**Local Structural Changes During Glass Formation in Zr80Pt20 Alloys**

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**Abstract.** Changes in the local atomic configurations during the glass formation in Zr80Pt20 alloys were studied using molecular dynamics simulations. Partial pair distribution functions and x-ray structure factors were calculated at different temperatures. The resulting x-ray total structure factor at 300 K coincides with previously reported experimental results. Neighboring Voronoi polyhedral analyses were performed to investigate the connections between atomic clusters in the Zr80Pt20 alloys. The growth of an interpenetrating medium-range order formed by icosahedral atomic clusters with central Pt atoms was observed during the glass formation, which could be considered a sign of glass transition in terms of static structure.

*Keywords: metallic glass, amorphous, molecular dynamics simulation*

# INTRODUCTION

The formation of glass from liquids has been reported in various material systems, and the dynamic and static structural changes have been discussed in depth. For metallic systems, it is well known that Zr-based and Pd-based alloys particularly have high glass-forming ability [1]. Especially for Zr-based alloys, it has been reported that icosahedral atomic clusters, which are known as local atomic environments peculiar to metallic glasses, are intrinsic, and their fractions increase significantly during the cooling process. Wang *et al.* also suggested that icosahedral atomic clusters, which are considered short-range order (SRO) structures, connect to form medium-range order (MRO) structures [2]. The Zr–Pt metallic glass is one of the alloys known to contain many icosahedral SRO and MRO structures, and detailed structure analyses of the glass and liquid states have been performed so far. As a result, a pronounced pre-peak at 1.69 Å-1 is observed in the x-ray structure factor of the Zr80Pt20 alloy, indicating a strong chemical SRO structure [3]. Celtek *et al.* also found that the second peak of the total pair distribution function (PDF) of the Zr80Pt20 alloy split at 1100 K during the cooling process, a characteristic sign of glass formation [4].

In this study, we focused on the MRO structures of Zr–Pt alloys and investigated their structural features and formation processes. Molecular dynamics (MD) simulations were used to investigate the changes in the atomic arrangement of the alloy at various temperatures during the glass formation. We also calculated the partial PDFs and total structure factors of the atomic configurations obtained by MD simulations at various temperatures. Furthermore, the formation of MRO structures composed of icosahedral atomic clusters near the glass transition temperature was investigated using Voronoi polyhedral analysis.

