± 0.01	-3.51 ± 0.02 E-4	5.08 ± 0.04 E-5	7.21 ± 0.09
$\text{Zr}_{76}\text{Ni}_{24}$	980 ± 5	6.67 ± 0.01	-2.94 ± 0.02 E-4	4.46 ± 0.03 E-5	6.87 ± 0.13

^aThe solidus temperature, T_s , was determined from DTA measurements; the liquid density at the solidus, ρ_s , rate of change of the liquid density with temperature, $d\rho/dT$, and the coefficient of liquid thermal expansion at the solidus, α_s , were determined using the BESL; the glass density at room temperature, ρ , was determined using Archimedes' method.

The liquid viscosity, η , was measured as a function of temperature for all liquid compositions (Fig. 2). It is not possible to present the Zr-Ni liquid viscosity in a typical Angell plot [2] since, consistent with previous reports [44, 45], no definitive T_g was observed in our DSC scans for the Zr-Ni glasses despite initially annealing the sample at low temperatures. Over the high temperature range where it could be measured, however, $\log_{10}(\eta)$ scales approximately linearly with inverse temperature, with only a subtle curvature evident (Fig. 2b). This indicates that the activation energy for flow is approximately constant over this temperature range, as expected for high-temperature metallic liquids [46, 47]. An effective activation energy was calculated from the slope of a linear fit to the Arrhenius region of $\ln(\eta)$ vs. $1/T$ using the form

$$\ln(\eta) = \ln(\eta_0) + \frac{E_A}{R} \frac{1}{T}, \quad (6)$$

where E_A is the activation energy, R is the ideal gas constant, and η_0 is the viscosity at infinite temperature (Table 2).

Figure 2 near here, high-resolution figure in attached files

Figure 2 – (a) Liquid viscosity, η , as a function of reduced inverse temperature. (b) $\log_{10}(\eta)$ versus reduced inverse temperature. In (b) a constant slope is observed over a significant portion of the temperature range studied, indicating a constant activation energy in the high temperature liquid (color online).

While, as mentioned, T_g is difficult to measure in the Zr-Ni glasses, the crystallization temperature, T_x , is easily measured due to the large enthalpy release. Previous studies have indicated that $T_x - T_g < 10\text{K}$ for Zr-Ni alloys [44]. Due to the difficulty in measuring T_g , $T_g \approx T_x$ is used here. DSC measurements of the onset temperature for crystallization were used to calibrate the temperature in the structural studies of the amorphous ribbons. Similar heating and quench rates were used for both measurements. The crystallization temperatures obtained at a heating rate of 40 K/min are presented in Table 2.

Table 2
DSC Crystallization Temperature and Effective Activation Energy for Viscosity

Sample	T_x (40 K/min)	Effective Activation Energy (E_A)
Zr ₃₆ Ni ₆₄	$568 \pm 3^\circ\text{C}$	$72.7 \pm 0.4 \text{ kJ/mol}$
Zr ₅₇ Ni ₄₃	$463 \pm 3^\circ\text{C}$	$54.6 \pm 0.6 \text{ kJ/mol}$
Zr ₇₆ Ni ₂₄	$353 \pm 3^\circ\text{C}$	$58.4 \pm 0.3 \text{ kJ/mol}$

Figure 3 near here, high-resolution figure in attached files

Figure 3 – Static Structure Factors for liquids and glasses of (a) Zr₃₆Ni₆₄, (b) Zr₅₇Ni₄₃ and (c) Zr₇₆Ni₂₄. (d) A comparison between the $S(q)$ s for all three compositions is shown for the liquids at the highest temperature studied ($\sim 1435^\circ\text{C}$) and (e) for the glass at room temperature, after structural relaxation. $S(q)$ s in a-c are each vertically offset by 0.5 for clarity (color online).

