EXPLOSIVE CONSOLIDATION OF (Bi,Pb)–Sr–Ca–Cu–O SUPERCONDUCTOR POWDERS DURING POWDER–IN–TUBE PROCESSING*

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Abstract

Superconducting (2212) Bi-Sr-Ca-Cu-O (BSCCO) and BSCCO-Ag composites were explosively consolidated in silver tubing and then drawn and rolled into tapes. The silver-sheathed tapes were then subjected to repeated cycles of pressing and heat treatment, which resulted in enhanced texturing and grain growth and a subsequent increase in critical current density (J_c). The effect of silver flake additions to the superconducting powder further increased texturing and J_c, with optimal properties occurring in powders with 10 vol.% silver flake. Density measurements on the superconductor tapes showed that near-theoretical densities had been achieved at the end of the thermomechanical treatment (TMT). Scanning electron microscopy indicated that grain alignment increased after TMT, with an apparent reduction in grain size after the fourth treatment. X-ray diffraction studies showed that grain orientation and conversion of 2212 to $Bi_2Sr_2Ca_2Cu_3O_{10-x}$ are improved when explosive consolidation is introduced before the drawing step in the powder-in-tube process.

MUCH OF THE RECENT RESEARCH ON HIGH-TEMPERATURE SUPERCONDUC-TOR (HTS) CERAMICS has focused on BiSrCaCuO compounds because of their relatively high superconducting transition temperatures (T_c), good phase stability, low toxicity, and low material costs. Two compounds are of the most interest: $Bi_2Sr_2CaCu_2O_{7-x}$ (2212), which exhibits a T_c of ≈90 K, and $Bi_2Sr_2Ca_2Cu_3O_{10-x}$ (2223), which exhibits a T_c of ≈107 K. Typically, the properties of 2212 are superior at 4.2 K at high magnetic fields, while the properties of 2223 are superior at 77 K at low magnetic fields (1).

One popular way to fabricate ceramic superconductors is the powder-in-tube (PIT) approach. Ceramic precursor powder is placed in silver tubes, which are then drawn into "wires" ≈2 mm in diameter by accepted techniques for drawing metal wire. These wires are then rolled in multiple passes into "tapes" with final thicknesses of ≈0.2 mm. The resulting tapes have a somewhat densified but highly fractured ceramic core with a silver exterior (which lends structural support and environmental protection) and are reasonably flexible (2).

The tapes then undergo a series of thermomechanical treatments (TMTs), which are the key to the PIT process. Each TMT consists of uniaxial pressing of the tape (or a proprietary rolling process for the fabrication of samples longer than a few inches), followed by a sintering heat treatment of 50 or 100 h. Ultimately, samples are treated between four and six times. A specific sample is referred to by the sum of its sintering times, for example, a 250-h sample (3). The samples are evaluated between treatments so that a progression of property changes can be illustrated. The TMTs have two primary effects: one is that much of the precursor powder (consisting of mostly 2212) is converted into 2223, and the other is that the microstructure becomes aligned and textured, and thus the tapes exhibit superior electrical properties, such as a high critical current (J_c) capacity, along the length of the tape (2).

A common improvement to PIT fabrication of HTS ceramics has been the use of silver powder along with the ceramic precursor powder when filling the silver tubes prior to drawing. The composite is then processed exactly like the pure ceramic. The improvements, which are due to the high ductility of silver and are primarily observed in mechanical properties (mainly strength and fracture toughness) (3) and J_c are attributable to increased texturing of the superconductor (4).

A novel approach to PIT fabrication is the use of explosive consolidation prior to the drawing step. It has been demonstrated that explosive consolidation can usually attain high densities in resultant compacts, usually 94–99% of theoretical (5). In addition, explosive treatment of ceramics can result in unique nonequilibrium microstructures with extremely high defect densities that do not anneal out as do defects that are introduced by mechanical deformation or radiation damage. A possible result is shock-induced recrystallization, in which during subsequent deformation (i.e., the subsequent steps of PIT processing), the ceramic recrystallizes at points of high stress and thus facilitates further plastic deformation (6).

