JOURNAL OF MATERIALS SCIENCE **25** (1990) 4477–4482

Structure changes on relaxation of differently cooled $Pd_{0.835}Si_{0.165}$ alloy glass

Y. NISHI, H. HARANO, S. UCHIDA, K. OGURI
Department of Materials Science, Tokai University, Hiratsuka, Japan

The radial distribution function (RDF) of X-ray diffraction was studied for liquid-quenched $Pd_{0.835}Si_{0.165}$ alloy glasses in relation to cooling conditions. The atomic distance (r_1), total coordination number (n) and volume (V) are obtained by a first peak of RDF. The faster the cooling rate, the larger the r_1, n and V become. Based on the relaxation theory, we show linear changes in r_1, n and V with the sample thickness (D) which indicates the reciprocal cooling rate.

$$\log_{10}(r_1 - 2.826) = -1.92 - 2.58D$$

$$\log_{10}(12.83 - n) = 0.130 - 2.50D$$

$$\log_{10}(V - 7.95) = 0.011 - 2.80D$$

The volume change is mainly dominated by n.

1. Introduction

Various properties, such as magnetic, electric and mechanical properties, have been reported in liquid-quenched glassy alloys [1–3]. It is important to know the effect of cooling conditions on the properties. However, the effect has never been investigated systematically. We have recently examined the cooling conditions in liquid-quenching [4, 5]. With this experience, we have recently started a study to observe the effects of cooling conditions on mechanical and magnetic properties in liquid-quenched glasses [6–8]. However, no one has ever quantitatively studied the dependence of relaxation state (atomic structure, such as atomic radius, coordination number and molar volume) on the cooling condition.

In particular, it is difficult to obtain the change in molar volume, because the boundary is often found in slowly cooled glasses (Fig. 1). Fig. 1 shows a micrograph of the slowly cooled $Pd_{0.835}Si_{0.165}$ alloy glass. Because the slowly cooled glass has a slow cooling curve and remains at a high temperature for a long time, the diffusivity pass of free volume [9] is large (the free volume is one of the defects and changes the glassy structure), i.e. relaxed glassy clusters are easy to grow. Because the migration pass is short at an aged temperature (low temperature below the glass transition temperature), the ageing may induce the growth of small glassy clusters and probably generates the fine boundary between the clusters. Although it is difficult to observe the boundary for the aged glass at low temperature, the aged glass is often brittle [10].

If the density of atoms is dilute in the boundary, it is impossible to measure the precise density of the slowly cooled glass by means of the usual Archimedean method [11, 12]. Thus, we have suggested a method to evaluate the structural change by means of X-ray diffraction. The purpose of the present work was to study the cooling condition dependence of the atomic structure (atomic radius, coordination number and molar volume) of the $Pd_{0.835}Si_{0.165}$ alloy glass.

2. Experimental procedure

An alloy of $Pd_{0.835}Si_{0.165}$ was prepared from elemental powders: Pd 99.8 wt % metallic purity and Si 99.99 wt % purity. The powders were compacted under high pressure with a hydraulic press, sintered and melted in an argon–hydrogen atmosphere. Glass plates were prepared by liquid-quenching [4, 5]. A piston–anvil type apparatus was constructed to quench the molten alloy in an argon–hydrogen atmosphere. The temperature of the liquid was about 1800 K. The cooling rate (R, $K\,sec^{-1}$) was varied by controlling the sample thickness (D, mm) as in the following equation [4]

$$\log R = -A \log D + C \tag{1}$$

where A and C are constants. Based on Newton's cooling condition, A is approximately equal to 1 [4, 5]. Because the heat transfer coefficient (h) between the molten sample and the copper plate of the apparatus is not very high [4, 5], the temperature slope in the sample should be small. The structure is monitored by X-ray diffraction (model no. RU-200B, Rigaku Denki, Tokyo). The diffraction is performed by a step scanning method (copper target, 30 kV, 50 mA, 0.05 deg/step, 10 sec/step).

3. Results

3.1. Total structure factor, $S(Q)$

The total structure factor, $S(Q)$, and radial distribution function, $4\pi r^2 \rho_0 g(r)$, were obtained from the measured intensity by the following procedures [13].

