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SINTERING OF BULK HIGH- T_c SUPERCONDUCTORS:
Bi-Sr-Ca-Cu-O*

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ABSTRACT

$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ (2212) and $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (2223) superconductors have orthorhombic crystal structures. They form platelike grains that at high temperatures grow primarily in the a-b planes and not in the c direction. The diffusional properties of Bi-Sr-Ca-Cu-O superconductors are so anisotropic that 2212 and 2223 cannot, in general, be densified by solid-state sintering. Improved densification can be achieved by application of pressure or by use of transient liquid phases.

Most useful bulk Bi-Sr-Ca-Cu-O superconductors are composites that contain Ag. The Ag lowers the melting points of the superconductors, which has significant effects on microstructural development. The results of disparate sintering studies are presented and discussed.

INTRODUCTION

$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ (2212) and $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (2223) have superconducting transition temperatures of 85-95 K and 110 K, respectively [1,2]. The formulas given are nominal stoichiometries. In fact, each compound has a fairly wide range of cation stoichiometry [3-5]. All of the high-temperature superconductors have highly anisotropic properties [1]. The Bi-Sr-Ca-Cu-O phases are the most anisotropic physically and have proved to be the most difficult to consolidate by conventional sintering [6-8]. At the sintering temperature, grain growth occurs in two dimensions only and a compact can actually become less dense with sintering time as the platelike grains push each other apart [7]. Owing to this platelike nature of the individual grains, which allow the grains to bend plastically under stress, the 2212 and 2223 phases have been successfully densified by hot isostatic pressing [9-14], hot pressing [15,16], or a combination of rolling and sintering of powder packed in a metallic sheath [17,18]. The physical and mechanical properties of Bi-Sr-Ca-Cu-O superconductors are so anisotropic,

however, that unless the grains are highly textured, poor superconducting properties result [17]. Thus, successful consolidation of Bi-Sr-Ca-Cu-O may require achievement of both high density and substantial preferred orientation of the grains.

This work will report on sintering of bulk 2212 and 2223. Since these phases are so difficult to consolidate effectively, they are often fabricated as composites with Ag sheaths or as films on Ag substrates. Ag is the only metal that is compatible with Bi-Sr-Ca-Cu-O superconductors [19,20], and it is also effective in promoting densification through formation of a liquid that melts at a lower temperature than does the superconducting phase [21].

EXPERIMENTAL METHODS

The composition selected for the 2212 powder was $\text{Bi}_2\text{Sr}_{1.7}\text{CaCu}_2\text{O}_x$, which has been found to yield 2212 of excellent phase purity [22]. 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, screened through a 30-mesh sieve, ground lightly with an agate mortar and pestle, and heated in an Al_2O_3 crucible. The heat treatment consisted of a period at 775°C in flowing O_2 at a pressure of 3×10^2 Pa, which caused complete decomposition of the carbonate precursors, followed by heating in air at higher temperatures to form the 2212 phase. Initial heating at 900°C for 0.2 h caused formation of a small amount of liquid phase from the peritectic melting of 2212. This step was introduced to enhance the reaction kinetics [22]. The partial-melt treatment was followed by heating for 48 h at 835 – 845°C . The resultant powder consisted of the 2212 phase and less than 5% total of the $\text{Bi}_2\text{Sr}_2\text{CuO}_x$ (2201) phase [1,2] and Ca-Cu oxides.

For the 2223, a starting stoichiometry of $\text{Pb}_{0.4}\text{Bi}_{1.8}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ was used [3,23]. (The Pb addition is needed to stabilize the 110 K superconducting phase [3,23].) Unlike 2212, 2223 cannot be heat treated effectively above the incongruent melting temperature. Significant phase segregation occurs and recovery of the superconducting phase through a diffusion mechanism is limited. Preliminary data have shown, however, that reactive-phase sintering, in which a transient liquid is employed, can produce dense, textured final products.

The 2223 powder was prepared by mixing appropriate amounts of PbO , Bi_2O_3 , SrCO_3 , CaCO_3 , and CuO powders and calcining under vacuum to 750°C and then in air at 800°C . The purpose of the vacuum was to ensure that CO_2 was removed from the starting materials. The calcined powder consisted of 2212, 2201, and a complex alkaline-earth cuprate. This partially synthesized powder was reacted to form the 2223 phase during subsequent sintering.

For all of the specimens, the final phases were studied by X-ray diffraction and differential thermal analysis (DTA). The microstructures were examined by scanning electron microscopy (SEM) and energy dispersive spectroscopy.

