The effect of plastic deformation of amorphous Pd–Si *alloys on their thermal properties*

Studies of metallic glasses give much attention to plastic deformation and to the thermal properties of these materials. However, only a few studies of amorphous metallic alloys have connected these characteristics. Masumoto *et al.* [1] have observed that plastic deformation stabilizes the structure of the amorphous phase, raising the crystallization temperature by about 20 to 30 K. According to Luborsky *et al.* [2], the amorphous alloy $Fe_{40}Ni_{40}P_{14}B_6$ subjected to cold-rolling shows no changes in crystallization heat, glass-formation temperature and crystallization temperature, as compared with the same alloy in the as-quenched state.

The present studies concern the effect of plastic deformation of metallic glasses belonging to the Pd–Si system on their thermal stability. Use was made of four alloys of the $Pd_{100-x}Si_x$ type ($x = 16, 18, 20, 22$ at%). Amorphous ribbons (thickness about 45 μm, width about 1.5 mm) were prepared by the melt-spinning method. The amorphous state of the structure of the ribbons was confirmed with the use of an X-ray diffractometer. Plastic deformation was performed by compression, in a press, of a pack made up of 10 pieces of ribbon, each about 40 mm long, placed between two steel plates. The decrease in thickness amounted to 35 to 40%. Deformation was carried out at room temperature, T_R. According to Argon [3], all the alloys were deformed within the low-temperature range, i.e. $T_R < 0.6\, T_g$ (assuming the glass transition temperature, T_g, to be close to the crystallization temperature, T_x). Thermal properties were studied using a Perkin Elmer differential calorimeter DSC-2, with application of continuous and isothermal heating.

The results obtained upon continuous heating are shown in Fig. 1. The nature of changes in the crystallization temperature (Fig. 1b) for $T_x = f(\text{at\% Si})$ is similar to that presented by Funakoshi *et al.* [4], because the alloys containing 18 to 20 at% Si exhibit maximal values of T_x. Plots in Fig. 1b and c point to two relationships. Firstly, plastic deformation causes a decrease in the crystallization temperature

$$\Delta T_x = T_x^d - T_x^q < 0, \qquad (1)$$

where T_x^q and T_x^d represent the crystallization temperatures of the material in as-quenched state and after plastic deformation, respectively. Secondly, the magnitude of changes in the crystallization temperature is a function of the chemical composition of alloy. The value of $|\Delta T|$ increases with a rise in the Si-content of the alloy. The above relationships apply also in case of other heating rates (40 and 10 K min^{-1}), the $|\Delta T|$ value decreasing with a drop in the heating rate.

Activation energies of crystallization, E_a, calculated according to Kissinger [5] using the crystallization peak temperatures, were determined for three heating rates (10, 40, 80 K min^{-1}), and are recorded in Fig. 1a. After plastic deforma-

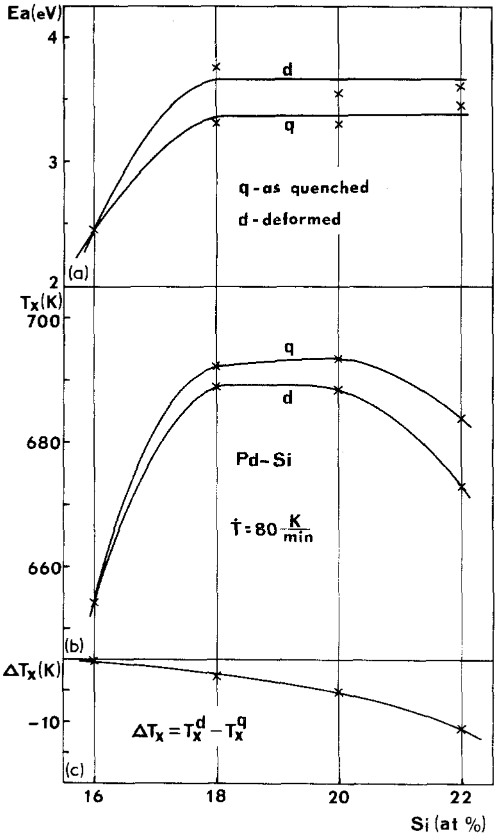

Figure 1 The results of continuous heating of amorphous Pd–Si alloys in the as-quenched (q) and deformed (d) states; (a) activation energy (E_a), (b) crystallization temperature (T_x), (c) difference in crystallization temperature (ΔT_x) between the alloys in both states.