0022-2461/90 $03.00 + .12 © *1990 Chapman and Hall Ltd.*

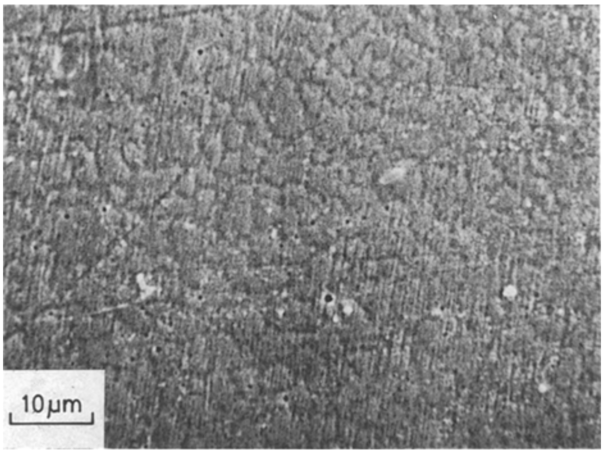

Figure 1 Scanning electron micrograph of the slowly cooled $Pd_{0.835}Si_{0.165}$ alloy glass.

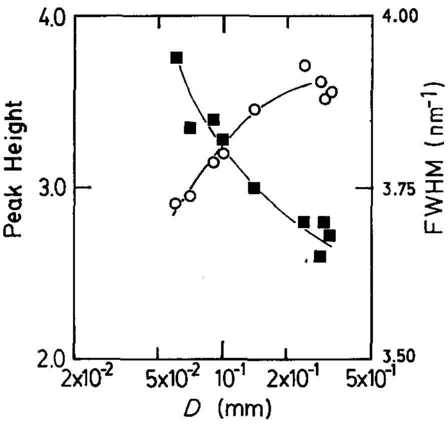

Figure 3 Changes in (○) peak height and (■) half value width (full-width at half-maximum; FWHM) of $S(Q)$ with sample thickness (D) of $Pd_{0.835}Si_{0.165}$ alloy glasses. D is inversely proportional to the cooling rate.

The correction of the background was carried out by subtracting the arithmetic mean intensity of the background (I_b) of pure palladium and pure silicon from the experimentally measured intensity (I_{exp}). The corrected intensity (I_{corr}) was obtained by dividing $I_{exp} - I_b$ by the product of the absorption (A) and polarization (P) corrections

$$I_{corr} = (I_{exp} - I_b)/PA \tag{2}$$

P and A are defined as

$$P = [1 + \cos^2 2\theta]/2 \tag{3}$$

$$A = [1 - \exp(-2\bar{\mu}t \operatorname{cosec}\theta)]/2\bar{\mu} \tag{4}$$

where θ, t and $\bar{\mu}$ are the scattering angle, the sample thickness and the linear total absorption coefficient [14], respectively. $S(Q)$ was defined by using I_{corr} as

$$S(Q) = [\bar{\beta}I_{corr} - \langle f^2\rangle - I_{inc}]/\langle f\rangle^2 \tag{5}$$

$$Q = 4\pi(\sin\theta)/\lambda \tag{6}$$

where $\bar{\beta}$, f and λ are the conversion factor, the total atomic scattering factor and the X-ray wavelength of 0.154 18 nm [14], respectively. I_{inc} is the Compton scattering intensity, which uses the results of Compton–Allison [15]. f was given by the equation [16, 17]

$$f = \sum_{i=1}^{4} a_i \exp[-b_i \sin^2\theta/\lambda^2] + C + f' + f'' \tag{7}$$

where a_i, b_i and C are the coefficients for fitting the atomic scattering factor. f' and f'' were the real and imaginary components of the anomalous dispersion. In the generalized Krogh–Moe–Norman method, the conversion factor $\bar{\beta}$ [18] was given by

$$\bar{\beta} = \left[\int_0^{Q_{max}} Q^2[(\langle f^2\rangle + I_{inc})/\langle f\rangle^2] \times \exp(-R^0Q^2)\,dQ - 2\pi^2\rho_0\right] \Big/ \left[\int_0^{Q_{max}} Q^2(I_{corr}/\langle f\rangle^2)\exp(-R^0Q^2)\,dQ\right] \tag{8}$$

$$Q = 4(\sin\theta)/\lambda \tag{9}$$

where Q_{max} is the Q at the scattering angle ($2\theta = 133°$), R^0 is the damping factor ($R^0 = 0.01$) [19], and ρ_0 the atomic number density of the sample.

