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Structural Relaxation in Pd-Ge Metallic Glass

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Abstract

We have measured small reversible changes of electrical resistance which occur following a small temperature change applied to an amorphous $\text{Pd}_{75}\text{Ge}_{25}$ alloy. Reversibility of this relaxation was demonstrated by the resistance returning (nearly) to the original value after repeated temperature cycling and equilibration. The reversible characteristic of the relaxation suggests that the mechanism is the change in chemical short-range order with temperature. Thus the measurements provide information on atomic mobility in this metallic glass. The relaxation kinetics indicate a broad spectrum of relaxation times which is best described as lognormal but skewed towards longer times. Parameters describing the breadth and shift in this spectrum with temperature will be described. We also observed an irreversible resistance change superimposed on the reversible changes. The kinetics of the irreversible change were found to obey the equation for free volume relaxation proposed by van den Buekel. However, his "mixed" CSRO-TSRO kinetics model fails to describe the slowing of the CSRO kinetics that occurs early in the annealing process.

Introduction

The structural relaxation of metallic glasses which occurs after the initial production of these materials has fascinated materials scientists for nearly a decade. Most investigators now believe that the relaxation can be divided into two distinct processes, namely, chemical short-range ordering (CSRO) and topological short-range ordering (TSRO). The latter process has been less widely studied than the former. It is a slower process and somewhat difficult to separate from the competing processes of CSRO and crystallization. Van den Buekel and co-workers [1,2] have made the most extensive studies of the kinetics of TSRO and have described it in terms of the annealing of free volume as proposed by Spaepen and co-workers [3,4].

The kinetics of CSRO in amorphous alloys are similar to the kinetics of CSRO in crystalline alloys. In the latter it is basically a first-order process with a distribution of relaxation times that is nearly lognormal with a width parameter of about 1.0 [5] for crystalline alloys. The lognormal distribution does not give a very accurate description of the relaxation spectrum for amorphous alloys, but if a fit is forced the width parameter is typically in the range 3 to 4. In crystalline alloys the mean relaxation time corresponds to the time required for about one to ten atomic jumps, depending on the alloy. This has been deduced by comparison with diffusion coefficients. For amorphous alloys there are not many cases where diffusion coefficients have been measured, but for the data available, the same conclusion regarding the relaxation time for CSRO and atomic jump times appears to hold. This correlation is important since if it is true, relaxation measurements can provide an alternative method for studying atomic mobility of amorphous metals.

It has been observed that the rate of CSRO is much greater in as-quenched metallic glasses than in metallic glasses which have been pre-annealed to allow some of the TSRO to occur. This is nicely demonstrated in the work of Balazsat et al [6] for some fourteen different metallic glasses. In this work as-quenched alloys were annealed isochronally up to a temperature where some small amount of TSRO would occur. They found that the

temperature range where CSRO occurred was lower for as-quenched samples than for samples that had been pre-annealed. This shift in the temperature at which ordering can occur is a clear indication that the atomic mobility is higher at a given temperature for a sample in the as-quenched from the melt condition than for one which has been pre-annealed. The theory of structural relaxation proposed by van den Beukel [1] incorporates a factor which decreases the rate of the CSRO kinetics as the free volume decreases during TSRO. The purpose of the present paper is to report the results of an extensive series of isothermal anneals made on melt-spun amorphous $\text{Pd}_{78}\text{Ge}_{22}$, and to present an analysis of this data in terms of CSRO and TSRO kinetics.

Experimental Procedures and Results

Electrical resistance measurements were used to follow changes in the state of order with time. Four platinum wires were spot welded to a Pd-Ge ribbon to serve as current and potential leads. The sample was placed in a low thermal inertia heater that allows the sample temperature to be changed by 25°C in less than one minute and held constant to within $\pm 0.1^{\circ}\text{C}$ for several weeks if necessary. In order to obtain maximum possible definition of the kinetic response, resistance measurements were made in situ using high sensitivity digital voltmeters and an automated data acquisition system [7].

The annealing history of the sample is indicated in Fig. 1 which is a plot of resistance versus temperature. Slanted lines on the figure indicate a rapid change in temperature and thus connect two states which are essentially isostructural. Vertical lines on the figure indicate an isothermal relaxation between two structural states with holding times between 10^4 and 10^6 seconds depending on the relaxation temperature. The relaxations are numbered sequentially from 1 to 39, but relaxations 10 through 35 are omitted from the figure to avoid confusion. A dashed line on Fig. 1 indicates our best estimate of the resistance in the equilibrium state of chemical short-range order for the as-quenched from the melt condition. Notice that the equilibrium CSRO state was not reached until the end of relaxation 4. Thus, relaxations 5 and above should show reproducible and reversible

CSRO effects.

