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Network connectivity in icosahedral medium-range order of metallic glass: A molecular dynamics simulation

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ABSTRACT

A molecular dynamics simulation study has been carried out to investigate the evolutions of network connectivities in icosahedral medium-range order of Ti–Al alloys during rapid solidifications. To overcome the shortcomings of previous quantitative methods, average connectable icosahedra parameter is applied to evaluate the network connectivity of interpenetrating connections of icosahedra in the medium-range order of metallic glass. According to the present investigations of the network connectivities in Ti–Al alloys, $TiAl_3$ alloy is predicted to have higher strength than TiAl alloy at amorphous state. Furthermore, the average connectable icosahedra parameter is a more precise and sensitive characterization method compared with previous parameters to describe the network connectivity of icosahedral clusters in a higher level of structural organization. As a good indicator to describe the interpenetrating icosahedral clusters in metallic glasses, the new parameter provides deeper insights into the relationship between network connectivity of icosahedral medium-range order and material properties in amorphous materials.

1. Introduction

Over the past years, icosahedral structure has been demonstrated to play an essential role in glass formation of amorphous alloys [1–5]. As the major structural unit in metallic liquids and glasses, icosahedral cluster provides an accessible signature of stability in metallic glasses (MGs) [6–8]. The icosahedral medium-range order (IMRO) structures are formed by the interconnections of atoms in icosahedral clusters. Among the IMRO structures, the interpenetrating connections of icosahedra (ICOI) have the lowest average potential energy and smaller average atomic volume compared with other types of connected icosahedral clusters [9–11]. The ICOI form a network that resists the flow in amorphous alloys, thus enhancing the mechanical properties of MGs [12–14]. The growth of the ICOI is considered to be the most important evolution in IMRO structures.

In order to gain deeper insight into the characteristics of network structures in IMRO, network connectivity is applied to describe the structural evolutions of ICOI networks. Network connectivity was demonstrated to be an essential factor in ICOI networks, and it has been found that the network connectivity has significant influence on both local and global mechanical properties [7,11]. In previous studies [11, 14–17], coordination number (CN), which only considers the center atoms of icosahedral clusters, was applied as a common parameter to indicate the network connectivity of ICOI networks. In 2010, M. Wakeda and Shibutani [9] proposed the clustering coefficient (X) to quantitatively indicate the degree of local clustering of an icosahedral network structure. In 2011, M. Lee et al. [11] employed the icosahedral connectivity parameter (C_{ico}) to quantitatively assess the network connectivity of ICOI networks. Although above parameters could investigate the neighboring atoms surrounding any center atom of icosahedral cluster in ICOI networks, the connection properties of the center atoms of icosahedral clusters beyond the icosahedral short-range order (ISRO) could not be fully indicated through these methods. Until now, the method which can comprehensively describe the network connectivity of ICOI networks in higher level of structural organization in MGs has not been established.

In this study, we propose a new quantitative method, average connectable icosahedra ($\overline{C}$) parameter, based on graph theory to indicate the network connectivity of ICOI networks with the structural unit beyond the ISRO. Ti–Al alloys as excellent engineering materials have attracted considerable interest because of the relatively high glass forming ability, which offers a good opportunity to analyze the structural evolution during the glass forming processes [18–25]. In this study, computer simulation based on molecular dynamics (MD) is applied as an effective tool to investigate the network connectivity in IMRO of liquid and amorphous Ti–Al alloys at atomic level. The radial distribution function (RDF) is applied to indicate the formation of MG. The connectivity of the ICOI networks is investigated through the original methods: C_{ico}, average CN, and $\overline{X}_{network}$. Moreover, we apply $\overline{C}$ parameter to indicate the network connectivities of Ti–Al alloys in IMRO, and then compare with the original parameters.

