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Thermal stability of Pd-based metallic glasses examined by electrical resistance measurement*

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Thermal stability of some Pd-based metallic glasses was investigated mainly by the electrical resistance measurement. Differential thermal analysis was also performed to compare the thermogram with the electrical resistance curve. The crystallization and glass transition temperatures were in good agreement between both measurements. The influence of gas atmosphere on the electrical resistance curve was examined under a purified Ar and a vacuum state. The amount of oxygen impurity was larger for Ar than vacuum. From the electrical resistance behavior in the supercooled liquid region it was concluded that the thermal stability of metallic glasses which contain Pd and/or B atoms was obviously affected by the oxygen impurity in the Ar atmosphere. Samples which were annealed to a temperature in the supercooled liquid region under an Ar atmosphere showed the precipitation of nano-crystallites.

KEYWORDS: Pd-based alloys, metallic glass, thermal stability, electrical resistance, oxygen impurity, glass transition, crystallization

1. Introduction

Great effort has been devoted to clarify the thermal stability[3)] and structure[4)] of Zr-, La- and Mg-based metallic glasses with a significant supercooled liquid region before crystallization, since their glasses were discovered by Inoue *et al.*[1-3)] In a typical $Zr_{60}Al_{15}Ni_{25}$ glass, the difference $\Delta T_x = T_x - T_g$, where T_x and T_g represent the crystallization and glass transition temperature, reaches to about 90 K[3)]. It has been pointed out[1)] that the origin of high thermal stability for these metallic glasses is well explained by the atomic size effect and the specific bonding nature between constituent atoms. In addition, it has been reported[4)] that the local structure of these metallic glasses is fairly different from that of intermetallic compounds which precipitate upon crystallization, leading to high resistance against their homogeneous nucleation. Recently, it has been reported[6)] that the addition of Cu to the ordinary Pd-Ni-P metallic glass enhances significantly the glass-forming ability and thermal stability. In this case, the minimum cooling rate necessary for formation of a single amorphous phase is as small as 0.10 K/s for the most stable $Pd_{40}Ni_{10}Cu_{30}P_{20}$ metallic glass. It has been reported[5)] that the thermal behavior of a $Zr_{60}Al_{15}Ni_{25}$ metallic glass is affected, especially in the supercooled liquid region, by the oxygen impurity contained in the gas atmosphere. Consequently, it is interesting to examine whether or not the ordinary Pd-metalloid metallic glass shows the similar behavior in the gas atmosphere containing the oxygen impurity. Besides, the clarification of such a basic property is important for the increase in the understanding of the supercooled liquid state.

In the present experiment, five metallic glasses, $Pd_{76}Cu_6Si_{18}$, $Pd_{76}Cu_6Si_{15}B_3$, $Pd_{61}Pt_{15}Cu_6Si_{18}$, $Pd_{61}Pt_{15}Cu_6Si_{15}B_3$ and $Pd_{40}Ni_{10}Cu_{30}P_{20}$, were used to examine the thermal stability and the influence of gas atmosphere. Instead of ordinary differential scanning calorimetry (DSC), the electrical resistance measurement was employed to investigate the thermal stability of supercooled liquid.

2. Experimental Procedure

Master ingots with the chemical composition of $Pd_{76}Cu_6Si_{18}$, $Pd_{76}Cu_6Si_{15}B_3$, $Pd_{61}Pt_{15}Cu_6Si_{18}$, $Pd_{61}Pt_{15}Cu_6Si_{15}B_3$ and $Pd_{40}Ni_{10}Cu_{30}P_{20}$ were produced by arc-melting. The amorphous ribbons with a cross section of about 0.05 x 2.00 mm^2 were prepared by a melt-spinning method. The amorphicity was confirmed by X-ray diffraction and transmission electron microscopy (TEM). Thermal stability was examined mainly by the electrical resistance measurement with d.c. four terminals. The DSC measurement was partly carried out in comparison with the electrical resistance curve. The thermal treatment was performed at a heating rage of 0.67 K/s in an inferred image furnace. To investigate the influence of gas atmosphere on the thermal stability, the electrical resistance measurement was performed in a purified Ar (99.9995%) and an evacuated (5.0x10^{-6} Torr) atmosphere.

