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AUTHOR(S): J. R. Cost, J. T. Stanley

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KINETICS OF STRUCTURAL RELAXATION IN METALLIC GLASSES

J. R. COST and J. T. STANLEY*
Los Alamos National Laboratory, Los Alamos, NM 87545

1. INTRODUCTION

When a metallic glass is annealed at temperatures below the glass transition temperature its structure changes with time. This structural change is observed to have an irreversible component and a reversible component. Our work has concentrated on studying the reversible component of the structural relaxation. In this paper we follow the practice of referring to the reversible component as chemical short-range order (CSRO) and the irreversible component as topological short-range order (TSRO).

Several investigators have studied the kinetics of CSRO in metallic glasses and reported that the kinetics follow a first-order response law with a very broad distribution of relaxation times[1,2]. We believe that it is important to determine if the spectrum of relaxation times has fine structure. In accord with this belief our experiments have been carried out to obtain the maximum possible detail about the kinetic behavior of the CSRO changes. Also a new method of analysis of the response curve, referred to as direct spectrum analysis, has been used that allows us to resolve fine structure in the spectrum of relaxation times.

2. EXPERIMENTAL

Electrical resistance measurements were used to follow changes in the state of order with time. In order to demonstrate reversible changes in order it is necessary to cycle the sample temperature. This was done over relatively narrow temperatures ranges since short-range ordering can only be expected to follow first-order kinetics when the total change in order is small[3].

The sample is placed in a low thermal inertia heater that allows the sample temperature to be changed by 25°C in about one minute and held constant to within ± 0.1 °C for several weeks if necessary. In order to obtain maximum possible definition of the kinetic response, resistance measurements are made in situ using high sensitivity digital voltmeters and an automated data acquisition system. The fractional change in resistance

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*On sabbatical leave from Arizona State Univ.

$f(t)=[R(t)-R_i]/[R_f-R_i]$ is assumed to be proportional to the fractional change in short-range order, $R(t)$ is resistance at time t, R_i is the initial resistance, and R_f is the final or equilibrium resistance. The specimens used in the present study were $Fe_{40}Ni_{40}P_{14}B_6$ (Metglas 2826) obtained from Allied Chemical and $Pd_{78}Ge_{22}$ melt spun ribbon kindly supplied by B. C. Giessen.

3. DIRECT SPECTRUM ANALYSIS

The direct spectrum analysis (DSA) method, which has recently been developed,[4] is a method which obtains an approximation of the relaxation time spectrum by an analysis of the total relaxation response curve. It does this without the usual force-fits to various spectra which are being tested for goodness-of-fit. Extensive validation of the DSA method using data generated from many different kinds of known input spectra and with varying amounts of random experimental error added has shown that it provides close approximations to the input spectra. This has been shown for spectra with single and multiple peaks and for peaks with different shapes and widths. Typically the position and width of single-peak spectra can be obtained with fractional uncertainties which are within a factor of one or two of that for the normalized data. This has been shown for data with fractional uncertainties of up to roughly 5%.

With the DSA method the integral equation describing the fractional approach to the new equilibrium state is unfolded to obtain the spectrum by making a sum approximation. The range of relaxation times in the spectrum is then divided up into n equally spaced bins (on a logarithmic scale) each of which makes its separate contribution to the total response. The sum approximation yields a set of equations which is then analyzed using a nonlinear regression least-squares method to obtain the spectrum approximation. Several DSA calculations were done for each data set. Typically the approximations to the spectrum for a given data set using various choices for n, the spectral limits, and the termination criteria differed by less than a few percent.

4. RESULTS AND DISCUSSION

4.1. PdGe

Both alloys showed reversible changes in resistance for temperature cycles carried out well below the crystallization temperature. Figure 1 shows a typical sequence of resistance measurements carried out on a PdGe sample. The reversibility of the CSRO is shown by the return to the initial state at the end of the temperature cycle.