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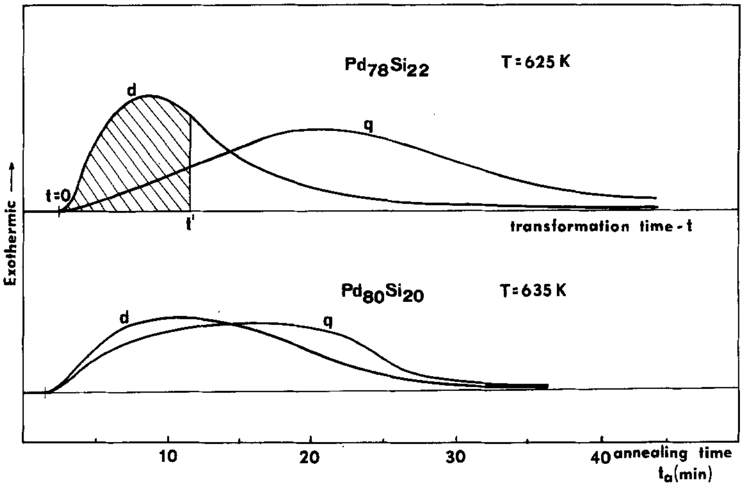

Figure 2 DSC thermograms for as-quenched (q) and deformed (d) $Pd_{78}Si_{22}$ and $Pd_{80}Si_{20}$ alloys obtained during isothermal annealing at temperatures about 50 K lower than the crystallization temperature T_x (80 K min^{-1}).

tion E_a increased slightly (0.2 to 0.5 eV) in the case of alloys with a Si-content $\geqslant$ 18 at %.

The results obtained upon isothermal heating, as shown in Fig. 2, are consistent with those observed for continuous heating. Also, in this case, the destabilizing effect of plastic deformation is manifested, and its intensity increases with a rise in the Si-content of the alloy.

Data from the thermograms, as in Fig. 2, are presented in a co-ordinate system $\ln \ln [1/(1-x)]$

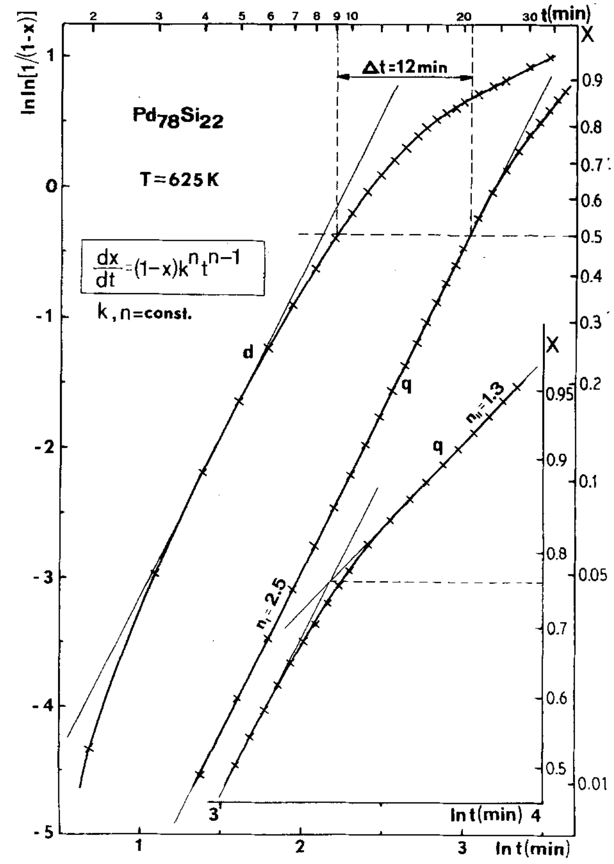

Figure 3 Experimental (cf. upper part of Fig. 2) plots of $\ln \ln [1/(1-x)]$ against $\ln t$ for as-quenched (q) and deformed (d) amorphous $Pd_{78}Si_{22}$ alloy (Johnson–Mehl–Avrami equation fitting).

and ln t (Fig. 3), where x is the fraction of volume crystallized in time t, and t is the annealing time minus incubation time.

Plots shown in Fig. 3 were prepared on the assumption that the percentage of alloy transformed from the amorphous phase to the crystalline phase is proportional to the amount of heat liberated during isothermal heating. The value of x for $t = t'$ was calculated as the ratio of the area under the calorimetric curve (Fig. 2) within the range of $0 \leqslant t \leqslant t'$ to the area under the curve within the range of $0 \leqslant t \leqslant 60$–$120$ min.

According to several communications [6–9], the crystallization of metallic glasses can be described by the Johnson–Mehl–Avrami equation (J–M–A).

$$x(t) = 1 - \exp(-kt^n),$$

where k is the reaction rate constant and n the exponent. If it is assumed that the crystallization kinetics of the investigated alloys can also be described by the above equation, the plots in Fig. 3 can be expected to be straight lines. In the case of the $Pd_{78}Si_{22}$ alloy in the as-quenched state, the results form two straight lines (Fig. 3). In contrast, for the same alloy deformed plastically, the plot shows distinct curvature. Thus, plastic deformation also changes the crystallization kinetics of the metallic glass $Pd_{78}Si_{22}$.