The purpose of the present study was to examine the effect of explosive consolidation and various amounts of silver flake additions on end-product superconducting 2223 tapes that were fabricated by the PIT process with 2212 precursor powder. It was hoped that the high densities of the HTS ceramic in the tape would lead to J_c values that are higher than those of tapes made with loose powder in the tubes. In addition, because microstructural differences are expected in explosively treated ceramics, the microstructures of the final tapes must be examined and quantified. This was done by scanning electron microscopy (SEM). In addition, X-ray diffraction (XRD) was used to determine the degree of 2212-to-2223 conversion and the degree of texturing of the 2223.

Experimental Procedure

The starting powders consisted of calcined 2212 powder with lead oxide and calcium cuprate additions to enable formation of 2223. Silver flakes were added to some of the pure BSCCO powders to form mixtures of 10, 15, and 20 vol.% silver. All compositions were ball-milled to ensure complete mixing.

The powders were uniaxially packed under a pressure of 300 MPa in silver tubes (6.35–mm outer diameter, 4.35-mm inner diameter) that were already in low-carbon steel canisters. Steel caps were welded onto the canisters, which were then ready for the explosive consolidation step. Details of the assemblies are shown in Fig. 1.

The steel canisters were centered in 6-in.–diameter buckets, then filled with ANFO (ammonium nitrate/fuel oil) explosive. The explosion yielded a calculated radial pressure of ≈10 GPa. The consolidated composite rods were then extracted from the canisters and processed by the PIT method, which entailed drawing the rods through a series of dies and then subjecting them to multiple rolling passes that produced silver-sheathed BSCCO or BSCCO/Ag composite tapes. The tapes were then

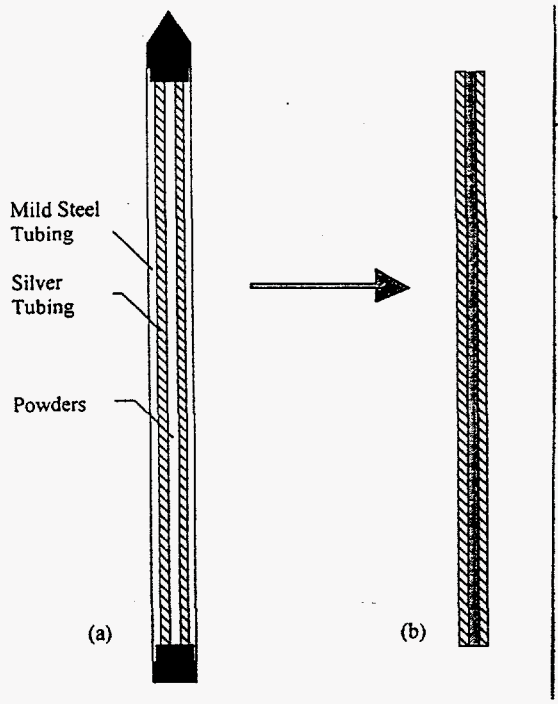


Fig. 1 - Explosive consolidation assembly: (a) sample is ready to be consolidated; in (b), consolidated rod has been extracted from the steel canister after the explosive consolidation step.

sectioned into short samples and sintered for 48 h in static air at 840°C. Samples for further heat treatment were pressed at ≈1000 MPa, then sintered for 100 h at 840°C, with the process repeated for samples that received third and fourth heat treatments.

The J_c values of the tapes were measured at 77 K with a standard four-probe DC setup against a 1–μV/cm criterion. Densities of both the consolidated rods and the final tapes were measured with an 86% glycerol/water solution and the Archimedes method of weighing samples both dry and wet. Microstructures of the samples with 10 vol.% silver were examined by SEM under relatively low magnification (500 and 1000x). A qualitative phase conversion analysis was performed by XRD, which compared the intensity of the 2223 (0 0 14) peak to that of the 2212 (0 0 12) peak. Two textural analyses were performed. The first was a qualitative comparison of the intensity of the 2223 (0 0 14) peak with the intensity of the 2223 (1 1 14) peak (to compare with published data). The second was a quantitative textural analysis, performed by calculating the Lotgering orientation factor f from the discernible 2223 peaks in each sample with the formula $f = (p - p_0) / (1 - p_0)$. (In the equation, p is the ratio of

the sum of the peak intensities of oriented peaks to the sum of all of the peaks, both oriented and unoriented, for the sample in question; and p_o is the same ratio, but for a randomly oriented powder sample.) The value of p_o is used as a constant throughout the analysis (7); in this study, it was determined from tabulated powder diffraction file intensity values, because a randomly oriented powder specimen could not be prepared reliably.