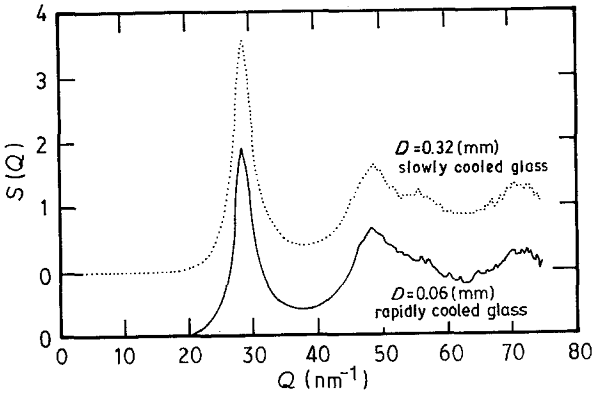

Figure 2 $S(Q)$ changes with Q of rapidly and slowly cooled $Pd_{0.835}Si_{0.165}$ alloy glasses.

Fig. 2 shows $S(Q)$ of Pd–Si glassy alloys obtained under different cooling conditions. The high and narrow first peak and the split second peak are particularly remarkable in the $S(Q)$ of the slowly cooled specimen in comparison with that of the rapidly cooled glass. The faster the cooling rate (the thinner

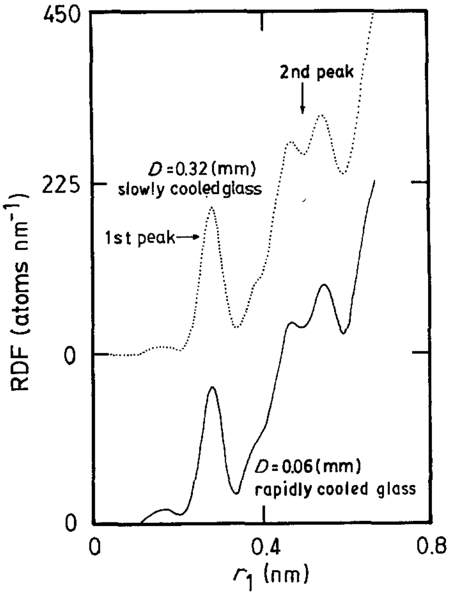

Figure 4 Radial distribution function changes with atomic distance of rapidly and slowly cooled $Pd_{0.835}Si_{0.165}$ alloy glasses.

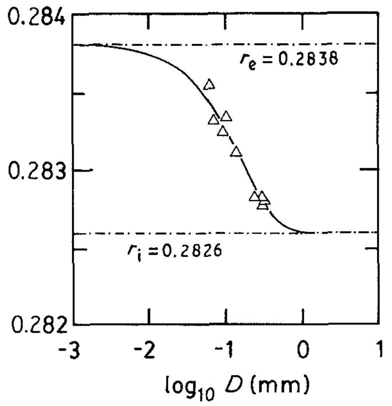

Figure 5 Changes in mean atomic distance (r_1) of the first peak in RDF with sample thickness (D) of $Pd_{0.835}Si_{0.165}$ alloy glasses. D is inversely proportional to the cooling rate. r_e and r_i are the mean atomic distance of extremely rapidly and slowly cooled glasses, respectively. (——) Calculated on the basis of the relaxation process (Equation 16).

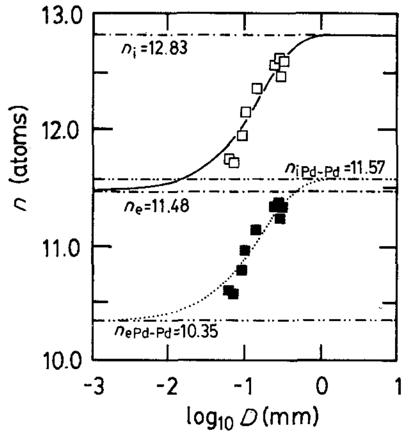

Figure 6 Changes in total coordination number (□) and corrected coordination number of Pd–Pd atoms (■) with sample thickness (D) of $Pd_{0.835}Si_{0.165}$ alloy glasses. D is inversely proportional to the cooling rate. n_e and n_i are the total coordination number of rapidly and slowly cooled glasses, respectively. $n_{ePd\text{-}Pd}$ and $n_{iPd\text{-}Pd}$ are the corrected coordination numbers of Pd–Pd atoms of rapidly and slowly cooled glasses, respectively. (——) and (– – –) Calculated using the relaxation process (Equations 17 and 18).

the sample thickness), the lower and broader the first peak becomes, as shown in Fig. 3.

