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Resistometric evidence of densification during structural relaxation in metallic glasses

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Abstract. We have studied experimentally the effects of long isothermal annealing treatments on electrical resistance in the $Pd_{82-x}V_xSi_{18}$ glasses ($x = 0, 1, 2$). In a separate experiment, we have determined the pressure coefficient of resistance in identical samples of these glasses. A correlation between these two sets of measurements suggests that densification, as brought about by hydrostatic compression, is an important component of irreversible structural relaxation in these materials.

1. Introduction

Detailed theories of electrical resistance in metallic glasses based on the interrelationship between structure and electronic properties are not yet available. Hence any experiment which provides information on the coupling between the structure and the electrical properties will be of use in modelling. The nature of structural relaxation in metallic glasses has frequently been investigated by kinetic analysis of the changes in physical properties during controlled heat treatments. An important model for the analysis of these results (van den Beukel and Radelaar 1983) asserts that property changes observed during irreversible structural relaxation are simply related to changes in the mean atomic volume, i.e. to densification. In the experiments reported here, we set out to test this idea more directly than is possible by kinetic analysis. We have compared the effects of structural relaxation and hydrostatic compression on the electrical resistance of a set of metallic glass ribbons, composition $Pd_{82-x}V_xSi_{18}$ ($x = 0, 1, 2$). The two experiments are described separately in § 3 and § 4 and then compared in § 5.

2. Characterisation of the ribbons

Metallic glass ribbons, made by melt-spinning, were supplied by the University of Sheffield. The absence of crystallinity both before and after annealing treatments was confirmed by x-ray diffractometry using Cu Kα radiation. The concentrations of vanadium in the metallic glasses with nominal compositions $Pd_{81}V_1S_{18}$ and $Pd_{80}V_2Si_{18}$ were determined by atomic absorption spectrophotometry; the true values of x were found to be $1.1 \pm 0.1\%$ and $2.2 \pm 0.2\%$; respectively. The temperature of onset of

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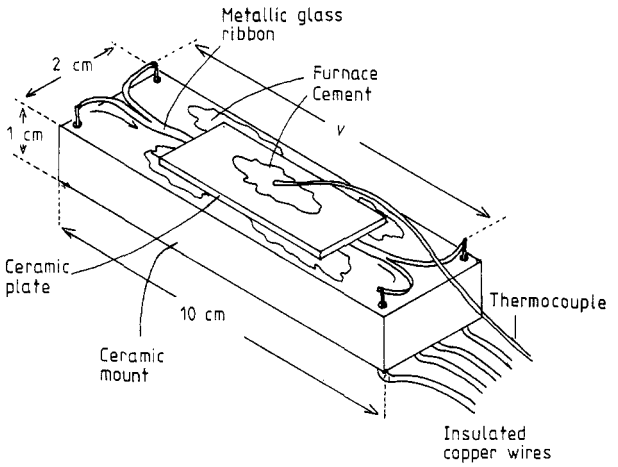

Figure 1. Sample and holder used for structural relaxation measurements on $Pd_{81-x}V_xSi_{18}$ metallic glasses.

crystallisation, T_x, at a heating rate of 5 K min^{-1} was measured for all three metallic glasses using a DuPont 9900 differential scanning calorimeter; T_x increases from 365 °C ($x = 0$) through 391 °C ($x = 1$) to 400 °C ($x = 2$).

3. Isothermal annealing treatments

The electrical resistance of short pieces of metallic glass ribbon was measured during isothermal anneals in an electrical furnace with large thermal mass. The required temperature was attained by switching on the heating element for an uninterrupted burst of predetermined duration; proportional control was then used to maintain the temperature of the metallic glass ribbon to with ±1 K. A Pyrex tube containing the sample was evacuated to a pressure of 5×10^{-2} Torr, using a rotary pump, in order to minimise oxidation (Marcus 1979) during the anneals.

Resistance was measured using a DC four-point method. The voltage across the potential contacts was compared potentiometrically with the voltage across a standard resistor in series with the sample. The effects of thermal EMFs were eliminated by repeating each measurement with the current reversed. Resistance changes were measured *in situ* with a resolution of 1 part of 10^5. The current, of about 60 mA, had a negligible heating effect. This fact was ascertained by observing that switching the current on and off had no effect on the temperature, as measured by the thermocouple, either at room temperature or during an anneal.