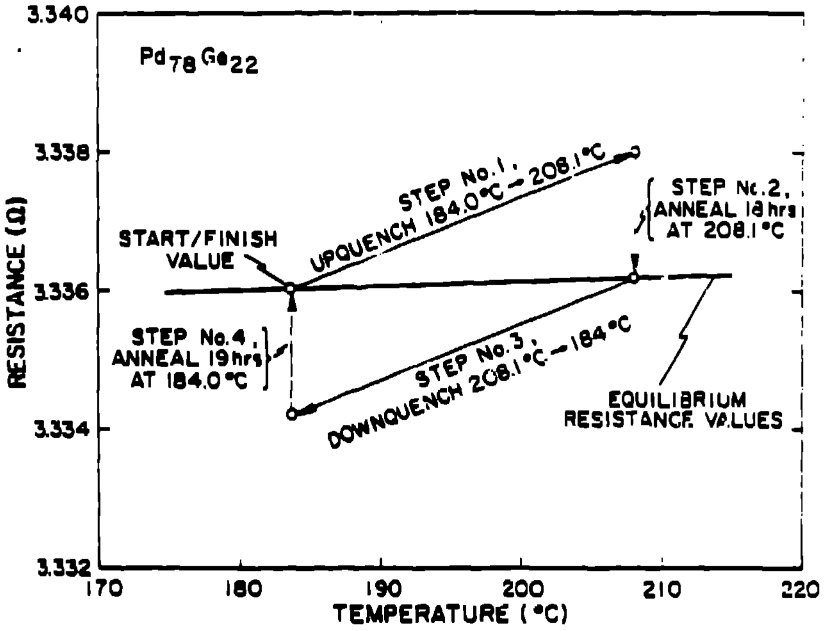

FIGURE 1

Typical resistance-temperature cycle for PdGe alloy.

This sample has not been stabilized with respect to changes in TSRO i.e., as the TSRO slowly changed there was an associated decrease in resistance. Since the TSRO is changing with time, it is not yet possible to obtain the exact spectrum of relaxation times associated with CSRO changes in PdGe. However, the relaxation strength defined as $(R_f-R_i)/R_f(T_A-T_Q)$ has magnitude 3 x 10^{-5} K^{-1} and it does not change significantly as TSRO changes. The relaxation time τ defined as the time at which the fractional change in resistance reaches a value of 1-1/e depends both on temperature and the TSRO.

Figure 2 compares our relaxation times in PdGe to some diffusion measurements of Chen, et al.[5] made on a PdCuSi alloy. We have calculated diffusion coefficients from relaxation times using the relation $D=d^2/6\tau$ where d is the interatomic spacing in the metallic glass. Chen, et al. found that much higher diffusion coefficients were obtained when the metallic glass was in an as-quenched condition than when it was given a pre-anneal. Our results tend to support these observations in that the relaxation time becomes longer at a given temperature as the TSRO relaxes. The numbers beside the data points in Figure 2 correspond to the relaxation numbers which increase as the degree of TSRO decreases.

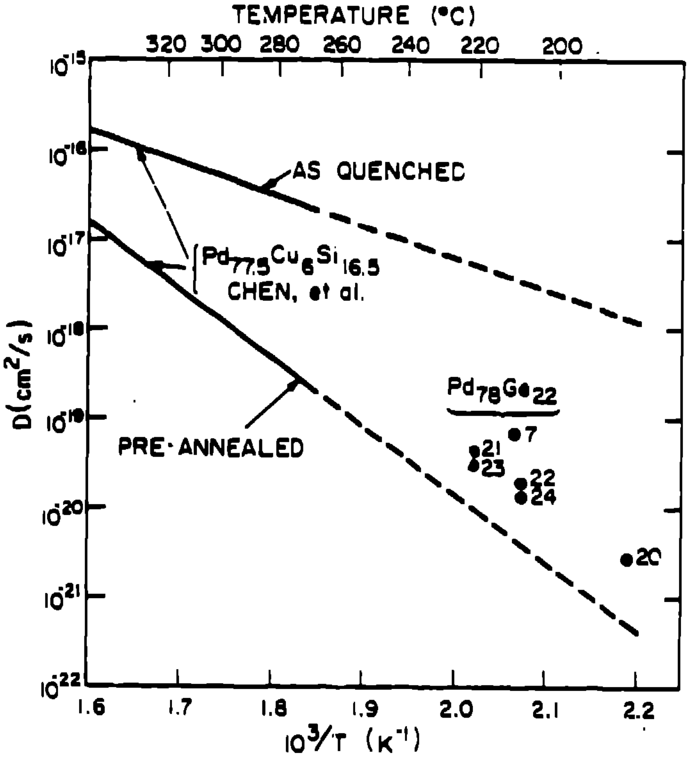

FIGURE 2
Diffusion coefficients and chemical short-range ordering rates versus reciprocal temperature. Straight lines are from Chen et al.[5]

4.2. FeNiPB

We now consider the application of the DSA method to structural relaxation of the FeNiPB amorphous alloy. The spectrum obtained from our direct analysis of a relaxation response curve for this alloy will be shown to be multimodal as had previously been reported by the conventional analysis method. The spectra obtained for the PdGe alloy have also been shown to be multimodal; these spectra will not be presented since, as previously described, the TSRO is still changing for this sample and hence the spectrum is still evolving.