The total structure factors, $S(q)$, for both the liquids and glasses were calculated from the measured intensity, $I(q)$, using Eq. 2; these are shown in Fig. 3. In all cases, $S(q)$ oscillates well around unity over the entire q -range, indicating the high quality of the experimental data. The amorphous ribbons were not pre-annealed prior to the structural measurements in BESL so that structural relaxation could be studied during heating. The ribbon was initially heated to a temperature well below the estimated glass transition temperature, then cooled to room temperature. In subsequent cycles, the maximum temperatures were increased until reversible behavior in the height of the first peak in the structure factor, $S(q_1)$, was observed. Structural relaxation was observed for all compositions, evidenced by an increase in the height of $S(q_1)$ and a decrease in its full width at half maximum.

For liquids of all compositions, the first peak position shifts towards larger q with decreasing temperature, consistent with an increasing density. The first peak also sharpens and increases in amplitude with decreasing temperature, indicating structural ordering in the liquid. The features in the

first and higher order peaks in the $S(q)$ s for the glasses are dramatically sharper than in the liquid, consistent with more structural order in the glass. A large- q shoulder on the second peak is often taken as evidence for icosahedral short-range order (ISRO) [9, 12, 48]. However, this is often distorted icosahedral order as is the case in the $Zr_{36}Ni_{64}$ glasses [22]. Further, results from MD simulations of Zr-rich Zr_2Ni [31] and $Zr_{64}Ni_{36}$ [33] have shown that the dominant Zr-centered clusters in the liquid are more closely related to higher-coordinated Frank Kasper (FK) polyhedra (coordination numbers (CN) of 14-16), while the Ni-centered clusters are primarily highly distorted icosahedra (CN of 11-13) with negligible ideal icosahedra (CN of 12). The higher-coordinated FK polyhedra are also present in small amounts in the $Zr_{36}Ni_{64}$ glass, with the relatively reduced population likely due to the smaller Zr concentration. Since the second peak in $S(q)$ varies in shape and position across a wide range of compositions (Fig. 3d-e), it is possible that there are evolving types of order as Zr is replaced by Ni. This is supported by the differences measured between the partial structure factors obtained from neutron scattering studies with isotopic substitution in the Ni-rich $Zr_{36}Ni_{64}$ glass [22, 49] and from RMC fits to neutron scattering data for the Zr-rich Zr_2Ni glass [30]. There have been numerous reports of a pre-peak in the experimentally measured $S(q)$ obtained from neutron scattering studies of the $Zr_{64}Ni_{36}$ amorphous alloy. This indicates the presence of medium-range order (MRO), attributed to the Ni-Ni correlation for both the high temperature liquid [25, 29] and the room temperature glass [30]. The pre-peak is also found from *ab initio* MD calculations of the high temperature liquid [33]. For the $Zr_{36}Ni_{64}$ glass [22, 49] the pre-peak is attributed to both Zr-Zr and Ni-Ni correlations, resulting from pronounced topological and chemical short-range order due to a preferred Zr-Ni bonding. However, the feature is not observed in X-ray diffraction measurements of the room temperature glass [22], consistent with our results. There is no evidence for a pre-peak for the Zr-Ni liquids and glasses studied here, which is expected due to the respective weighting factors of the Zr-Zr, Zr-Ni and Ni-Ni partial structure factors [50].

