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Local structure of Al- and Fe-based metallic glasses

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Abstract

The local atomic structures of Fe- and Al-based amorphous metallic glasses have been investigated by the pair density function (PDF) analysis of neutron diffraction data. In the Fe system, chemical substitution at the transition metal ion sites induces significant changes of the local structural environment. With the substitution of Nb for Zr and Mn for Fe, a pre-peak in the structure function is observed that is indicative of short-range chemical rearrangement. This is accompanied by a reduction of volume in real space and a contraction of interatomic pair correlations that could in turn be associated with stronger glass forming ability. In the Al–Ni–Nd system, using the isotope difference neutron PDF technique, the local environments for Ni and Nd were separately determined. The Ni ions tend to form strong interactions with Al with significant shortening of the bond length and weaker interactions with Nd. The local Ni–Al cluster is almost spherical with a coordination close to twelve nearest neighbours, while Ni–Ni chemical short-range ordering is quite strong as indicated by the change of amplitude of the pre-peak with the isotopic substitution. On the other hand, the local Nd environment is more disordered with two separate Nd–Al coordination environments and weaker clustering.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The number of systems that can form bulk metallic glass is still quite small in spite of years of research. This is partly due to the limited understanding of the basic glass forming ability and partly to the absence of a predictive mechanism for searching for new glasses other than what is empirically derived. In the current understanding, glass synthesis is mainly guided by at least three rules, such as the negative heat of formation, a large difference in the atomic size of constituent atoms along with a low liquidus eutectic [1]. In the past decade or so, new kinds of amorphous alloy have been synthesized and studied, especially in zirconium-based and aluminium-based systems [2–5]. New amorphous alloys exhibiting a wide supercooled liquid region before crystallization, greater than 50 K, were found to form by melt spinning

in Zr–Al–M (M = Ni or Cu) systems consisting of constituent elements with significantly different atomic sizes. So far, the largest thickness, in excess of 10 mm, for glass formation has been found in the Zr-based systems [1, 6].

We investigated the local atomic structure of Fe- and Al-based glasses using neutron scattering. The bulk ferrous metallic glasses investigated in this study are selected with a view to obtaining desirable mechanical and corrosion properties including a low ferromagnetic transition temperature [7]. But to predict the glass formability of new Fe-based glasses, it is important to know how the different substitutional elements interact at the atomic level, what the structural changes induced by the different ionic sizes are and how these are in turn related to the macroscopic properties. In this paper we present how the local atomic structure changes due to alloying, while these changes cannot be described by a dense-random-packed model. A distinct pre-peak is observed in reciprocal space because of specific chemical ordering that might be significant with regard to enhancing interactions. This is also accompanied by short-range structural ordering where the local interactions between Fe/TM and the refractory metal and metalloids change with the detailed balance of chemical substitution and hence ionic size. In particular, the local bond lengths between ions get shorter, indicating an increase in their interaction strength. Consequently, the local ‘structural unit’ volume gets smaller for compositions that exhibit good glass forming criteria. Such volume contraction can be significant in destroying ferromagnetic coupling between the Fe ions and is consistent with the suggestions made by [8, 9].

We also report on the local atomic structure in the vicinity of Ni and Nd in Al₈₇Ni₇Nd₆ amorphous alloy as determined by neutron scattering experiments. Earlier neutron and x-ray structural studies of melt-spun Al₉₀Fe_xCe_{10-x} alloys revealed a strong interaction in the vicinity of the first coordination sphere of Fe [4, 10]. It was shown that Fe–Al bond lengths were anomalously short (about 8% contraction), and that this feature was accompanied by anomalous low coordination numbers (45% reduction) as compared to values based on a model of dense random packing (DRP) of hard spheres. In this study, we investigated the Al₈₇Ni₇Nd₆ system using Ni and Nd isotopes (⁵⁸Ni, ⁶⁰Ni, ¹⁴²Nd and ¹⁴⁴Nd) to separate the contribution to the local structures from these two elements. Using the difference in the neutron scattering lengths of the isotopes, differential pair density functions (DPDF) with respect to Ni and Nd were obtained, in an analogous way to in an x-ray absorption fine-structure or an anomalous x-ray scattering measurement performed at the Ni or Nd absorption edge. The results show that Ni ions form strong interactions with Al with significant shortening of the bond length just as in Al₉₀Fe_xCe_{10-x} and weaker interactions with Nd. The local Ni–Al cluster is almost spherical, with a coordination close to twelve nearest neighbours, while Ni–Ni chemical short-range ordering is quite strong. On the other hand, the Nd rare-earth environment is more disordered, with two separate Nd–Al coordination environments and weaker clustering.

