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STRUCTURAL RELAXATION RATES IN AMORPHOUS METGLAS ALLOYS $Fe_{40}Ni_{40}P_{14}B_6$ AND $Fe_{80}B_{80}$*

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INTRODUCTION

It is well known that the properties of amorphous materials change with time as the as-quenched structure evolves from a relatively disordered state towards a more ordered state. In the case of metallic glasses these structural and property changes often occur at appreciable rates below the crystallization temperature, and thus, the study of the kinetics of these changes is of practical significance and also provides information about the fundamental nature of atomic mobility in these materials.

There is much evidence that the amorphous state can be characterized by two different types of short range order, topological and chemical (1). Indirect evidence for chemical short range order in ferromagnetic alloys such as $Fe_{40}Ni_{40}P_{14}B_6$ comes from studies of the effects of annealing on the Curie temperature (1) and induced magnetic anisotropy (2-4). It is argued that the existence of these effects depends on changes in the number of Fe-Fe nearest neighbors in the alloy and thus is primarily due to changes in chemical short range order. Dalanzat (5) showed that the electrical resistance of amorphous $Fe_{40}Ni_{40}P_{14}B_6$ (Metglas 2826) changed with time in a similar way as the magnetic anisotropy. These changes were found to be reversible in cycling the temperature between high and low values. This implies that there is a characteristic state of order for each temperature that can be achieved in a reasonable annealing time at the given temperature. We shall refer to this as the equilibrium state of order, although it is not a true equilibrium state.

In a recent article (6) we reported results of electrical resistance measurements on a Metglas 2826 specimen which demonstrated reversible time-dependent resistance changes induced by changing temperature, a type of behavior associated with changes in short range order. The resistance change measured at 200°C after equilibrating and rapidly cooling from 250°C followed a curve that could be decomposed into four simple first order processes. This and other evidence suggested that each separate process might be associated with movement of a particular chemical species. In this article we report additional measurements made on the Metglas 2826 alloy at an anneal temperature of 250°C which again strongly indicate that the temperature-change induced reaction involves four simple first order processes. In addition, we report results of an unsuccessful attempt to find a similar effect in the binary metallic glass $Fe_{80}B_{20}$.

EXPERIMENTAL PROCEDURE

The experimental technique for monitoring sample resistance has been previously described (6), but the fractional error of a measurement has been decreased to roughly 1 ppm. During measurements the sample was maintained at a constant temperature to ± 0.1°C. The temperature changes referred to as quenches in this report were carried out at a rate of approximately 0.5°C/sec.

The $Fe_{40}Ni_{40}P_{14}B_6$ sample used in this study was different from the one on which results were previously reported (6); it was, however, taken from the same production spool. Microprobe scans showed the chemical composition of this alloy to be homogeneous within ± 1 at % across the width and thickness of the ribbon. The average composition was as follows: Fe-40.1 at %, Ni-38.1 at %, P-18.4 at % and B(by difference)-3.2 at %.

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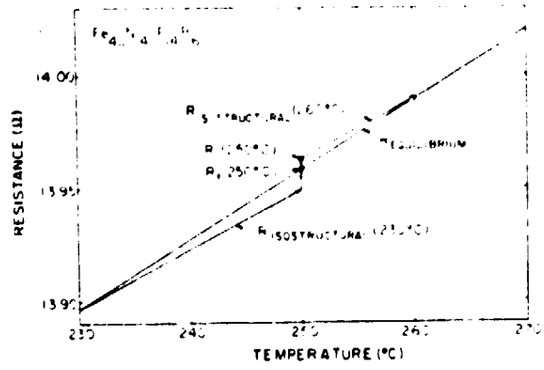


Fig. 1

Equilibrium and isostructural resistance vs temperature for a $Fe_{40}Ni_{40}P_{14}B_6$ metallic glass up-quenched and down-quenched to 250°C.

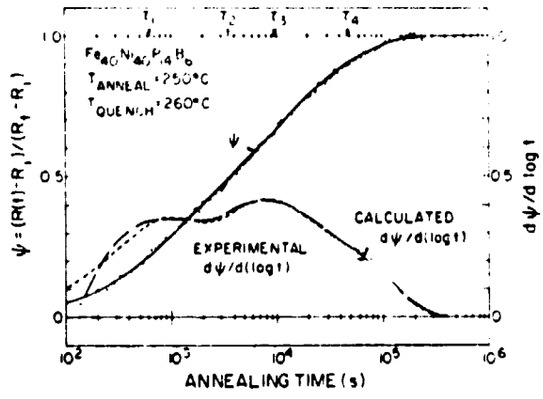


Fig. 2

Time dependence of the normalized change in resistance, Ψ, and experimental and calculated derivative curves, $d\Psi/d(\log t)$, for a $Fe_{40}Ni_{40}P_{14}B_6$ alloy quenched to 250°C from 260°C.

