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Stored energy in a cold-rolled metallic glass

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The relaxation spectra of a cold-rolled Pd-Cu-Si glass are very similar to that of the initially quenched glass, except for the low-temperature peak at 400°K. About 4% of expended energy is stored in the glass. A possible mechanism is that the stored energy arises from local heating and quenching in shear bands. The bandwidth and the stored energy in the shear bands are of the order of 2500 Å and 2.5×10^4 erg/cm^2, respectively.

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A few investigations have been reported on the effect of plastic deformation on mechanical properties in metallic glasses. Barmatz *et al.*[1] observed that the damping and dispersion of sound in the low-temperature region observed previously in initially quenched glassy metals are appreciably enhanced by cold rolling in a Fe-based glass. The present author[2] found that the Young's modulus of metallic glasses decreases slightly upon cold rolling. Upon subsequent heating, the deformed samples exhibit two distinct relaxation peaks, one near 100°C and the other about 100°C below the glass temperature. These two peaks indicate two different modes of atomic rearrangement in the glass.

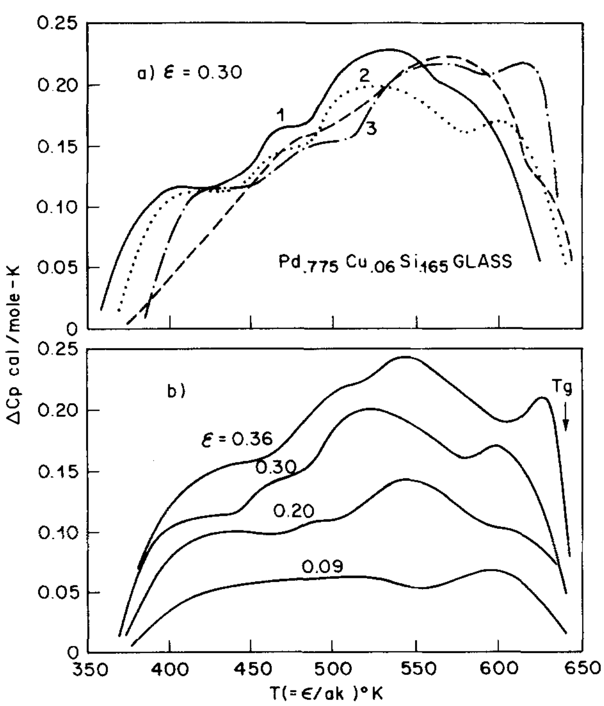

FIG. 1. Relaxation spectrum, ΔC_p-vs-T curve, of cold-rolled metallic glasses of $Pd_{0.775}Cu_{0.06}Si_{0.165}$ alloy (a) at various scanning rate: 20 °K/min (1), 40 °K/min (2), and 80 °K/min (3); reduction in thickness $\epsilon = 0.30$; the dashed line is the relaxation spectrum of the quenched glass at 20 °K/min scanning rate, scaled down by a factor of 5; (b) at various ϵ, scanning rate = 40 °K/min, T_g is the glass temperature.

Recently, Chen and Chuang[3] have studied the structure of a cold-rolled Pd-Cu-Si glass using position annihilation methods. Based on the observation that only slight changes occurred in both the position lifetime and angular correlation of the glass upon cold rolling, they concluded that cold rolling of the metallic glass induces no vacancylike defects, and plastic deformation in metallic glasses is accompanied by atomic regroupings somewhat analogous to the viscous flow of liquids.

We report here, for the first time, the stored energy and relaxation spectrum in a glassy state. The stored energy density in the shear bands is evaluated, and its implication for the structure and flow in metallic glasses is discussed.

$Pd_{0.775}Cu_{0.06}Si_{0.165}$ glassy ribbons about 60 μm thick and 2 mm wide were prepared using a roller quenching technique.[4] In order to eliminate the frozen-in structure of the quenched state, the quenched glassy ribbons were heated to the glass temperature T_g and then cooled slowly (≈ 20°K/min) to room temperature.[5] The annealed samples were then rolled to various reductions in thickness ϵ ($=\Delta t/t$) at room temperature. Here t is the thickness of the sample.

The apparent specific heat C_p of glassy samples was first scanned to T_g to obtain data on the deformed state, then cooled at 20°K/min to room temperature. The measurement was repeated *in situ* to obtain data on annealed (or underformed) samples. Because of the small specific heat change ΔC_p (≤ 0.25 cal/mole °K) between the deformed and undeformed samples, care was taken to ensure reproducibility of ΔC_p to within 0.01 cal/mole °K.