3.2. Radial distribution function (RDF)

The radial distribution function (RDF) was obtained as a Fourier transform of $S(Q)$

$$\begin{aligned} \mathrm{RDF} &= 4\pi r^2 \rho_0 g(r) \\ &= 4\pi r^2 \rho_0 + (2r/\pi) \\ &\quad \times \int_0^{Q_{\max}} Q[S(Q) - 1] \sin(Qr)\, \mathrm{d}Q \qquad (10) \end{aligned}$$

Fig. 4 shows RDFs as Fourier transforms of $S(Q)$. The remarkable split second peak, the high and narrow first peak are found in the RDF of the slowly cooled glass. The faster the cooling rate (the thinner the sample thickness), the lower and broader the first peak becomes.

3.3. Atomic distance

Fig. 5 shows the change in the mean atomic distance (r_1, nm) with the sample thickness (D, mm). The slowly cooled glass (the thick sample thickness) shows small r_1. r_1 increases with an increase in cooling rate (decrease in sample thickness). The atomic distance of the rapidly cooled glass is 0.27% larger than that of the slowly cooled glass.

3.4. Coordination number

The coordination number was calculated from the area under the first peak in the RDF as follows

$$n = \int_{r'}^{r''} 4\pi r^2 \rho_0 g(r)\, \mathrm{d}r \qquad (11)$$

where r' is the value below which the RDF is zero, and r'' is the position of the first minimum of the RDF. In other words, although the first peaks of Pd–Pd and Pd–Si of this wavelength cannot be divided, the mean coordination number (n) was obtained by the area of the first peak of RDF.

Fig. 6 shows the change in the total coordination number (n) with the sample thickness (D). The rapidly cooled glass (the thin sample thickness) shows small n. n increases with increasing D. From the results of the neutron diffraction analysis, separated first peaks were found (see Fig. 7). Both peaks are for Pd–Pd atoms and Pd–Si atoms. The two coordination numbers of Pd–Pd atoms ($n_{Pd\text{-}Pd}$) and Pd–Si atoms ($n_{Pd\text{-}Si}$) are 10.6 ($15.5 < \mathrm{at\%\ Si} < 20$) and 1.38 ($n_{Pd\text{-}Si} = 7.58 \times 10^{-2}\,\mathrm{at\%\ Si} + 0.133$; $15.5 < \mathrm{at\%\ Si} < 20$) for the rapidly cooled glasses produced by a roll-quenching method [13, 20].

Based on the metallographic method (changes in mean distance of dendrite and crystal orientation), the cooling condition of the piston–anvil method can be assumed to be nearly equal to that of the roll-quenched method for the thin and fast-cooled specimens of Al–Cu alloys, though both methods show different conditions at the same sample thickness for the slowly cooled specimens [21]. Therefore, n of the X-rays is assumed to relate to $n_{Pd\text{-}Pd}$ (10.6) for the rapidly cooled $Pd_{0.835}Si_{0.165}$ glass ($D = 0.06$ mm). If the fraction ($n/n_{Pd\text{-}Pd} = 1.10$ for the $Pd_{0.835}Si_{0.165}$ alloy

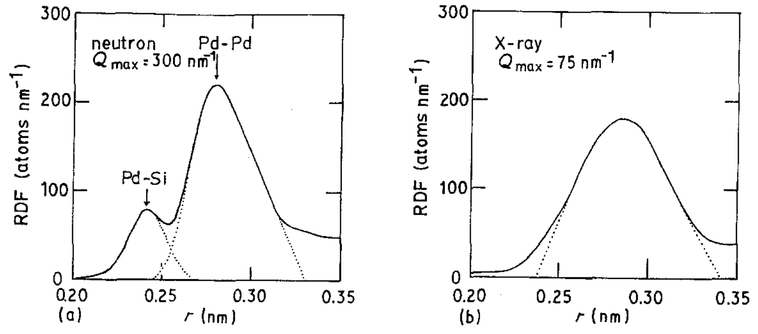

Figure 7 First peaks of RDF by (a) neutron diffraction, $Q_{\max} = 300\,\mathrm{nm}^{-1}$ [13] and (b) X-ray diffraction, $Q_{\max} = 75\,\mathrm{nm}^{-1}$, present work.