3. Results and Discussions

Figure 1 shows the typical electrical resistance curve of

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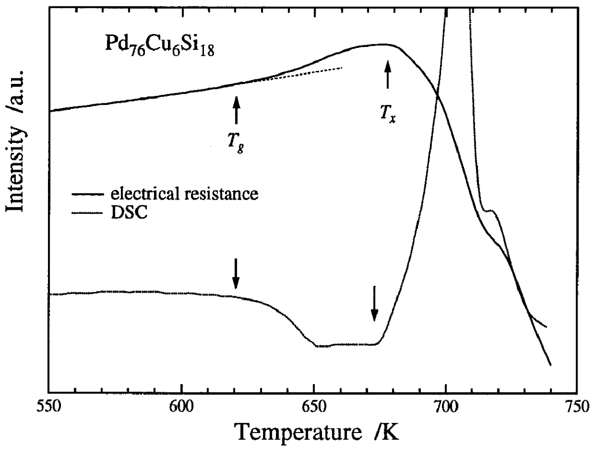

Fig. 1 Comparison the DSC thermogram around the supercooled liquid region of a $Pd_{76}Cu_6Si_{18}$ metallic glass with the electrical resistance curve. The measurements were carried out in an Ar atmosphere at a heating rate of 0.67 K/s.

the $Pd_{76}Cu_6Si_{18}$ metallic glass as a function of annealing temperature together with the DSC curve. he measurement was made at a heating rate of 0.67 K/s in an Ar atmosphere. The T_x (675 K) agrees between both measurements. The glass transition around 630 K on DSC curve can be also observed on the electrical resistance curve and T_g is in

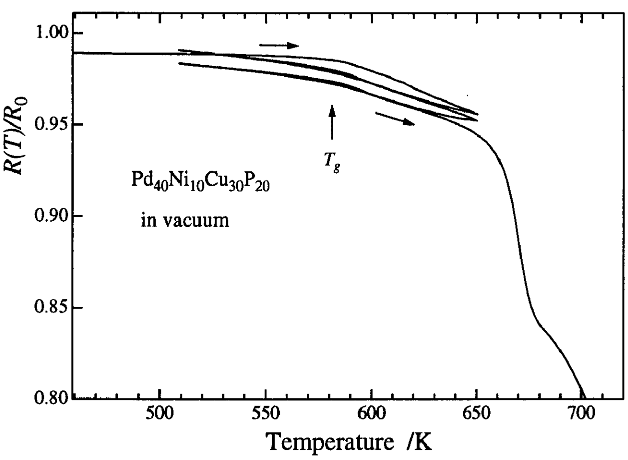

Fig. 2 Reproducible behavior of the electrical resistance curve around T_g for a $Pd_{40}Ni_{10}Cu_{30}P_{20}$ metallic glass. The measurement was performed at a heating rate of 0.33 K/s in an evacuated atmosphere of $5.0x10^{-6}$ Torr.

agreement with one defined from DSC curve. It should be noticeable that the temperature coefficient of resistance TCR increases slightly in the temperature region above T_g. As T_x and T_g can be defined from the electrical resistance curve, the electrical resistance curve is hereafter used to investigate the thermal stability of metallic glasses hereafter. To examine the reproducibility of the glass transition phenomenon for the typical $Pd_{40}Ni_{10}Cu_{30}P_{20}$ metallic glass, the annealing treatment across T_g was repeated. Simultaneously, the change in the electrical resistance was measured at a heating rate of 0.33 K/s in vacuum. Figure 2 shows the reproducibility of the glass transition. By repeating the annealing treatment, the electrical resistance slightly decreases presumably because of the annihilation of quenched-in free volume. However, the reproducibility of T_g is excellent and this alloy system possesses a high resistance against crystallization. The similar reproducibility of glass transition was also observed in other metallic glasses of $Zr_{60}Al_{15}Ni_{25}$[5] and $Pd_{58}Ni_{25}Si_{17}$[7]. In addition, TCR is negative for this metallic glass and the negative value increases further after glass transition. We have reported[5] that the electrical resistance behavior in the supercooled liquid region undergoes significantly the influence of gas atmosphere for Zr-based metallic glasses.