2. Experiment

The alloy ingots with compositions Fe₆₈Zr₁₀B₂₂, Fe₆₈Zr₄Nb₄B₂₄ and (Fe₇₀Mn₃₀)₆₈Zr₄Nb₄B₂₄ were prepared by arc melting in an argon atmosphere using nominal amounts of each element. The ribbons were melt spun in a partial helium atmosphere using a copper wheel (20 cm in diameter) with a typical circumferential velocity of 40 m s⁻¹. Typical dimensions were: 15 μm thick, 1–2 mm wide and up to several metres long. The melt-spun ribbons were very flexible and could easily be bent in half without fracturing. Amorphous ribbons of Al₈₇Ni₇Nd₆ and four isotope-substituted samples were prepared by the same method, using the isotope elements ⁵⁸Ni, ⁶⁰Ni, ¹⁴²Nd and ¹⁴⁴Nd to prepare four different samples.

The neutron data were collected using the glass, liquid and amorphous materials diffractometer (GLAD) and the special environment powder diffractometer (SEPD) at the intense pulsed neutron source (IPNS) of Argonne National Laboratory. Data were collected at room temperature for all compositions. Corrections for inelastic, multiple scattering and absorption were applied and the background was measured separately and subtracted from the data. The structure function, $S(Q)$, was Fourier transformed to determine the pair density function (PDF). The PDF is a real-space representation of atomic pair correlations and the analysis provides direct information with regard to the local structure without requiring long-range structural periodicity. It is quite commonly used in the structure analysis of amorphous systems. Since the Fe samples contain boron that has a high neutron absorption cross-section, data were collected over long periods of time to compensate for the reduction in counting statistics.

For the DPDF analysis, the functions for the four isotopic compositions were processed under identical conditions using the same termination point as well as the same background subtraction. Subtraction of $\rho(r)$ for one isotope material from that for the other provides the DPDF with respect to the corresponding elements alone, in this case, Ni or Nd. It is normalized by the corresponding average scattering lengths, $\langle b \rangle$, so the true intensity is recovered and the difference in peak amplitude is due only to the difference in neutron scattering amplitude for Ni or Nd:

$$\text{DPDF} = [\langle b_{58\text{Ni}} \rangle^2 \rho(r)_{58\text{Ni}} - \langle b_{60\text{Ni}} \rangle^2 \rho(r)_{60\text{Ni}}]. \quad (1)$$

Any pair that does not include the Ni (or Nd) atom will be subtracted out. This allows one to discern the contribution from the corresponding element without obscuring the peaks that include this pair with other undesirable pair correlations. Details of this analysis can be found in [11].

3. Results and discussion

3.1. Fe-based metallic glasses

The local atomic topology of bulk Fe-based metallic glasses changes in a distinct way with chemical substitution providing information on important trends towards better glass forming ability. It appears that in this multi-component system, size factor effects alone cannot account for the changes observed in the atomic structure, but, when they are combined with strong hybridization by enhancing bonding interactions, possible network formation can lead to more stable glasses. By substitution in the base composition $\text{Fe}_{68}\text{Zr}_{10}\text{B}_{22}$ of Nb for Zr and Mn for Fe, several changes are observed in the structure function as seen in figure 1 (the structure function for FeZrB is not shown because it is the same as that for FeZrNbB). In particular, a small pre-peak becomes visible with Mn substitution around 1.5 \AA^{-1} that is not observed for either the Zr or Zr/Nb compositions. Because Mn has a negative neutron scattering length it is also possible that the pre-peak is enhanced by Mn substitution. The Fourier transformations of the structure functions are shown in figure 2. The local atomic structure for $\text{Fe}_{70}\text{Zr}_{10}\text{B}_{20}$ was determined earlier by means of extended x-ray absorption fine structure [12] and the results are comparable to the present neutron PDF. The shortest bond length in the structure is the Fe–B correlation which is about 2.12 \AA . This is followed by the Zr–B, Fe–Fe and Zr–Fe correlations in the range of correlation length up to 3.4 \AA . With Nb substitution for Zr, the intensity of the first correlation peak corresponding to Fe–B pairs increases while the intensity of the main correlation peak that is dominated by Fe–Fe correlations decreases in intensity and shifts to higher r -values. Since Nb and Zr atoms have very similar neutron scattering lengths,