As annealing to reach the equilibrium state of CSRO takes place the TSRO state is also changing. Figures 2a and 2b show two typical resistance versus time measurements for isothermal relaxations at 209.0°C and 221.5°C, respectively. Figure 2a is for a down-quench and the resistance change due to CSRO shows an increase. Figure 2b is for an up-quench and the change in CSRO produces a resistance decrease with time. For both measurements there is a long term decrease of resistance that appears linear with time, see the dashed lines in the two figures. This linear resistance decrease was subtracted from the data leaving the contribution due to CSRO only. The linear decrease is due to changes in TSRO which is evolving more slowly than CSRO. The reversibility of the CSRO contribution to the resistance is shown by the fact that when the linear TSRO contribution is subtracted, the resistance increase shown in Fig. 2a is equal to the resistance decrease shown in Fig. 2b.

To study the evolution and temperature dependence of TSRO the slopes of the linear resistance decreases obtained for the full sequence of relaxations are plotted in an Arrhenius plot in Fig. 3. It is apparent that the rate of resistance decrease at a given temperature decreases with an increase in the relaxation number and hence with an increase in the total annealing time. Although this linear resistance contribution is decreasing at a given temperature, if we take the slope of a straight line between two consecutive relaxations, we can obtain a good approximation of the activation energy. Doing this for the various pairs of relaxations gives activation energies in the range 1.66 eV to 1.8 eV. We believe that the most accurate value is 1.66 eV obtained from the line between relaxations 38 and 39 since the rate of change of TSRO is less for these latest relaxations than for earlier ones.

An example of the part of the relaxation due to CSRO is shown in Fig. 4 for the sample quenched from 258.8°C and annealed at 221.5°C. Here the resistance change remaining after the TSRO contribution has been subtracted has been normalized so that the

fractional change in resistance between initial and equilibrium values is shown as a function of time on a logarithmic scale. Similar analysis of the various relaxations at different temperatures yielded curves that superimpose on the one shown in Fig. 4 but with an appropriate shift of the curve on the time scale due to the temperature dependence of the relaxation times.

We have tried fitting the relaxation curves such as shown in Fig. 4 with various relaxation time spectra. Unfortunately none that we tried showed a good fit. The fit to a single lognormal distribution showed that this distribution gives an adequate description but that the actual spectrum is skewed toward longer relaxation times. An average width of the lognormal distributions fit to all of the CSRO data is $\beta=2.9$. This means that the relaxation spectrum is roughly 2.5 decades wide at $1/e$ of maximum. To show the temperature dependence of the relaxation time spectrum we have determined the times for one-fourth, one-half, and three-fourths completion of the relaxation and plotted them according to the Arrhenius relation as shown in Fig. 5. The activation energies and pre-exponential factors for these various fractions of the relaxation are shown in Table I. The activation energy of roughly 1.68 eV for CSRO can best be interpreted as an average activation energy of the relaxation time spectrum. Our finding that TSRO has roughly the same activation energy is in agreement with the prediction [1] that this energy lies within the spectrum of energies for CSRO.

Discussion of Results

According to the model of van den Beukel et al [1], the change in resistance due to TSRO should be proportional to the change in free volume and hence

$$\Delta R = K \log_{10}(1 + t/\tau) \quad (1)$$

where K is a constant and τ is the relaxation time for TSRO. It has been postulated [1] that a single activation energy, Q , should apply to TSRO and therefore

$$\tau = \tau_0 \exp(-Q/kT). \quad (2)$$

The linear change of resistance with time that we attribute to TSRO for each relaxation is not inconsistent with Eq. 1 as long as the time for each relaxation is small compared to τ . In order to evaluate the TSRO contribution summed over all the relaxations and thus check on Eq. 1, we have plotted the cumulative irreversible resistance changes versus the temperature-corrected cumulative annealing times of the various relaxations. The annealing times were corrected using

$$t_{\text{effective}} = t \exp(Q (1/T_{\text{ref}} - 1/T)/k), \quad (3)$$

where $t_{\text{effective}}$ is an effective time at the reference temperature, T_{ref} , and t is the actual time of a relaxation at the temperature T . The resulting plot on a logarithmic time scale for annealing times corrected to 221.5°C is shown in Fig. 6. For annealing times long compared to τ Eq. 1 shows that such a plot should yield a straight line with slope K and time axis intercept, τ , at $\Delta R = 0$. Our data clearly show this linear region at long annealing times. The values of K and τ obtained from the straight line through the long time data were used to plot Eq. 1 on Fig. 6; see the dashed curve. It may be seen that the early TSRO data show a good fit to Eq. 1.