Figure 1 shows how the contacts were made. A 10 cm length of ribbon was cut longitudinally at its ends to make four arms which formed the potential and current leads. These arms were spot-welded to stiff copper wires, held in place by a rigid ceramic mount. The section of ribbon contributing to the resistance measurement is well separated from all spot-welds in this geometry; any crystallisation around the spot-welds would therefore contribute nothing to the measured resistance value. The central section of the ribbon was trapped between the top of the ceramic mount and a thin ceramic

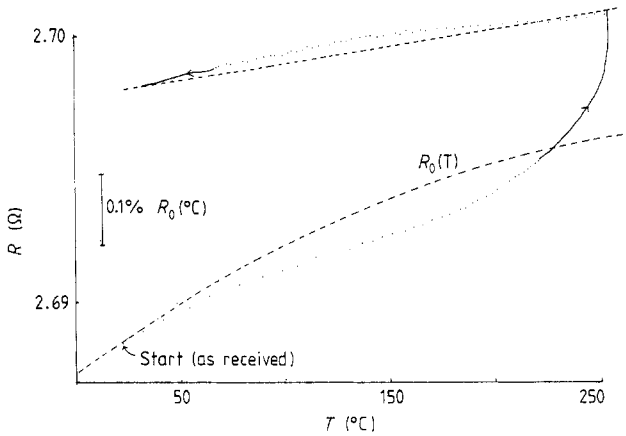

Figure 2. Resistance of as-received $Pd_{80}V_2Si_{18}$ during an isothermal anneal at 253 °C. Dots represent individual data points, replaced by a full curve when very close together. See § 3 of text for explanation of broken curves.

plate, held in place with furnace cement. Temperature was measured using a calibrated chromel–alumel thermocouple in contact with the ribbon.

The results of a typical experiment can be seen in figure 2, which shows the resistance, R, of an as-received sample of $Pd_{80}V_2Si_{18}$ as a function of its temperature, T, as T is increased from room temperature to 253 °C over a period of about twenty minutes, held there for several days, and then returned to room temperature. The dots represent data points, replaced by a full curve when they are very close together. The broken curve is the estimated temperature dependence of the resistance, R_0 of the sample in its initial structural state. It was constructed by extrapolating a quadratic curve fitted to four values of resistance, measured in a separate experiment, at temperatures between −200 °C and 150 °C:

$$R_0(T) = R_0(0\,^\circ\mathrm{C})[1 + \alpha(T - 0\,^\circ\mathrm{C}) + \beta(T - 0\,^\circ\mathrm{C})^2] \tag{1}$$

The data points lie below the broken curve; this is because the temperature of the sample lags slightly behind that of the thermocouple during rapid changes in temperature.

Using the following equation, we can define the fractional departure $\Delta R/R_0$ of the observed curve $R(T)$ from the as-received curve $R_0(T)$:

$$\Delta R/R_0 = (R(T) - R_0(T))/R_0(T) \tag{2}$$

In figure 3, $\Delta R/R_0$ and T are plotted as functions of annealing time $(t - t_0)$. Here t_0 is the effective starting time, calculated using a method given by Hygate (1988) and Hygate and Gibbs (1989). This takes into account the relaxation of the structure during the heating process. The resistance change curve is drawn full where the temperature lies within ±1 K of its steady value, 253 °C, and broken otherwise. The dotted line is a guide to the eye, indicating approximately where the initial part of the resistance change curve would lie in an ideal isothermal treatment with zero warm-up time.

Identical experiments were performed on samples of $Pd_{82}Si_{18}$ and $Pd_{81}V_1Si_{18}$. The results obtained are displayed in figures 4 and 5. The isothermal resistance change is negative when $x = 0$ and $x = 1$, in contrast to its positive value when $x = 2$.

