CHANGES IN CURIE TEMPERATURE, PHYSICAL DIMENSIONS, AND MAGNETIC ANISOTROPY DURING ANNEALING OF AMORPHOUS MAGNETIC ALLOYS

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Abstract

We have measured the effects of annealing in air on various properties of several amorphous alloys. Reported here are results on the changes in Curie temperature, in the physical dimensions of lengths of amorphous ribbon, and in the magnetic anisotropy. Increases in Curie temperature up to 35°C have been measured. All the alloys examined show a steady increase in T_C on annealing at low temperatures, but some compositions show a smaller increase in T_C on annealing near the crystallization temperature than on annealing at lower temperatures. There appear to be two competing mechanisms influencing T_C. All the alloys examined show a clearly measurable decrease in length on annealing; we interpret this as an increase in bulk density. The kinetics of the annealing are similar to those of the stress relaxation. Finally, annealing experiments on the shape of 60 Hz hysteresis loops show a decrease in the anisotropy associated with non-uniform internal stresses, but in some cases also show the slow development of a fairly strong uniaxial anisotropy with its easy axis perpendicular to the ribbon axis. This uniaxial anisotropy is tentatively ascribed to the development of an oxide layer during annealing, which in turn produces a uniform compressive stress due to differential thermal contraction and therefore a stress-magnetostriction anisotropy. The changes in Curie temperature and in sample dimensions cannot be ascribed to oxidation. All the results described above are for annealing treatments that do not cause crystallization. The time for crystallization at various temperatures has been measured, and activation energies for crystallization derived.

Changes in Curie Temperature

Changes in T_C were studied in three alloys: $Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$, $T_C \simeq -20°C$; $Fe_{29}Ni_{49}P_{14}B_6Si_2$, $T_C \simeq 100°C$; and $Fe_{27}Ni_{53}P_{14}B_6$, $T_C \simeq 90°C$. The first two compositions are Metglas[R] alloys 2826A and 2826B, respectively, made by Allied Chemical Corp., and the third was made in this laboratory. Compositions with low Curie temperature were chosen so that T_C could be measured without the measurement itself causing any annealing effects. The Curie temperature was determined by heating or cooling a short length of amorphous ribbon in a small (<0.2 Oe) magnetic field while measuring its moment with a vibrating-sample magnetometer. A sharp break in the curve of induced moment vs. temperature is observed at (or very slightly below) the Curie temperature.[1] The samples were annealed in the same apparatus, which was designed so that the sample temperature could be increased rapidly but without overshooting. This permitted well-defined annealing times as short as 2 minutes at temperatures up to 500°C. Since there were slight variations in T_C in the as-prepared samples, the results are presented as values of ΔT_C, the change in the initial T_C caused by an anneal of fixed time and temperature. Fig. 1 shows plots of ΔT_C vs. annealing temperature, for various times. Changes in T_C up to 35°C are observed, in general agreement with the results of Chen et al.[2] There are, however, striking differences between alloys of different compositions. In one case, ΔT_C increases monotonically with time and temperature until crystallization begins, but in the other two cases there is a maximum in ΔT_C at an intermediate annealing temperature, followed by a sharp decrease. At annealing temperatures near 400°C, a constant value of T_C is attained in a very short time, and no further change in T_C occurs until crystallization takes place. The same data is presented in another way in Fig. 2, which gives contour lines of ΔT_C on a temperature-log time plot. These plots suggest that all three alloys show similar behavior at low temperatures, but that in two of the compositions a competing process occurs at higher temperatures. One possible explanation of the competing process is that a phase separation occurs in the amorphous state. Samples annealed near the maximum in ΔT_C (Fig.1) and then further annealed at higher temperature show a drop in ΔT_C to the apparent equilibrium.

The appearance of crystallization is clearly detected from the magnetization vs. temperature measurements, and has been confirmed by x-ray diffraction. From the measured times to crystallization at several temperatures, activation energies for crystallization have been derived from Arrhenius plots. The numerical values are given in Fig. 2, and are in reasonable agreement with the values given by Luborsky[3] for similar alloys.