RESULTS AND DISCUSSION

Pellets for the 2212 sintering studies were uniaxially cold pressed to about 50% of the theoretical density. Sintering was conducted in air at 800 to 910°C . The onset of melting in air for the 2212 phase used here was about 885°C [22], 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 of 6.5–6.6 g/cm³. This density did not change appreciably with time and was not a strong function of temperature. This lack of densification from solid-state sintering has been observed previously [6-8]. It was due, in part, to rapid initial grain growth. As shown in Fig. 1, however, for microstructures of randomly oriented grains, little total grain growth occurred. After the initial growth, the platelike grains impinged upon each other and essentially stopped growing. Subsequent diffusional processes were incapable of causing additional densification or significant grain growth to take place because of the highly anisotropic diffusion characteristic of the 2212 phase.

As shown in Fig. 2, when partial-melting heat treatments were used, very large, aligned microstructures resulted. Alkaline-earth cuprates were produced during melting. Upon cooling, the 2212 reformed, but in most cases, some of the alkaline-earth cuprates remained in the final microstructure. The densities of partially melted pellets averaged 80–85% of theoretical after a heat treatment in air that incorporated 0.2–0.5 h at 900°C. The densities were higher when thick films were partially melted on substrates because of substantially better preferred orientation of the grains induced by the presence of the substrate (Fig. 2).

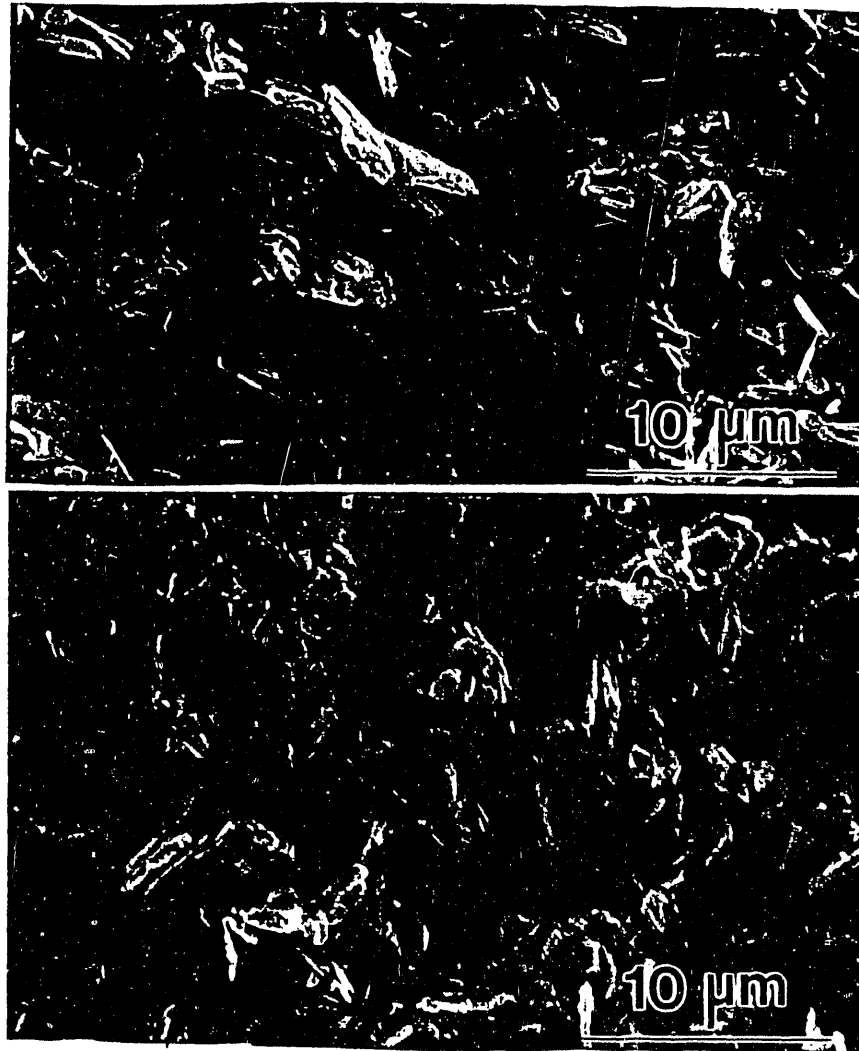


Figure 1. SEM photomicrographs of 2212 pellets sintered in air for 18 h at (a) 800°C and (b) 835°C; note that in (a) and (b) the grains are randomly oriented and approximately the same size.



