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CONSOLIDATION AND PLASTICITY OF Bi-Sr-Ca-Cu-O SUPERCONDUCTORS*

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ABSTRACT

The $Bi_2Sr_2CaCu_2O_x$ (2212) superconductor consists of platelike grains that grow very rapidly in two directions at high temperature. The grain growth is so fast that this superconductor can not be sintered by conventional means. Densification can be achieved, however, by hot isostatic pressing or by a combination of flat rolling and sintering.

Results from 2212 and 2212 + 15 wt.% Ag specimens produced by these consolidation methods are compared with those from sintering studies. Scanning and transmission electron microscopy were used to assess the mechanisms by which 2212 densifies. The superconducting properties of each type of specimen were measured. It was found that only forms in which the platelike grains exhibited substantial preferred orientation were capable of carrying large amounts of current. This result has important implications to the thermomechanical processing of Bi-Sr-Ca-Cu-O superconductors.

INTRODUCTION

All of the high-temperature superconductors have highly anisotropic properties [1]. The Bi-Sr-Ca-Cu-O system exhibits the strongest mechanical anisotropy. The most widely studied phase in the system [1,2] has a superconducting transition temperature of 80-90 K and has a nominal stoichiometry of $Bi_2Sr_2CaCu_2O_x$ (2212). This phase has proved to be very difficult to consolidate by conventional sintering methods [3,4]. At the sintering temperature, rapid grain growth occurs in two dimensions and a compact can actually become less dense with sintering time [4]. The 2212 phase and other Bi-based superconductors have been successfully densified by hot isostatic pressing [6-9], hot pressing [10,11], or a combination of rolling and sintering of powder packed into an Ag tube [12,13].

The mechanisms by which the 2212 phase consolidates constitute an important subject of study. In addition, it has been shown that metallic Ag additions can promote densification kinetics in the high-temperature superconductor $YBa_2Cu_3O_x$ [14], but the effects of Ag on 2212 remain unclear [7,15,16]. The goals of this study were to examine the sintering and deformation behaviors of the 2212 phase and the effects of the addition of Ag particles on these behaviors. Microstructural development and superconducting properties have been examined for sintered pellets, hot isostatically pressed pellets, and Ag-clad flat wires. The behavior under stress of individual crystals of 2212 has also been studied by transmission electron microscopy.

EXPERIMENTAL METHODS

The composition selected for the powder was $Bi_2Sr_{1.7}CaCu_2O_x$, which has been found to yield 2212 of excellent phase purity [17]. The 2212 was made by calcination of Bi_2O_3, $SrCO_3$, $CaCO_3$, and CuO powders. The powders were mixed by ball milling for 24 h in polyethylene jars containing methanol and ZrO_2 grinding media. After being milled, the powders were pan dried, ground lightly with an agate mortar and pestle, and heated in air for 48 h at 815-820°C. Intermittent grinding was performed to promote homogeneity. The resultant powder consisted of the 2212 phase and less than 5% total of $Bi_2Sr_2CuO_x$ and residual Ca-Cu oxides.

A similar routine was applied to obtain 2212 with 15 wt.% Ag additions. A mortar and pestle were used to mix 2 µm metallic Ag particles into the 2212 [15]. The 2212 and 2212 + Ag powders were processed into bulk forms by conventional pressureless sintering, by cold rolling in an Ag tube, and by hot isostatic pressing. Results from each of these methods will be discussed individually.

For all of the specimens, scanning electron microscopy (SEM) and energy dispersive spectroscopy were conducted on fracture surfaces. Superconducting transition temperatures were determined by magnetization: specimens were cooled in zero field below T_c, a field of 0.5-20 Oe was applied, and magnetization was monitored during warming. Critical current densities were obtained for some of the specimens. A four-probe technique and a criterion of 1 µV/cm were used.

SINTERING

Pellets for the sintering studies were uniaxially cold pressed to about 50% of the theoretical density. Sintering was conducted in air at 850 to 910°C. The onset of melting for the 2212 phase in air is about 885°C [17], and hence some of the pellets were sintered in the presence of a liquid. The pellets that were sintered in the absence of a liquid averaged less than 60 % of the theoretical density. The lack of densification from solid-state sintering has been observed before [3,4,15] and is due to very rapid grain growth.