RESULTS AND DISCUSSION

The experiments we report for the $Fe_{40}Ni_{40}P_{14}B_6$ alloy all involve measurement of time-dependent resistance changes at a measuring temperature of 250°C after the sample was previously equilibrated at a quench temperature in the range from 230°C to 270°C and then quenched to 250°C. Equilibration was achieved by holding at the quench temperature until there was no further resistance change. Examples of these experiments are shown in the resistance vs temperature plot of Fig. 1. Here the equilibrium curve for resistance is shown for the temperature range from 230°C to 270°C. Also shown are the resistance values for a downquench from 260°C to 250°C. As determined by our results, this quench takes place rapidly relative to the time for the reaction which we measure in the sample. Thus this upper line between 260°C and 250°C, $R_{isostructural}$ (260°C), shows how the resistance varies with temperature at the constant structure which is quenched in at 260°C. The values R_i(250°C) and R_f(250°C) show the initial and final values of the resistance at 250°C following the quench. Monitoring and then analyzing the time dependence of the resistance as it varied between these two values provided the kinetic parameters for the temperature-change induced structural modification reaction in this alloy.

Resistance behavior for an upquench from 230°C to 250°C is also represented in Fig. 1. For this quench the values have been corrected to fit the $R_{equilibrium}$ curve for the 260°C to 250°C quench. This correction was for a small ($1/R\ dR/dt \simeq 5 \times 10^{-10}$ per sec at 250°C) linear increase in the resistance which appeared to be due to a much slower process than the one of this study. This correction was made for all the results we report for this alloy. It is emphasized that after correction for this relatively small linear resistance increase, the temperature-change induced resistance behavior was fully reversible, e.g., the same equilibrium resistance value was obtained at 250°C for all quenches. Also the total resistance change $\Delta R = R_f - R_i$ was found to be proportional to $\Delta T = T_a - T_q$, where T_a and T_q are the annealing temperature and quenching temperature, respectively. This reversibility and proportionality between ΔR and ΔT are important because they indicate that, ignoring the small linear change referred to above, the same equilibrium state is reached at a given temperature independent of previous specimen history. These conditions were also found for a similar quenching study involving structural ordering kinetics of stainless steel (7).

Experimental results for a downquench from 260°C to 250°C are shown in Fig. 2. Here data for the normalized time-dependent resistance change, ψ, are plotted vs time on a logarithmic scale. Also shown in Fig. 2 are two derivative curves, $d\psi/d(\log t)$, one experimental and one calculated. The experimental derivative curve was

obtained from many (~ 20) different overlapping polynomial fits to the ψ vs time data. The calculated curve, which agrees very well with the experimental, was predicted from the analysis. It has been shown that use of the derivative curve provides a particularly sensitive method for analyzing data and distinguishing between various models (8). In this study the experimental derivative curve exhibits several well defined peaks and inflection points. The presence of multiple peaks in the experimental derivative curve provides strong evidence that more than a single relaxation is occurring in the quench-induced reaction.

The previous temperature-change induced structural relaxation results for this alloy (6) showed quite emphatically that the kinetic process was best fit by a set of discrete relaxations described by

$$\psi(t) = 1 - \sum_{i=1}^{n} A_i \exp(-t/\tau_i) \qquad \text{(Eqn. 1)}$$

where A_i are the relaxation strengths, τ_i are the relaxation times and n is the number of relaxations involved. Furthermore, it was demonstrated quite clearly that the best fit for the result was n = 4, i.e., that there are four separate nearly first order processes taking place. In addition, this previous study also showed that the results were best fit when the four discrete relaxations had nearly a single time constant as opposed to a relaxation spectrum of appreciable breadth.

The results of this present study further confirm the previous finding that this reaction involves four separate very nearly single relaxations as given in Eqn. 1 with n = 4. The calculated derivative curve in Fig. 2 was obtained using a non-linear regression analysis to determine the A_i and τ_i for the minimum sum of squared residuals using n = 4. The agreement between the experimental and the calculated derivative curves in Fig. 2 is quite satisfactory, especially for the location and magnitudes of the peaks. Again, as in the previous study, (6) attempts to fit Eqn. 1 with n < 4 did not show the proper number, location and magnitude of the peaks and were clearly less appropriate. The τ_i values with i = 1 to 4 obtained for the quench from 260°C to 250°C are shown in the upper portion of Fig. 2 and also in Table I with the appropriate A_i values. It may be observed that the peaks in the derivative

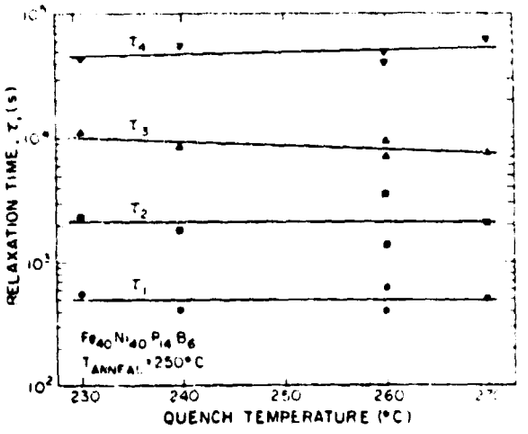
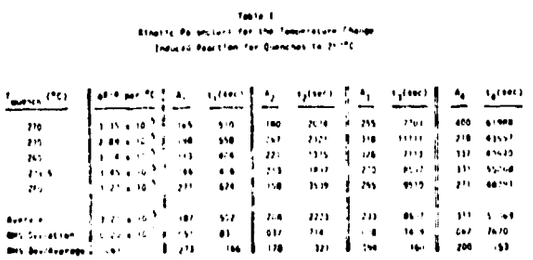