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2. Simulation details

MD technique was applied to simulate the rapid solidifications of liquid Ti–Al alloys in this study, and we selected two model alloys from the Ti–Al binary systems: $TiAl_3$ and TiAl. The systems were performed in cubic boxes (side lengths = 7.9 nm) with 32,000 atoms for the $TiAl_3$ and TiAl compositions under three dimensional periodic boundary condition. The simulations employed the embedded-atom model (EAM) which was developed for the Ti–Al alloys to indicate the interatomic interactions in a many-body framework [26]. The simulations were performed under constant pressure and constant temperature (NPT ensemble) with zero pressure. The time step was 1.0 fs. Since the melting points of $TiAl_3$ and TiAl alloys are around 1623 K and 1753 K [19], the simulations were started at 2000 K. At the beginning of the simulation, the systems were run for 200 ps at 2000 K to guarantee equilibrium liquid states and the microstructures were proved to be in liquid states after this operation. Subsequently, the systems were cooled down from 2000 K to 200 K under cooling rate of 10^{11} K/s. Meanwhile, the atomic positions in the boxes were recorded with an interval of 100 K during the rapid solidifications. In this study, cluster-type index method (CTIM) was applied to indicate the formations and evolutions of the short-range order structures [27]. Finally, several quantitative methods were applied to evaluate the network connectivities of $TiAl_3$ and TiAl alloys during the quenching processes.

3. Results and discussions

3.1. Glass formation of Ti–Al alloys

It is necessary to investigate whether the $TiAl_3$ and TiAl alloys have formed MGs during the solidifications. RDF, as a widely used structural characterization method, was applied to describe the probability of finding a neighboring atom in the spherical shell of a central atom. It is defined as

$$g_{\alpha\beta}(r) = \frac{V}{N_\alpha N_\beta}\left\langle \sum_{i=1}^{N_\alpha} \frac{n_{i\beta}(r)}{4\pi r^2 \Delta r} \right\rangle \quad (1.1)$$

where V is the volume of the simulation box; N_α and N_β denote the number of atoms α and β, respectively. $n_{i\beta}(r)$ denotes the average number of β-type atoms around ith α-type atoms in the spherical shell ranging from r to r + Δ r. As shown in Fig. 1(a) and (b), remarkable splits in the second peaks of $g_{total}(r)$ curves could be observed at the end of the solidifications. Since the split of the second peak in the $g_{total}(r)$ curve is the evidence of glass formation, $TiAl_3$ and TiAl alloys have formed MGs after solidifications. In Fig. 1(a) and (b), the first peaks of $g_{Ti-Al}(r)$ curves are higher than $g_{Ti-Ti}(r)$ and $g_{Al-Al}(r)$ curves, which indicates that a strong interaction between different kinds of atoms existed in the rapidly solidified $TiAl_3$ and TiAl alloys. As shown in Fig. 1(a), the first peak of $g_{Ti-Ti}(r)$ curve is lower than other $g_{partial}(r)$ curves, and second peak of $g_{Ti-Ti}(r)$ curve is relatively high compared with other $g_{partial}(r)$ curves, which is caused by the relatively weak interaction between Ti atoms and relatively low Ti content in amorphous $TiAl_3$ alloy. The insets of Fig. 1(a) and (b) show the evolutions of internal energy of Ti–Al alloys during the quenching processes. The glass transition temperatures (T_g) of $TiAl_3$ and TiAl alloys were around 810 K and 865 K, respectively.