Dimensional Changes

Although experience and concepts based on the behavior of silicate glasses would lead one to expect an increase in density on annealing of an amorphous alloy,[4] we are not aware of any reported experiments establishing this effect. Although we have not been able to make density measurements of sufficient precision, we have clearly shown significant changes in length of amorphous ribbons on annealing. The measurements were made on 15cm lengths of ribbon cut to a point at each end and clamped lightly between grooved steel plates. Changes in length could be measured with a six-inch micrometer to about 0.001 cm, or better than 0.01%. We believe that the measured decrease in length corresponds to an increase in density, but this remains unproved. Fig. 3 shows selected results; typically there is a rapid decrease in length occurring within 15 minutes (the shortest time in these experiments), followed by a much slower shrinkage that appears to continue until crystallization occurs. This behavior is very similar to the behavior of the stress relaxation observed in earlier work[5]. There is no evidence in the length measurements of an anomaly corresponding to the drop in ΔT_C with increasing annealing in Figs. 1 and 2.

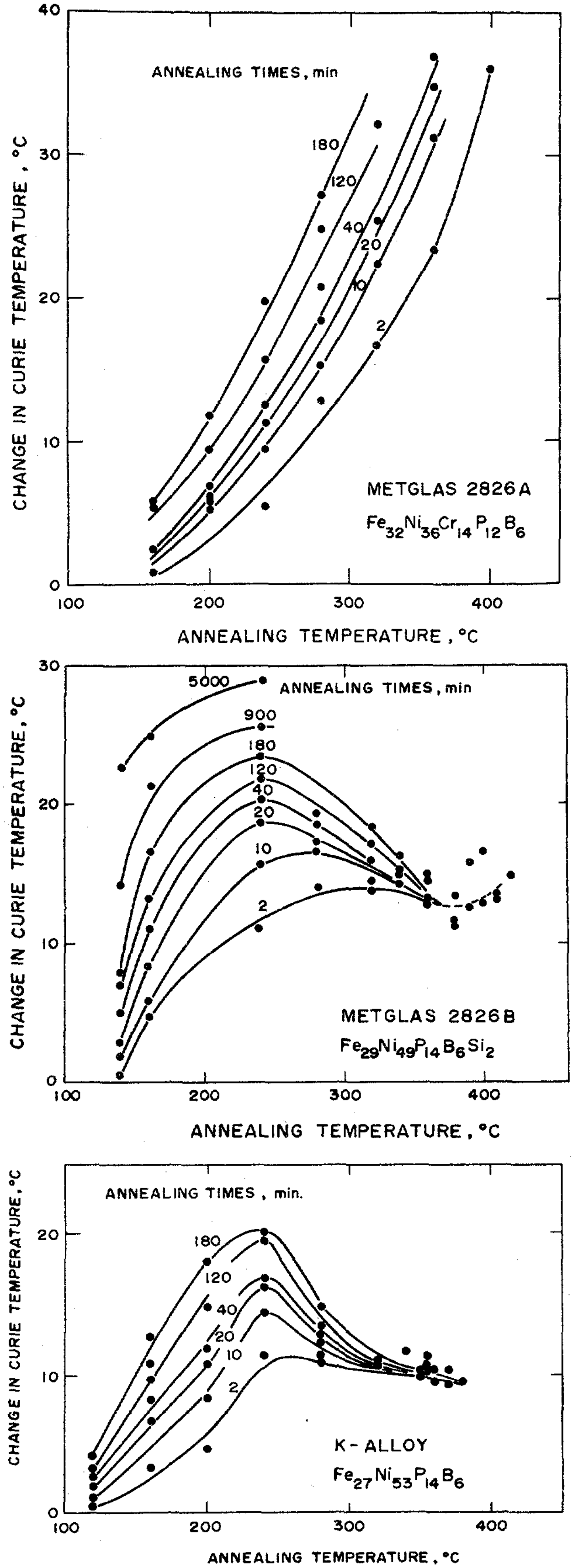

Fig. 1. Isochronal response of Curie temperature to annealing for three compositions