Results and Discussion

Critical Current and Critical Current Density. Figure 2a illustrates the effect of the thermomechanical treatments on the critical current (I_c) of the tapes. The best sample transported 36 A, and the best properties were attained after the fourth heat treatment of samples that contain 10 vol.% silver. This contrasts with the results of other researchers, who report superior I_c at 15 vol.% silver (3). It is generally believed that the increase in I_c with silver content is due to the presence of elongated silver particles, which improve grain alignment and increase connectivity between the grains. Degradation of properties occurs with increasing silver content, and can be attributed to a reduction in the volume fraction of the superconducting phase.[4] It has also been suggested that in this case, the relatively low but increasing concentration of silver particles might interfere with successive layers of grain nucleation and thus cause a decrease in the I_c of the tape (8).

To obtain Fig. 2b, cross-sectional areas of the tapes were used to calculate the J_c of the tapes. The peak at 10 vol.% silver is now more pronounced than the other peaks, especially when compared with pure BSCCO samples. The more pronounced peak is caused by smaller measured cross-sectional areas in the silver composite tapes, which should be due to the improved reduction properties that exist in the Ag/BSCCO composite tapes during the deformation process. Because the cross-sectional areas of processed tapes are relatively large, the highest J_c value obtained in this study was only 17,000 A/cm^2, which does not compare favorably with J_c values in published work (9). This can be attributed to the poor reduction properties of the consolidated ceramic during the drawing process (resulting in cross-sectional areas approximately twice as large) when compared with the normally unconsolidated powder in the silver tube used in the PIT process.

Densities Densities of the explosively consolidated rods before PIT processing were ≈85% of theoretical density, with the highest value of 88% occuring in the composite that contained 10 vol.% silver flake. Densities of the processed tapes were 60-70% of theoretical for the 48-h samples, whereas densities of the

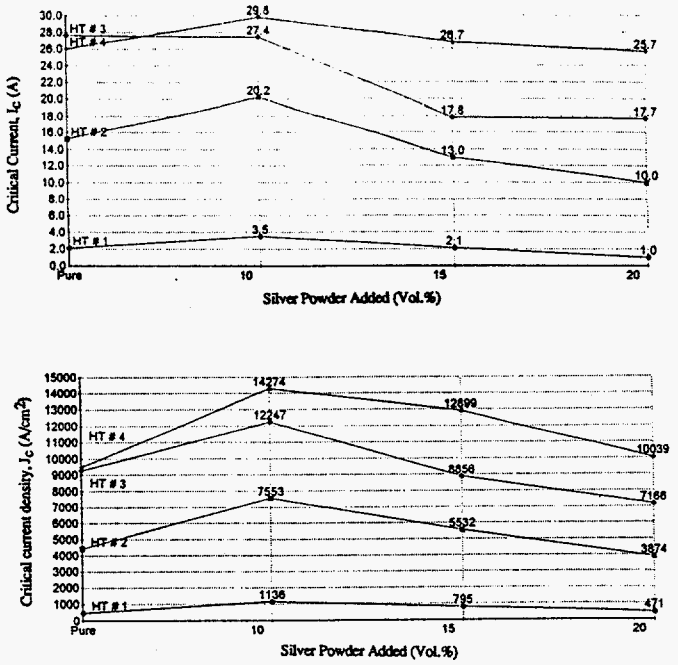


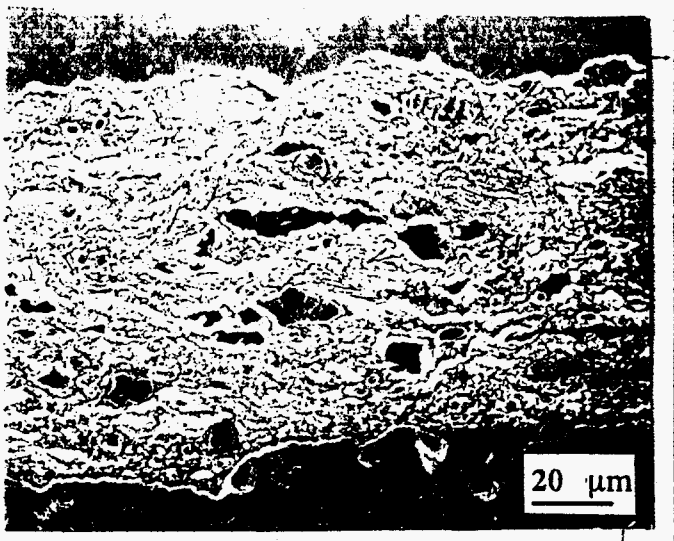
Fig. 2 - Effect of silver content on (a) critical current I_c and (b) critical current density J_c of BSCCO tapes. HT = heat treatment.

