Existence of covalent-like bonding in $Pd_{40}Cu_{20}Ge_{40}$ metallic glass observed by anomalous x-ray scattering

T Yamamoto[1], S Hosokawa[2,3], J-F Bérar[4], N Boudet[4], W-C Pilgrim[3], K Hayashi[5], H Kato[5]

[1]Department of Mechanical and Intelligent Engineering, Utsunomiya University, Utsunomiya 321-8585, Japan

[2]Department of Physics, Graduate School of Science and Technology, Kumamoto University, Kumamoto 860-8555, Japan

[3]Department of Chemistry, Physical Chemistry, Philipps University of Marburg, D-35032 Marburg, Germany

[4]Institut Néel, Centre National de la Recherche Scientifique/Université Joseph Fourier (CNRS/UJF), 38042 Grenoble Cedex 9, France

[5]Institute of Materials Research, Tohoku University, Sendai 980-8577, Japan

E-mail: `hosokawa@sci.kumamoto-u.ac.jp`

Abstract. To elucidate the local structure of $Pd_{40}Cu_{20}Ge_{40}$ metallic glass having curious thermodynamic properties of a low melting point and an extremely small ratio of glass transition- and melting temperatures, anomalous x-ray scattering experiments were performed close to the Pd, Cu, and Ge K edges. The results were analyzed using reverse Monte Carlo modeling to obtain partial structure factors and pair correlation functions. Covalent-like bondings between the Pd and Ge atoms are realized in this metallic glass, which may be related to the thermodynamic anomalies.

1. Introduction

The ratio of glass transition- and melting temperatures, T_g/T_m, is widely employed as a simple index to characterize glass-forming abilities of glasses [1]. Generally, values of $3/2$ or at smallest $1/2$ were observed in various types of glasses, such as oxide, organic, and metallic glasses. Exceptions are only observed in simple polymer glasses, such as polyethylene (0.35) and polytetrafluoroethylene (0.26) [2, 3]. Recently, Yamamoto *et al.* [4] have found a curious metallic glass, $Pd_{40}Cu_{20}Ge_{40}$, having a very low T_g and an extremely small T_g/T_m of 0.36, where $T_g = 52°C$ and $T_m = 625°C$. Surprisingly, this metallic glass is formable even in hot water.

To investigate an origin of such a small T_g/T_m value in $Pd_{40}Cu_{20}Ge_{40}$ metallic glass from a partial structural point of view, we have measured anomalous x-ray scattering (AXS) close to the Pd, Cu, and Ge K x-ray absorption edges. The obtained differential structure factors, $\Delta_k S(Q)$, were analyzed using reverse Monte Carlo (RMC) modeling to clarify local- and intermediate-range partial correlations between the constituent elements. In this paper, we report our finding of clusters of Pd and Ge atoms with a highly covalent-like nature.

2. Experimental procedure and data analysis

A $Pd_{40}Cu_{20}Ge_{40}$ metallic glass sample was manufactured by a normal melt-spinning technique with a tapered silica nozzle. The glass phase of the obtained ribbons was examined by x-ray diffraction and transmission electron microscopy. The composition of the ribbons was confirmed to be nominal value by an electron-probe micro-analysis equipment.

AXS experiments were carried out at room temperature using a standard $\omega-2\theta$ diffractometer installed at the beamline BM02 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. Scattering measurements were performed at two incident x-ray energies below each K edge, i.e., –30 eV for Pd, –20eV for Cu and Ge, and –200 eV for all elements. For discriminating elastic signals from $K\beta$ fluorescence- and Compton scattering contributions, a bent graphite crystal analyzer was mounted at the middle of a 1-m-long detector arm. An energy resolution was about 120 eV near the Pd K edge and about 50 eV near the Cu and Ge K edges, with which the $K\beta$ contribution is estimated to be less than 0.1%. More than three or five million counts were collected at the maximum of the structure factor, $S(Q)$, within a reasonable beamtime for this AXS experiment. The feasibility of this detecting system is given elsewhere [5]. For AXS data analysis, Sasaki's theoretical values [6] were used for the anomalous terms together with theoretical usual terms [7]. Following the procedure given in Ref. [8], $\Delta_k S(Q)$'s were calculated for each K edge.

RMC modeling [9] is a useful tool to construct three-dimensional atomic configurations of disordered materials using only experimental diffraction data. In the RMC calculations, atoms are moved from an initial configuration so as to minimize deviations from experimental data, e.g., in this study, three $\Delta_k S(Q)$'s and $S(Q)$ measured near the Pd K edge, using a standard Metropolis Monte Carlo algorithm [10].