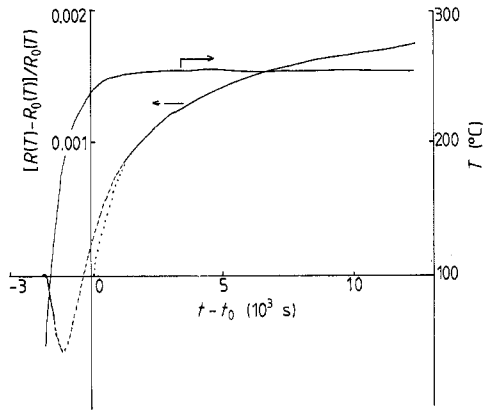

Figure 3. Evolution of fractional resistance change in as-received $Pd_{80}V_2Si_{18}$ during an isothermal anneal at 253 °C. See § 3 of text for explanation of broken and dotted curves.

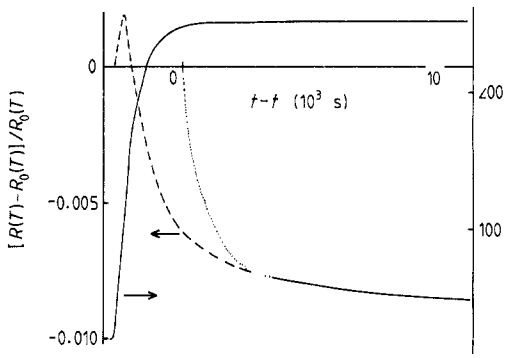

Figure 4. Evolution of fractional resistance change in as-received $Pd_{82}Si_{18}$ during an isothermal anneal at 253 °C. See § 3 of text for explanation of broken and dotted curves.

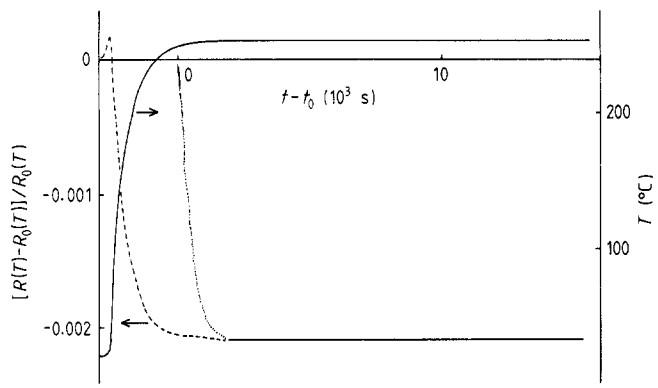

Figure 5. Evolution of fractional resistance change in as-received $Pd_{81}V_1Si_{18}$ during an isothermal anneal at 253 °C. See, § 3 of text for explanation of broken and dotted curves.

The results of these three experiments are summarised in table 1. The first two rows of this table give the coefficients α and β of the isostructural temperature-dependence of resistance in the as-received state, defined by equation (1).

The effects of irreversible structural relaxation on resistance have been characterised by taking the value of $\Delta R/R_0$ and the value of $(1/R_0)(dR/d\ln t)$ at 10^4 s for each alloy. The effects of irreversible structural relaxation on the isostructural temperature

Table 1. Summary of results of isothermal annealing measurements on $Pd_{82-x}V_xSi_{18}$ metallic glasses.

			Composition		
			$Pd_{82}Si_{18}$	$Pd_{81}V_1Si_{18}$	$Pd_{80}V_2Si_{18}$
Isostructural temperature dependence of resistance	α (10^{-4} K^{-1})		1.243	0.400	0.212
	β (10^{-8} K^{-2})		−1.56	−1.14	−3.21
Irreversible structural relaxation	$(\Delta R/R_0)$		-8.70×10^{-3}	-2.06×10^{-3}	1.67×10^{-3}
	$(1/R_0)(dR/d \ln t)$		-8.6×10^{-4}	0.0×10^{-4}	3.9×10^{-4}
Effect on temperature coefficient of resistance	$(1/R)(dR/dT)$	As-received	1.20×10^{-4}	0.37×10^{-4}	0.13×10^{-4}
		Relaxed	1.26×10^{-4}	0.28×10^{-4}	0.05×10^{-4}
		Change	0.06×10^{-4}	-0.09×10^{-4}	-0.08×10^{-4}
Reversible structural relaxation	$(1/R)(d\Delta R/d\Delta T_A)_{TA}$ (10^{-6} K^{-1})		−10	−5	−8

dependence of resistance have been compared by calculating the average temperature coefficients of resistance (TCR), in both as-received and annealed states, between 0 °C and 250 °C in the three cases. The change in TCR upon annealing is positive in $Pd_{82}Si_{18}$ and negative in $Pd_{81}V_1Si_{18}$ and $Pd_{80}V_2Si_{18}$ (see table 1).