The pair correlation function, $g(r)$, for all liquids and glasses was calculated from the $S(q)$ s using Eq. 3; these are shown for all liquids and glasses studied in Fig. 4. The higher order peaks behave in a similar manner for all liquids, increasing in amplitude and shifting towards smaller- r with decreasing temperature. These trends indicate an increase in the correlation length for structural order and an increasing density. The smallest- r peak (i.e. first peak), however, shows an anomalous expansion, shifting towards larger r with decreasing temperature. This is now emerging as common behavior, reported in many metallic glass-forming liquids [51, 52]. The character of the first peak in $g(r)$ for the different glasses is one of the more interesting features (Fig. 4d-f). The $Zr_{57}Ni_{43}$ liquid and glass shows a distinctly split first peak with the two sub-peaks having nearly equal amplitudes. In contrast, the $g(r)$ for the $Zr_{36}Ni_{64}$ liquid has an asymmetric first peak that develops into a small shoulder at large- r in the glass, consistent with that observed by Georgarakis *et al.* [20]. The $Zr_{76}Ni_{24}$ liquid shows a similar asymmetry, but with the shoulder appearing at small- r in the glass. That the sharper features in the $g(r)$ s for the glasses appear at the same positions as the asymmetries in the liquid $g(r)$ s suggests that the short-range order in the liquid and glass is similar. An asymmetry was also observed in the first peak in $g(r)$ in Cu-Zr/Hf liquids and glasses [15, 16, 20], although the features are more subtle than observed here and only become distinct in the glass.

Figure 4 near here, high-resolution figure in attached files

Figure 4 – Pair correlation functions, $g(r)$, calculated from the $S(q)$ s for the liquids and glasses of (a) $Zr_{36}Ni_{64}$, (b) $Zr_{57}Ni_{43}$ and (c) $Zr_{76}Ni_{24}$. The first peaks, corresponding to the first coordination shell, for each alloy (d-f) show a marked asymmetry or peak splitting corresponding to the positions of the average bond distances, indicated by the dashed lines. The amplitudes of the peaks giving rise to the asymmetry scale with their respective Faber-Ziman weighting, indicated by the height of the solid bars. The $g(r)$ s in a-c are each vertically offset by 0.5 for clarity (color online). The peaks of the $g(r)$ s in d-f increase in amplitude as the temperature is decreased.

EXAFS [24, 53] and neutron diffraction [26, 28] measurements of room temperature glasses have shown that the Zr-Ni and Ni-Ni bond lengths are almost identical and essentially constant across a range of compositions, while the Zr-Zr bond length is compositionally dependent, increasing to larger r as the Zr concentration is decreased. MD calculations of Zr_2Ni liquids indicate a small increase of all bond lengths with decreasing temperature, as well as a separation of the Zr-Ni and Ni-Ni bond lengths similar what is observed in the glass [31]. Based on these measured average bond distances, the large- r feature in the first coordination shell (Fig. 4d-f) corresponds to the Zr-Zr bond, with the position of this feature shifting to larger r as the Zr content decreases. This is consistent with the Zr-Zr bond length increasing with decreasing Zr concentration. The small- r feature corresponds to the combined Ni-Ni and Ni-Zr bonds and shifts very little in position across the compositional range studied, consistent with other measurements [24]. The average length of the Zr-Ni bond in other studies is 5-7% shorter than the sum of their individual atomic radii [20, 24, 31], consistent with the 6-7% decrease observed here. In the Cu-Zr/Hf liquids and glasses, the average length of the Cu-Zr/Hf bond is very close to the sum of the atomic radii, resulting in much more overlap of the distribution of the Cu-Zr/Hf and Zr/Hf-Zr/Hf bond lengths in the first coordination shell. Since the atomic sizes of Cu and Ni are very similar, this difference in behavior is likely due to the higher enthalpy of mixing between Zr and Ni compared with that between Cu and Zr (-49 and -23 kJ/mol, respectively [54]). The reduced average length for the Zr-Ni bonds results in a distinct separation of the peaks of the Zr-Zr and Zr-Ni bond length distributions, indicating an increase in the chemical ordering of Zr with Ni.

