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# Magnetic Annealing and Directional Ordering of an Amorphous Ferromagnetic Alloy

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The amorphous ferromagnetic alloy $Fe_{75}P_{15}C_{10}$ has been found to respond reversibly to magnetic annealing treatments. The response has been studied (a) by measurements of the $\Delta E$ effect, which is unusually large, (b) by measurements of the magnetostriction, and (c) by torque curves which yield a value of 550 erg/cm$^3$ for the uniaxial anisotropy parameter $K_u$. Internal-friction measurements reveal that the alloy is also susceptible to stress-induced ordering, with an activation energy of 2.2 eV.

It is well known that the structure-sensitive ferromagnetic properties of certain crystalline solid-solution alloys can be significantly modified and made uniaxially anisotropic by annealing in a magnetic field.[1,2] This behavior has been successfully explained in terms of a directionality induced in the state of short-range order of the alloy by the magnetization $\vec{M}$, a process which necessitates local atom motion below the Curie point, $T_C$. Although developed to explain the behavior of crystalline alloys, this mechanism is actually of wide generality and should also apply to amorphous alloys, since only *short-range* directional order is involved. In confirma-

tion of this view, we report here the observation of reversible magnetic annealing effects in an amorphous ferromagnetic alloy of nominal composition (in atomic percent) $Fe_{75}P_{15}C_{10}$, prepared at California Institute of Technology by the technique of splat cooling[3] and generously supplied by Professor Pol Duwez. For present purposes the alloy combines a reasonably high Curie point ($T_C = 330°C$) with the advantages that it can be heat treated up to and above $T_C$ without crystallization, and can be saturated in moderate fields (~ 100 Oe). Crystallization of the amorphous alloy has been studied by Rastogi and Duwez,[4] who concluded that the amorphous condition is largely preserved to about 420°C. In the present work crystallization has been found to produce several well-marked irreversible property changes, including the total elimination of the large $\Delta E$ effect described below.

Measurements of the internal friction and $\Delta E$ effect were performed on vibrating-reed samples about 2 cm long and 0.3 cm wide, cut from foils of 0.004 cm thickness. The $\Delta E$ effect refers to the variation of the uniaxial elastic constant $E$ (Young's modulus) with the intensity of magnetization of a ferromagnetic material. The modulus for the saturated condition, $E_S$, is larger than that for any other level of magnetization. The difference $\Delta E = E_S - E$ is caused by the interaction of the applied stress (in this case the oscillatory stress) with the domain configuration,[5] which results in the addition of a magnetostrictive strain to the ordinary elastic strain. The ratio of these strains is readily shown to be given by the ratio $\Delta E/E$ used in Fig. 1. These measurements were made with a vibrating-reed apparatus[6] equipped for *in situ* annealing in fields of 100–500 Oe. After cooling to room temperature, removal of the annealing field, and application of a standard ac demagnetization treatment, the $\Delta E$ effect was obtained as a function of a longitudinal magnetizing field via measurements of the resonant frequency of the sample. For references, curve $Z$ shows the behavior after a zero-field anneal of 30 min at 360°C. $\Delta E/E$ starts off with a value of 0.24 in the demagnetized condition and doubles in size before decreasing to zero with the approach to saturation. It is noteworthy that the $\Delta E$ effect is two orders of magnitude larger than for crystalline iron. This striking difference is attributed largely to the lack of magnetocrystalline anisotropy in the amorphous alloy, which allows a much greater response to the applied stress by domain rotation.[7] Another sig-

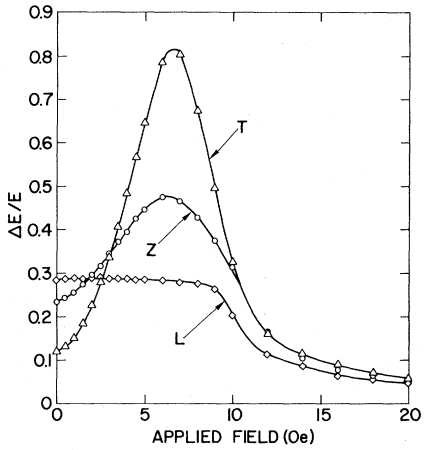


FIG. 1. The $\Delta E$ effect of the amorphous Fe-P-C alloy, determined from measurements at the second tone of vibration near 400 Hz. $Z$, after a zero-field anneal; $T$, after a transverse-magnetic anneal; $L$ after a longitudinal-magnetic anneal.