The liquid-phase sintered specimens were only about 80-85% dense. In addition, because the 2212 phase melts incongruently, upon solidification the specimens were no longer phase pure. Additions of Ag improved the densities substantially, with some of the specimens being over 90% dense. Phase purity was a problem for these specimens also. Most of the Ag segregated to the grain boundaries. It was found that the Ag-rich regions were also rich in Cu [16].

All of the as-sintered specimens had good superconducting transition temperatures from 85 to 89 K, but none was able to carry large amounts of current. Only the liquid-phase sintered specimens had critical current densities of more than 100 A/cm^2 at 77 K in zero applied magnetic field. The random orientation of the grains is thought to be largely responsible for the poor current-carrying capability.

COLD ROLLING

Cold uniaxial or isostatic compaction of the 2212 superconductor by pressures up to 200 MPa yields compacts that are at most 70% of theoretical density. This is a relatively high value and appears to be a consequence of two effects. First, rearrangement and fracturing occur during compaction. Second, the platelike 2212 grains bend under load. The extent of deflection can be quite large (Fig. 1). If a compact is then sintered, however, little if any densification results because of severe grain growth within the plane of each 2212 platelet.

Transmission electron microscopy (TEM) was used to examine the structures produced by bending of the platelike grains. An adhesive tape was applied to an [0 0 1] oriented 2212 crystal. Small platelets were pulled off. The tape was then dissolved and the platelets examined. Those that were transparent to electrons were severely bent by the stripping procedure. Very high concentrations of dislocations were found in the (0 0 1) plane. Almost all of the dislocations were split into partials (Fig. 2). The SEM and TEM observations indicated that dislocation motion was relatively easy in the (0 0 1) basal plane, but was difficult in other planes. No evidence was found for dislocation motion occurring on a sufficient number of slip systems to produce generalized plasticity of 2212 at room temperature.

Superconducting wires and tapes can be fabricated by packing 2212 powder into an Ag tube and cold working the composite. Efforts at optimizing the properties of the 2212/Ag superconductors have included attempts to increase densification of the 2212 core. Standard processing by various combinations of drawing/swaging/extrusion/rolling have generally produced densities of about 70% [12,18,19]. It has proved possible to increase densities substantially by orienting the grains within the core. This is accomplished by alternating cold rolling with heat treatments designed to grow the 2212 grains [13,20].