The last row of table 1 shows the effects of reversible structural relaxation on the resistance, measured at the annealing temperature, of the three alloys. These effects were studied in separate experiments in which samples of each alloy were pre-annealed at 253 °C until the isothermal resistance change had become imperceptibly slow; this took between two and four days. In each case, the sample was cooled rapidly by about 18 K and annealed isothermally at a lower temperature of about 235 °C. A small isothermal increase in resistance was seen in each case. This is a reversible effect, as was demonstrated by raising the temperature again, once the resistance had stopped changing at the lower temperature, to the original annealing temperature of 253 °C. The increase previously observed was reversed.

These reversible changes were too small to justify presentation on graphs of the type of figures 3 to 5. The ratio $(1/R_0)(d\Delta R/d\Delta T_A)$ of the fractional reversible change in resistance to the change in annealing temperature, T_A, is given in table 1; this quantity is negative in all three cases, indicating that reversible ordering is accompanied by an increase in resistance in these three metallic glasses. In contrast, the sign of the change in resistance with irreversible ordering varies with composition, as demonstrated above.

Our results on irreversible structural relaxation are in good quantitative agreement with the results of Kelton and Spaepen (1984) on a similar range of Pd–V–Si glasses. To our knowledge there has been no previous comparison of reversible resistance change in these three glasses. Our results on reversibility in $Pd_{82}Si_{18}$ are consistent with those of Kelton and Spaepen (1982); they found that irreversible ordering increased the resistance, measured at 40 °C, but their results do not allow a numerical estimate of the magnitude of the effect to be made.

It seems that reversible and irreversible ordering in $Pd_{82}Si_{18}$ affect the electrical resistance, measured at a single temperature, in an opposite sense.

4. The effect of hydrostatic pressure

The effect of hydrostatic pressure up to 3 kbar (0.3 GPa) on the electrical resistance of the three metallic glasses was studied experimentally by immersing short pieces of ribbon in an oil-filled cylinder and compressing the oil with a piston, the resistance being measured *in situ*. The sample was passed through holes in a cylindrical ceramic mount (see figure 6), attached to the end of the piston by a screw fitting.

Resistance was measured using the DC four-point method described above, but a different method of making the contacts was employed. Both potential and current leads were soldered onto the ribbon directly; soldering was considered preferable to spot-welding in this geometry because solder joins metals by surface adhesion, without melting them, and therefore without causing crystallisation.

Pressure was measured using a seasoned manganin coil (Bridgman 1958); its pressure coefficient of resistance at room temperature was $(2.4 \pm 0.1) \times 10^{-3}$ kbar^{-1} (Samara and Giardini 1964, Wang 1967). The oil used was silicone fluid. Pressure was applied to the piston with a secondary, hand-pumped, hydraulic pressure system.

A thermocouple close to the metallic glass ribbon monitored changes in the temperature of the oil to within 0.1 K. Each time more pressure was applied, the temperature

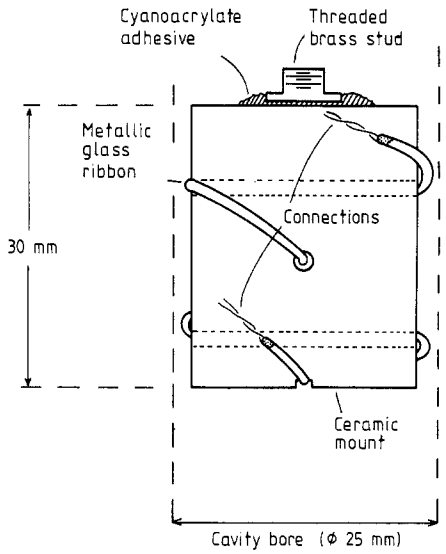

Figure 6. Ceramic mount for pressure measurements on $Pd_{18-x}V_xSi_{18}$ metallic glasses.