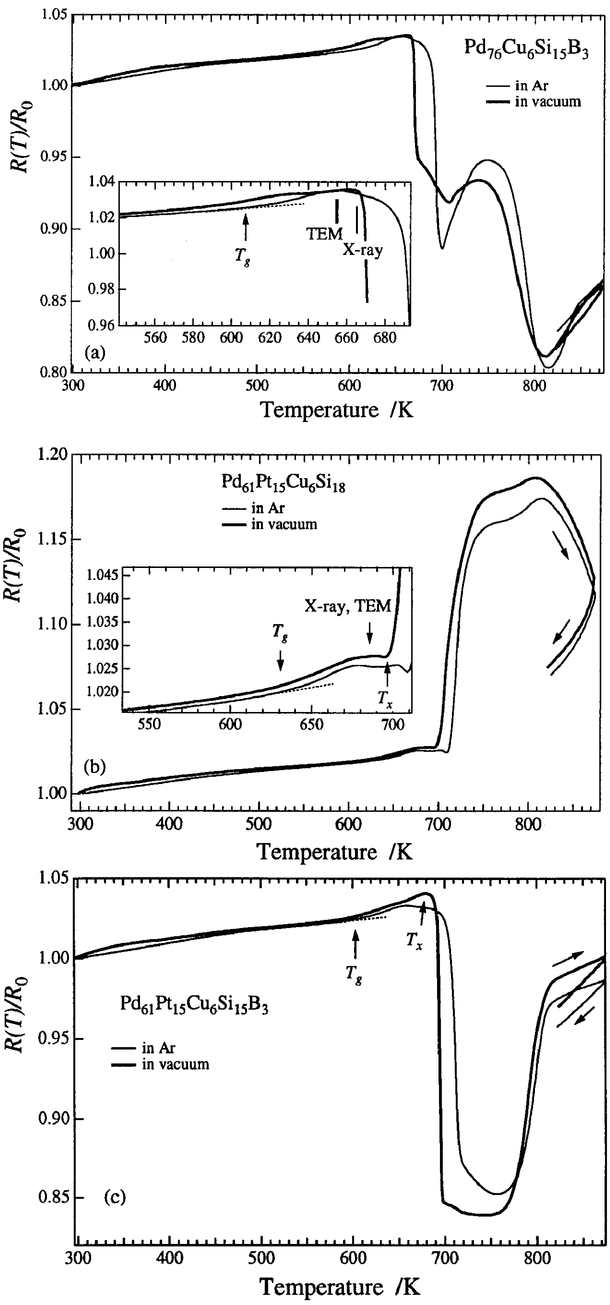

Fig. 3 Comparison the electrical resistance curve measured in an Ar atmosphere with that in the evacuated state for (a) $Pd_{76}Cu_6Si_{15}B_3$, (b) $Pd_{61}Pt_{15}Cu_6Si_{18}$ and (c) $Pd_{61}Pt_{15}Cu_6$-$Si_{15}B_3$ metallic glasses.

To confirm whether or not the similar result is obtained for Pd-based metal-metalloid glasses, we performed the electrical resistance measurements in a purified Ar and an evacuated atmosphere. Three metallic glasses, $Pd_{76}Cu_6Si_{15}B_3$, $Pd_{61}Pt_{15}Cu_6Si_{18}$ and $Pd_{61}Pt_{15}Cu_6Si_{15}B_3$ were chosen. Figure 3(a) to (c) shows the electrical resistance curves of $Pd_{76}Cu_6Si_{15}B_3$, $Pd_{61}Pt_{15}Cu_6Si_{18}$ and $Pd_{61}Pt_{15}Cu_6Si_{15}B_3$ metallic glasses, together with the insets enlarged around the supercooled liquid region. The T_g appears to be independent of the gas atmosphere. However, the T_x is affected by the gas atmosphere. All T_x values are shifted to a lower temperature side in the case of the measurement in the Ar atmosphere. Besides, the decrease of the electrical resistance in the supercooled liquid region is seen in the Ar atmosphere. Figure 4 shows X-ray diffraction pattern and TEM image for $Pd_{76}Cu_6Si_{15}B_3$ metallic glass which was heated to 665 and 654 K respectively in the Ar and evacuated atmospheres, and then cooled to room temperature. The sharp peak, due to a crystalline phase, is seen in the principal hallo pattern. On the other hand, in the TEM image (bright-field image and Laue pattern), no crystallite is observed. Therefore, it is concluded that the decrement of electrical resistance in the supercooled liquid region is attributed to the precipitation of a crystalline phase. As, however, no corresponding exothermic peak is observed in the DSC curve, the volume fraction of the crystalline phase is presumed to be extremely small. Figure 5 shows the similar experimental result for the $Pd_{61}Pt_{15}Cu_6Si_{18}$ metallic glass, where the sample was annealed to 685 K in the Ar or the evacuated atmosphere at a heating rate of 0.67 K/s and subsequently cooled to room temperature. Although no crystallite is observed in the X-ray diffraction pattern for the sample annealed in the evacuated atmosphere, the Laue pattern of the sample annealed in the Ar atmosphere reveals the trace of a crystallite which is not detected in the bright-field image. The similar result is presumably valid for a $Pd_{61}Pt_{15}Cu_6Si_{15}B_3$ metallic glass. The amount of oxygen impurity is larger in the Ar atmosphere than vacuum in the present experiment. Therefore, it is concluded that the oxygen impurity, although the amount is slight, affects the thermal stability of the Pd-based metallic glass in the supercooled liquid region. However, the detailed mechanism on the oxygen-induced precipitation remains unclear up to date.