The experimental procedure and data for the FeNiPB alloy have previously been described as part of an extensive study involving several samples which demonstrated reversibility and reproducibility of the CSRO relaxation[6,7]. The results which have been analyzed here are for a sample equilibrated at 250°C and rapidly cooled to the measurement temperature of 200°C. Several different DSA's were calculated for these data and they all yielded self-consistent approximations of the spectra. Similarly, data

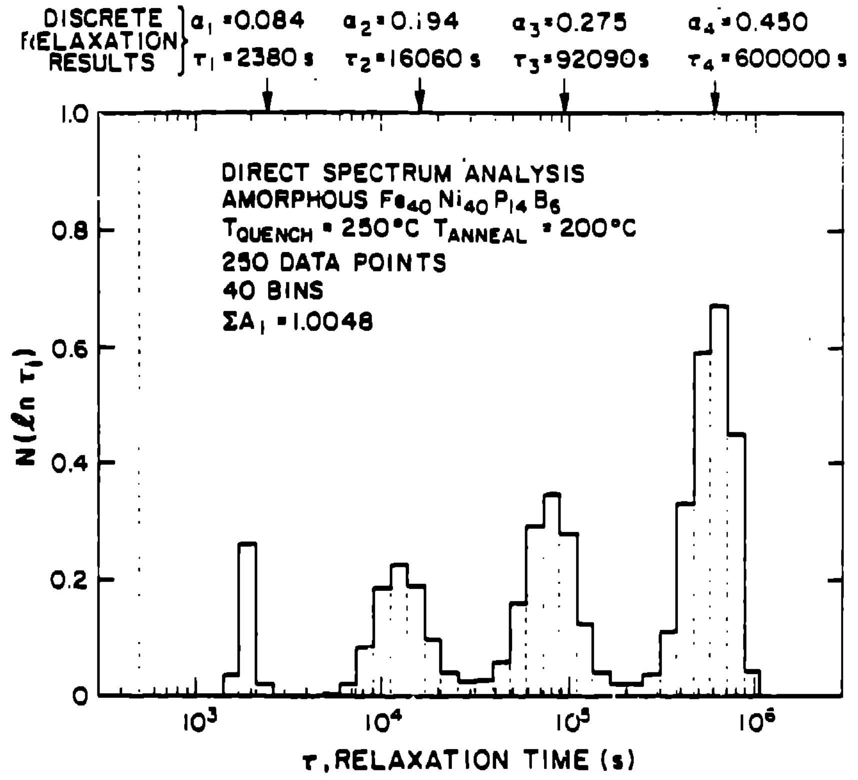

FIGURE 3
Histogram of relaxation time spectrum for FeNiPB alloy showing fine structure consisting of four nearly-discrete peaks.

from other relaxations of this alloy yielded spectra which showed the same salient features. A histogram of a typical spectrum obtained by the DSA method for the annealing temperature of 200^0C is shown in Figure. 3. Here $N(\ln \tau_i)$, the strength of the relaxation in the i^{th} bin is plotted vs relaxation time. The limits for calculating the spectrum are shown by the dotted, full scale, vertical lines in Figure 3. The calculation was for 40 bins.

The finding that the spectrum has four relatively narrow well-separated peaks of varying height is of particular interest. It corroborates the previously reported result that this relaxation is multimodal and can best be described by four nearly-discrete processes. In addition, it shows the power of the DSA method in that it enables analysis without the necessity of assumptions as to the number and form of the spectral peaks. At the top of Figure 3 the relaxation strengths α_i and times τ_i are shown for the analysis of the same data based upon four discrete relaxations. It may be seen that there is good general agreement between these parameters and the magnitudes and positions of the spectral peaks.

The significance of the finding of fine structure in the form of four relatively narrow peaks in the relaxation time spectrum is difficult to determine without further experiments. These will need to be on a variety of alloys so that general behavior patterns can be identified. Our finding that the spectrum in PdGe is also multimodal shows that the FeNiPB result is not just an isolated case. By analogy to studies of short-range ordering in crystalline alloys, we know that an average atom makes at most a few atomic jumps during the rearrangements leading to a new state of short-range order. Furthermore, stainless steel which has also been studied by the temperature-change-induced relaxation method has been shown to have only a single peak in its relaxation time spectrum[8]. Thus the multimodal spectra may well be unique to metallic glasses. If this is true, then the explanation for fine structure in the spectrum may lie in the microscopic structure of the metallic glass. For instance, there may be four (or more) different kinds of regions or domains in the glass, each of which has a uniquely different structure in which the atomic rearrangements for the ordering process take place at different rates. Furthermore, it seems reasonable that the relaxation would have nearly the same rate in all of the regions with the same structure. Thus the nearly-discrete nature of the spectral peaks would be accounted for.

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