Figure 2. SEM photomicrograph of 2212 pellet sintered in air at 900°C for 0.2 h, and then at 850°C for 18 h.

It has been found that specimens that were partially melted have much higher critical current densities than did those that were sintered entirely in the solid state [6,24]. The reasons for this effect are not known with certainty, but it is clear that in the absence of a liquid phase during sintering, the connectivity between grains in 2212 is poor.

No studies were conducted in an oxygen partial pressure (P_{O_2}) other than air. Unlike the high-temperature superconductor $YBa_2Cu_3O_x$, the 2212 phase does not exhibit significant changes in stoichiometry with changes in P_{O_2} [1]. Thus, one may not expect sintering to be affected strongly by P_{O_2} . Furthermore, there is evidence that the 2212 phase is stable over a limited range of P_{O_2} and air is within that range [25].

Results similar to those for 2212 have been obtained for the 2223 phase. Pressed pellets were placed on Ag substrates and heat treated between 840 and 860°C. Partial melting was observed above 850°C. A study was therefore carried out as a function of time at 850°C. Very close control of the temperature was required for this study; a thermocouple placed adjacent to the specimens during each run. The density results are summarized in Fig 3. The pellets became more dense initially, suggesting at least some liquid-phase formed. A retrograde densification process [7] occurred for longer times as a result of anisotropic grain growth of particles of nearly random orientation, which indicates that the total concentration of liquid must have been small.

The interior and the region of one pellet near the Ag substrate were examined by SEM (Fig. 4). The bulk of the specimen exhibited the characteristic platelike grain morphology and a large amount of porosity. The region near the Ag interface exhibited larger grains and, at the interface, a high degree of grain alignment. It is suggested that grain growth was enhanced near the Ag substrate

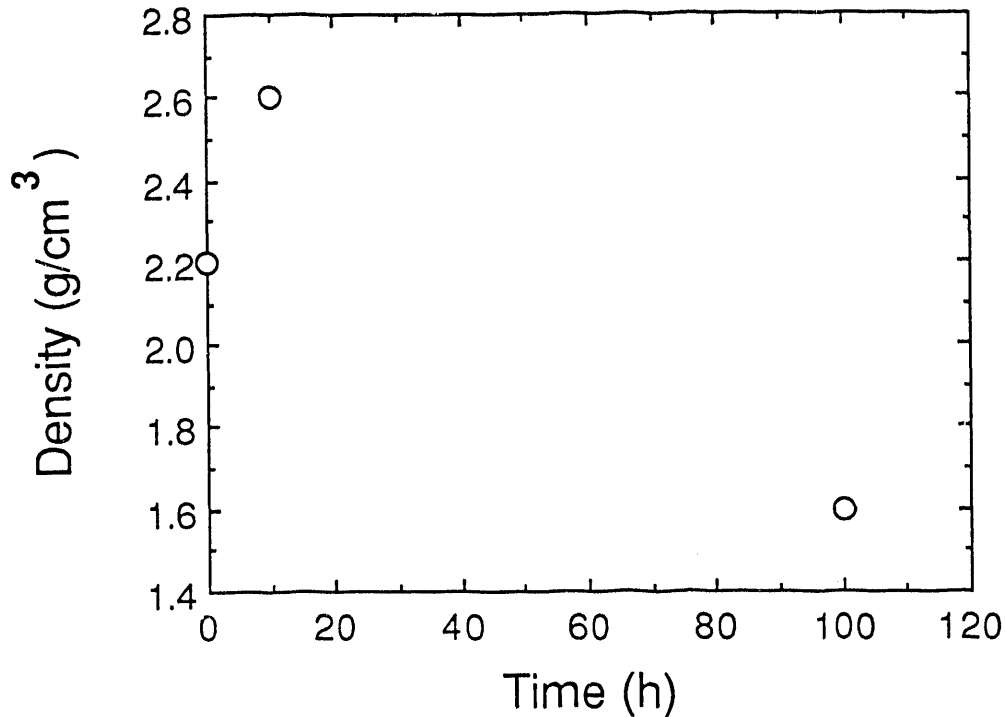


Figure 3. Density versus time for 2223 pellet sintered on Ag in air at 850°C.

owing to a melting reaction [21] between the 2223 and Ag. DTA data support this conclusion [26]. It has not yet been determined how much liquid was formed by the interaction between 2223 and Ag.