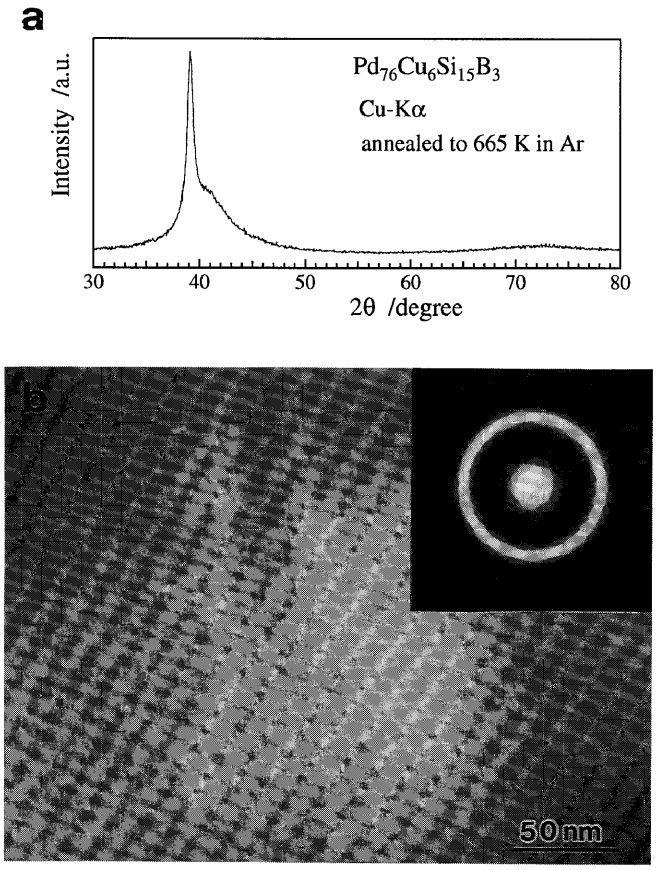

Fig. 4 (a) X-ray diffraction pattern and (b) TEM image for a $Pd_{76}Cu_6Si_{15}B_3$ metallic glass annealed to 665 and 654 K at a heating rate of 0.67 K/s respectively in the Ar and the evacuated atmosphere.

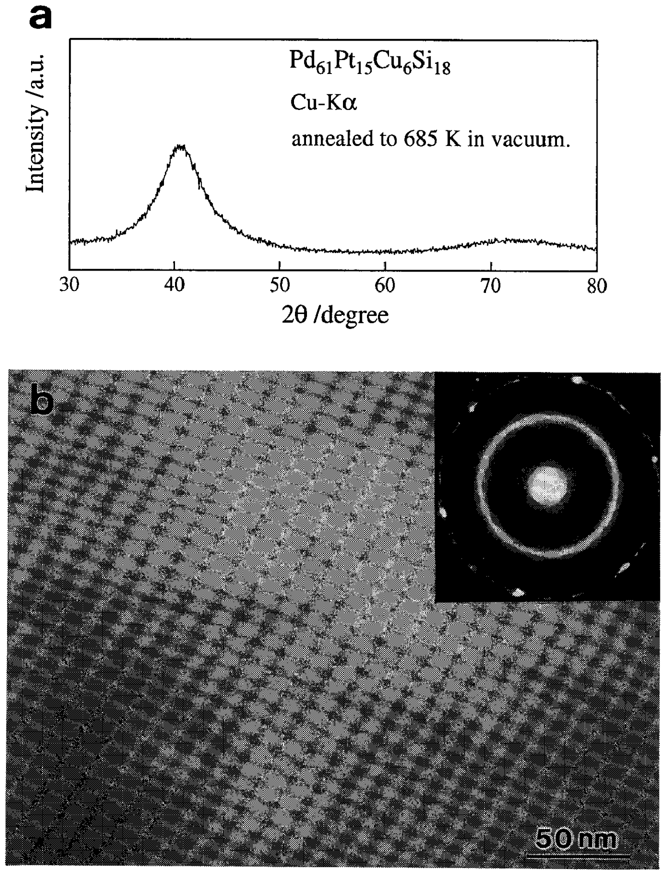

Fig. 5 (a) X-ray diffraction profile and (b) TEM image for a $Pd_{61}Pt_{15}Cu_6Si_{18}$ metallic glass annealed to 685 K at a heating rate of 0.67 K/s in the Ar or the evacuated atmosphere.