nificant feature of Fig. 1 is that the measurements refer to the complete or fully relaxed $\Delta E$ effect, free from eddy-current shielding which, for higher frequencies and thicker samples, is known to modify the field dependence and limit the observed magnitude of the effect.[8] The anisotropy introduced into the $\Delta E$ effect by magnetic annealing was observed by repeating the above measurements after anneals with a field applied along either the longitudinal or the major transverse axis of the reed. The standard annealing schedule consisted of 30 min at 360° to erase any previously induced anisotropy, followed by cooling to room temperature in a field of 100–500 Oe with holds of 30 min each at 325°C, 315°C, 290°C, and 260°C. It is clearly evident that the longitudinal anneal suppresses the maximum and lowers the overall magnitude of the $\Delta E$ effect, while the transverse anneal has the opposite effect, increasing the maximum $\Delta E$ effect to the very substantial magnitude of 0.8. These differences are readily explained in terms of an induced easy axis of magnetization lying parallel to the magnetic annealing direction. The main point is that the easy axis causes a nonrandom or nonideal demagnetized condition[9] in which most domains have magnetization vectors along the easy axis and are separated by 180° walls. In this condition the $\Delta E$ effect tends to be relatively small because 180° walls are not stress active and the predominant domain orientations are not susceptible to stress-induced rotation. If the sample is subsequently magnetized by a

field applied along the easy axis (curve $L$), the $\Delta E$ effect can be decreased by the removal of the residual stress-active walls (those with a 90° component). On the other hand, when the magnetizing field is perpendicular to the easy axis (curve $T$), magnetization must necessarily be accompanied by domain rotation or growth into orientations which enhance the stress sensitivity and cause the $\Delta E$ effect to increase.

The measurements of Fig. 1 have been repeated on several different samples using various tones of vibration. While the results show differences of detail the major characteristics described above are consistently reproduced and appear to be stable indefinitely at room temperature. Additionally, it has been clearly established by repeated sequences of anneals that the changes induced in the $\Delta E$ effect are reversible in the sense that any of the curves $T$, $Z$, or $L$ can be recovered by repeating the appropriate anneal. Taken together these observations show that an anisotropy can be reversibly induced and frozen into the alloy, and thus provide clear evidence for a directional-ordering model involving thermally activated local atom movements. Although a detailed study of the magnetic annealing kinetics has not been performed, it has been concluded from experiments with different cooling rates that an anisotropy close to the maximum obtainable is developed in about an hour at 300°C. Since by hypothesis this is roughly the time for an atom to jump just once, we may estimate its activation energy $Q_m$ from the relationship

$$w = A\nu_0 \exp(-Q_m/kT), \tag{1}$$

where $w$ is the atomic jump rate, $A\nu_0$ is a frequency factor whose value can be expected to be about $5\times 10^{13}$ sec$^{-1}$, $k$ is Boltzmann's constant, and $T$ is the absolute temperature. The value of $Q_m$ estimated in this way is 2.0 eV. An independent and more accurate measurement of the activation energy for atomic movement in the amorphous alloy has been obtained from high-temperature internal-friction measurements (Fig. 2). These data reveal a thermally activated relaxation behavior attributable to stress-induced ordering. An activation energy $Q_r = 2.2$ eV is obtained from Fig. 2 by the frequency-shift method.[10] The similarity of $Q_m$ and $Q_r$ is significant because it indicates that similar atomic movements are involved in both the magnetic annealing and the internal friction behavior. This is to be expected if directional ordering is involved in both effects.

Further evidence of magnetic annealing in the Fe-P-C alloy is shown by the magnetostriction results of Fig. 3. These data were obtained from the sample of Fig. 1 in a separate sequence of anneals. The measurements were made with a Talysurf instrument in the manner described by Simpson and Brambley,[11] with the flexible reed mounted in a guide to keep it straight. The larger magnetostriction seen after magnetic annealing in a direction transverse to the magnetization direction is precisely the effect expected since

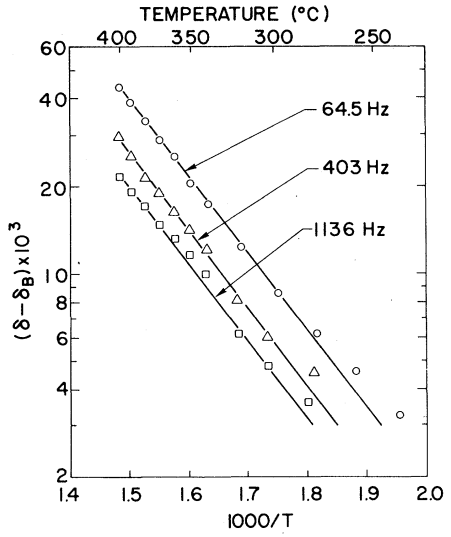


FIG. 2. Thermally activated internal friction of the amorphous Fe-P-C alloy. The observed logarithmic decrement ($\delta$) is corrected for a background loss $\delta_B$ due mainly to thermoelastic damping. Magnetoelastic losses, normally present below $T_C$, were suppressed by a magnetic field of 80 Oe.