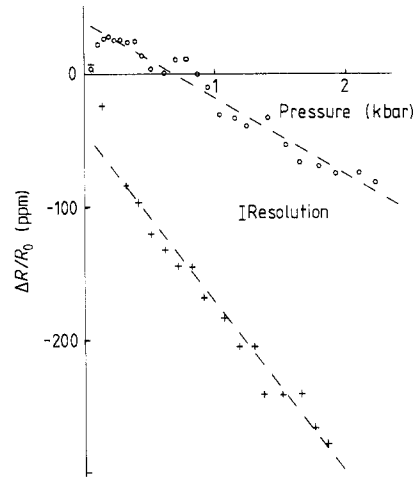

Figure 7. Effect of pressure on resistance for $Pd_{82}Si_{18}$. Crosses, as-received; open circles, after anneal of 22 hours at 230 °C.

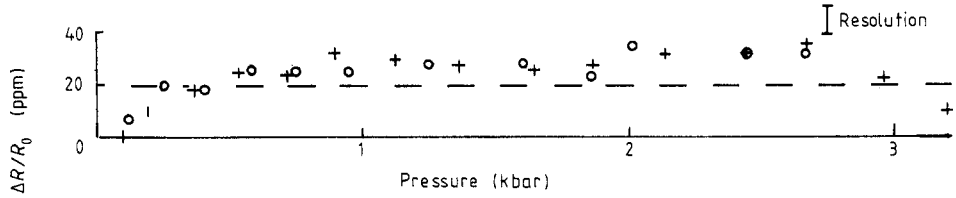

Figure 8. Effect of pressure on resistance for $Pd_{81}V_1Si_{18}$. Crosses, as-received; open circles, after anneal of 22 hours at 230 °C.

of the oil and the temperature of the metallic glass (deduced from its resistance at constant pressure) increased sharply and then began to decay slowly. Each measurement was made several minutes after the application of extra pressure when the temperature at the thermocouple had fallen back to a precisely measured value T_0, about 0.5 K above ambient temperature. Any difference in temperature between the metallic glass and the thermocouple was therefore constant from one measurement to the next.

Figures 7, 8 and 9 show the effect of hydrostatic pressure on the resistance of $Pd_{82}Si_{18}$, $Pd_{18}V_1Si_{18}$ and $Pd_{80}V_2Si_{18}$, respectively, in their as-received states. The difference ΔR between the resistance at atmospheric pressure and at pressure P is expressed as a fraction of R_0, the resistance at atmospheric pressure, in ppm. The crosses represent data on as-received samples. The open circles in these figures show the results of similar experiments with fresh samples pre-annealed for 22 hours at 230 °C in a vacuum of 5×10^{-2} Torr. The point (0.001 kbar, 0) was not used because R_0 was not known exactly at temperature T_0. The effect of this uncertainty in R_0 on the normalisation of the vertical axes is negligibly small. The vertical bar, of height 10 ppm, on each graph represents the limit of resolution of the resistance measurement.

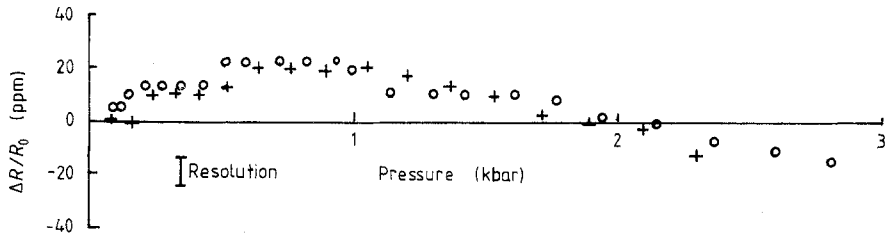

Figure 9. Effect of pressure on resistance for $Pd_{80}V_2Si_{18}$. Crosses, as-received; open circles, after anneal of 22 hours at 230 °C.