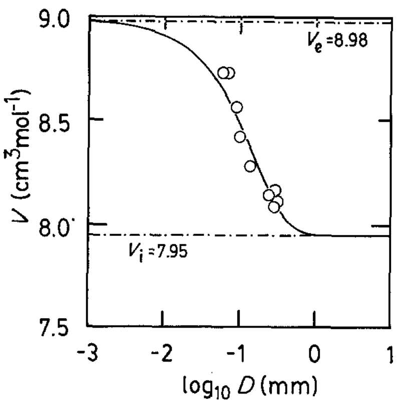

Figure 8 Changes in molar volume (V) with sample thickness (D) of $Pd_{0.835}Si_{0.165}$ alloy glasses. D is inversely proportional to the cooling rate. V_e and V_i are the molar volumes of extremely rapidly cooled and slowly cooled glasses, respectively. (——) Calculated on the basis of the relaxation process (Equations 14 and 15).

glass) does not depend on the cooling condition, the change in $n_{Pd\text{-}Pd}$ with cooling condition is shown in Fig. 6 (see dotted line). $n_{Pd\text{-}Pd}$ are between 8.6 for the liquid [22] and 12 for the fcc crystal. $n_{Pd\text{-}Pd}$ increases with D increasing.

3.5. Molar volume (V)

Atomic volume, V, is estimated from the coordination number (n), the first nearest distance between atoms (r_1) and the following equation [18, 23–25]

$$V/V' = (r_1/r_1')^3(n'/n). \qquad (12)$$

n and r_1 are measured by the RDF of X-ray diffraction; r_1' and n' are the values when the molar volume (V') is known. V' is assumed to be estimated from the density of the rapidly cooled Pd–Si alloy glass ($Pd_{0.835}Si_{0.165}$ alloy glass, $0.02\,\text{mm} < D < 0.06\,\text{mm}$, roll-quenched method) [13]

$$\begin{aligned}&[V' - V(\text{Pd–14.5 at\% Si glass})]/\\&[V(\text{Pd–14.5 at\% Si glass})\\&- V(\text{Pd–19.8 at\% Si glass})]\\&= 0.337 \qquad (13)\end{aligned}$$

Taking into account the changes in the mean distance of dendrite and crystal orientation, the cooling condition of the piston–anvil method can be assumed to be nearly equal to that of the roll-quenched method for the thin and rapidly cooled specimens, although the cooling conditions of both methods are different at the same D for the slowly cooled specimens [21].

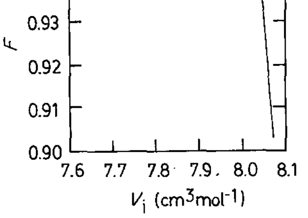

Figure 9 Changes in correlation coefficient (F) with V_i. V_i is molar volume of an extremely slowly cooled glass.

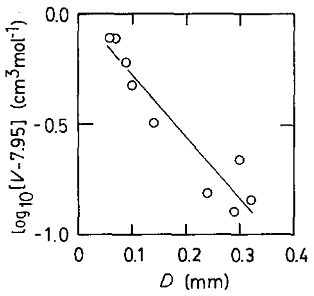

Figure 10 Linear plots between $\log_{10}(V - 7.95)$ and sample thickness (D) of $Pd_{0.835}Si_{0.165}$ alloy glasses, where V is molar volume. D is inversely proportional to the cooling rate. (——) Calculated using the relaxation process (Equation 15).

Therefore, V' is assumed to be $8.74\,\text{cm}^3\,\text{mol}^{-1}$ for the rapidly cooled $Pd_{0.835}Si_{0.165}$ glass ($D = 0.06\,\text{mm}$).

Fig. 8 shows the changes in the molar volume (V) with sample thickness (D). The slowly cooled glass (the thick sample thickness) shows small V, i.e. the faster the cooling rate, the larger V becomes.

4. Discussion

4.1. Relaxation process

The density of vacancies in a crystal depends on the relaxation time [26]. A free volume (V_f) is defined in a liquid [27]. If the concept of free volume is similar to that of a vacancy in the crystal, the molar volume (V) depends mainly on the relaxation time (t, sec), which is inversely proportional to the cooling rate (R, K sec^{-1}). Here, R is inversely proportional to the sample thickness (D) (see Equation 1). A reduced molar volume (X_v) is expressed by the following equation.

$$\begin{aligned}X_v &= [(V - V_i)/(V_e - V_i)]\\&= \exp(-k't)\\&= \exp(-k''/R)\\&= \exp(-kD) \qquad (14)\end{aligned}$$

where V_i, V_e, k, k' and k'' are constants. If the cooling rate (R) is extremely high, i.e. D is extremely small, V approaches the maximum free volume (V_e) of Equation 14. We suggest that the physical meaning of V_i is the volume of an extremely slowly cooled glass. The glass may have an extremely small amount of free volume. V_i is $7.95\,\text{cm}^3\,\text{mol}^{-1}$, when the correlation coefficient (F) of Equation 14 is maximum ($F = 0.946$) as shown in Fig. 9.

