

# Atomic packing and short-to-medium range order evolution of Zr-Pd metallic glass

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Received June 1, 2011; accepted August 31, 2011

A larger-scale  $Zr_{70}Pd_{30}$  alloy system has been simulated using molecular dynamics (MD) to investigate structure evolution in  $Zr_{70}Pd_{30}$  metallic glass. The simulated pair distribution function of  $Zr_{70}Pd_{30}$  metallic glass agrees well with the experimental results. Voronoi polyhedron analysis indicates that the icosahedra are not randomly distributed in space, but form characteristic intercrossed icosahedral clusters with medium-range order. Intercrossed icosahedral clusters are the dominant local configurations in  $Zr_{70}Pd_{30}$  metallic glass and probably cause the quasicrystalline phase discovered in  $Zr_{70}Pd_{30}$  metallic glass.

**molecular dynamics simulation,  $Zr_{70}Pd_{30}$  metallic glass, icosahedra, medium-range order**

**Citation:** Qi L, Liu M, Zhang S L, et al. Atomic packing and short-to-medium range order evolution of Zr-Pd metallic glass. Chinese Sci Bull, 2011, 56: 3908–3911, doi: 10.1007/s11434-011-4841-0

In recent years, quasicrystals have been found to form in many Zr based binary metallic glasses (MGs) such as Zr-Pd and Zr-Pt [1,2]. The bulk quasicrystalline alloys exhibit high strength and good ductility [3]. In the Zr-Pd binary system, the nature of the amorphous-to-quasicrystalline phase transition has been clarified [4,5]. However, the characteristic structure in the  $Zr_{70}Pd_{30}$  MGs is currently unknown. We also do not know whether the structures of  $Zr_{70}Pd_{30}$  MGs directly affect the transition into the quasicrystalline phase. In the present study, the transition of the  $Zr_{70}Pd_{30}$  alloy from the supercooled liquid to the solid is simulated using molecular-dynamics (MD). The structure of the  $Zr_{70}Pd_{30}$  metallic glass is investigated in detail by means of the pair distribution function (PDF), pair analysis method (PA) [6,7] and Voronoi polyhedron analysis method.

Based on the hypothesis that linking icosahedra can form the quasicrystalline phase, there has been considerable interest in the icosahedral medium range ordering (IMRO) of MGs's [8–13], which probably affects the glass formability as well as the mechanical properties, including Young's modulus and shear banding resistance [14]. Recently, some

models for IMRO in MGs have been suggested by experimental and computational studies [15–22].

## 1 Simulation methods

Theoretical models of liquid and amorphous structures are often obtained from MD simulations using either *ab initio* methods or empirical pair potentials. However, finite computational resources restrict the size of the ensembles that can be considered in *ab initio* calculations to a few hundred atoms. The systems simulated with pair potentials show an increase in the number of icosahedra during liquid cooling [23–26]. Therefore, the embedded-atom method (EAM) potential [27], which has been successfully applied to a wide range of aspects of the liquid and amorphous states, is adopted in the present simulations [28–33].

Based on the constant temperature and constant pressure (NPT) method, the simulations are performed with a system consisting of 100000 atoms in a cubic box with periodic boundary conditions along all three directions. The Newton equations were integrated using the Verlet [34] algorithm with a time step of 5 fs. The initial liquid state was obtained

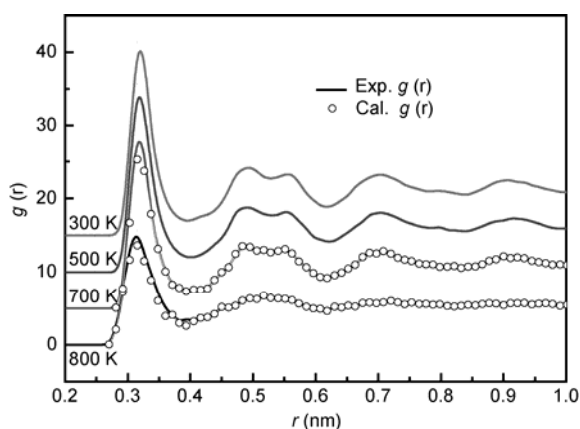
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by holding the system well above a liquidus temperature. The system was melted, homogenized, and then quenched by rescaling particle velocities to room temperature at a rate of  $1 \times 10^{12}$  K/s. The dependences of the volume and the local structure on the temperature were examined. The structural analysis of liquids and glasses was performed using the PA technique and index of Honeycutt-Anderson in a separate program. Using the PA technique, the fivefold symmetry bonds plus the icosahedral short-range ordering can be easily seen at the atomic level. For the larger clusters with IMRO, the local structure in the models was analyzed using the Voronoi method.