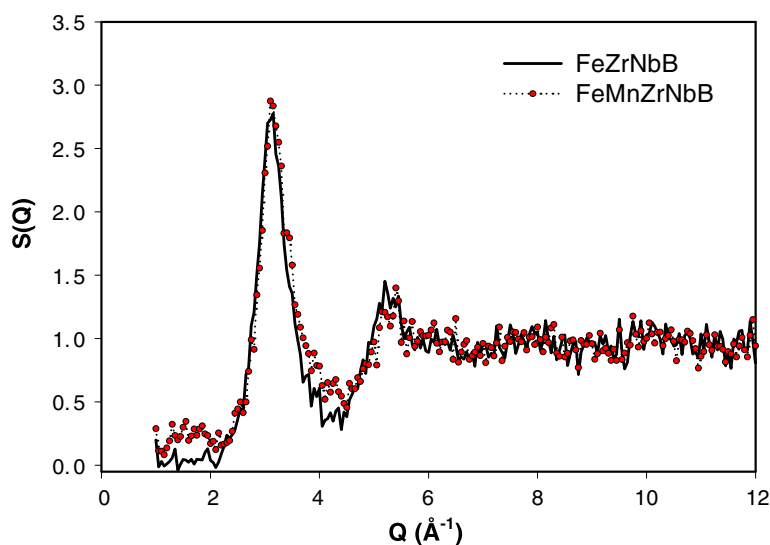


Figure 1. The structure function for the Fe–Zr-based alloy system. The pre-peak at about 1.5 \AA^{-1} is accentuated with Mn doping. This pre-peak is a manifestation of short-range chemical ordering.

the observed changes in the intensity are not due to the difference in the normalized intensity. Also, changes in the bond lengths due to change in the size of Zr and Nb are small. The increase in intensity of the Fe–B peak occurs because of the increase in the Fe–B coordination shell or number of neighbours which seems to be enhanced with Nb substitution. On the other hand, the decrease in the intensity of the main correlation peak might be due to a reduction in the coordination number of Nb/Zr–B pairs or Fe–Fe pairs. These two peaks cannot be resolved because the bond lengths are very similar. It is clear though that Nb does not merely substitute for Zr; its role is in some way affecting the local structure.

With Mn substitution, several changes occur in the atomic structure. Along with the pre-peak in the structure function shown in figure 1, the Fourier transformation for the local atomic structure shown in figure 2 changes significantly with Mn doping. In particular, the bond lengths get shorter as they continuously shift to lower r -distances. It is estimated that the bond lengths are reduced by $0.05\text{--}0.1 \text{ \AA}$. The nearest-neighbour correlations are affected the most where the Fe/Mn–B pair correlation peak changes intensity and the bonds get shorter. This is also an indication that the structural unit volume contracts with Nb and then Mn substitutions. Thus it is clear that the atomic environment is changing with the chemical substitution and that the bond lengths in the first and second coordination shells are reduced with the addition of Mn, indicating an increase in the strength of bonding between the ions.

3.2. Al-based metallic glass, $\text{Al}_{87}\text{Ni}_7\text{Nd}_6$

In the Al system, we investigated a single composition that exhibits a good glass forming ability, $\text{Al}_{87}\text{Ni}_7\text{Nd}_6$. Natural Ni and Nd were each substituted for with two different isotopes that have very different neutron scattering lengths to provide a contrast in the structure function as regards each element and obtain their local environments separately. Similarly to the case for the Fe system, a pre-peak is observed in the structure function of this system as well, as shown in figure 3(a), that serves as strong evidence for a good glass forming system.

