Available online at www.sciencedirect.com
ScienceDirect
Acta Materialia 58 (2010) 3963–3969
Acta MATERIALIA
www.elsevier.com/locate/actamat

Icosahedral clustering with medium-range order and local elastic properties of amorphous metals

M. Wakeda [a], Y. Shibutani [b,*]

[a] Department of Mechanical Engineering, Iwate University, 4-3-5, Ueda, Morioka, Iwate 020-8551, Japan
[b] Department of Mechanical Engineering, Osaka University, 2-1, Yamadaoka, Suita, Osaka 565-0871, Japan

Received 3 November 2009; received in revised form 10 February 2010; accepted 18 March 2010
Available online 13 April 2010

Abstract

The paper focuses on the relationship between icosahedral clustering with medium-range order in amorphous metals and local elastic properties. Using a Cu–Zr binary amorphous model constructed by rapid quenching in the framework of molecular dynamics simulations, Voronoi polyhedra analysis shows that the icosahedra are not randomly distributed in space, but form characteristic interpenetrating icosahedral clustering with medium-range order. It is shown that the center atoms of icosahedra within the highly developed interpenetrating icosahedral clusters have higher local elastic moduli than those of independently existing icosahedra and other polyhedra with lower coordination numbers.

Keywords: Metallic glasses; Medium-range order; Elastic behavior; Molecular dynamics simulations

1. Introduction

Bulk metallic glasses (BMG) have high glass-forming ability (GFA), and therefore large bulky bodies up to 50 mm diameter can successfully be realized [1]. Their high strength, high fracture toughness and high corrosion resistance, which are essentially attributed to the disordered atomic configuration, have already been reported. In recent years, there has been considerable interest in their medium-range ordering (MRO), which probably affects the glass formability as well as mechanical deformability, closely linked to Young's modulus and also shear banding resistance. Some MRO model ideas have been suggested by experimental and computational studies [2–5] and, among them, the atomic cluster model made of interpenetrating icosahedra is considered to be one of the prospective candidates. Such analyses go back more than two decades. In the early study of the molecular dynamics (MD) amorphous model, Tomida and Egami [6] investigated the orientation order of interpenetrating icosahedral clusters in liquids and glasses, and discussed its influence on glass transition in detail. In recent years, Shimono and Onodera [4,7] have shown the existence of both icosahedral short-range ordering (SRO) and network-like MRO composed of icosahedra in supercooled liquid and also in the glass state of metals. Moreover, *ab initio* MD, which gives a more physically reliable internal structure, has shown that there is vertex shared and interpenetrating (intercrossed) icosahedral MRO in metallic glasses [5]. Experimental studies for some alloy compositions have also supported evidence of the existence of icosahedral SRO and MRO in metallic glasses [8–10].

In the present MD study, the relationship between the development of icosahedral clustering and the occurrence of elastic rigidity is taken up. Of primary interest is the question of whether the distribution of icosahedra in space really has any order of difference from artificially random distribution. SRO is, in this study, defined as some ordering atomic polyhedra in the range of the first neighbor,

* Corresponding author.
E-mail address: sibutani@mech.eng.osaka-u.ac.jp (Y. Shibutani).

1359-6454/$36.00 © 2010 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.actamat.2010.03.029

which can be detected by Voronoi polyhedra, and thus MRO is categorized as the ordering structure in the range more than the first nearest neighbor. Of secondary interest is the question of whether icosahedral clustering makes any contribution to the mechanical properties of amorphous metals. Although MRO have been studied for decades, these two issues have still been not fully discussed. In the framework of the MD scheme, this study first investigates the morphological features characterized by both the Voronoi technique, which is modified to handle the size difference of components, and the parameters used in network science. Moreover, as one of the basic mechanical properties, the atomic-level elastic constants which respect only the potential energy contribution are estimated for icosahedral MRO structures, and then their morphological and mechanical relations are qualitatively discussed.