248-h samples were 95-100% dense. These results compare favorably with the 70% dense tapes that have been achieved by other researchers, whether the process was initiated with loose powder (50% dense) or cold isostatically pressed powders (70% dense) (10), or even hot isostatically pressed powders (95% dense) (11). It is expected that these near-theoretical densities would lead to better electrical and mechanical properties from the lack of porosity alone, but mechanical properties were not examined in this study.

Microstructure. Figure 3 illustrates a longitudinal cross section of a tape with 10 vol.% silver prior to heat treatment. Although heavily deformed silver particles, secondary darker phases, and an irregular silver sheath/ceramic core interface can be seen (especially in the higher-magnification photomicrograph), no desired microstructure is visible.

Figure 4 depicts the microstructure of a tape with 10 vol.% silver after the first heat treatment. Excellent grain structures can be observed, but visual examination shows that grain alignment is relatively poor and the silver/ceramic interface is still somewhat irregular.

Figure 5 shows that grain alignment is improved by the second heat treatment, but in Figs. 6 and 7 (the third and fourth heat treatments, respectively), the grains appear to be smaller and visual evaluation of grain



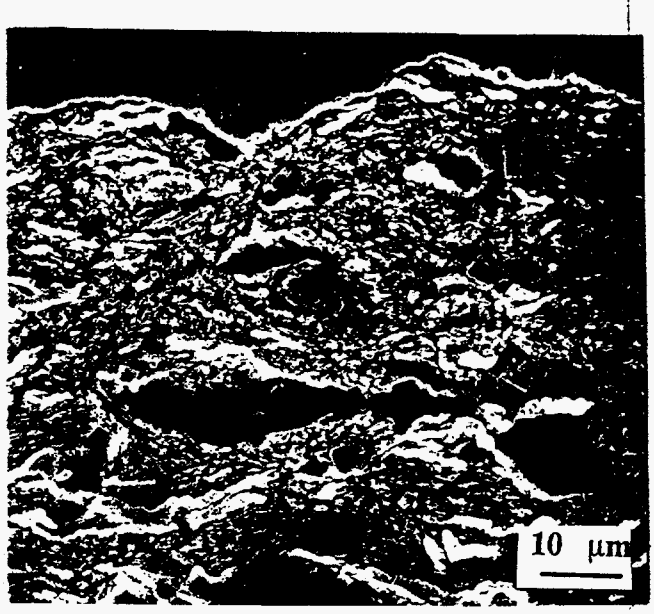
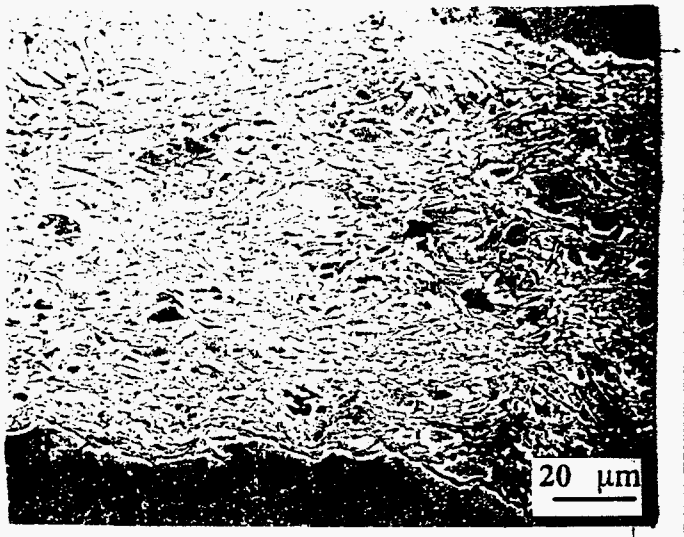


Fig. 3. SEM photomicrographs in two magnifications of longitudinal cross section of as–rolled tape, before thermomechanical treatment.