The relative amplitudes of the first coordination shell features can be described within the Faber-Ziman formalism [55], where the partial pair distribution functions (PPDF), $g_{ij}(r)$, are related to the partial structure factors (PSF), $S_{ij}(q)$, by

$$g_{ij}(r) - 1 = \frac{1}{4\pi\rho_0} \frac{1}{\pi} \int (S_{ij}(q) - 1) \frac{\sin(qr)}{qr} q^2 dq. \quad (6)$$

The total $g(r)$ is related to the partials using the q -dependent Faber-Ziman (FZ) weighting factor, w_{ij} , where, as $q \rightarrow 0$,

$$w_{ij}(0) = c_i c_j \frac{Z_i Z_j}{\langle Z \rangle^2} \quad (7)$$

where c_i is the concentration of the i^{th} atomic species and Z_i is the number of electrons in each species. When the features in the partial structure factors vary quickly compared to the atomic form factors, the total pair-correlation function can be approximated as a simple weighted sum of the partial pair-correlation functions,

$$g(r) \cong \sum_i \sum_j w_{ij}(0) g_{ij}(r). \quad (8)$$

This approximation is valid for amorphous metallic alloys and is discussed in more detail elsewhere [15, 56-58]. The relative heights of the peaks and shoulders in the first coordination shell are well correlated with the relative amplitudes of the FZ factors for the corresponding atomic bond distances (Table 3). While the small- r feature corresponds to the combined first peaks of the Ni-Ni and Ni-Zr PPDFs, the FZ factor for Ni-Ni is small for all alloy concentrations, indicating that the Ni-Ni PPDF contributes very little to the total $g(r)$. The split peaks in the first coordination shell then correspond primarily to contributions from the Ni-Zr and Zr-Zr PPDFs. Their sharpening indicates an increase in the coherence length and frequency of Zr-Ni and Zr-Zr bonding, signaling chemical ordering for all of the alloys studied. The sharpening of these peaks also indicates an increase in topological ordering, but the well-separated bond lengths show that the change in structure is not chemically random but rather is tied to specific chemical contributions. The chemical ordering in Zr-Ni, then, is not restricted to the glass, but also occurs in the high temperature liquid. Such chemical ordering is, therefore, not unique to Cu-Zr/Hf liquids, but may be quite common in metallic alloy liquids.

Table 3
Faber-Ziman Weighting Factors for Each Amorphous Alloy

Composition	$w_{Ni-Ni}(0)$	$w_{Zr-Ni}(0)$	$w_{Zr-Zr}(0)$
Zr ₃₆ Ni ₆₄	0.307	0.494	0.199
Zr ₅₇ Ni ₄₃	0.120	0.452	0.428
Zr ₇₆ Ni ₂₄	0.033	0.296	0.671

Figure 5 near here, high-resolution figure in attached files

Figure 5 – (a) The thermal processing program for Zr₅₇Ni₄₃ glass. The maximum temperature is slowly increased to observe structural relaxation. (b) The maximum in the first peak in $S(q)$ ($S(q_1)$) in the Zr₅₇Ni₄₃ glass as a function of temperature over several processing cycles. The final cycle is fully reversible after a nearly 8% increase in $S(q_1)$ at room temperature from the as-quenched structure to the fully relaxed structure. The error bars reflect the imprecision in the height of the first peak in the static structure factor.

A dramatic sharpening of the first peak in $S(q)$ on going from the liquid to the glass is observed for all alloy compositions (Fig. 3a-c) and indicates an increase in the ordering of the liquid on a larger scale, accompanying the increasing density. The increasing height of the first peak, $S(q_1)$ is correlated with a decreasing peak width. One benefit of the experimental design is the ability to extract quantitative information from these changes with temperature. As already discussed, the as-quenched glasses were thermally cycled to allow structural relaxation to be measured. For illustration, the processing cycle for Zr₅₇Ni₄₃ is shown in Fig. 5a, with the change in $S(q_1)$ shown in Fig. 5b. In the case of Zr₅₇Ni₄₃, pronounced changes in $S(q)$ accompany structural relaxation, with $S(q_1)$ increasing by nearly 8% from the as-quenched state to the fully relaxed state (measured at room temperature).