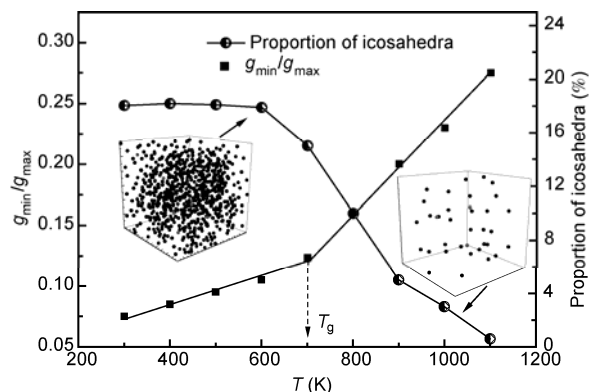
## 2 Results and discussions

Since the PDF is a Fourier transformation of the structure factor obtained from a diffraction experiment, it can be used to compare the simulation results with the experimental ones for liquid and glass structures. Figure 1 shows the evolution of the total PDF during the rapid quenching process of  $Zr_{70}Pd_{30}$  liquid alloy at a cooling rate of  $1 \times 10^{12}$  K/s. The splitting of the second peak in the total PDF becomes pronounced with decreasing temperature, which indicates the formation of  $Zr_{70}Pd_{30}$  metallic glass and the enhancement of ISRO during the quenching process. The simulated total PDFs for the liquid and glass structures both agree well with the experimental results, although their first peaks are slightly higher.

The glass transition temperature  $T_g$  can be obtained from the relationship between the Wendt-Abraham ratio  $R$  [35] and temperature. In Figure 2, both the proportion of icosahedra and  $R$  are represented as functions of temperature for a cooling rate of  $1 \times 10^{12}$  K/s. The glass transition temperature  $T_g$  is about 700 K, which is lower than the experimental value ( $\approx 750$  K) [18]. Considering that the much higher cooling rate adopted in the present simulation compared with that occurring experimentally will reduce the  $T_g$ , our



**Figure 1** Evolution of total PDF during the liquid quenching process of  $Zr_{70}Pd_{30}$  alloy.



**Figure 2** Relationship between Wendt-Abraham ratio  $R = g_{\min}/g_{\max}$  and temperature obtained from Figure 1, and the proportion of icosahedra during the quenching process from the liquid state at a cooling rate of  $1 \times 10^{12}$  K/s. The two embedded images are spatial distributions of the center atoms of icosahedra at 1100 and 600 K, respectively.

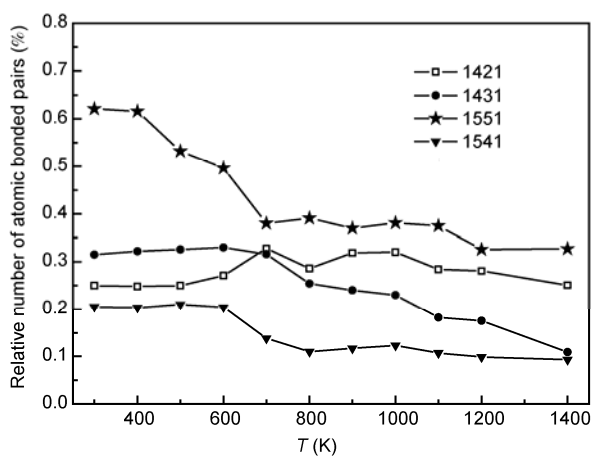
calculations are reasonable. There is a decrease in the proportion of icosahedra going from slightly above  $T_g$  to  $T_g$ ; this fact has already been reported in many MD studies [10,36].

The PDF reflects the statistical average of the ISRO structures, but is incapable of describing the topological structures of the ISRO. The pair analysis method has been widely used to assess the local configurations of the liquid, amorphous and crystal structures. In this method, a set of four integers,  $ijkl$ , is designed to describe the different local configurations. The first integer  $i$  is used to identify the bonding of two given atoms.  $i$  is 1 when they are bonded in the root pair, otherwise  $i$  is 2. The second integer  $j$  is the number of common near-neighbor atoms shared by the root pair. The third integer  $k$  is the number of bonds among the shared neighbors. The fourth integer  $l$  is needed to distinguish configurations having the same first three indices but being different bond geometries. Different local atomic structures have different PA indices and general observations are as following: the fcc crystal structure leads only to 1421 bonds; the hcp crystal structure leads to 50% 1421 bonds and 50% 1422 bonds; and the bcc crystal structure has 43% 1441 bonds and 57% 1661 bonds. The 1551 bond represents the two neighboring atoms with five common neighbors that form a pentagon of near-neighbor contacts, and is therefore situated in a fivefold symmetry environment. The number of 1551 bonds is a direct measurement of the degree of icosahedral ordering. The 13-atom icosahedron has twelve 1551 bond-types. When one bond between a pair of outer atoms in an icosahedron is broken, two of the 1551 bonds become transformed into 1541 bonds and two are transformed into 1431 bonds.