A starting configuration of a system containing a total of 10,000 atoms with the measured number density of 69.86 nm^{-3} was generated using a hard-sphere Monte Carlo simulation (a random configuration except short bonds). To avoid unphysical atomic configurations, only a constraint of shortest atomic distances was applied to the RMC calculations, i.e., 0.19, 0.21, and 0.22 nm for Ge-Ge, (Pd,Cu)-Ge, and other inter-metallic (Pd,Cu) correlations, respectively. The RMC calculations were performed using the RMC++ program package coded by Gereben *et al.* [11].

3. Results and discussion

Circles in Fig. 1 show $\Delta_k S(Q)$'s close to the Pd, Cu, and Ge, together with $S(Q)$, obtained from the present AXS measurements. The limited Q ranges in the $\Delta_{Cu} S(Q)$ and $\Delta_{Ge} S(Q)$ are due to the low incident energies near the Cu and Ge K absorption edges. Of special interest is the spectral shape of $\Delta_{Ge} S(Q)$, i.e., there is a steep minimum at 19 nm^{-1}, and the first peak at about 28 nm^{-1} is not high. These features look far from those of usual metallic glasses, and are similar to those of covalent chalcogenide glasses [8].

The $\Delta_{Pd} S(Q)$ and $S(Q)$ functions have small shoulders at about 20 nm^{-1}. Since the shoulder in $\Delta_{Pd} S(Q)$ is more prominent than that in $S(Q)$, and no clear indications are seen in $\Delta_{Cu} S(Q)$ and $\Delta_{Ge} S(Q)$, the origin of the shoulder seems to be Pd-related partial correlations. The $\Delta_{Cu} S(Q)$ function shows an enhancement in the low Q range, and thus, a density or concentration fluctuation is expected around the Cu atoms.

Solid curves in Fig. 1 show the best fits of the RMC modeling. Although the $\Delta_k S(Q)$ functions have features very different from each other as mentioned above, they surprisingly coincide well with the corresponding experimental diffraction data.

Figure 2(a) shows partial structure factors, $S_{ij}(Q)$, obtained from the present RMC modeling. As seen in the figure, large prepeaks are realized at about 19 nm^{-1} in all of the homopolar correlations of $S_{PdPd}(Q)$, $S_{CuCu}(Q)$, and $S_{GeGe}(Q)$. It should be noted that only a small and broad shoulder was observed in Pd- [12] and Zr-based [13] metallic glasses so far, and this is the
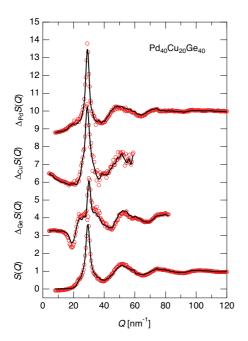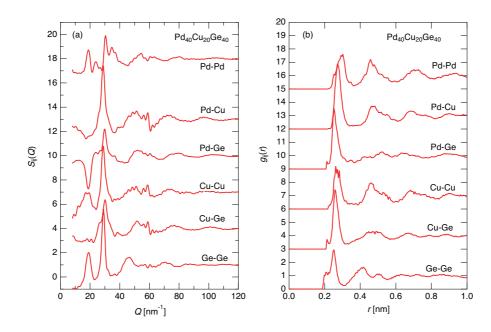
Figure 1. (Color online.) From top to bottom: $\Delta_k S(Q)$'s close to the Pd, Cu, and Ge K edges, and $S(Q)$. Circles indicate those obtained from the AXS experiments, and solid curves denote best fits of the RMC modeling. For clarity, the spectra are displaced upwards by three each.

first finding of such a large prepeak in metallic glasses.

On the contrary, the heteropolar $S_{\mathrm{PdGe}}(Q)$ function has a large and negative minimum at the Q position of the prepeaks, indicating very strong Pd-Ge heteropolar correlations analogous to chalcogenide glasses [8]. However, the remaining Cu-related heteropolar correlations, Pd-Cu and Cu-Ge, show features similar to usual metallic glasses indicating metallic bondings around the Cu atoms. Only the $S_{\mathrm{PdCu}}(Q)$ function indicates a weak concentration fluctuation tendency in the low Q region below 18 nm^{-1}.

Figure 2. (Color online.) (a) $S_{ij}(Q)$ and (b) $g_{ij}(r)$ functions obtained from the RMC fits. For clarity, the spectra are displaced upwards.