# METHODS

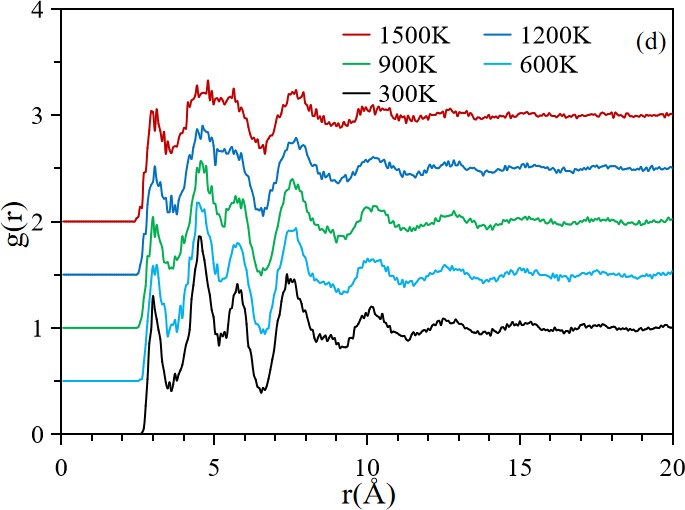
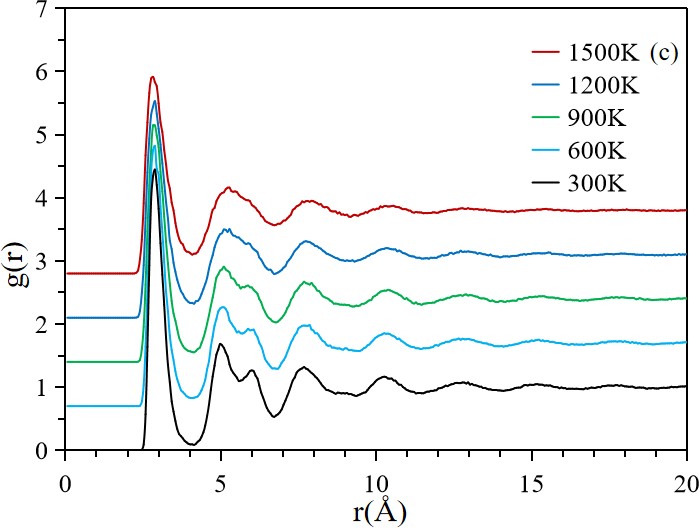
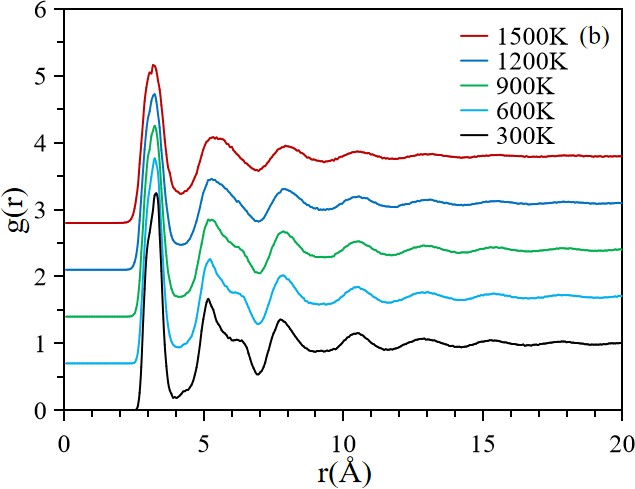
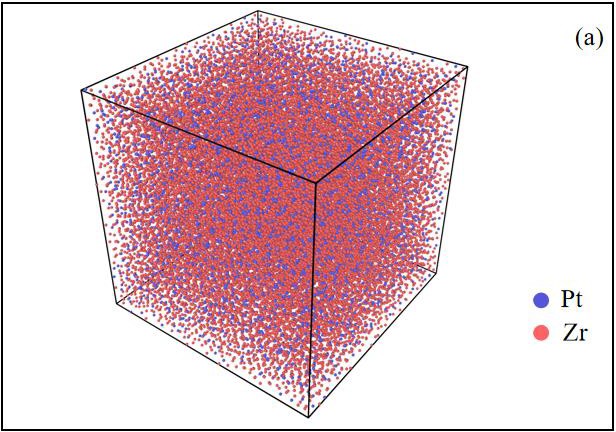
MD simulations were performed using the LAMMPS Molecular Dynamics Simulator [5] with the NPT ensemble to calculate the cooling process of the Zr80Pt20 alloys. The embedded atom method (EAM), which includes many-body

effects approximately, was employed for the interatomic potential [6]. The atomic arrangements were initially set to have a face-centered-cubic structure containing 32000 atoms (25600 Zr atoms and 6400 Pt atoms) under three- dimensional periodic boundary conditions. The simulation was performed under constant isothermic-isobaric (NPT) conditions. The temperature and pressure of the system were controlled using a Nose-Hoover thermostat and barostat. After equilibration of 20000 steps in the liquid state at 3000 K, the configurations were cooled to 300 K at a cooling rate of 1.0×1013 K/s, followed by 10000 steps for relaxation. The atomic configurations at 1500K, 1200K, 900K, and 600K were captured in the middle of the cooling process. The time step was set to 1 fs. To investigate the structural features of Zr80Pt20, we calculated pair distribution functions (PDF) of its atomic configurations at different temperatures. The total x-ray structure factors for different temperatures were obtained by the Fourier transform of the total PDF profiles. Neighboring Voronoi polyhedral analyses, which we propose in the present study, were also used to reveal the details of the SRO and MRO in Zr80Pt20.