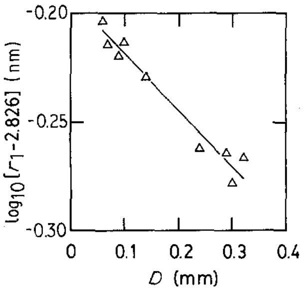

Figure 11 Linear plots between $\log_{10}(r_1 - 2.826)$ and sample thickness (D) of $Pd_{0.835}Si_{0.165}$ alloy glasses, where r_1 is the mean atomic distance, D is inversely proportional to the cooling rate. (——) Calculated using the relaxation process (Equation 16).

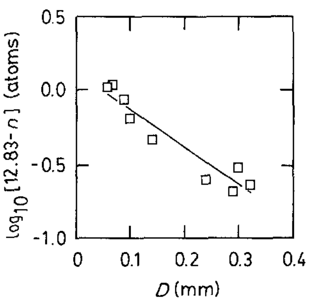

Figure 12 Linear plots between $\log_{10}(12.83 - n)$ and sample thickness (D) of $Pd_{0.835}Si_{0.165}$ alloy glasses, where n is the total coordination number, D is inversely proportional to the cooling rate. (——) Calculated using the relaxation process (Equation 17).

Based on the relaxation process of Equation 14, V is expressed by the following linear equation for $Pd_{0.835}Si_{0.165}$ alloy glasses (see solid lines in Fig. 10).

$$\log_{10}(V - 7.95) = 0.011 - 2.80D \tag{15}$$

If Equation 14 is applied for r_1, n and $n_{Pd\text{-}Pd}$, they are expressed by the following linear equations of $Pd_{0.835}Si_{0.165}$ alloy glasses (see solid lines in Figs 11 to 13).

$$\log_{10}(r_1 - 2.826) = -1.92 - 2.58D \tag{16}$$

$$\log_{10}(12.83 - n) = 0.130 - 2.50D \tag{17}$$

$$\log_{10}(11.57 - n_{Pd\text{-}Pd}) = -0.086 - 2.51D \tag{18}$$

where r_i, n_i and $n_{iPd\text{-}Pd}$ are 0.2826 nm, 12.83 and 11.57, respectively, when the correlation coefficients (F) are maximum ($F = 0.978$, 0.935 and 0.935), as shown in Figs 14 to 16. If the cooling rate (R) is extremely low, i.e. D is extremely large, V approaches r_i, n_i, $n_{iPd\text{-}Pd}$ and V_i. If the cooling rate (R) is extremely high, i.e. D is extremely small, the molar volume (V) approaches V_e ($V_e = 8.98\,\text{cm}^3\,\text{mol}^{-1}$) and the free volume ($V - V_i$) approaches the maximum free volume ($V_e - V_i$) of Equation 14. Thus, ($V_e - V_i$) is $1.03\,\text{cm}^3\,\text{mol}^{-1}$; $[(V_e - V_i)/V_i]$ is about 1/8.

The plots in Figs 10 to 13 confirm the assumptions of Equation 14. The equations are applied for the values of r_i, n_i, $n_{iPd\text{-}Pd}$ and V_i ($\text{cm}^3\,\text{mol}^{-1}$) in Figs 5, 6 and 8. On the other hand, the reduced atomic distance ($X_r = [(r_1 - r_i)/(r_e - r_i)]$), the reduced total coordination number ($X_n = [(n_i - n)/(n_i - n_e)]$) are applied for the following linear equations, as shown in Fig. 17.

$$\log_{10}X_r = 4.787 \times 10^{-4} - 2.58D \tag{19}$$

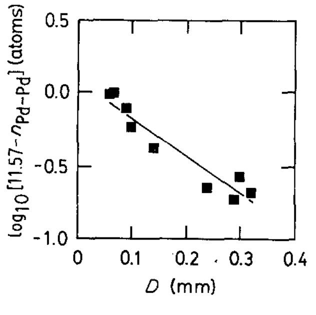

Figure 13 Linear plots between $\log_{10}(11.57 - n_{Pd\text{-}Pd})$ and sample thickness (D) of $Pd_{0.835}Si_{0.165}$ alloy glasses, where $n_{Pd\text{-}Pd}$ is the coordination number of Pd–Pd, D is inversely proportional to the cooling rate. (——) Calculated using the relaxation process (Equation 18).

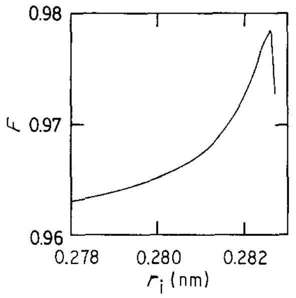

Figure 14 Changes in correlation coefficient (F) with r_i where r_i is the mean atomic distance of an extremely slowly cooled glass.