Figure 2(b) shows partial pair distribution functions, $g_{ij}(r)$, obtained from the RMC modeling. At a glance, all of the $g_{ij}(r)$ functions seem to be usual as of metallic glasses, i.e., dense-packed features with a large first peak followed by damping oscillations. However, the first peaks in the homopolar $g_{ij}(r)$ functions are small in height compared with the corresponding second peaks, which is the reason of the existence of prepeaks in the corresponding $S_{ij}(Q)$ spectra.

The first coordination shells were defined up to mostly the first minima of the $g_{ij}(r)$ functions, i.e., 0.35 nm around the Pd atoms and 0.33 nm around the Cu and Ge atoms. The total coordination numbers around the Pd, Cu, and Ge atoms are about 13.0, 12.5, and 10.7, respectively, which seem to indicate the dense-packed features of 12. As expected from the features of the $g_{ij}(r)$ functions, however, the portions of homopolar partial coordinations of Pd-Pd, Cu-Cu, and Ge-Ge pairs are 35.8%, 16.4%, and 31.8% , respectively, which are much smaller than the nominal values of 40%, 20%, and 40%, in particular, Ge-Ge exceeding 20% of the discrepancy. Thus, the heteropolar correlations are much favorable in the first shells of this metallic glass.

From these analyses, we found a heterogeneous nature of the structure of $Pd_{40}Cu_{20}Ge_{40}$ metallic glass. The Pd and Ge atoms are strongly bound to form covalent-like clusters, while the Cu atoms seem to connect with the Pd and Ge atoms in a manner of weak metallic bonding. In relation to the small small $T_g/T_m = 0.36$ value in this metallic glass, these structural findings suggest the existence of covalent-like bondings between the Pd and Ge atoms.

4. Conclusion

AXS measurements were performed close to the Pd, Cu, and Ge K edges on $Pd_{40}Cu_{20}Ge_{40}$ metallic glass to search the local structural origin of curious thermodynamic properties of a low $T_g = 52°C$ and an extremely small $T_g/T_m = 0.36$. The results were analyzed using reverse Monte Carlo modeling to obtain $S_{ij}(Q)$'s and $g_{ij}(r)$'s. The existence of covalent semiconductor-like configurations between the Pd and Ge atoms may be related to the thermodynamic anomalies in the $Pd_{40}Cu_{20}Ge_{40}$ metallic glass.

Acknowledgments

References

[1] Inoue A 2000 *Acta Mater.* **48** 279
[2] Andrews R J and Grulke E A 1999 *Glass Transition Temperatures of Polymers*, in Brandrup J, Immergut E H and Grulke E A (Eds.), *Polymer Handbook 4th Ed.* (John Wiley & Sons, Inc., New York) p. VI/193-277
[3] R. L. Miller 1999 *Crystallographic Data and Melting Points for Various Polymers*, in Brandrup J, Immergut E H and Grulke E A (Eds.), *Polymer Handbook 4th Ed.* (John Wiley & Sons, Inc., New York) p. VI/1-192
[4] Yamamoto T, Hayashi K, Seki I, Suzuki K and Ito M 2013 *J. Non-Cryst. Solids* **359** 46
[5] Hosokawa S and Bérar J-F 2007 *AIP Conf. Proc.* **879** 1743
[6] Sasaki S 1989 *KEK Report 1989* (Nat. Lab. High Energy Phys., Tsukuba) p. 1
[7] MacGillavry C H and Rieck G D (ed.) 1969 *International Table for X-ray Crystallographie, 2nd ed.* (Kynoch, Birmningham) Vol. III
[8] Hosokawa S, Oh I, Sakurai M, Pilgrim W-C, Boudet N, Bérar J-F and Kohara S 2011 *Phys. Rev. B* **84** 014201, and references therein
[9] McGreevy R L and Pusztai L 1988 *Mol. Simul.* **1** 359
[10] Metropolis N, Rosenbluth A W, Rosenbluth M N, Teller A. H and Teller E 1953 *J. Phys. Chem.* **21** 1087
[11] Gereben O, Jóvári P, Temleitner L and Pusztai L 2007 *J. Optelectr. Adv. Mater.* **9** 3021
[12] Hosokawa S, Sato H, Ichitsubo T, Nakatake M, Happo N, Bérar J-F, Boudet N, Usuki T, Pilgrim W-C, Matsubara E and Nishiyama N 2009 *Phys. Rev. B* **80** 174204
[13] Hosokawa S, Bérar J-F, Boudet N, Kohara S, Pilgrim W-C, Joester M, Stellhorn J, Zeidler A, Maruyama K, Nasu T, Zhang W and Kato H 2012 *Int. J. Mater. Res.* **103** 1108