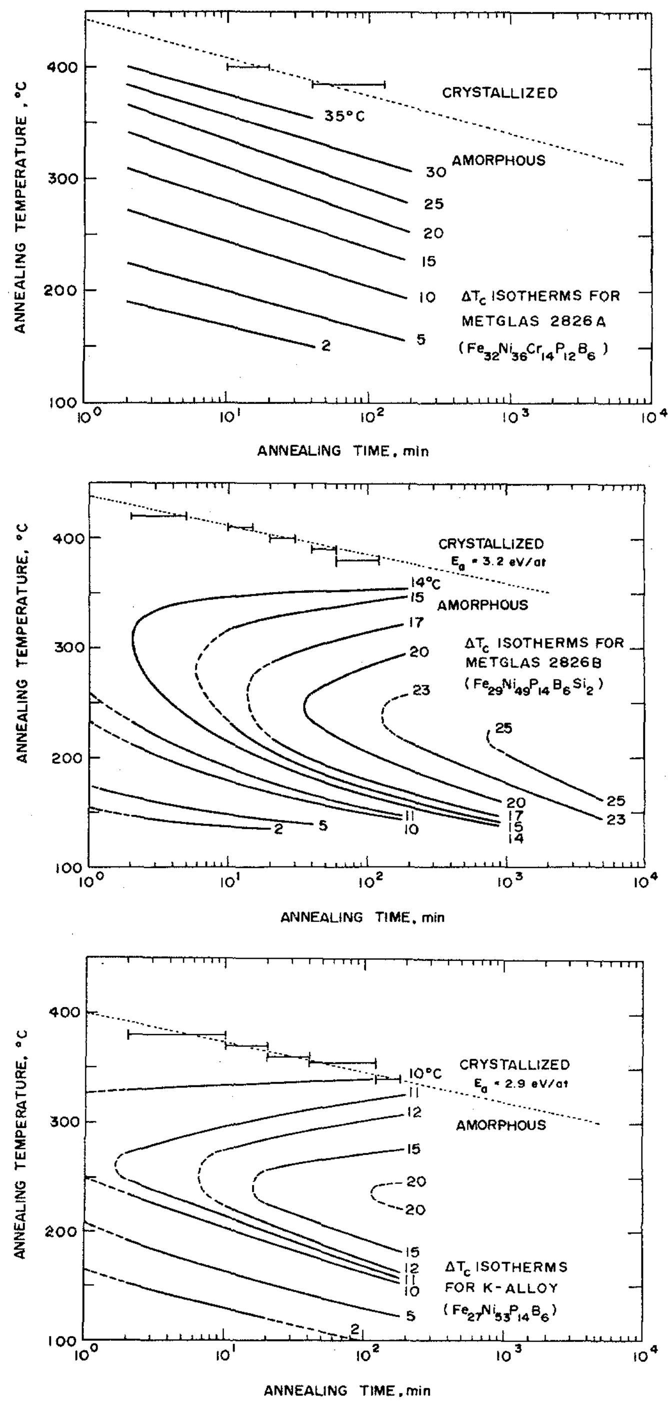

Fig. 2. Curie temperature isotherms as a function of annealing treatment for three compositions

Anisotropy and Oxide Effects

Low-field magnetic properties were measured from 60 Hz hysteresis loops on 20cm straight lengths of ribbon, after various annealing treatments. All the samples showed an initial decrease in anisotropy, defined as the area bounded by the magnetization axis, the magnetization curve, and the value of M_S. This decrease is attributed to the relaxation of internal stress, with a consequent reduction of stress-magnetostriction anisotropy[5]. However, two compositions, Metglas 2826 ($Fe_{40}Ni_{40}P_{14}B_6$, T_C=250°C) and 2826B, slowly developed a uniaxial magnetic anisotropy with its easy axis perpendicular to the ribbon axis (see Fig. 4). The value of the uniaxial anisotropy in this case is about 500 erg/cm^3. The anisotropy does not appear to originate from any magnetic annealing phenomenon. Various experiments to change the magnitude and direction of the magnetic field applied to the sample during the anneal (earth's field, furnace winding fields) had no effect on the anisotropy. However, the uniaxial anisotropy does not appear in samples annealled in vacuum, which suggests that the anisotropy is caused by the formation of an oxide layer. Differential thermal contraction of the oxide and the amorphous alloy, interacting with the relatively large positive magnetostriction of the alloy, could account for the magnitude of the observed anisotropy and for its lack of dependence on the field present during the anneal.

Comparison measurements on samples annealed in air and in vacuum have shown that the oxide layer is not responsible for the observed changes in Curie temperature and in length.