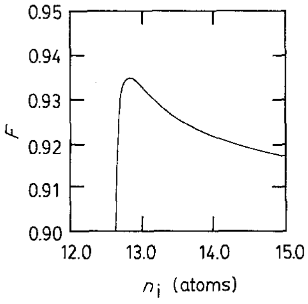

Figure 15 Changes in correlation coefficient (F) with n_i where n_i is the total coordination number of an extremely slowly cooled glass.

$$\log_{10}X_n = -1.653 \times 10^{-4} - 2.50D \tag{20}$$

$$\log_{10}X_v = -1.814 \times 10^{-3} - 2.80D \tag{21}$$

The changes in the reduced values are approximately equal. These results show that the structure changes depend on the cooling condition, simultaneously.

The plots in Figs 10 to 12 confirm the assumptions of Equation 14. The equation is applied for the values of r_i, n_i, $n_{iPd\text{-}Pd}$ and V in Figs 5, 6 and 8.

Taking into account Equations 12 and 17, the fine solid line in Fig. 18 shows the change in the molar volume which depends on the atomic radius at the constant coordination number of n_i. On the other hand, the dotted line in Fig. 18 shows the change in molar volume which depends on the coordination number at the constant atomic radius of r_i by the use of Equations 12 and 16. Considered in conjunction with the results of the coordination number and the molar volume, one of the coordinated atoms seems to convert the free volume at extremely fast cooling. Thus, we conclude that the dominant factor in volume change is the coordination number.

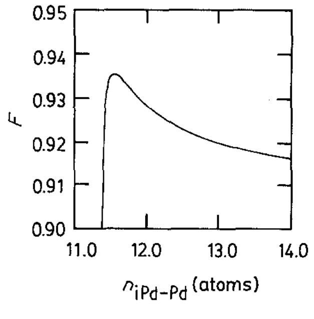

Figure 16 Changes in correlation coefficient (F) with $n_{iPd\text{-}Pd}$ where $n_{iPd\text{-}Pd}$ is the coordination number of Pd–Pd of an extremely slowly cooled glass.

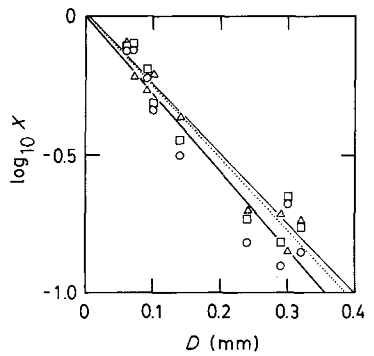

Figure 17 Linear changes of (△) $\log_{10}X_r$, (□) $\log_{10}X_n$ and (○) $\log_{10}X_v$ with sample thickness (D) of $Pd_{0.835}Si_{0.165}$ alloy glasses. D is inversely proportional to the cooling rate. (——) Calculated using the relaxation process (Equation 14).

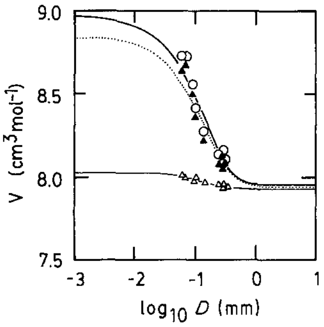

Figure 18 Change in (—○—) molar volume (V) with sample thickness (D) of $Pd_{0.835}Si_{0.165}$ alloy glasses. D is inversely proportional to the cooling rate. (···▲···) Change in the molar volume which depends on the coordination number at constant atomic radius of r_i. (—△—) Change in the molar volume which depends on the atomic radius at constant coordination number of n_i.

5. Conclusion

The RDF change with the cooling condition is studied for the liquid-quenched $Pd_{0.835}Si_{0.165}$ alloy glass. The rapidly cooled glasses show larger atomic distances (r_1) and smaller coordination numbers. The faster the cooling rate, the larger the volume (V) becomes. The reduced atomic distance ($X_r = [(r_1 - r_i)/(r_c - r_i)]$), the reduced total coordination number ($X_n = [(n_i - n)/(n_i - n_e)]$ and the reduced molar volume ($X_v = [(V - V_i)/(V_c - V_i)]$) are applied for the following linear equations:

$$\log_{10}X_r = 4.787 \times 10^{-4} - 2.58D$$

$$\log_{10}X_n = -1.653 \times 10^{-4} - 2.50D$$

$$\log_{10}X_v = -1.814 \times 10^{-3} - 2.80D$$

Based on the equations, we conclude that the dominant factor in volume change is the coordination number.