The temperature dependence of $S(q_1)$ for the liquids and glasses of all three compositions is shown in Fig. 6. At high temperature, $S(q_1)$ increases linearly with decreasing temperature with very similar rates ($dS(q_1)/dT$) for all liquid alloys. After complete structural relaxation, the temperature dependence of $S(q_1)$ for the glass is small, primarily arising from atomic vibrations, which are described within the Debye theory [59]. For all three alloys studied, a discontinuity is observed between a linear

extrapolation to T_g of the $S(q_1)$ s for the liquids and the $S(q_1)$ s measured for the completely relaxed glasses at T_g . The structurally relaxed state was chosen to ensure consistency of the measurements between glasses prepared using different techniques and with different effective quench rates. From Eq. 1, the calculated structural fragility index, γ , is $15 \pm 5\%$ for $Zr_{36}Ni_{64}$, $7 \pm 4\%$ for $Zr_{57}Ni_{43}$ and $7 \pm 5\%$ for $Zr_{76}Ni_{24}$. These indicate that a large acceleration of structural ordering must occur in the liquid upon approaching the glass transition temperature. This is the behavior expected for fragile liquids [8], with the $Zr_{36}Ni_{64}$ appearing more fragile than the other two Zr-Ni liquids. GFA is often argued to correlate with liquid fragility, consistent with the low GFA and high fragility for these alloy liquids.

Figure 6 near here, high-resolution figure in attached file

Figure 6 – The maximum in the first peak in $S(q)$, $(S(q_1))$, in the glass and liquid as a function of temperature for (a) $Zr_{36}Ni_{64}$, (b) $Zr_{57}Ni_{43}$, and (c) $Zr_{76}Ni_{24}$. The glass data were obtained after complete structural relaxation. The respective crystallization (T_x), solidus (T_s), and liquidus (T_l) temperatures are indicated in each panel. When extrapolated to T_g , the liquid $S(q_1)$ values are smaller than those for the relaxed glass. The computed values of the structural fragility, γ , reflect this difference. The error bars reflect the total uncertainty, incorporating estimates of both accuracy and precision. Fitting parameters from the linear extrapolations are available in the supplementary materials section, which is available online.

Conclusions

In summary, density, volume, thermal expansivity, viscosity, and high-energy X-ray diffraction studies of Zr_xNi_{100-x} ($x = 36, 57$, and 76) equilibrium and supercooled liquids were made in a containerless environment using the electrostatic levitation capabilities of the BESL facility. Complementary X-ray data were obtained in the BESL from rapidly-quenched glasses made from these liquids. The smaller background than is possible in capillary measurements gave higher quality data that could be compared with the liquid data. For all alloys, the pair correlation function, $g(r)$, showed evidence of chemical ordering between Ni and Zr with decreasing temperature that starts in the liquid and becomes more prominent in the glass. This is a manifestation of the strong bonding between Zr and Ni. Similar evidence for chemical ordering was observed earlier by us in Cu-Zr and Cu-Hf liquids and glasses. The results presented here indicate that this may be a common feature in many binary metallic liquids and glasses, hinted at by simulations of Zr-transition metal binary alloys [31]. A deeper experimental investigation of this ordering requires the measurement of the partial structure factors from, for example, neutron diffraction studies. Topological ordering accompanies the chemical ordering. A rapid acceleration in the structural ordering near the glass transition temperature is observed in the temperature evolution of $S(q_1)$, indicating a high fragility of the Zr-Ni liquids [8]. Normally, fragility is determined by the temperature dependence of the viscosity, which is often difficult to measure. The ability to determine fragility from structural studies provides a new avenue for studies of the origin of fragility and for investigating the relationship between fragility and glass forming ability.

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Figure 1 - single column

Figure 2 - single column

Figure 3- double column

Figure 4 - double column

Figure 5a - double column

Figure 5b - double column

Figure 6 - single column

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Fig3_2column_grayscale

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