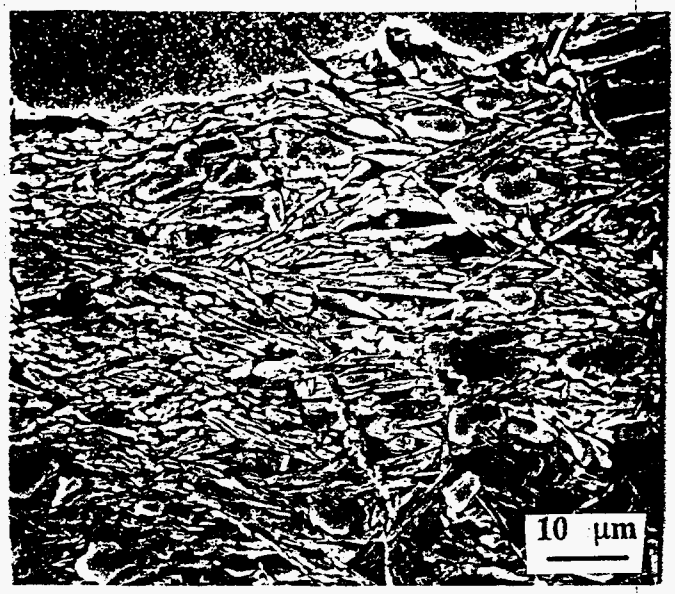
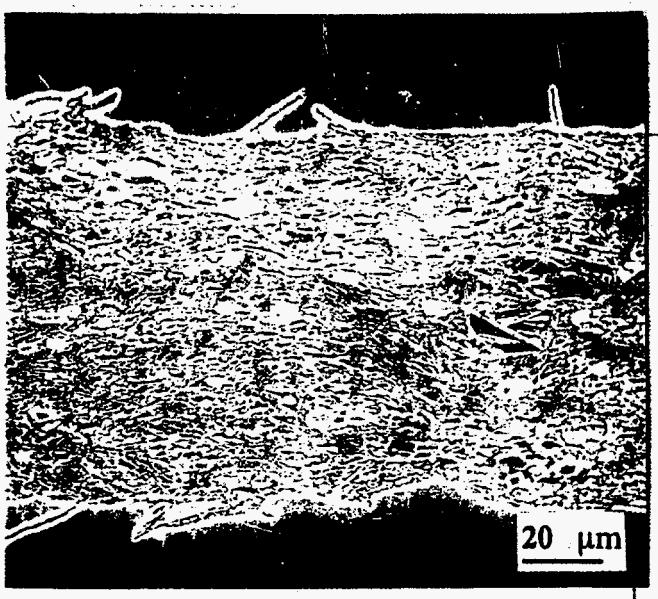


Fig. 4 - SEM photomicrographs in two magnifications of tape after first heat treatment (48 h).

alignment becomes difficult. It can be seen that the interface between the silver sheath and the ceramic core becomes very uniform at the end of the TMT schedule.

Phase and Textural Analysis. Examples of XRD patterns obtained from BSCCO are presented in Fig. 8. Figure 8a was obtained from a pure BSCCO tape after the first heat treatment. Already, most of the primary peaks are in the (0 0 ℓ) orientation of 2223. This is illustrated further in Fig. 8b, where after the third heat treatment, a pure BSCCO tape, exhibits almost exclusively, the preferred orientation of 2223.