# RESULTS AND DISCUSSION

* 1. Pair distribution functions

The PDF measures the existence probability of an atom at a distance of *r* away from a central atom and can be calculated using the atomic arrangement data obtained from the MD simulation. By specifying the type of atomic pair, we can calculate the partial PDF using the following equation [4].



**FIGURE 1.** (a) Atomic configuration at 300 K, (b) Zr–Zr partial PDFs, (c) Zr–Pt partial PDFs, (d) Pt–Pt partial PDFs.

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| --- | --- |
| 𝑁 𝑁  𝑉  𝑔𝛼𝛽(𝑟) = 4𝜋𝑟2𝑁 𝑁 〈∑ ∑ 𝛿(𝑟 − 𝑟𝑖𝑗)〉  𝛼 𝛽 𝑖 𝑗≠𝑖 | 1) |

where V represents the volume of the structural model, *Nα* and *Nβ* represent the numbers of atoms of type *α* and type *β*, brackets represent the time average of summation of the Dirac delta function *δ(r-rij)*, and *rij* is the distance between atoms *i* and *j*.

In this study, we focus on the data at temperatures of 1500, 1200, 900, 600, and 300 K to characterize the structural changes during the cooling process. The atomic configuration at 300 K obtained by MD simulations with an amorphous structure is shown in Fig. 1(a). The partial PDFs for the Zr–Zr, Zr–Pt, and Pt–Pt atomic pairs at each temperature are shown in Fig. 1(b), (c), and (d), respectively. The partial PDFs for each pair indicate that a pronounced splitting of the second peak at around 5.3–5.7 Å occurs with a temperature decrease. Our present results show that the second peaks of the Zr–Zr and Zr–Pt partial PDFs started to split at 900 K, whereas the second peak of the Pt–Pt partial PDF split at 1200 K. These results are reasonably consistent with those of Celtek *et al.* [4], where the second peak of the total PDF of Zr80Pt20 splits at 1100 K, implying the formation of pronounced MRO structures at approximately 900–1200 K. Additionally, Fig. 1(d) shows that the second peak of the Pt–Pt partial PDF was the highest peak at all temperatures, indicating that Pt atoms are mainly placed at a distance of 4.3–5.0 Å away from another Pt. This result implies the presence of a strong chemical SRO in the glass state of Zr80Pt20.

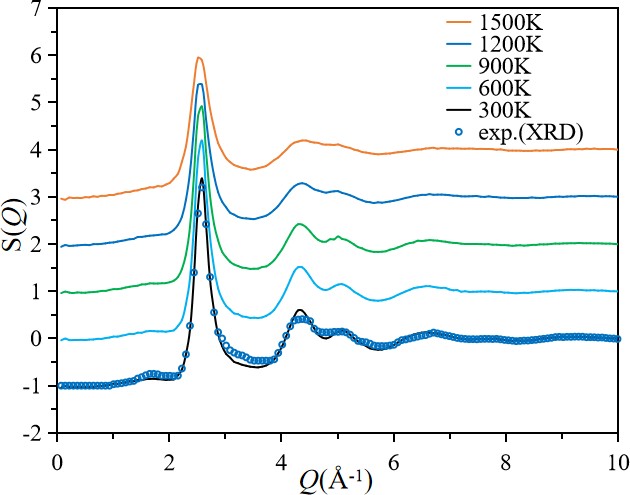
* 1. Structure factor

The partial structure factors for the simulated atomic configurations at different temperatures were obtained by Fourier transform of the partial PDFs [7]:

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| --- | --- |
| sin𝑄𝑟  𝑆𝑖𝑗(𝑄) = 1 + 4𝜋𝜌𝑖𝑗 ∫[𝑔𝑖𝑗(𝑟) − 1] 𝑟2𝑑𝑟  𝑄𝑟 | 2) |

where *ρij* is the partial density, which can be calculated from the average atomic density *ρ0* and the atomic concentrations of the two types of atoms a*i* and a*j* using

|  |  |
| --- | --- |
| 𝜌𝑖𝑗 = 𝜌0√𝑎𝑖𝑎𝑗 | 3) |



**FIGURE 2.** Total structural factors obtained by MD simulation (1500, 1200, 900, 600, and 300 K) and XRD measurements (300

K) [8].

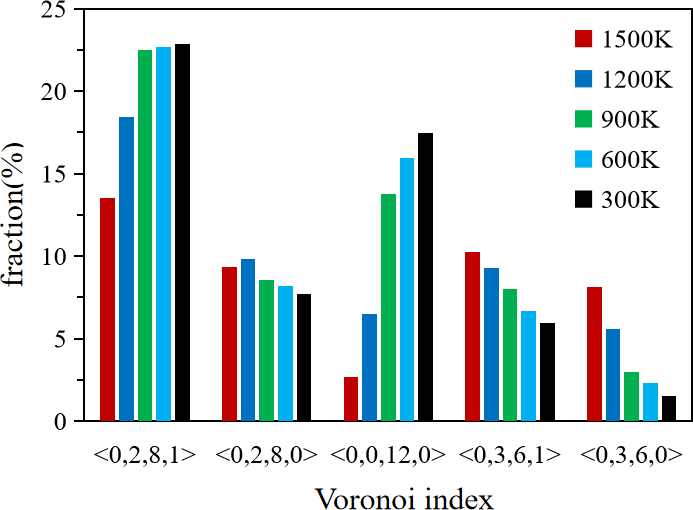
The x-ray total structure factor was obtained by summing the three partial structure factors with the weighting factors as coefficients. The total structure factors of Zr80Pt20 at different temperatures (1500, 1200, 900, 600, and 300

K) are shown in Fig. 2. The simulated S(*Q*) profile at 300 K coincides with the experimental S(*Q*) profile [8] obtained by x-ray diffraction measurements, although the second peak of the simulated profile was slightly higher than that of the experimental profile. A pre-peak appearing at approximately 1.7 Å-1, widely reported in the previous studies [2, 4, 9], was also observed, although it is unclear. As the temperature decreased, the shoulder of the second peak became visible below 900 K, probably because of the glass transition.

* 1. Voronoi polyhedral analysis

Voronoi polyhedral analysis is a widely used method to analyze the structural characteristics of atomic clusters. The planes that bisect the line segments connecting a central atom with its nearest atoms form a Voronoi polyhedron [10], whose shape can be described by the Voronoi index. Figure 3 shows the fractions of each Voronoi index for the atomic clusters with central Pt atoms at different temperatures. The <0,2,8,1> polyhedron with a coordination number of 11 was the most common structure of atomic clusters with central Pt atoms at all temperatures, followed by the

<0,0,12,0> polyhedron, which was identical to the icosahedral cluster, except in the liquid state (1500 and 1200 K). When the temperature drops, the fractions of both the <0,2,8,1> and <0,0,12,0> polyhedra increase, whereas those of both the <0,3,6,1> and <0,3,6,0> polyhedra decrease. The <0,3,6,1> and <0,3,6,0> polyhedra have coordination numbers of 10 and 9, respectively. These results indicate that the atomic clusters with central Pt atoms having larger coordination numbers, such as 11 or 12, tend to be more stable in the glassy state, resulting in the formation of a large number of icosahedral or icosahedral-like atomic clusters in Zr80Pt20 alloys. These results are consistent with previously reported experimental observations [6, 11, 12] and MD simulations [13] of Zr–Pt alloy systems reported previously.

