Journal of Alloys and Compounds 732 (2018) 585–592

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Inhomogeneity of local packing density and atomic bonding of $Ni_{67}Zr_{33}$ amorphous alloy

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ARTICLE INFO

Article history:
Received 5 September 2017
Received in revised form
21 October 2017
Accepted 23 October 2017
Available online 27 October 2017

Keywords:
Amorphous materials
Atomic scale structure
Neutron diffraction
X-ray diffraction

ABSTRACT

Pulsed neutron diffraction and synchrotron X-ray diffraction measurements were performed on a melt-quenching $Ni_{67}Zr_{33}$ amorphous alloy sample. The Ni-Ni, Ni-Zr and Zr-Zr nearest neighbour distributions were obtained from differences in the scattering intensities between the two probes in conjunction with the Gaussian fitting. The results demonstrate that the Ni-Zr and Zr-Zr nearest neighbour distributions are respectively represented by single Gaussian peaks but the Ni-Ni one is an asymmetric shape. Three-dimensional structure models were constructed by using reverse Monte Carlo (RMC) modelling method with fitting to the neutron and X-ray diffraction data sets. The Voronoi-Delaunay method was used on the RMC configurations to investigate the local packing properties of each coordination cluster. With reference to the macroscopic packing fraction, inhomogeneous structural feature arising from dense and loose packing domains is observed in the structure of $Ni_{67}Zr_{33}$ amorphous alloy.

1. Introduction

Despite of the long-standing interest in amorphous alloys and metallic glasses, their structural properties are not totally understood. Structural studies of these alloys have been conducted by means of not only several experimental techniques but also three-dimensional structure modelling. Voronoi polyhedral analysis is useful to investigate the local topology in the three-dimensional atomic configurations [1,2]. A shape of Voronoi polyhedron reflects the coordination environment around each atom, providing the local coordination cluster around the atom. The nearest neighbours are defined as those atoms whose Voronoi polyhedra share a face, namely they are geometrically determined. Various types of local coordination clusters are generally observed in the structure models of amorphous alloys. One of the most remarkable polyhedral structures may be an icosahedral cluster formed by 13 atoms because of its densely-packed and energetically-stable structure. It was pointed out by Franc that the icosahedral cluster is significantly lower in energy than the corresponding face-centred cubic and hexagonal close-packed clusters [3]. Indeed, Voronoi polyhedra corresponding to the icosahedral and/or icosahedral-like clusters are observed in the three-dimensional structure models of amorphous alloys and metallic glasses [4–9].

On the other hand, the macroscopic densities of typical amorphous alloys are about 2–3% lower than those of corresponding crystals, indicating that the amorphous structures have loosely-packed regions, which are often regarded as free volumes. In order to get a full understanding of the structures of amorphous alloys, detailed information about the packing properties is needed. A simple way to examine the packing properties is the dense random packing (DRP) of hard spheres model. Empirical and simulation studies of the DRP model show that the packing fraction of equal sized spheres is about 0.64 [10–13]. A mixture of different sized spheres can generate a more dense packing, and its packing efficiency is dependent on the radius ratio of spheres. When the radius ratio of small sphere to large sphere is about 0.8, the packing fraction of binary mixtures is up to about 0.65 [13,14], which is much below the values of densely-packed crystal structures [15,16].

Inhomogeneous structures arising from the dense and loose packings were observed in the three-dimensional atomic configurations of some amorphous alloys but these results are simply based on the appearances of the atomic arrangements [17,18]. In a multi component system consisting of different sized atoms, the packing densities depend on the atomic sizes, i.e., a large atom occupies more space than small one. A local cluster formed by

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https://doi.org/10.1016/j.jallcom.2017.10.188
0925-8388/

mainly large atoms inevitably has the low local number density. Hence the packing properties should be investigated in terms of packing fraction rather than number density.

Recently, the glass-forming ability of metallic glasses has been discussed from the aspect of atomic packing efficiency [19,20]. For instance, Ward et al. studied the structural evolution and kinetics in Cu-Zr binary liquids by using molecular dynamics simulation [20]. They used a radical Voronoi tessellation [21] to characterise the models and showed that atomic packing features are important information for understanding the glass-forming ability.

In this work the local packing properties of $Ni_{67}Zr_{33}$ amorphous alloy are investigated by using the pulsed neutron, synchrotron X-ray diffraction measurements and reverse Monte Carlo (RMC) modelling method [22]. The Voronoi-Delaunay analysis was used on the RMC configurations in order to investigate the local packing fractions of respective coordination clusters.