Table 2. PCRs for the metallic glasses $Pd_{81-x}V_xSi_{18}$.

		Composition		
		$Pd_{82}Si_{18}$	$Pd_{81}V_1Si_{18}$	$Pd_{80}V_2Si_{18}$
PCR (10^{-4} K^{-1})	As-received	-1.3 ± 0.2	0.0 ± 0.1	0.0 ± 0.1
	Pre-annealed at 230 °C for 22 h	-0.6 ± 0.1	0.0 ± 0.1	0.0 ± 0.1

Straight lines were interpolated by eye through the two sets of points in figure 7, yielding the values for the PCR of $Pd_{82}Si_{18}$ given in table 2. In the other two metallic glasses, any linear term in the dependence of resistance on pressure was zero, to within the experimental resolution of 10^{-5} $kbar^{-1}$, both before and after annealing.

The PCR of as-received $Pd_{82}Si_{18}$ is approximately halved upon annealing and is reduced to zero by the substitution of vanadium atoms for palladium atoms.

Our value for the PCR of as-received $Pd_{82}Si_{18}$ is in good agreement with work by McNeil (1983), who reports a value of $(-1.3 \pm 0.1) \times 10^{-4}$ $kbar^{-1}$.

5. A correspondence between structural relaxation and compression

In the three metallic glasses studied here, there is a correlation between the effects of irreversible structural relaxation and hydrostatic compression on electrical resistance. Both cause a decrease in the resistance of amorphous $Pd_{82}Si_{18}$. The substitution of vanadium for palladium at first reduces the magnitude of the resistance decrease seen during relaxation (when $x = 1$) and then changes it to a small increase ($x = 2$); the negative PCR of $Pd_{82}Si_{18}$ is reduced approximately to zero as the vanadium is added.

Since the changes brought about by compression are presumably the effects of densification, this correlation suggests that densification is an important component of irreversible structural relaxation in these glasses.

Similar evidence has been found, although not universally, in other metallic glasses. In amorphous $Fe_{80}B_{20}$, both PCR (McNeil 1983) and the change $\Delta R/R_0$ in resistance during isothermal anneals (Riontino and Marino 1984, Cost and Stanley 1982) are negative. The same two facts are true of the metallic glass $Fe_{32}Ni_{36}Cr_{14}P_6B_{12}$ (McNeil 1983, Cote and Meisel 1982, Cochrane *et al* 1980, Mulder *et al* 1981). In $Fe_{40}Ni_{40}P_{14}B_6$

however, the PCR is negative according to both Ast and Krenitsky (1976) and Cochrane *et al* (1980), whereas $\Delta R/R_0$ is positive according to Sonius *et al* (1983).

Interpretation of the marked effect of structural relaxation on the PCR in $Pd_{82}Si_{18}$ depends on our understanding of the mechanism whereby changes in density bring about changes in resistance. If we suppose that the dominant effect of densification is, as in crystalline metals, a change in the amplitude of vibration of the ions about their mean positions, then we would expect both the PCR and the TCR to show the same dramatic sensitivity to structural state, since both coefficients depend on the anharmonicity of the interatomic potential. The results given above show that TCR changes by only about 5% during irreversible structural relaxation.

If, on the other hand, we suppose that the resistance change seen upon compression is due mostly to changes in the mean positions of the atoms, then we would expect to see a change of about 50%, upon relaxation, in other properties which, like PCR, depend directly on the stiffness of the inter-atomic bond. Young's modulus and the coefficient of thermal expansion are examples of such properties; small changes in both have been reported (Mulder *et al* 1984, Leonardsson 1984), but the effect is not as great as would be expected. This appears to refute the second hypothesis.

Further studies of the effects of structural relaxation on physical properties of $Pd_{82}Si_{18}$ might contribute usefully to the understanding of this unexplained result.

6. Conclusion

We have observed a correlation between the effects of hydrostatic compression and isothermal annealing on electrical resistance in the $Pd_{82-x}V_xSi_{18}$ glasses ($x = 0, 1, 2$). This supports the notion that densification is a major component of irreversible structural relaxation in these alloys.

Acknowledgments

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