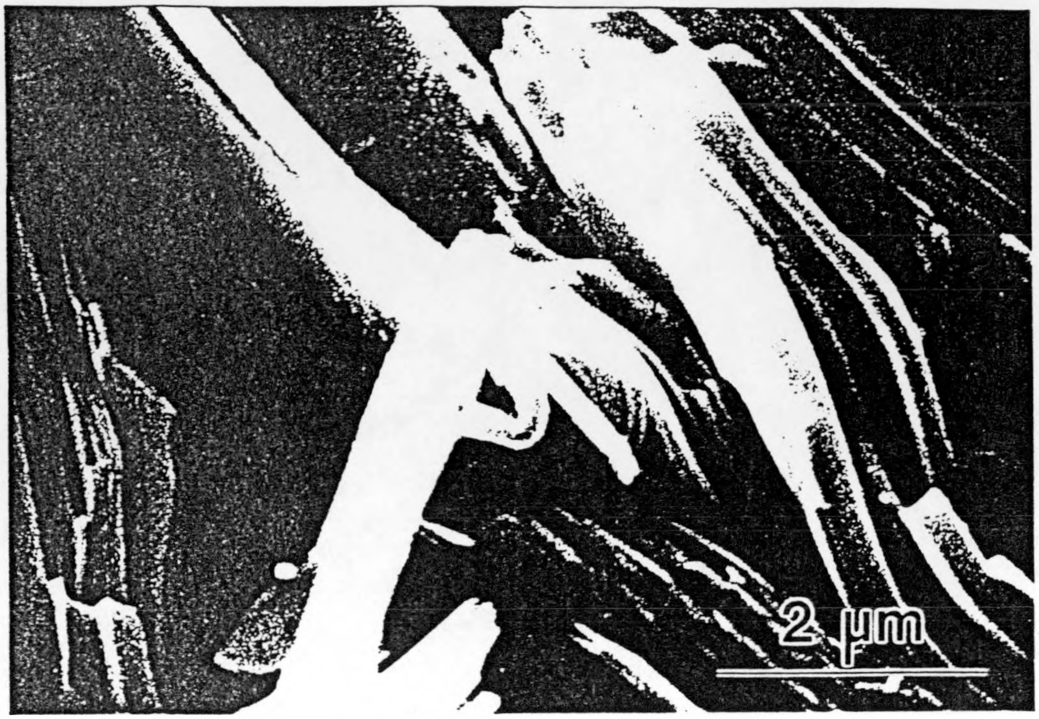

Figure 1. SEM micrograph of 2212 grains bent during cold working (from Ref. 3).

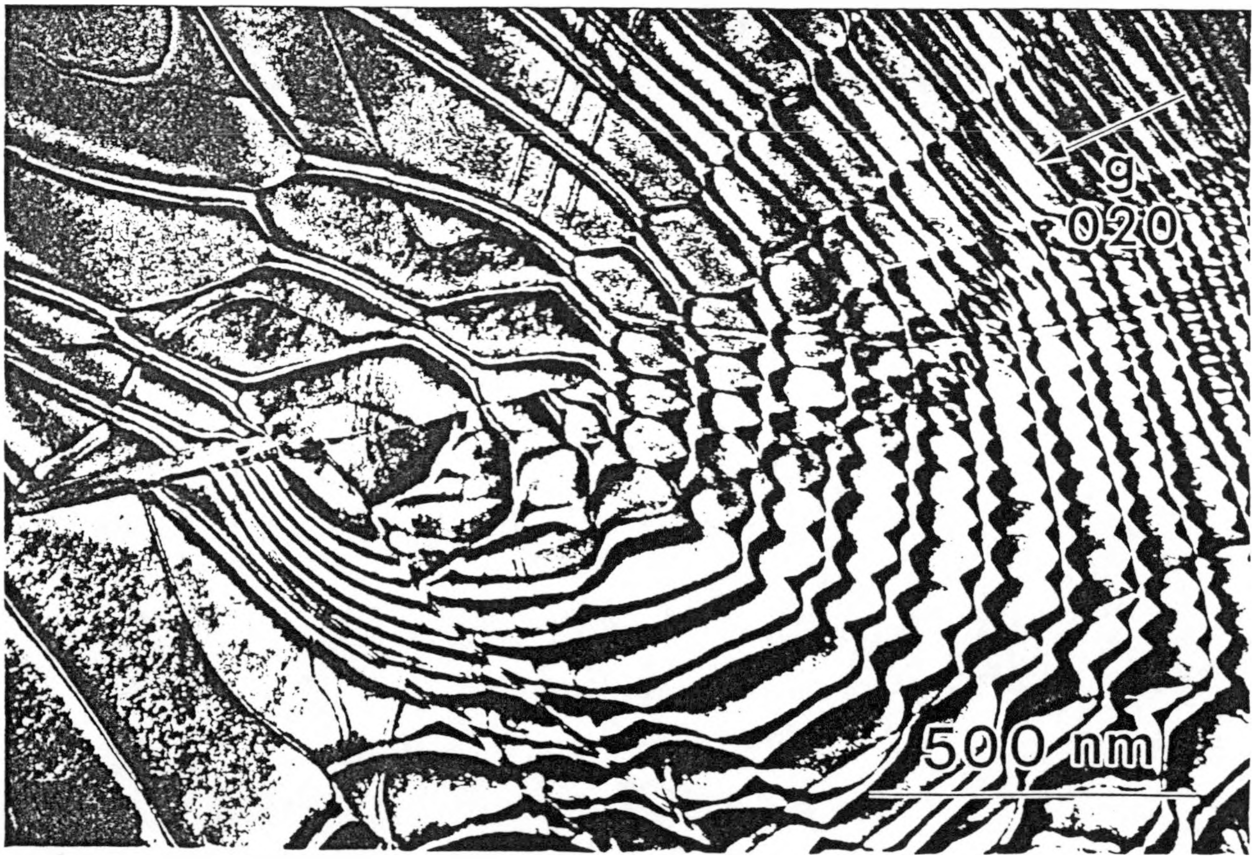

Figure 2. TEM micrograph of dislocations introduced into a 2212 single crystal by bending.