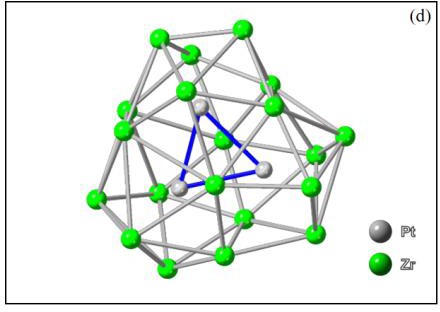
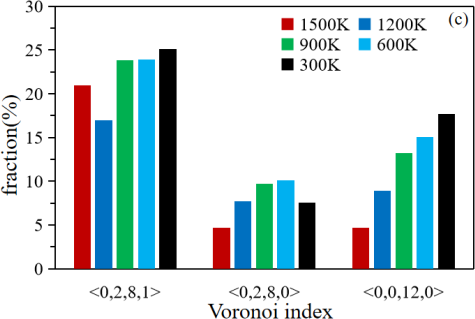
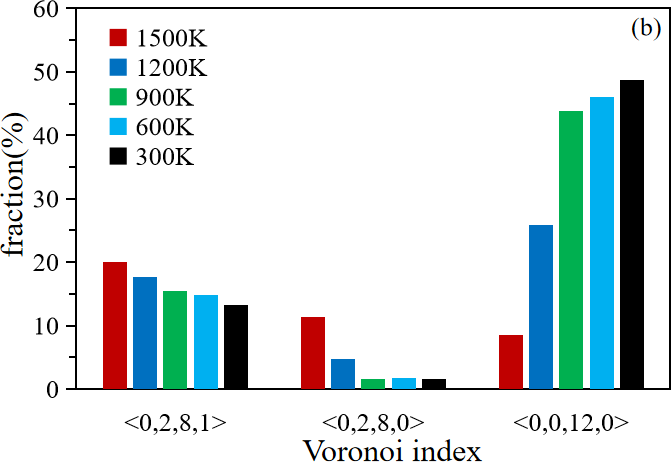
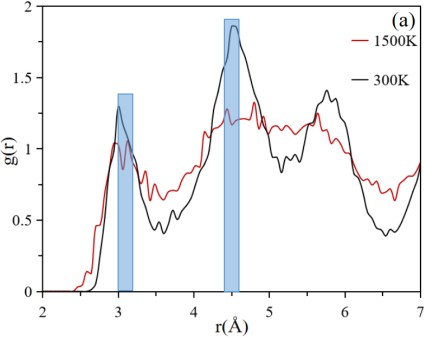


**FIGURE 3.** Fractions of dominant Pt-centered Voronoi polyhedra at different temperatures.

* 1. Neighboring Voronoi polyhedral analysis

To understand the correlation between atomic clusters, we have developed a method of neighboring Voronoi polyhedral analysis, which enables us to determine the cluster correlation not only in the nearest neighbor range but also in the next-nearest range or more. By setting the type of atomic cluster as the central cluster, the existence probability of each type of atomic cluster at a specified distance can be obtained. In this study, we chose <0,0,12,0> icosahedral atomic clusters with central Pt atoms as the central clusters and set the ranges of distance to 3.0–3.2 Å and 4.4–4.6 Å, corresponding to, respectively, the first and the second peaks of the Pt–Pt partial PDF, as shown in Fig. 4(a). The analysis results of the ranges 3.0–3.2 Å and 4.4–4.6 Å are shown in Fig. 4(b) and (c), respectively. The results show that the fraction of <0,0,12,0> clusters continued to increase at both distance ranges during the cooling process. A similar tendency can be seen in the results obtained by the Voronoi analysis for the entire structure. However, the fraction of <0,2,8,1> clusters slightly decreased in the range of the first peak, whereas that for the entire structure increased. Furthermore, the fraction of <0,2,8,0> clusters increases in the range of the second peak at the beginning of glass formation, whereas that for the entire structure decreases. These results indicate that, in the glass

state, <0,0,12,0> clusters connect to each other at a closer distance and therefore form the interpenetrating MRO [13], whereas clusters with lower coordination numbers, such as <0,2,8,1> or <0,2,8,0>, tend to exist on the second-nearest neighbor for the central <0,0,12,0> clusters.