Fig. 3
Values of τ_i obtained from analysis of the ψ vs time curves using Eqn. 1 and n = 4 for a $Fe_{40}Ni_{40}P_{14}B_6$ alloy quenched to 250°C from the temperatures indicated.

curve at short and long annealing times correspond to τ_1 and τ_4 respectively, and that the large central peak near 8000 sec is a superposition of the kinetic response from τ_2 and τ_3.

In Fig. 3 are shown the four different values of τ_i measured at an annealing temperature of 250°C for different quench temperatures. The time-dependent resistance behavior for each of these quenches was analyzed using various values of n and for each, the results of the analysis indicated that n = 4 was the proper fit. The consistancy of this finding, both for the different quenches in this study and for the different samples of this and the previous study, (6) provides further evidence that the analysis using Eqn. 1 with n = 4 is correct and that four discrete first order reactions are intrinsic to the reaction.

Least squares straight lines have been fit to the data in Fig. 3 for each of the four τ_i. Within experimental error these lines all have a slope of zero. The relative magnitudes of the resistance changes, as well as the A_i and τ_i for the results of Fig. 3, are presented in Table I. Here it may be observed that there is good agreement between the various values for these parameters. The standard deviations for the relaxation times and the relaxation strengths are roughly 20% of the average values. The slope of zero for the data for each τ_i in Fig. 3 is a significant finding since the absence of an effect due to varying the quench temperature indicates that, at least for this



small temperature range, the different structural order which is frozen-in from the quench temperature does not affect the rate constants for the reaction. This suggests that atomic mobility is not sensitive to the temperature dependent structural changes which account for the relatively large resistance changes ($\Delta R/R$ per °C of quench is 32 ppm/°C). However, this point is still controversial since Chambron and Chamberod (9) found for the same alloy that the reaction rate at 160°C was enhanced by a factor of about four when the quench temperature was changed from 200°C to 340°C.

Studies of the temperature dependence of τ_i are still in progress. However, based upon previous results on a different sample (6) and preliminary results on the present sample each of the four relaxations appears to be governed by a thermally activated process with activation energies in the range 1 eV to 2 eV.

It was predicted that if the four discrete relaxations observed for the $Fe_{40}Ni_{40}P_{14}B_6$ alloy were indeed due to some type of long range atomic regrouping of the four kinds of atoms, e.g., changes in specific atomic volume (5), then it would be desirable to test this by investigating temperature-change induced reactions in a binary or ternary alloy. Accordingly, we attempted measurements in the metallic glass $Fe_{80}B_{20}$ (Metglas 2605) Unfortunately, no reversible reactions were observed in this alloy. Instead, it was found that the resistance decreased monotonically with time; this is in agreement with recent results by Hillairet, et al (10). This behavior is shown in fig. 4 where resistance is plotted vs measuring temperature and the thermal history is indicated for the isothermal measurements at points A through J. At each of these points (and others not conveniently shown which cycled several times between some of these points)

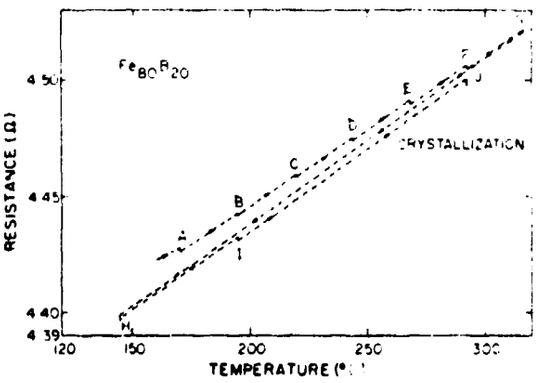


Fig. 4
Effect of thermal history upon the resistance of a $Fe_{80}B_{20}$ metallic glass. Isothermal anneals are indicated by the letters.

the resistance was found to decrease. Finally, at point J the resistance dropped in a way which suggested the onset of crystallization.

Because the $Fe_{80}B_{20}$ alloy has not been found to exhibit a reversible temperature-change induced structural modification reaction analogous to that in the $Fe_{40}Ni_{40}P_{14}B_6$ alloy, the proposal that the reaction involves discrete relaxations due to long range atomic motion of each of the component elements has still not been tested. It is planned to check this prediction in other binary or ternary metallic glasses. When this process is better characterized, it can be expected to provide useful understanding of atomic mobility in the amorphous state.

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