The relaxation spectra, ΔC_p-vs-T curves, are illustrated in Fig. 1. The spectra exhibit several broad relaxation peaks; a low-temperature one which peaks at ~400°K and high-temperature peaks, which are similar to those previously observed for the quenched glass,[5] composed of two distinguishable broad distributions. The relaxation spectrum of the quenched glass has been scaled down by a factor of 5 and is reproduced for comparison (a dashed line) in the figure. From the shift of spectrum with scanning rate, the activation energy of relaxation $\mathcal{E}$ is evaluated and related to the temperature T as $\mathcal{E} \approx akT$ with $a \approx 25$, where k is Boltzmann's constant. $\mathcal{E} \approx 0.9$ eV for the low-temperature peak. The intensity of the relaxation spectra decreases with decreasing strain ϵ. At small ϵ (< 0.10), the low-temperature relaxation appears to become dominant.

The total stored energy E_s increases linearly with cold rolling strain ϵ as shown in Fig. 2. Neglecting lateral expansion, the energy expended during cold rolling is approximated as $E_a \approx \sigma_f \epsilon \bar{V}$. Here, σ_f (≈ 150 kg/mm^2) is the flow stress, $\bar{V}$ (≈ 8.67 cm^3/mole)[6] is the molar volume. The ratio of stored energy to the expended energy, E_s/E_a, is shown in Fig. 2(b). E_s/E_a is about 4% but appears to be higher for $\epsilon \lesssim 0.1$.

Typical SEM micrographs of the cold-rolled surface clearly reveal highly localized shear bands which are characteristic of metallic glasses.[7,8] The deformation is not uniform and it changes in morphology from the edge to the center of ribbons. As ϵ increases, the average density of shear bands increases but at a slower rate. This implies that further plastic deformation occurs in the previously deformed regions as well as in undeformed regions in which new shear bands have been created.

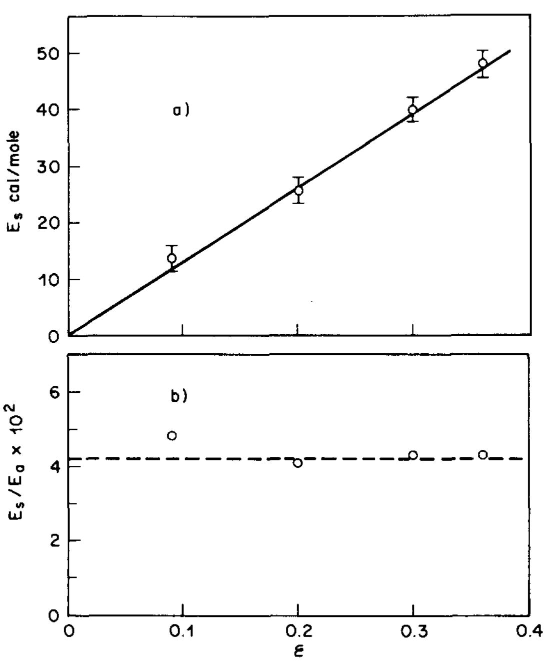

FIG. 2. Stored energy E_s and ratio of stored energy to expended energy (E_s/E_a) vs ϵ of the Pd-Cu-Si glass.

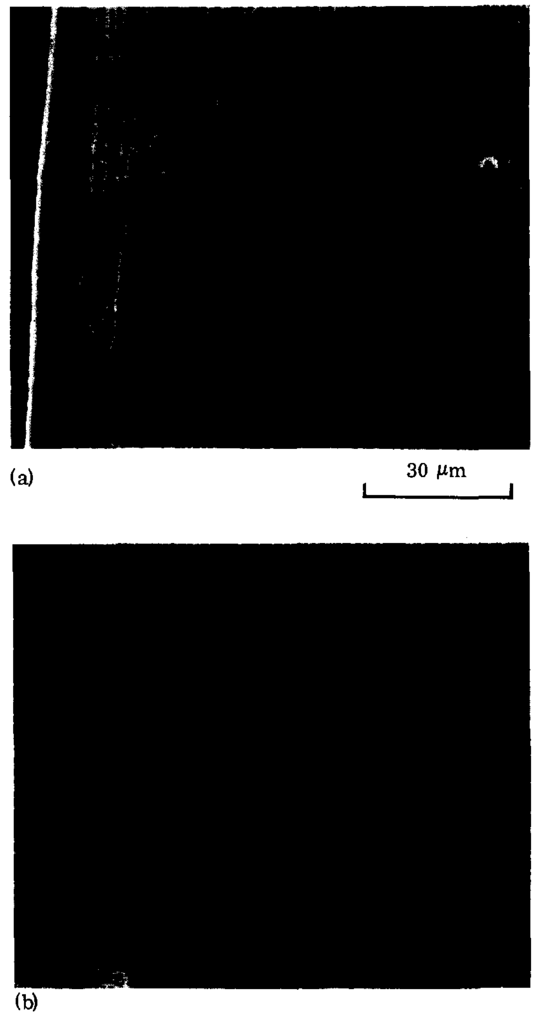

FIG. 3. SEM micrographs of the cold-rolled surfaces; near edge (a) and center (b) of the ribbon, $\epsilon = 0.30$. The direction of rolling is vertical.