Additions of Ag particles to the pellets can improve the density substantially. Specimens greater than 90% dense can be fabricated routinely. Phase purity can be a problem, however. Most of any Ag addition will migrate to grain boundaries. Segregation of Cu to these Ag-rich regions has been observed [27]. In addition, Ag will diffuse relatively rapidly into Bi-Sr-Ca-Cu-O superconductors, although the solubility limits are unknown at present [28]. It has been established that Ag will diffuse into the $\text{YBa}_2\text{Cu}_3\text{O}_x$ superconductor [29-31] and that Cu from the $\text{YBa}_2\text{Cu}_3\text{O}_x$ will diffuse into Ag [32]. It is expected that the situation will be similar for the Bi-Sr-Ca-Cu-O superconductors, which share the Cu-O layer structure with $\text{YBa}_2\text{Cu}_3\text{O}_x$.

Although Ag does not appear to affect superconducting properties appreciably in most cases, as discussed, its effect on processing is pronounced. An extreme example of the effects of Ag on microstructural development during sintering of Bi-Sr-Ca-Cu-O superconductors is shown in Fig. 5. An Ag-clad 2212 tape produced by a standard powder-in-tube method consisting of swaging, drawing, and flat rolling [17] was heated for 15 min at 920°C in flowing Ar, cooled to 815°C, and then annealed in flowing air for 44 h. A substantial amount of melting occurred during the heat treatment. Dissolution of the Ag by the 2212 grains that grew upon cooling resulted in the grains growing into the Ag sheath [33]. Because of the interaction between the two phases, when partial-melt heat treatments are used for Bi-Sr-Ca-Cu-O/Ag composites, attempts are made to



Figure 4. SEM photomicrographs of 2223 pellet sintered on Ag foil for 100 h at 850°C in air: (a) center of pellet, (b) region near Ag foil, and (c) at Ag interface; the presence of the Ag enhances densification and grain growth through formation of a liquid phase.

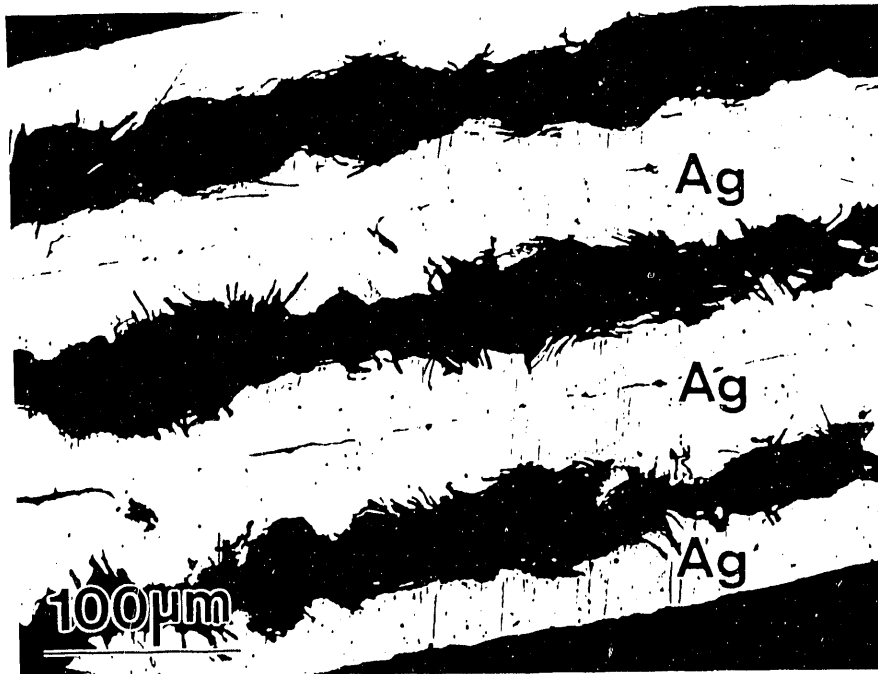


Figure 5. Optical photomicrograph of Ag-clad 2212 powder-in-tube tape for in which the 2212 core has grown into the Ag sheath.

have the grains oriented as much as possible with their a-b planes parallel to the Ag interface. Since the grain growth occurs almost entirely within the a-b plane, intrusion into the Ag is limited by this configuration. Thus, the integrity of the Ag sheath is preserved and the beneficial effects of a transient liquid phase can be realized.

SUMMARY

Conventional solid-state sintering does not appear to be an effective means of densifying the 2212 or 2223 superconductors. Partial melting heat treatments can be used to help densify 2212, but because of gross phase separation, not 2223. Reactive sintering by a transient liquid can be effective for sintering of 2223. Metallic Ag can be used to create that liquid.

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