A number of structural studies of Ni-Zr binary amorphous alloys have been carried out by using several experimental techniques such as neutron diffraction [8,9,23–25], X-ray diffraction [23,26–29], anomalous X-ray scattering (AXS) [30,31] and extended X-ray absorption fine structure (EXAFS) [28,32–34]. The amorphous structure of a binary alloy is described by three independent pair correlation functions [35]. The full set of partial structure factors and partial pair distribution functions were separately obtained by means of the neutron diffraction measurements with isotopic substitution [24,25]. Moreover, the local environments around Ni and Zr were investigated through the AXS [30,31] and EXAFS [28,34] techniques. However, these results are too limited to provide detailed information about the short-range order because of the lack of real-space resolution. In the present study, the nearest neighbour distributions of respective pairs are obtained from the high-resolution real-space neutron and X-ray data sets in conjunction with the Gaussian fitting.

2. Theory

The neutron and X-ray total structure factors, $S^{N,X}(Q)$, can be obtained from scattering intensities, $I^{N,X}(Q)$, based on the Faber-Ziman definition [35] as follows:

$$S^{N}(Q) = \frac{I^{N}(Q) - \left\{\langle b^2\rangle - \langle b\rangle^2\right\}}{\langle b\rangle^2}, \tag{1}$$

$$S^{X}(Q) = \frac{I^{X}(Q) - \left\{\left\langle f(Q)^2\right\rangle - \langle f(Q)\rangle^2\right\}}{\langle f(Q)\rangle^2}, \tag{2}$$

where Q is the momentum transfer. Furthermore,

$$\left\langle b^2\right\rangle = \sum_k c_k b_k^2, \quad \langle b\rangle = \sum_k c_k b_k, \tag{3}$$

$$\left\langle f(Q)^2\right\rangle = \sum_k c_k f_k(Q)^2, \quad \langle f(Q)\rangle = \sum_k c_k f_k(Q), \tag{4}$$

where c_k, b_k and $f_k(Q)$ are respectively the concentration, the neutron coherent scattering length and the X-ray atomic form factor of the component atom k.

The $S^{N,X}(Q)$ of a Ni-Zr binary mixture can be described as a weighted sum of three partial structure factors, $S_{kl}(Q)$:

$$S^{N}(Q) = \sum_{kl}^{k\geq l} w_{kl}^{N} S_{kl}(Q), \tag{5}$$

$$S^{X}(Q) = \sum_{kl}^{k\geq l} w_{kl}^{X}(Q) S_{kl}(Q), \tag{6}$$

and the neutron and X-ray weighting factors, $w_{kl}^{N,X}$, are respectively defined as,

$$w_{kl}^{N} = (2-\delta_{kl})\frac{c_k c_l b_k b_l}{\langle b\rangle^2}, \tag{7}$$

$$w_{kl}^{X}(Q) = (2-\delta_{kl})\frac{c_k c_l f_k(Q) f_l(Q)}{\langle f(Q)\rangle^2}, \tag{8}$$

where δ_{kl} is the Kronecker delta.

The neutron (or X-ray) total pair distribution function, $g^{N,X}(r)$, can be obtained from the Fourier transform of $S^{N,X}(Q)$ as follows:

$$g^{N,X}(r) = 1 + \frac{1}{2\pi^2 r\rho_0}\int_0^\infty Q\left(S^{N,X}(Q)-1\right)\sin Qr dQ, \tag{9}$$

where ρ_0 is the average number density.

3. Experimental procedure

3.1. Sample preparation and density measurement

A master ingot of $Ni_{67}Zr_{33}$ alloy was produced by arcmelting from high-purity Zr (99.9 mass%) and Ni (99.9 mass%) in a purified argon atmosphere. An amorphous ribbon sample was prepared by single-roller melt spinning with a roll speed of 40 ms^{-1}.

The density of the $Ni_{67}Zr_{33}$ amorphous alloy sample was measured at room temperature using a gas pycnometer (Quantachrome, Micro-Ultrapyc 1200e) with helium as the displacing fluid. The measurement value is 7.90 (1) g/cm^3 ($\rho_0 = 0.0684$ $Å^{-3}$). The result is about 2% smaller than the value of 8.05 (4) g/cm^3 reported by Altounian and Stron-Olsen [36] but is agreed with the value of ~7.9 g/cm^3 that estimated through extrapolation of data sets reported by Dong et al. [37].

3.2. Neutron and X-ray diffraction measurements

The neutron diffraction measurement was carried out in BL21 (NOVA) spectrometer at the MLF pulsed neutron source of J-PARC facility. The amorphous alloy sample was placed into a vanadium can with an inner diameter of 6 mm and a 0.1 mm thickness. The total structure factor was obtained from the scattering intensity after correction for the background, absorption [38], and multiple scattering [39] and normalization with a vanadium rod. The neutron scattering lengths and cross sections were taken from Ref. [40].

The X-ray diffraction measurement was carried out using a horizontal two-axis diffractometer with a photon energy of 61.57 keV ($\lambda = 0.2014$ Å) on the BL04B2 beam line at the SPring-8 facility. After corrections for the background, polarization, absorption [41] and Compton scattering [42], the scattering intensity was converted to the total structure factor [43]. The X-ray atomic form factors were taken from Ref. [44].