References

1. H. S. CHEN, S. D. FERRIS, E. M. GYORGY, H. J. LEAMY and R. C. SHERWOOD, *J. Appl. Phys. Lett.* **26** (1975) 405.
2. M. MITERA, T. MASUMOTO and N. S. KAZAMA, *J. Appl. Phys.* **50** (1979) 7609.
3. M. HAGIWARA, A. INOUE and T. MASUMOTO, *Met. Trans.* **13A** (1982) 373.
4. Y. NISHI, K. SUZUKI and T. MASUMOTO, *J. Jpn. Inst. Metals* **45** (1981) 1300.
5. Y. NISHI, T. MOROHOSHIM, T. KAWAKAMI, K. SUZUKI and T. MASUMOTO, "Proceedings of Fourth International Conference on Rapidly Quenched Metals", Sendai, 1981, edited by T. Masumoto and K. Suzuki (Japan Institute of Metals, Sendai, 1981) pp. 111–14.
6. Y. NISHI, H. HARANO and H. ISHIZUKI, *J. Mater. Sci. Lett.* **6** (1987) 1445.
7. Y. NISHI, M. TACHI, T. KAI and T. ONO, *Scripta Metall.* **19** (1985) 1367.
8. Y. NISHI, T. KAI, M. TACHI, T. ISHIDAIRA and E. YAJIMA, *ibid.* **20** (1986) 1099.
9. P. B. MACEDO and T. A. LITOVITZ, *J. Chem. Phys.* **42** (1965) 245.
10. A. INOUE, T. MASUMOTO and H. KIMURA, *J. Jpn. Inst. Metals* **42** (1978) 303.
11. N. HAYASHI, T. FUKUNAGA, M. UENO and K. SUZUKI, "Proceedings of Fourth International Conference on Rapidly Quenched Metals", Sendai, 1981, edited by T. Masumoto and K. Suzuki (Japan Institute of Metals, Sendai, 1981) pp. 355–8.
12. T. MASUMOTO, H. KIMURA and A. INOUE, *Mater. Sci. Engng* **23** (1976) 141.
13. T. FUKUNAGA, PhD thesis, Tohoku University (1979) pp. 55–63, 78–80, 96.
14. C. H. MACGALLAVRY and G. D. RIECK, in "International Tables for X-ray Crystallography", Vol. III, edited by C. H. Macgallavry and G. D. Rieck (The International Union of Crystallography, Birmingham, 1968) pp. 75, 157–67.
15. A. H. COMPTON and S. K. ALLISON, "X-ray in Theory and Experiments" (Van Nostrand, New York, 1935).
16. D. T. CROMER and J. B. MANN, *Acta Crystallogr.* **A24** (1968) 395.
17. D. T. CROMER, *ibid.* **18** (1968) 17.
18. K. FURUKAWA, "Reports on Progress in Physics", Vol. XXV (The Institute of Physics and the Physical Society, London, 1962) pp. 395–440.
19. B. E. WARREN, "X-ray Diffraction" (Addison-Wesley, Reading, Massachusetts, 1969).
20. T. FUKUNAGA and K. SUZUKI, *Sci. Rep. Res. Inst. Tohoku Univ. Ser.* **A29** (1981) 153.
21. M. SUGIYAMA, E. YAJIMA and Y. NISHI, Reports of Grant in Aid for Science Research of Ministry of Education, Science and Culture (56460159), Tokyo, 1982).
22. K. SUZUKI, T. FUKUNAGA, M. MISAWA and T. MASUMOTO, *Mater. Sci. Engng* **23** (1976) 215.
23. K. FURUKAWA, *Discuss. Faraday. Soc.* **32** (1961) 53.
24. H. OHNO, K. FURUKAWA, K. IGARASHI and J. MOCHINAGA, *J. Chem. Soc. Faraday Trans.* **1** 78 (1982) 1555.
25. Y. NISHI, H. HARANO, T. FUKUNAGA and K. SUZUKI, *Phys. Rev. B* **37** (1988) 2855.
26. Y. NISHI, M. TACHI and E. YAJIMA, *Scripta Metall.* **19** (1985) 865.
27. Y. NISHI, H. WATANABE, K. SUZUKI and T. MASUMOTO, *J. De Phys. Suppl.* **C8** (1980) 359.

Received 12 May
and accepted 15 November 1989