In view of the similarity of the relaxation spectra (except for the low-temperature peak at 400°K) for the cold-rolled and initially quenched glass, and considering the positron annihilation studies on the structure of the cold-rolled glass, we suggest that the cold-rolling-induced structural disorder is similar to the "frozen-in" structure in the quenched glass. We may suppose as a possible mechanism that the volume near a shear band is locally heated to or above T_g during plastic flow and then quenched to room temperature immediately at the completion of the deformation. This would lead to the "frozen-in" structure at shear bands. In what follows, the shear band thickness and possible temperature rise at the shear bands will be discussed.

On this model, the stored energy density in the shear bands, $\mathcal{E}_s$, may be evaluated from the shear band density ρ and the stored energy E_s as $\mathcal{E}_s = E_s/\rho\bar{V}$. Assuming that the structural disorder in shear bands is similar to that of the quenched state, the shear bandwidth is given by $h \approx \mathcal{E}_s \bar{V}/\Delta H_s$. Here, ΔH_s is the heat of relaxation of the quenched glass. Taking, for example, the sample with $\epsilon = 0.30$ and $\rho \approx 8\times 10^3$ bands/cm (see Fig. 3), $E_s = 40$ cal/mole and $\Delta H_s = 200$ cal/mole.[5] We obtain $\mathcal{E}_s = 2.5\times 10^4$ erg/cm^2 and $h \approx 2500$ Å. This shear bandwidth is in agreement with micrographic observations.

The stored energy arises from local heating due to local deformation. With $\sigma_f = 150$ kg/mm^2, the shear step $\Lambda \geq 10^{-5}$ cm,[9] and specific heat $C_p \approx 6$ cal/mole°K, the possible temperature rise at the shear bands is $\Delta T \approx \sigma_f \Lambda \bar{V}/C_p h \geq 400$°K. This is sufficient to heat the shear bands above the glass temperature T_g (≈ 636°K).

Only a small fraction of expended energy, ~4%, is stored in the glass and most of the energy is dissipated as heat during cold rolling as is the case for crystalline metals.[10] One may expect that E_s/E_a will decrease with further increase in ϵ since the shear deformations will occur more frequently at the existing shear bands, and shear bands begin to overlap. However, at $\epsilon = 0.4$, only 10% of the volume is filled with slip bands.

The low-temperature relaxation near 400°K of the cold-rolled glasses seems to be unique and may be attributed to local atomic rearrangements which are distinguishable from the cooperative atomic regroupings of glasses near T_g. This local atomic rearrangement is believed to be responsible for the kink at 100°C in the Young's modulus E-vs-T relaxation curve and possibly for the enhancement in the low-temperature anomalies of the cold-rolled glass.

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Ferromagnetic properties of some new metallic glasses

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Continuously cast metallic glasses [METGLAS® (trademark of the Allied Chemical Corporation) alloys] based on the transition metals (TM) iron, cobalt, and nickel can now be synthesized containing boron as the only metalloid. The different electron-donor effects of boron and phosphorus are clearly seen for the first time; each atom of these metalloids gives ~1.6 and 2.4 electrons, respectively, to the TM d bands. Extrapolation of the available magnetic moment data suggests a nonzero moment on nickel in $(TM)_{80}B_{20}$ glasses. The boron-containing metallic glasses generally show higher Curie temperatures and room-temperature saturation magnetizations than mixed-metalloid glassy alloys of the same TM content.

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The magnetic properties of metallic glasses have been the subject of considerable investigation over the past several years.[1] The interest in these materials has been stimulated, in part, by the availability of long ribbons and wires, produced by continuous rapid quenching from the melt.[2] Such filaments are most attractive from the point of view of sample form suitable for a variety of measurements and applications; it has been demonstrated that they exhibit excellent soft ferromagnetic properties.[3-7] However, continuously cast ferromagnetic glassy alloys available to date always contained metalloids in doublet or triplet combination, hindering interpretation of results and obscuring trends in data.

We report here the magnetic properties of new METGLAS alloys based on transition metals, alone or in combination (totalling 80 at.%), and boron (20 at.%) as the only metalloid. Specifically, we examine two series of magnetic glassy alloys $(FeCo)_{80}B_{20}$ and $(FeNi)_{80}B_{20}$ *including the binary end members* of the first series. These metallic glasses have been produced for the first time in ribbon form by continuous quenching from the melt. The properties of these new metallic glasses are discussed with respect to (a) their dependence on the systematic variation of the alloy metal composition for a given metalloid, and (b) their dependence on the nature of the metalloid content, i.e., B alone, as opposed to B-P-C-Si-Al doublet, triplet, etc., combinations.

Alloys were prepared from constituent elements of high purity (> 99.9%) and rapidly quenched from the melt in the form of long and thin glassy ribbons.[2] Typical