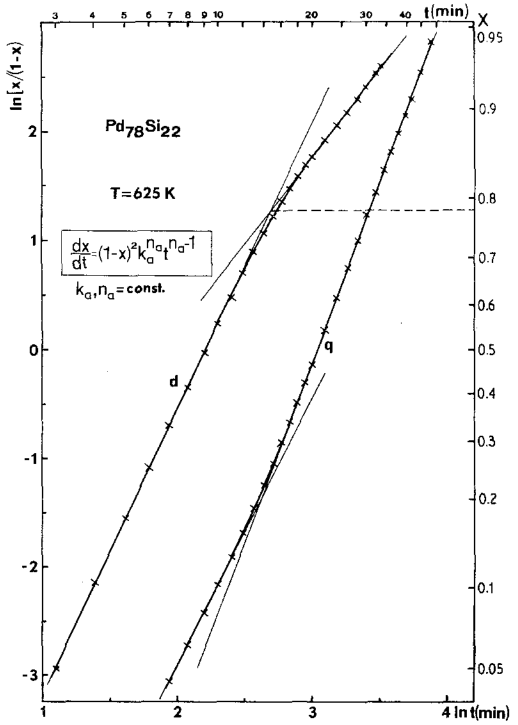

Figure 4 Experimental plots of $\ln[x/(1-x)]$ against $\ln t$ for as-quenched (q) and deformed (d) amorphous $Pd_{78}Si_{22}$ alloys (Austin–Ricketts equation fitting).

Fig. 4 illustrates the crystallization kinetics of alloy $Pd_{78}Si_{22}$ (in both states) on the assumption that crystallization can be described by the Austin–Ricketts (A–R) equation [10]. Also in this case, distinct differences in the crystallization kinetics between the alloy in the as-quenched state and the plastically deformed one are found.

Comparison of Figs 3 and 4 indicates that the J–M–A equation is appropriate for the description of the crystallization of alloy $Pd_{78}Si_{22}$ in the as-quenched state, whereas the A–R equation is preferable for the description of the state after plastic deformation. It is noteworthy that in both cases (Curve q in Fig. 3 and Curve d in Fig. 4) the curves exhibit an inflection at the same values of x. The intersection of the tangents gives $x \approx 0.75$. The times of attainment of 50% crystallization in glass $Pd_{78}Si_{22}$ in the as-quenched state and after plastic deformation differ considerably. For example, upon isothermal heating at 625 K, the half-transformation time is more than twice as long for the material in the as-quenched state (21 min) than in the deformed state (9 min) (Fig. 3).

The fact that plastic deformation fails to influence the crystallization temperature, T_x, of certain metallic glasses, e.g. $Fe_{40}Ni_{40}P_{14}B_6$ [2], is not inconsistent with the results presented above obtained for alloys of the Pd–Si system. In particular, the intensity of destabilization of the investigated glasses was found to depend on their chemical composition. It can also be assumed that in the alloy $Pd_{84}Si_{16}$ plastic deformation exerts no effect on T_x, because the observed changes are minimal ($\Delta T = -0.5$ to -1 K) and may remain within the limits of the experimental error. On the other hand, a comparison of the present results with those reported by Masumoto *et al.* [1] for $Pd_{80}Si_{20}$ is surprising; namely, the latter authors observed a stabilizing effect of plastic deformation, i.e. an opposite one to that found in our experiments. It is possible that the dissimilarities of the effects result from the use of different methods for deformation (compression in our studies and cold-rolling in those of Masumoto *et al.*).

The change in the amorphous structure, caused by plastic deformation, involves an increase in its disorder [1, 11–14], i.e. a decrease in the short-range order similar to that found in crystalline materials [15].

Many examples indicate that a decrease in the short-range order lowers the crystallization temperature of metallic glasses [16–19] and of chalcogenide glasses [20, 21]. Thus, the present observations are consistent with the results of other authors, even if the decrease in the short-range order has been achieved by another procedure, e.g. by a reduction of the metalloid content in the alloy [16] or by an increase in the cooling rate from liquid state [17–21]. The present results and those quoted above are consistent with the results of measurements of the diffusion coefficient in metallic glasses. The more the structure of a given glass departs from a fully relaxed structure, the higher the diffusion coefficient; this fact has been confirmed by direct investigations of diffusion [22] and by studies of stress relaxation [2, 18, 23] and creep [24]. It can be expected that the higher the diffusion coefficient, the lower the temperature required for the initiation of glass crystallization. The decrease in $|\Delta T|$, with a drop in the continuous heating rate observed for all investigated alloys, can be attributed to the more advanced structural relaxation upon slower heating and, consequently, to a reduction of the structural differences between the alloy in the as-quenched state and after plastic deformation.

A rise in the metalloid content of the TM–M (transition metal–metalloid) type alloy elevates the number of bonds between the TM and M atoms, and increases the short-range order [16]. It can be expected that the intensity of changes in the short-range order during plastic deformation may increase with a rise in the metalloid content of the alloy; this phenomenon ought to manifest itself as an increased destabilization of the alloys richer in metalloid, as observed in the present studies.

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