In our study, the diameter of the Ag tube was reduced by swaging in 15% increments from 6.35 to 1.0 mm. The 2212 core began to densify, and because of the platelike shape of the grains, some alignment of the grains occurred along the axis of the tube. In the process, the grains also fractured and deformed. The tube was then heated in air at 840°C for 50 h. Long 2212 grains resulted and the degree of alignment along the axis increased slightly. Cold rolling at 10% reduction per pass caused the core to densify further and the platelets to align better along the length of the flat tape. An additional heat treatment and cold rolling cycle, followed by a final heat treatment, produced a nearly fully dense core (Fig. 3). The grains were highly aligned; in the absence of such alignment, the final heat treatment would not have resulted in a dense product.

The superconducting properties of the 2212/Ag tapes have been reported in Ref. 13. The transition temperature was about 85 K and the critical current density at 77 K is 1×10^3 A/cm^2 and at 4.2 K was greater than 3×10^4 A/cm^2. The degree of alignment of the 2212 appears to be related to the superconducting properties and efforts are now focused on quantifying and improving the alignment. It is noted that high densities and good superconducting properties have also been obtained in well-aligned thick films of 2212 [21,22], which is in agreement with the conclusion that superconducting properties are related to texture.

HOT ISOSTATIC PRESSING

Hot isostatic pressing has been found to produce fully dense 2212 specimens [6–9]. In this study, 2212 and 2212 + 15% Ag pellets were placed between Ag foil, loaded into steel cans, and then evacuated. The sheathed specimens were hot isostatically pressed for 2 h in an inert atmosphere at a pressure of 105 MPa. Three temperatures were used: 800, 825, and 850°C.

All of the resultant specimens were nearly fully dense. The specimens pressed at 850°C were greater than 99 % dense [7]; the specimens pressed at 800 and 825°C contained a few percent porosity. The specimens pressed at 800°C appeared to contain microcracks, which may be related to the lower plasticity associated with the lower processing temperature. In contrast to the sintered 2212 + Ag samples, the 2212 + Ag samples that were hot isostatically pressed at 825°C exhibited alloy segregation in which the Ag-rich regions were Cu-depleted rather than Cu-rich. The reason for this difference is not known, but may be related to variations in the elemental diffusion rates with temperature and pressure.

During the pressing, oxygen was lost from the specimens and the superconducting transition temperatures were reduced to 75 ± 1°C. An anneal in air at 760°C raised the transition temperatures to 83–88 K. The transitions for the 2212 + 15 % Ag specimens were generally sharper than those for the pure 2212 specimens, but also occurred at slightly lower temperatures (Fig. 4). The effects of Ag on superconducting properties are complex and are still under study.