Icosahedral cluster is the major structural unit in metallic liquids and glasses. Based on the Honeycutt–Andersen (HA) bond-type index [28] and Wang's work [29], CTIM defines the basic cluster as the smallest cluster composed of one central atom and its nearest-neighbor atoms. CTIM adopts four indices (N, n1, n2, n3) to denote different types of basic clusters, where N is the number of the nearest-neighbor atoms, namely, the coordination number, and n1, n2, and n3 denote the number of 1441, 1551 and 1661 bond-types formed between the surrounding atoms and the central atom. The (12 0 12 0) denotes an icosahedral cluster. Furthermore, the numbers of perfect icosahedra and imperfect icosahedra are added as total icosahedra in the investigation, since clusters are not required to be perfect icosahedra; they are considered "full" as long as the distortion is not significant enough to change the complete fivefold bonding environment [7]. Fig. 2(a) demonstrates the evolutions of icosahedral clusters in $TiAl_3$ and TiAl alloys during the rapid solidifications. The icosahedral clusters in $TiAl_3$ and TiAl alloys both increased remarkably around the T_g, and kept moderate growth below the T_g. At the end of the solidifications, the numbers of icosahedral clusters in $TiAl_3$ and TiAl alloys came up to 4128 and 2399, respectively. According to the statistical numbers of icosahedral clusters, the growth of ISRO in $TiAl_3$ alloy is better than TiAl alloy.

The insets of Fig. 2(a) show the center atoms of icosahedral clusters in $TiAl_3$ and TiAl alloys at the end of the solidifications. At 200 K, nearly 99.8% center atoms of icosahedral clusters in $TiAl_3$ alloy were Al atoms. In TiAl alloy, nearly 94.9% icosahedral clusters were Al-centered at 200 K. The atomic radius of Al is little smaller than Ti and the electron density of Al atom is higher than Ti atom, thus, the stability of Al-centered icosahedral cluster is higher than Ti-centered icosahedral cluster [30,31]. At the end of the solidifications, 100% and nearly 95.6% icosahedral clusters which built the ICOI networks were Al-centered icosahedral clusters in $TiAl_3$ and TiAl alloys, respectively. Fig. 2(b) shows the percentages of atoms in different CNs which only consider the center atoms of icosahedral clusters at 200 K. The CN of center atom of icosahedral cluster presents the environment around icosahedral cluster in

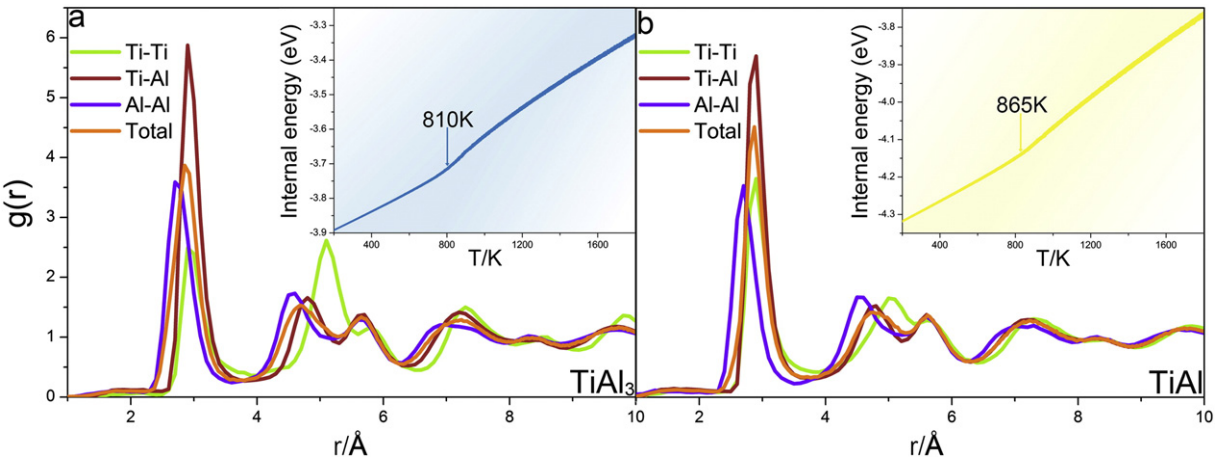

Fig. 1. The $g_{total}(r)$ and $g_{partial}(r)$ curves of (a) $TiAl_3$ and (b) TiAl alloys at 200 K. The insets show the evolutions of internal energy of (a) $TiAl_3$ and (b) TiAl alloys during the rapid solidifications.