Acknowledgements

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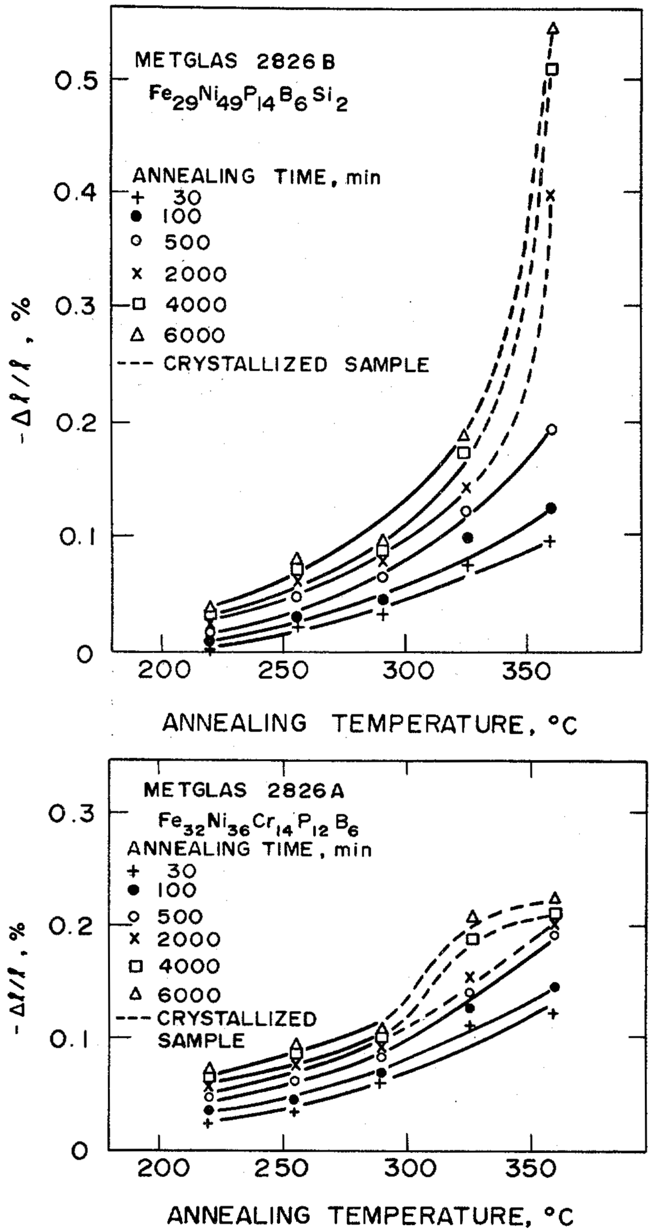

Fig. 3. Change in length as a function of annealing treatments for two compositions

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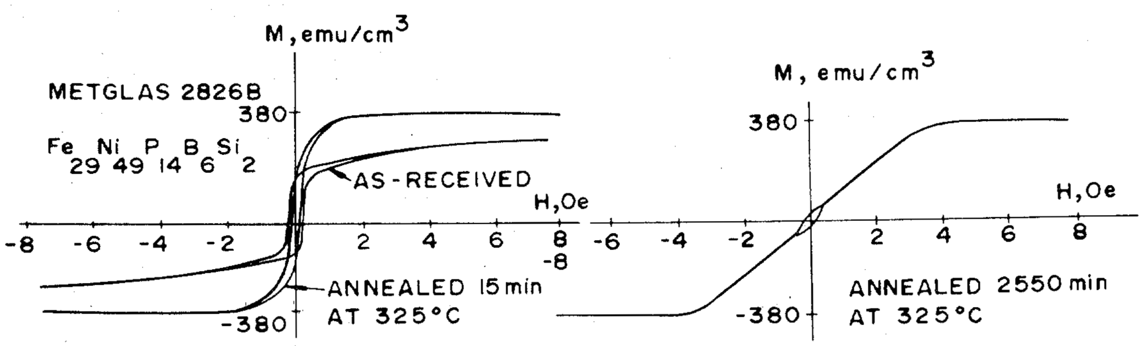

Fig. 4. Change in 60 Hz magnetic hysteresis loop with annealing.