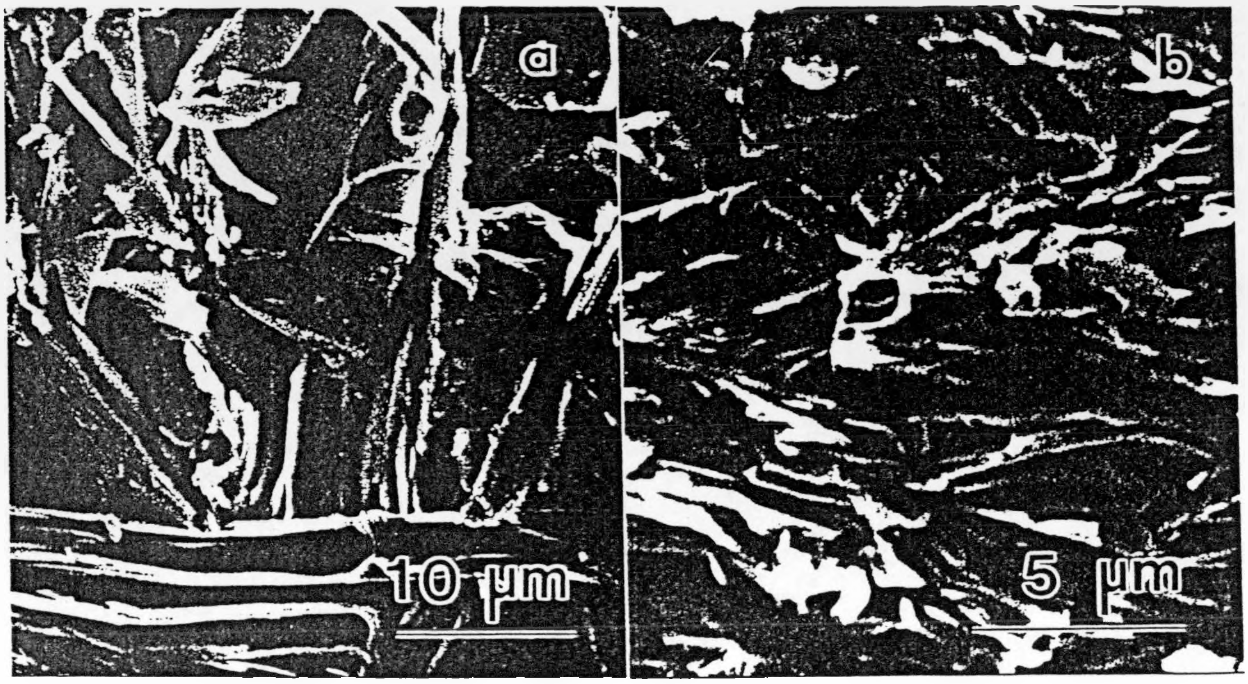

Figure 3. SEM micrographs of (a) randomly oriented 2212 compact that is about 70% dense and (b) core of a 2212/Ag tape that exhibits preferential alignment of grains and high density.

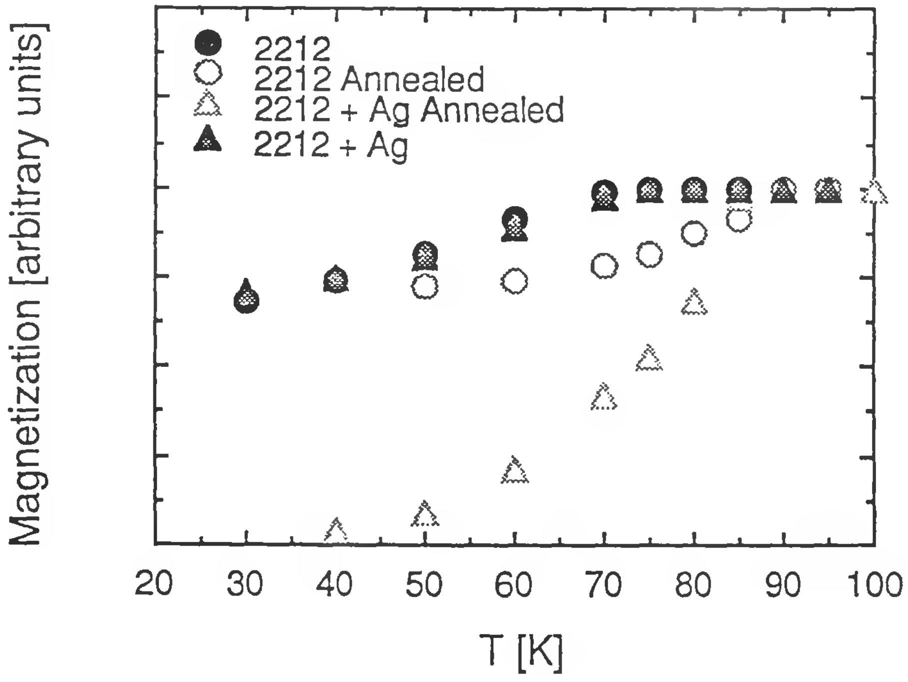

Figure 4. Zero-field-cooled magnetization data indicating the superconducting transition temperature for 2212 and 2212 + 15 wt.% Ag specimens hot isostatically pressed at 825°C; the final annealing treatment was 20 h in air at 760°C.