We have reported[5)] that the electrical resistance curve in the supercooled liquid region for Zr-based metallic glasses is significantly affected by the oxygen impurity contained in the gas atmosphere. It has further been pointed out that the density of state of the conduction electron at Fermi energy level was changed by the formation of a new bonding state between zirconium and oxygen atoms. The electron transport property of the Pd-based metallic glasses is predicted to be significantly different from that of the Zr-based metallic glass. Table 1 summarizes the electrical resistivity and TCR at room temperature for metallic glasses. All resistivity values for the Pd(Pt)-Cu-Si(B) metallic glasses are fairly lower than 2.0 μΩ m, which is indicative of the limit for the application of Faber-Zimann theory[8] to the interpretation of the electron transport property. Their glasses possess the positive TCR at room temperature. On the other hand, the $Pd_{40}Ni_{10}Cu_{30}P_{20}$ metallic glass shows the relative large value of the resistivity and the negative TCR at room temperature. The relation between resistivity and TCR for these Pd-based metallic glasses is consistent with Mooij's criterion[9]. Also, the compositional dependence of Hall coefficient (negative value) for the Pd-Cu-Si metallic glass has been interpreted by Faber-Zimann theory[10]. We have confirmed that the $Pd_{61}Pt_{15}Cu_6Si_{18}$ glass shows similarly the negative Hall coefficient. On the other hand, the typical $Zr_{60}Al_{15}Ni_{25}$ metallic glass shows the electrical resistivity of 2.1 μΩm at room temperature[5] and has been reported to possess the positive Hall coefficient[11]. Therefore, it is reasonably assumed that the electron transport property of the present Pd-based metal-metalloid glasses is interpreted within the framework of the usual Faber-Zimann theory. The typical value of $2k_F$ (twice of Fermi wave number) has been reported to be 24.8 nm^{-1} for the $Pd_{77.5}Cu_6Si_{16.5}$ glass[10]. The Q_p which corresponds to the first peak position in the static structure factor is calculated to be 28.3 nm^{-1} for the $Pd_{76}Cu_6Si_{18}$ glass. The $2k_F<Q_p$, which manifests the condition for the appearance of the positive TCR, is satisfied for this metallic glass. The increment of TCR in the supercooled liquid may be interpreted by expected broadening and lowering of the 1st peak intensity of the structure factor because the average displacement of atom is then predicted to increase by the reduction of the bonding strength between atoms, leading to the enhancement of the Debye-Waller factor. The detailed mechanism for the decrement of the electrical resistance in the supercooled liquid region remains unknown. The nano-crystalline precipitates are predicted to possess a smaller electrical resistivity than these for metallic glasses.

Table 1 Resistivity (μΩm) and TCR(K^{-1}) at room temperature for Pd-based metallic glasses

glass	resistivity	TCR
$Pd_{76}Cu_6Si_{18}$	0.807	8.32×10^{-5}
$Pd_{76}Cu_6Si_{15}B_3$	0.640	9.93×10^{-5}
$Pd_{61}Pt_{15}Cu_6Si_{18}$	0.899	7.06×10^{-5}
$Pd_{61}Pt_{15}Cu_6Si_{15}B_3$	0.772	8.95×10^{-5}
$Pd_{40}Ni_{10}Cu_{30}P_{20}$	2.33	1.11×10^{-4}

4. Conclusion

Thermal stability of Pd-based metal-metalloid glasses was investigated mainly by the electrical resistance measurement, and the DSC measurement was partly utilized in comparison with the electrical resistance curve. The variation in the electrical resistance curve was clearly recognized when the glass transition occurred. This behavior seems to be interpreted qualitatively by assuming Faber-Zimann transport theory. The T_g and T_x were in good agreement with those defined from the DSC thermogram. The reproducibility of the glass transition phenomenon was excellent in repeating the thermal treatment across T_g. The influence of the gas atmosphere on the thermal stability was examined by employing an Ar and an evacuated atmosphere. The T_g remained unchanged in different circumstances. However, the T_x was shifted to a lower temperature side for the measurement in the Ar atmosphere. Also, the electrical resistance of the metallic glasses contained Pt and B atoms decreased in the supercooled liquid region. On the other hand, in the evacuated atmosphere, the electrical resistance continued to increase in the supercooled liquid region. The X-ray diffraction and TEM image suggested that the decrease in electrical resistance is due to the precipitation of nanocrystalline phase.

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