Figure 3 shows the evolution of the relative numbers of various bonds during the rapid quenching process of  $Zr_{70}Pd_{30}$  alloy. It is clear that the numbers of 1551, 1541 and 1431 bonds which are closely related to icosahedra or defective icosahedra, are significantly higher than the other

types; their summation reaches 74.2% of the glass structure at 300 K. Moreover, the number of 1551 bonds increases remarkably during the glass transition process, whereas others only change a little. This means that various icosahedral ISRO structures in the  $Zr_{70}Pd_{30}$  alloy are inherent to the glass structure during the rapid quenching process, and the icosahedral ISRO structures play a critical role in the formation of the  $Zr_{70}Pd_{30}$  metallic glass. Although the existence of ISRO in the glassy state of some metals has been proven, in some MGs the ISRO is absent. The first evidence for structural identification of the icosahedral cluster in the  $Zr_{70}Pd_{30}$  glassy alloy was provided by Saida et al. [18], which presents a high-resolution TEM image of the  $Zr_{70}Pd_{30}$  glassy alloy. Although the diffraction spots are quite weak due to the small area of the ordered region and the fine electron beam, the fivefold symmetry is clearly identified, which indicates that the cluster has an icosahedral structure. These results imply that the icosahedral clusters observed in the as-quenched state are attributable to the high stability of the icosahedral atomic configuration during the cooling process from the melt [18].

One can now ask what kinds of relationships are there among the large number of icosahedral or defective icosahedral clusters, and also what further kinds of characteristic IMRO structure the  $Zr_{70}Pd_{30}$  glassy alloy has. To answer these questions, we adopt the Voronoi polyhedron analysis method. Voronoi polyhedron analysis gives hundreds of types of polyhedra, among which the most popular polyhedron corresponds to the icosahedral atomic configuration. Just as the 1551 bond only reveals the presence of fragments of icosahedra, the PA method is incapable of characterizing the larger clusters with IMRO. To examine the local structure in the fully relaxed glass models, the atomic coordinates in the models were analyzed using the Voronoi method. Based on the pattern of two linking icosahedra, there are four types of configuration: vertex-sharing (VS), edge-sharing (ES), face-sharing (FS) and intercross-sharing

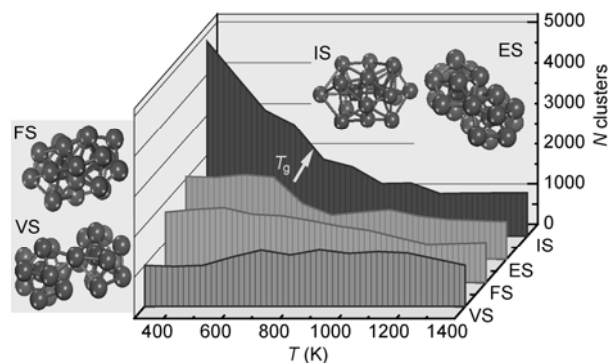


**Figure 3** Evolution of relative numbers of different bond types during the rapid quenching process.

(IS) atoms, as shown in the four embedded images in Figure 4. Thus, IMRO structure with extended icosahedral clusters can be formed. Figure 4 also shows the evolutions of the four types of configuration with temperature during rapid quenching. The figure shows that at high temperature, the numbers of VS, ES, FS and IS clusters are small, indicating that most icosahedra in the system are isolated from each other. As the temperature continuously decreases, more and more icosahedra are linked with each other to form VS, ES, FS and IS types. Among the four cluster bond-types, the IS bond-type increases remarkably and is the dominant cluster bond-type in the supercooled liquid and glass structures. This indicates that the extended icosahedral clusters in the  $Zr_{70}Pd_{30}$  supercooled liquid and glass structures are mainly composed of the IS cluster bond-type. Since the central atoms of two icosahedra bond with each other by sharing four atoms in the IS cluster bond-type as shown in Figure 4, it is high densely packed and will be more stable than other cluster bond-types. Based on the idea that linking icosahedra can form quasicrystals, we can infer that the intercrossed icosahedral clustering with medium-range order is the direct reason for the formation of the quasicrystalline phase discovered in the  $Zr_{70}Pd_{30}$  metallic glass.

### 3 Conclusion

The present study investigated the atomic structure and the relationship between the IMRO and quasicrystal transition of  $Zr_{70}Pd_{30}$  alloy using the binary amorphous MD model. The simulation results show that highly icosahedral clusters exist in the amorphous state. The detailed analysis of the cooling process from liquid showed that the icosahedral structure does not form randomly. More intercrossing icosahedral clusters form, leading to the characteristic network structures in the glassy state. This is likely to be the direct reason for the quasicrystalline phase discovered in the  $Zr_{70}Pd_{30}$  metallic glass.



**Figure 4** Evolutions of the numbers of VS, ES, FS, and IS clusters in the system with temperature at a cooling rate of  $1 \times 10^{12}$  K/s. The four embedded images are schematic configurations of the VS, ES, FS, and IS clusters between two icosahedra.

This work was supported by the National Basic Research Program of China (2010CB731600) and the National Natural Science Foundation of China (50901066, 50771090 and 50821001).

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