To examine the conversion of 2212 to 2223, the (0 0 14) 2223 peaks were compared with the (0 0 12) 2212 peaks. The relative phase content was represented by the peak intensity ratio of 2223 (0 0 14) to 2223



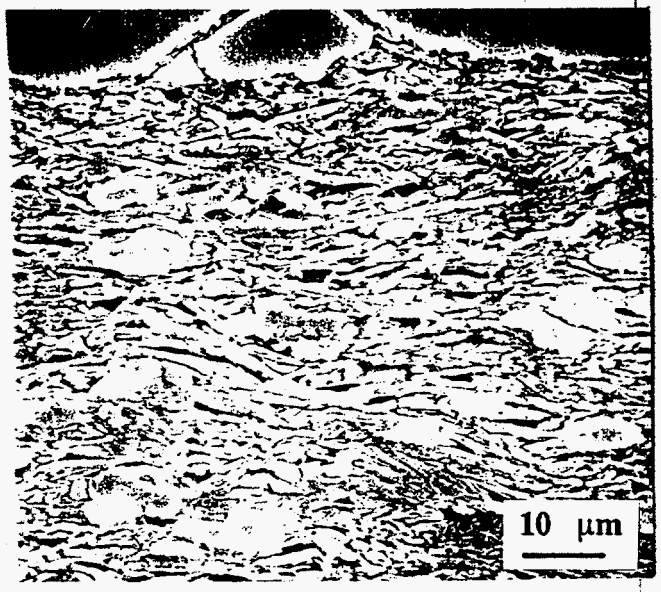
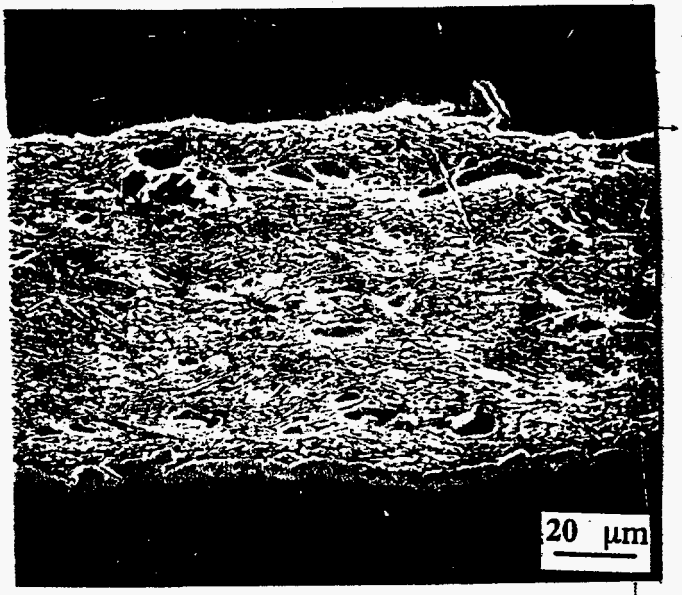


Fig. 5 - SEM photomicrographs in two magnifications of tape after second heat treatment (148 h).



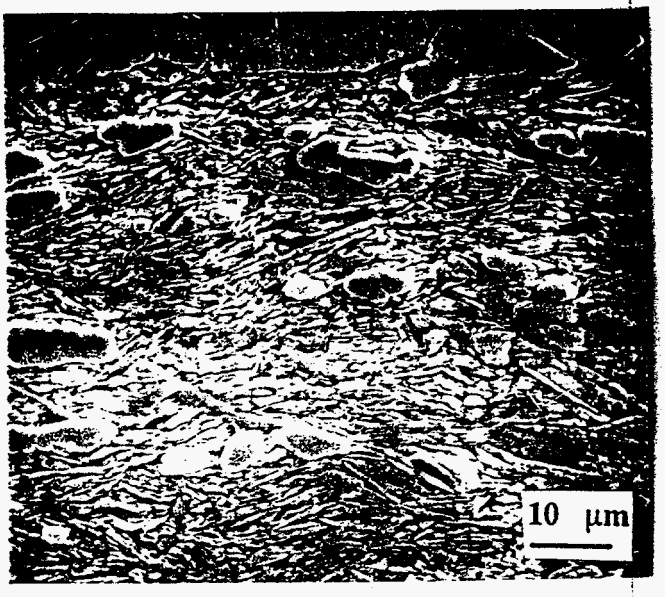
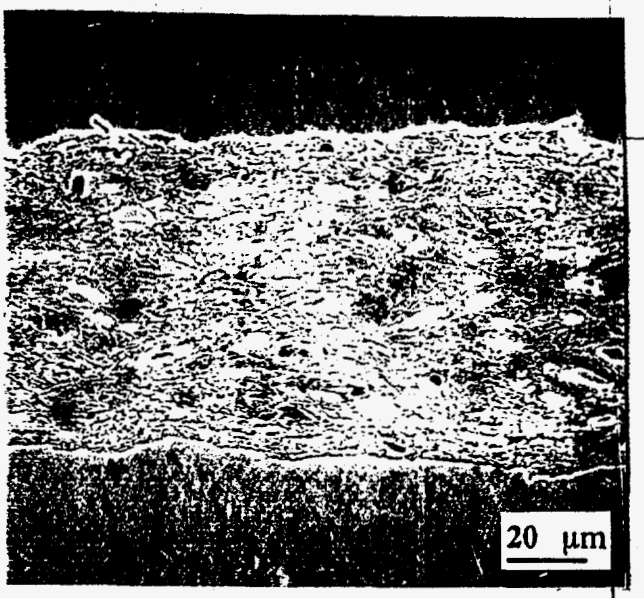