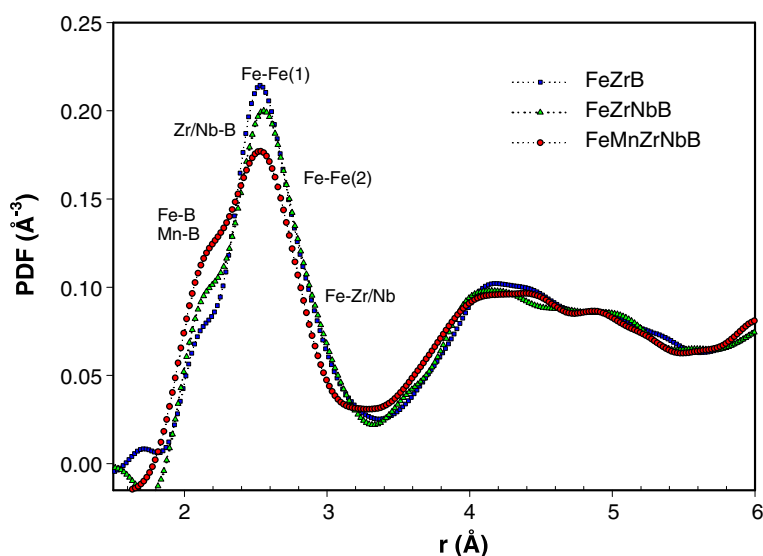


Figure 2. The local atomic structure for the Fe–Zr system determined as a function of chemical substitution at room temperature. Note how the peaks shift to lower r -distances because of volume contraction.

The pre-peak is a distinct feature and corresponds to a quasi-periodic arrangement of atoms in real space that extends over an intermediate range [13]. The pre-peak is present in the natural sample without any isotopic substitution, but when ^{58}Ni is substituted, with its strong neutron scattering length, the intensity under the pre-peak is considerably enhanced. With ^{60}Ni , the pre-peak is still present, but with reduced intensity. In the samples made with the Nd isotopes, the difference in the intensity under the pre-peak upon substitution of ^{142}Nd and ^{144}Nd is minimal. This would suggest that Ni primarily contributes to the intensity of the pre-peak. The quasi-periodic arrangement may be estimated by $R = 7.5/Q_{pp}$, where R is a characteristic distance related to the structural unit size and Q_{pp} is the momentum transfer position of the pre-peak in reciprocal space. Thus the structural correlation length is estimated at about 5 Å, which corresponds to a quasi-periodicity of correlations between Ni clusters.

The total PDF of natural $\text{Al}_{87}\text{Ni}_7\text{Nd}_6$ is shown in figure 3(b). The first peak is quite broad and consists of at least three subpeaks with contributions from Al–Ni, Al–Al and Al–Nd nearest-neighbour pair correlations. To resolve the contribution of each pair, the difference of the total PDF for each isotope, such as $\text{Al}_{87}^{60}\text{Ni}_7\text{Nd}_6$ and $\text{Al}_{87}^{58}\text{Ni}_7\text{Nd}_6$ for Ni, is considered. The DPDF for Ni is shown in figure 4. Similarly, the Nd-DPDF can be obtained by subtraction of the total PDF of $\text{Al}_{87}\text{Ni}_7^{144}\text{Nd}_6$ from $\text{Al}_{87}\text{Ni}_7^{142}\text{Nd}_6$. The first peak in the Ni-DPDF is centred at 2.46 Å and corresponds to Al-around-Ni nearest-neighbour pair correlations while the second small peak corresponds to Ni–Al next-nearest-neighbour pair correlations. The bond length of the Ni–Al pair (2.46 Å) is less than the sum of the atomic radii of Al (1.43 Å) and Ni (1.24 Å) by about 0.2 Å. While such drastic shortening may appear surprising, a similar effect has been observed for the Fe–Al pairs in the amorphous Al–Fe–Ce system [10]. The shortening of the Ni–Al bond indicates strong Ni–Al interactions and may be explained from the electronic structure point of view: electrons with s–p character of the Al atoms are transferred to the d states of the Ni atoms. However, the bond lengths of the Nd–Al (3.26 Å) and Al–Al (2.75 Å) pairs are close to the expected Nd–Al (3.24 Å) and Al–Al (2.86 Å) bond lengths.