2. Atomic amorphous model

A Cu–Zr binary amorphous metal is chosen in the present study because it has high GFA among binary systems [11]. Moreover, the Cu–Zr amorphous system is suitable for MD calculations since the system does not have strong directional bonding, and thus the structures are expected to be basically formed by random packing. The $Cu_{57}Zr_{43}$ binary amorphous model, containing about 30,000 atoms, was constructed via the quenching process. The interatomic potentials employed here are the empirical ones suggested by Kobayashi et al. [12], which refer to two-body effects. In total, three types of potential parameter sets are prepared to describe Cu–Cu, Cu–Zr and Zr–Zr interactions. In the case of the multi-component amorphous model, the local elastic constant depends not only on the geometrical structure, but also on local atomic composition, which should be reflected in the interaction with the neighbors. The present potentials employed give almost the same elastic moduli for the respective Cu and Zr pure crystalline models [12]. This is not realistic, but is an advantage in discussion of the influence of the geometrical factor on the elastic moduli, since the influence of local composition might be practically ignored as in a single component model.

The alloy model was quenched and relaxed as follows. First, a randomly packed initial state was numerically heated up to 2000 K. After sufficient relaxation for 20 ps, the model was cooled down to 0 K at a rate of 10^{12} K s^{-1}. The external pressure during this heat treatment was kept at zero by the Parrinello–Rahman ensemble, and the temperature of the whole cell was controlled by scaling the velocities of the atoms. Periodic boundary conditions were applied in three-dimensional directions in order to eliminate the inhomogeneous surface effects. The details of this treatment are given in Ref. [13].

3. Formation of interpenetrating icosahedral cluster

Icosahedral configuration is composed of one center and 12 neighbor atoms, and it is characterized by fivefold symmetry. It is suggested by Tanaka [14] that the stable icosahedral order in the supercooled liquid prevents the formation of a long-range crystalline order, resulting in enhancement of GFA. From the standpoint of this idea, the fully developed icosahedral MRO stunts the nucleation and growth of the crystalline nucleus more easily than the dispersion of isolated icosahedra. In computational amorphous models, icosahedral atomic configuration is detected by Voronoi polyhedron analyses, which are good at exploring the local geometrical structure and estimating the local atomic volume quickly. However, this might be accompanied by some technical problems, especially for the case of disorderly condensed matter. The Voronoi polyhedron is determined by relative configuration of the nearest-neighbor atoms, which cannot be clearly defined in the case of a disordered state, thus there is some possibility of judging the severely distorted icosahedron as the other polyhedron and vice versa. Although this inevitable problem would produce no small quantitative error to the structural analyses of highly disordered structures, one can obtain their qualitative characteristics via the Voronoi technique. In addition, attention should be paid to the case of multi-component alloys because of different atomic radii. In the ordinary Voronoi method, a polyhedron has faces placed in just a middle position between the corresponding and nearest-neighbor atoms. Therefore, it cannot take into account the size of individual atoms. An alternative radical plane technique was applied to binary and ternary metallic glasses by Park and Shibutani [15]. This method respects a division of space according to the face placed in a position roughly proportional to the atomic size ratio. This technique is adopted here, and the individual atomic volume is calculated more precisely, which is necessary for the calculation of atomic elastic moduli described below. A significant error of $\sim$20% for typical atomic volume estimation between the two methods was confirmed in the preliminary calculations.

Both the proportion of icosahedron among all the polyhedra and the total volume normalized by the value at 0 K are represented as functions of temperature in Fig. 1. The glass transition temperature T_g is about 850 K, because the volume–temperature curve changes its gradient explicitly. There is a remarkable increase in the proportion of icosahedron from the slightly higher temperature than from T_g, which fact has already been reported in many MD studies [16,17]. For the present atomic composition (Cu 0.57 and Zr 0.43), it is appreciably difficult to identify what kind of background ordered-alloy the present MD model has. This means that there is no information on the precise melting point. Alternatively, as for the other referred simulations, a heating–cooling process was performed for the Zr_2Cu crystalline model with C11b structure, constructed using the same potentials. The melting point obtained for the Zr_2Cu model is about 2400 K, and the glass transition temperature is about 900 K. This implies that the $Cu_{57}Zr_{43}$ model may be in the supercooled liquid state at 2000 K, because the glass transition temperature is about 850 K from Fig. 1.