As was found for the sintered 2212 specimens. the critical current densities were very low. At 77 K. for example, the values were less than 50 A/cm^2. Despite the high densities of the hot isostatically pressed specimens, no improvements in superconducting properties arose. However, as for the sintered specimens, these specimens exhibited little preferred orientation of grains.

It was not clear what the principal mechanisms of deformation were during hot isostatic pressing. To provide insight, compressive creep tests were attempted on some of the densified material. Similar studies of the $YBa_2Cu_3O_x$ superconductor have revealed that general deformation is possible by diffusional flow and that the activation energy for the process is about 1 MJ/mole [23,24]. For temperatures greater than 90% of the melting temperature and strain rates of about 10^{-5} s^{-1}, $YBa_2Cu_3O_x$ deforms by diffusional flow and strain rate is proportional to stress [24]. Under similar conditions, the 2212 superconductor appeared to deform, but the strain rate and stress were nearly independent (Fig. 5).

It was found that the 2212 specimens had not undergone true creep. Instead, the specimens had fractured and bent. Each specimen was deformed to about 15% true strain. Friction at the compression surfaces resulted in barrelling. A few longitudinally oriented fractures were evident. This deformation is illustrated schematically in Fig. 6. In addition to fracturing, much plasticity in the form of platelet bending occurred. Thus dislocation motion appears to have contributed more to the plasticity than did diffusional flow. This contention may apply to the hot isostatic pressing as well.

Dislocations have been reported to have a significant effect on the superconducting properties of high-T_c superconductors [25,26]. It is thought that dislocations can act to pin flux lines in these Type II superconductors, and hence can raise the inherent critical current densities. Dislocation structures in Bi-based superconductors are beginning to be studied [27-30], and their effects on superconducting properties have yet to be understood. The intragranular critical current densities of the specimens that have been hot isostatically pressed are now being measured.

ASSESSMENT

Conventional sintering does not appear to be an effective means of densifying the 2212 superconductor, but additions of Ag can promote better densification. Evidence from the cold-working and hot isostatic pressing experiments indicate that the 2212 platelike grains bend easily at room and elevated temperatures, but can not easily undergo plasticity on several independent slip systems by dislocation motion. General plasticity of 2212 by diffusional flow may be possible, but the temperature will have to be near the melting point and the stresses will have to be very low, lower than those for the $YBa_2Cu_3O_x$ superconductor. Cold rolling produces a dense superconductor that exhibits substantial alignment of grains. Improved ability to carry current is associated with the grain alignment. The effects of dislocations on superconducting properties remain uncertain, but there are a few reports of improved current-carrying capability attributable to