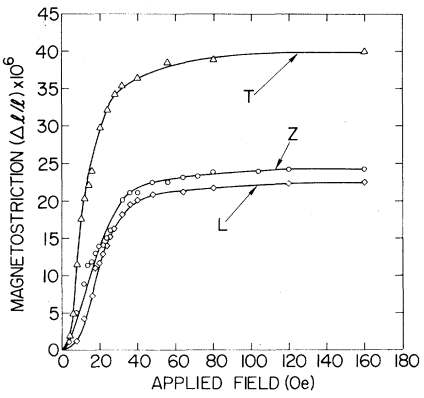


FIG. 3. Magnetostriction of the amorphous Fe-P-C alloy after a zero-field anneal (curve $Z$), and after longitudinal- ($L$) and transverse- ($T$) magnetic anneals.

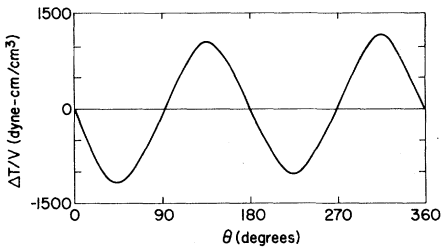


FIG. 4. Determination of the anisotropy induced in the amorphous Fe-P-C alloy by magnetic annealing. The curve shown is the difference between the torque curves obtained after magnetic anneals in two orthogonal directions, each measured with a saturating field of 800 Oe.

magnetization in this case involves the reorientation of most domains through 90°. Overall, the results show that the magnetostriction is of positive sign, is of substantial magnitude, and varies with magnetization in a considerably simpler manner than is the case for crystalline iron. The proximity of curve $Z$ to curve $L$ was somewhat unexpected, and serves to suggest that, because of shape anisotropy or other causes, curve $Z$ does not start from a truly random or ideal demagnetized state.

To characterize the induced anisotropy in the Fe-P-C alloy in quantitative terms, the uniaxial anisotropy parameter $K_u$ has been determined by torque measurements on a disk sample nominally 0.004 cm thick and 1.6 cm in diameter. The measurements were made with a taut-suspension magnetometer of simple design, calibrated by the usual oscillation method.[12] To eliminate the effect of a residual shape anisotropy (due to minor nonuniformity in the thickness of the splat-formed foil), Fig. 4 shows the difference in the torque curves obtained after standard magnetic anneals along and perpendicular to a reference direction defining the sample orientation $\theta$ with respect to the measurement field. Following these measurements further anneals were performed to demonstrate that the induced torque difference could be both removed by annealing in zero field and reintroduced with an appropriately shifted phase by further magnetic anneals along other directions. For the situation of Fig. 4, the difference in the energies per unit volume can be written

$$\mathcal{E}_1 - \mathcal{E}_2 = K_u(\sin^2\theta - \cos^2\theta), \qquad (2)$$

and the torque difference per unit volume follows as

$$\Delta T/V = -d(\mathcal{E}_1 - \mathcal{E}_2)/d\theta = -2K_u \sin 2\theta. \qquad (3)$$

Comparing Eq. (3) with Fig. 4, it is seen that the data exhibit the expected $\sin 2\theta$ dependence, and provide from the peak torque the value $K_u = 550$ erg/cm$^3$. Since $K_u$ is thus not particularly large, but its effects are nonetheless substantial, we are led to the general conclusion that a small induced anisotropy can be of greater relative importance in an amorphous alloy because there is no magnetocrystalline anisotropy to compete against it.

As a final comment it may be remarked that an amorphous solid is frequently simply thought of as a material possessing a random structure, whose properties are therefore necessarily isotropic. Through the observation of phenomena linked to directional short-range ordering, the present experiments serve to emphasize that, more precisely, it is the absence of long-range order, rather than total randomness, that is the characteristic feature of an amorphous solid.

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