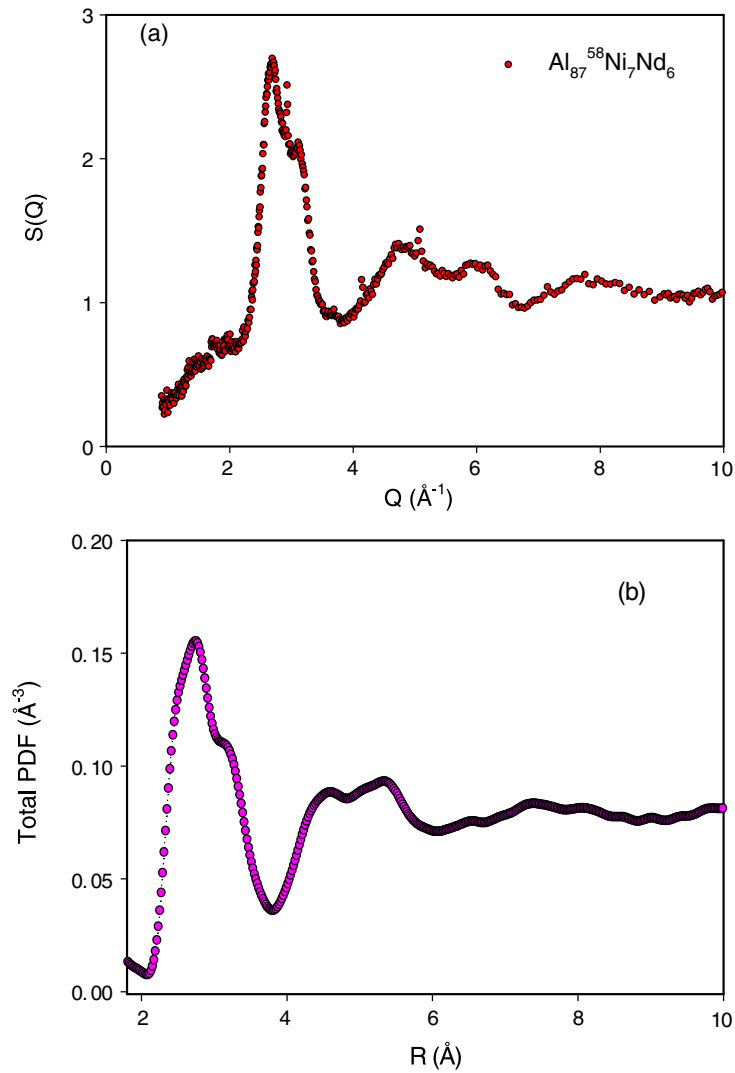


Figure 3. (a) The total structure function of the Ni isotope $\text{Al}_{87}^{58}\text{Ni}_7\text{Nd}_6$ system. The intensity under the pre-peak is enhanced with the ^{58}Ni isotope. (b) The local atomic structure of natural $\text{Al}_{87}\text{Ni}_7\text{Nd}_6$ amorphous metallic glass.

The coordination number around Ni and Nd ions can be obtained using the following expression:

$$N_{\text{Ni-Al}} = A_{\text{Ni-Al}} \frac{\langle b \rangle^2}{b_{\text{Ni}} b_{\text{Al}}} \frac{1}{2c_{\text{Al}}} \quad (2)$$

This formula represents the number of Al atoms bound to Ni ($N_{\text{Ni-Al}}$), where $A_{\text{Ni-Al}}$ is the area under the peak corresponding to the Ni-Al pair, b_i is the neutron scattering length and c_i is the atomic fraction of element i and $\langle b \rangle = \sum_i c_i b_i$. The coordination numbers for each pair are listed in table 1. The coordination number of Al around Ni is determined as close to 11, while the first-nearest-neighbour coordination number of Al around Nd is about 14. The second-nearest-neighbour coordination number of Al around Nd (at a distance of 3.61 Å) is about 4.