It should be mentioned that relaxation 8 had a large enough change in TSRO to make the linear approximation inaccurate. The CSRO curve that resulted from the linear correction did not match the shape of the other CSRO curves. We therefore used Eq. 1 to make the TSRO correction for relaxation 8. This resulted in a CSRO curve that matched the shape of the other CSRO curves. There were some relaxations that were not continued long enough to determine the TSRO correction by the linear subtraction method. These were mainly the relaxations 1-6. In these cases we used Eq. 1 to calculate the approximate resistance change for these relaxations. This made only a small change in the overall curve

of Fig. 6 from the one originally determined by ignoring these relaxations.

The activation energy of 1.66 eV that we determined for the TSRO is very close to the activation energy of 1.77 eV determined by van den Beukel for $\text{Pd}_{82}\text{Si}_{18}$; however the pre-exponential factor that we determined, $\tau_0 = 9.9 \times 10^{-18}$, is a factor of 200 larger than that reported for Pd-Si. This factor may be accounted for by the experimental uncertainty for the determination of the activation energies, which is probably greater than ± 0.1 eV. Thus we conclude that the irreversible resistance changes that we have observed are in excellent agreement with the free-volume annealing theory and are most probably due to TSRO changes. There is, however, one important area of disagreement with the extended free-volume annealing theory of van den Beukel. This is explained in the following paragraphs.

According to the van den Beukel model the temperature independent factor for the CSRO relaxation time contains a factor which depends exponentially upon the free volume. Thus the model predicts a shift to longer relaxation times for CSRO as the free volume decreases with TSRO. One can show that from the van den Beukel model,

$$\tau_0(t)/\tau_0(t_{\text{initial}}) = 1 + t/\tau \quad (4)$$

where $\tau_0(t)$ and $\tau_0(t_{\text{initial}})$ are respectively pre-exponential factors for CSRO relaxation times at time, t , and as-quenched, t_{initial} and τ is the relaxation time for TSRO. Figure 7 shows a plot of equation 4 at the same annealing temperature used for Fig. 6 together with experimental values of $\tau_0(t)/\tau_0(t_{\text{initial}})$. The latter values being the ratio of the average relaxation time for a given relaxation to that of relaxation 2 adjusted to the given relaxation temperature by using the activation energy determined experimentally for CSRO. It can be seen that the van den Beukel model fails to predict the shift of CSRO kinetics that occurs early in the annealing process and predicts that the relaxation times should be rising when they have actually leveled off. We have proposed using a model in

which atomic mobility in the metallic glasses is controlled by the concentration of a vacancy like defect in order to account for this early shift in CSRO kinetics [8].

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Table I

Activation energies and Pre-exponential Time Factors for CSRO

Fraction of Relaxation	t_0, s	Activation energy, eV
1/4	$1.6 \cdot 10^{-15}$	1.7
1/2	$2.4 \cdot 10^{-14}$	1.66
3/4	$8.9 \cdot 10^{-14}$	1.67

Figure Captions

Fig. 1. Thermal annealing history of $\text{Pd}_{73}\text{Ge}_{27}$. resistance versus temperature.

Fig. 2a. Resistance versus time at 209°C after a down-quench from 221.5°C.

Fig. 2b. Resistance versus time at 221.5°C after an up-quench from 209°C.

Fig. 3. Arrhenius plot of the rate of resistance decrease due to TSRO for relaxations as indicated on the figure.

Fig. 4. Fraction of CSRO resistance contribution versus time (logarithmic scale) for relaxation 39 at 221.5°C.

Fig. 5. Arrhenius plot for CSRO relaxation times at fraction x of the relaxation ($x=1/4, 1/2, 3/4$).

Fig. 6. Cumulative resistance change due to TSRO versus $t_{\text{effective}}$ (logarithmic scale) for annealing at 221.5°C.

Fig. 7. Ratio of average relaxation time to average relaxation time for relaxation 2, T/T_{initial} , versus $t_{\text{effective}}$ (logarithmic scale) for annealing at 221.5°C.

Pd₇₀Ge₃₀ - Annealing history

Fig. 1

Fig. 2a

Fig. 2b

Fig. 4

RELAXATION TIME (S)

Fig. 6

Fig. 7