Fig. 6 - SEM photomicrographs in two magnifications of tape after third heat treatment (248 h).

(0 0 14) + 2212 (0 0 12). Although this is not a quantitative analysis, it was chosen for comparison with published phase conversion studies by Singh et al. (4), and will be used for relative comparisons only.

The phase conversion trend in Fig. 9 illustrates the presence of more 2223 in the tapes, when compared with published work, and stabilization after the first heat treatment. This is in contrast to the lower but steadily increasing intensity ratios of published work (4). Silver additions have the effect of slightly increasing the conversion of 2212 to 2223, which is consistent with work done by Singh et al (4); however, the effect is less pronounced in this study.

The texturing trends that can be seen in Fig. 10 show significantly more texturing in the explosively consolidated samples than in those of Singh et al. (4). It can be seen that the samples with 10 vol.% silver give the best texturing results, with texturing apparently



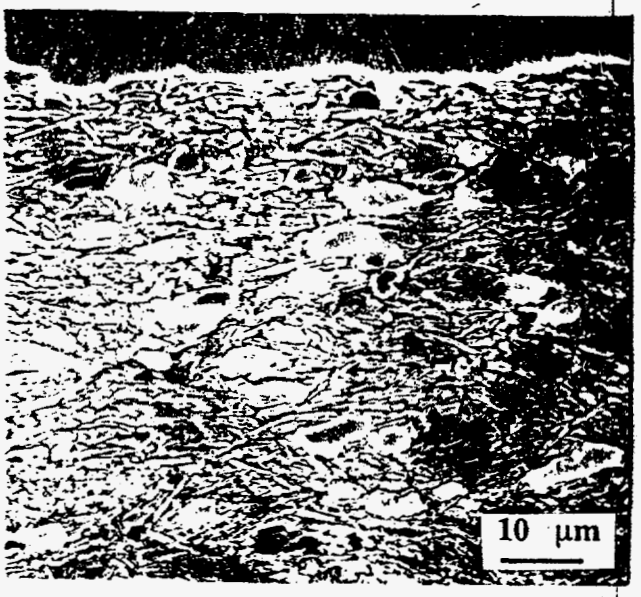


Fig. 7 - SEM photomicrographs in two magnifications of tape after fourth heat treatment (348 h).

leveling off at the fourth heat treatment, as observed with the average of the other compositions we studied. Again, this is not meant to be a quantitative textural analysis and is used only for qualitative comparison.

The data from the Lotgering orientation factor calculations are illustrated in Fig. 11. They detail a high degree of orientation, with a maximum of 91% orientation of the grains in the 10 vol.% Ag samples after the third heat treatment. Orientation trends after the