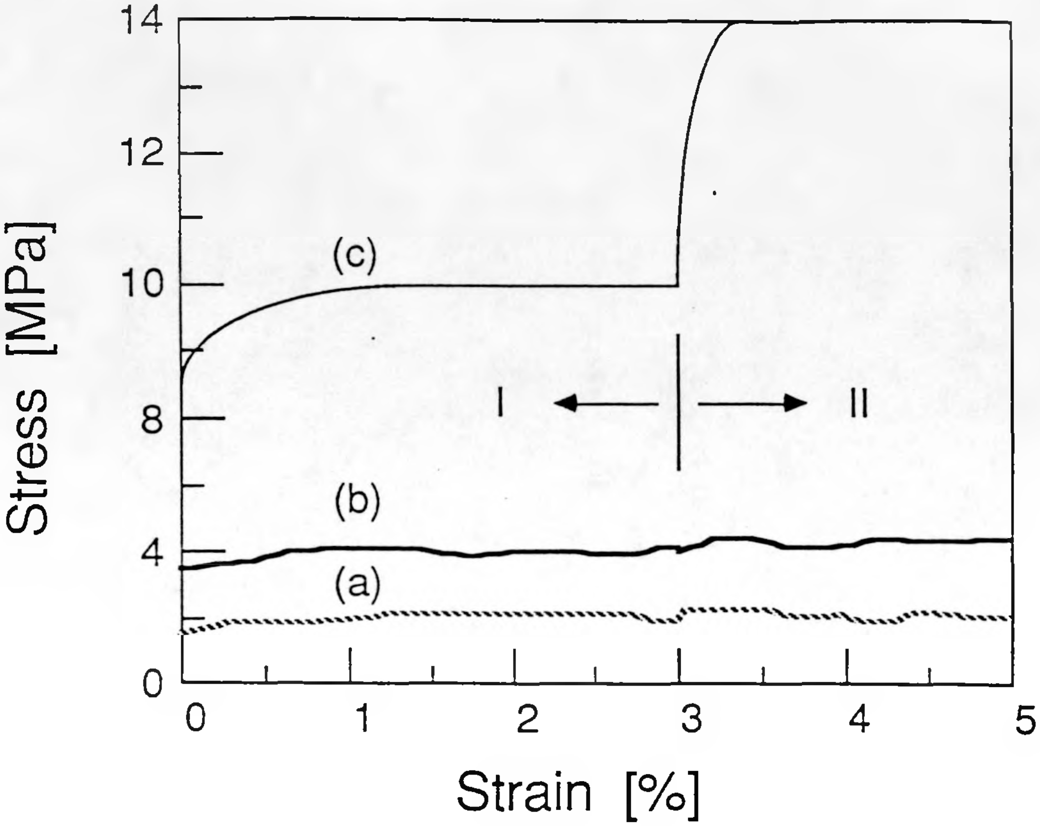

Figure 5. Stress–strain curves for (a) 2212, (b) 2212 + 15 wt.% Ag, and (c) $YBa_2Cu_3O_x$ specimens deformed at 0.94 % of the melting temperature; in Region I the strain rate was 10^{-5} s^{-1} and in Region II the strain rate was 2×10^{-5} s^{-1}; the data for the $YBa_2Cu_3O_x$ specimen are from Ref. 24.

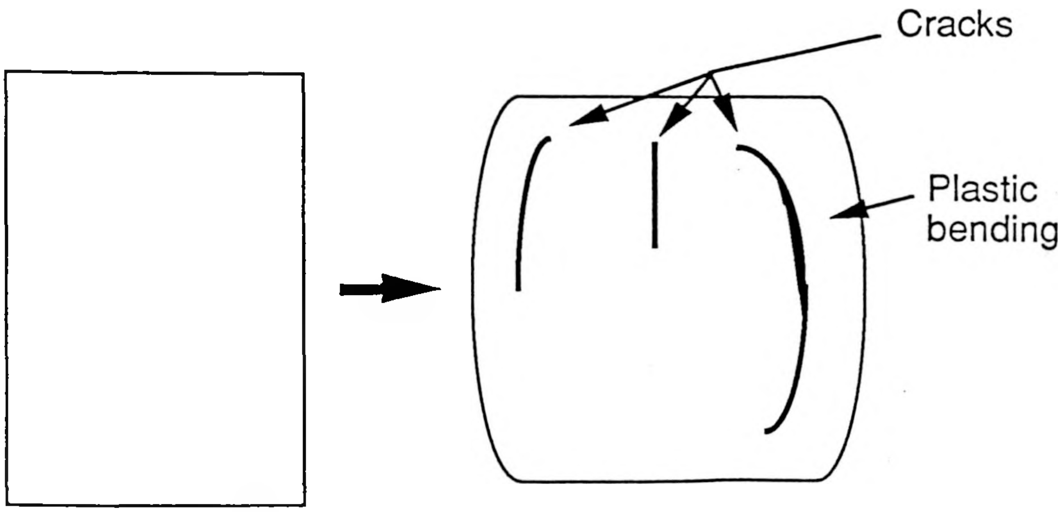

Figure 6. Schematic diagram of 2212 specimen that was compressed at 825°C.

dislocations and this possibility merits careful study. Ag additions also appear to affect superconducting properties. The transition temperature is slightly suppressed, but the transition is sharpened. Ag also has chemical effects on 2212 and these need to be examined more extensively.

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