**FIGURE 4.** (a) Pt–Pt partial PDFs at 1500 and 300 K with two high-lighted parts marking the ranges of neighboring Voronoi polyhedral analysis, (b) the result of neighboring Voronoi polyhedral analysis implemented in the range of 3.0–3.2 Å at different temperatures, (c) the result of neighboring Voronoi polyhedral analysis implemented in the range of 4.4–4.6 Å at different temperatures, (d) an interpenetrating MRO consisting of icosahedral clusters obtained from the atomic configuration at 300 K.

# CONCLUSION

In this study, we investigated the structural changes that occur during the glass formation process in terms of the connection of atomic clusters using MD simulations. The partial PDFs of Pt–Pt differ from those of Zr–Zr and Zr–Pt in that the first peak is weaker than the second peak. This indicates that the atomic clusters with central Pt atoms are connected through intermediate Zr atoms. However, the fraction of interpenetrating MRO consisting of icosahedral clusters that contain nearest neighbor Pt atoms increased significantly during the glass formation process compared to the fractions of the other cluster connections. These large-sized MRO units could play a crucial role in slowing down the dynamics around the glass transition temperature.

# REFERENCES

1. A. Inoue, Acta Mater. **48**, 279-306 (2000).

1. S. Y. Wang, C. Z. Wang, M. Z. Li, L. Huang, R. T. Ott, M. J. Kramer, D. J. Sordelet, and K. M. Ho, Phys. Rev. B **78**, 184204 (2008).
2. M. Kitada, M. Imafuku, J. Saida, and A. Inoue, J. Non-Cryst. Solids **312–314**, 594–598 (2002).
3. M. Celtek and S. Sengul, J. Non-Cryst. Solids **498**, 32-41 (2002).
4. A. P. Thompson, H. M. Aktulga, R. Berger, D. S. Bolintineanu, W. M. Brown, P. S. Crozier, P. J. in 't Veld, A. Kohlmeyer, S. G. Moore, T. D. Nguyen, R. Shan, M. J. Stevens, J. Tranchida, C. Trott, and S. J. Plimpton, Comp. Phys. Comm. **271**, 10817 (2022).
5. A. Hirata, L. J. Kang, T. Fujita, B. Klumov, K. Matsue, M. Kotani, A. R. Yavari, M. W. Chen, Science **341**, 376–379 (2013).
6. N. A. Mauro, V. Wessels, J. C. Bendert, S. Klein, A. K. Gangopadhyay, M. J. Kramer, S. G. Hao, G. E. Rustan,

A. Kreyssig, A. I. Goldman, and K. F. Kelton, Phys. Rev. B **83**, 184109 (2011).

1. J. Saida, K. Itoh, S. Sato, M. Imafuku, T. Sanada, and A. Inoue, J. Phys. Condens. Matter. **21**, 375104 (2009).
2. K. Sugiyama, T. Kawamata, and T. Muto, J. Phys. Conf. Ser. **809**, 12005 (2017).
3. V. S. Stepanyuk, A. Szasz, A. A. Katsnelson, O. S. Trushin, H. Müller, H. Kirchmayr, J. Non-Cryst. Solids **159**, 80–87 (1993).
4. J. Saida, M. Matsushita, and A. Inoue, J. Appl. Phys. **90**, 4717–4724 (2001).
5. H. W. Sheng, W. K. Luo, F. M. Alamgir, J. M. Bai, and E. Ma, Nature **439**, 419–425 (2006).
6. A. Hirata, Quantum Beam Sci*.* **6**, 28 (2022).