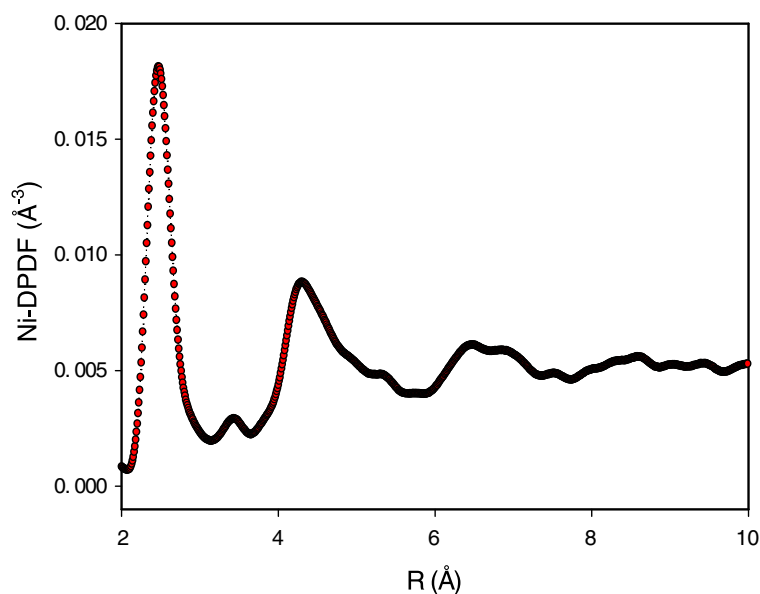


Figure 4. The DPDF with respect to Ni. Note that the first peak, due to Ni–Al pairs, is particularly sharp. The second most prominent peak is due to Ni–Ni compositional ordering.

Table 1. A list of peak positions and coordination numbers for the $\text{Al}_{87}\text{Ni}_7\text{Nd}_6$ system.

Pairs	Bond length (Å)	Coordination number
Al–Ni	2.46	10.9
Al–Nd(1)	3.26	14.2
Al–Nd(2)	3.60	4.1

These numbers are fairly close to what one would expect assuming a dense-random-packed model (16.4).

4. Conclusions

The local atomic topology of amorphous metallic glasses was investigated by alloying in the Fe-based system and by isotopic substitution in the Al system. The structural ordering observed in both systems is consistent with good glass forming criteria. The quasi-periodicity supported by the presence of the pre-peak is enhanced by the substitution of Mn in the Fe-based glass but some evidence of a pre-peak, even without Mn, simply on substituting Nb for Zr is also observed. Interactions between Mn and other ions modify the structure of the glass, leading to changes in the local structure. It becomes apparent that as a consequence of the strong orbital hybridization, the bond between the atoms is enhanced with improved glass forming ability. This is reflected in the reduction of the cell volume, particularly for the first coordination shells. Such reduction in volume continues with the alloying of Nb and Mn, thus strongly suggesting that this is an important criterion in improving glass formability.

For the Al system, the DPDF analysis showed that the transition metal and the rare-earth ions have very different local environments. In the case of Ni, the sharpness of the peaks in the DPDF suggests that it forms a quasi-periodic lattice with distinct bonds in real space and that it does not enter the glass randomly. Also, the presence of the pre-peak in reciprocal

space supports the suggestion of the existence of strong compositional and geometrical order around Ni. The bond distance in the Ni–Al pairs is less than the sum of the atomic radii, suggesting a strong interaction between Al and Ni that is consistent with the effects observed with alloying in the Fe system (volume reduction). In contrast, the Nd sublattice is not well defined. Evidence for Nd geometrical ordering is weak and the broadening of the DPDF local structure peaks is indicative of weakness of interactions of Nd with other ions. Evidence for Ni–Nd bonds has also not been observed that suggests that the interaction between these two ions might be repulsive. While the Ni ions are uniformly surrounded by almost twelve Al ions, the Nd bond length to Al is close to the expected sum of atomic radii for neutral ions and the Al–Nd coordination number of about 18 is close to the coordination number (16.4) calculated from the DRP model. Thus in both systems, the transition metal appears to play a far more vital role in changing the local structure than any other ion.

Acknowledgments

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