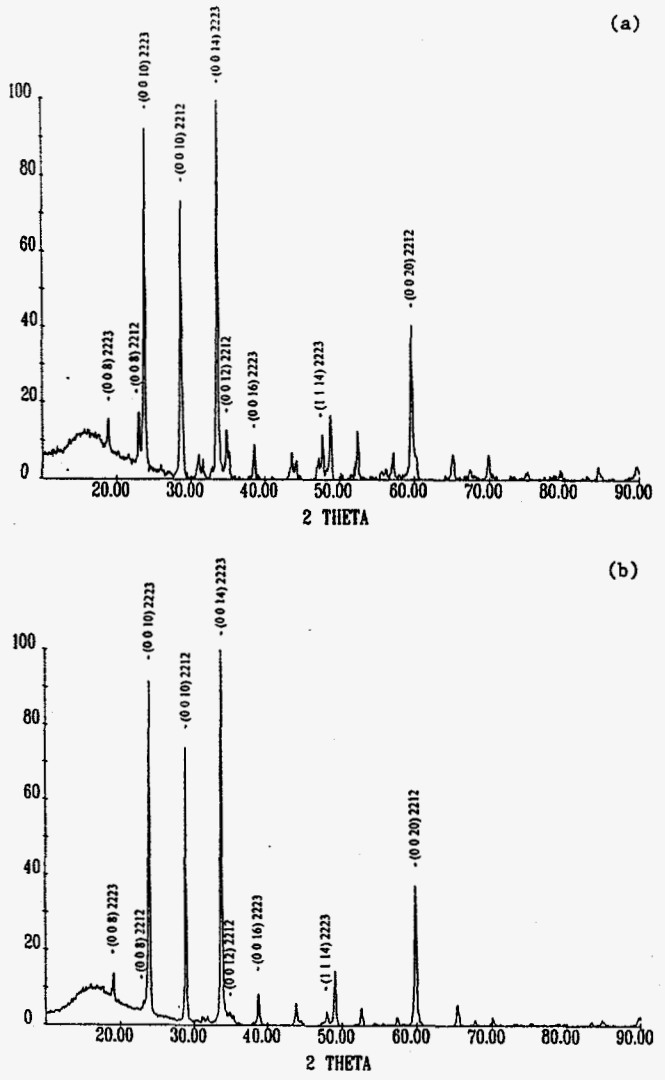


Fig. 8 - XRD plots of pure BSCCO tape after (a) first heat treatment (48 h) and (b) third heat treatment (248 h).

fourth heat treatment are inconclusive, because some compositions show an increase while others exhibit a decrease.

Conclusions

Although the I_C values of tapes produced by explosive consolidation are promising, the relatively large cross-sectional area of the tapes reduce the J_C further than would be expected. This problem may be solved by using silver tubing with a smaller inside diameter to counteract the tendency of the consolidated ceramic to

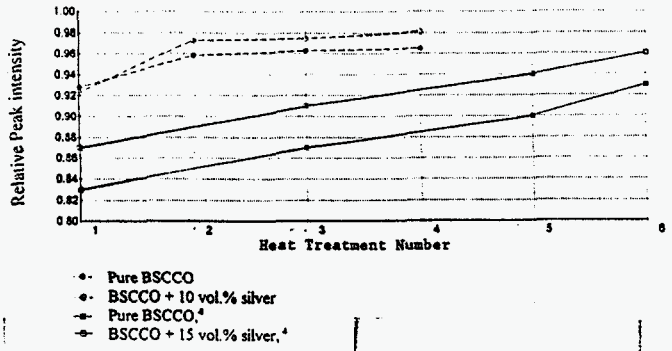


Fig. 9 - Effect of heat treatment on conversion of 2212 to 2223. Relative phase content was represented by peak intensity ratio of 2223 (0 0 14) to 2223 (0 0 14) + 2212 (0 0 12).

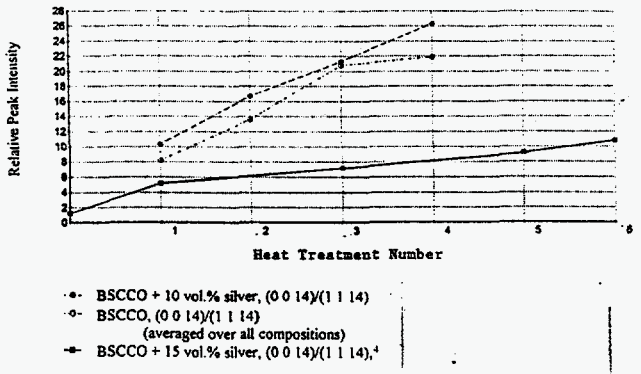


Fig. 10 - Effect of heat treatment on (0 0 ℓ) texturing of 2223 phase. The degree of texturing was represented by peak intensity ratio of (0 0 14) to (1 1 14). Also represented is relative peak intensity before heat treatment.

resist reduction in area during drawing. Studies indicate that the density of the final tapes is almost 100% of theoretical, so better electrical and mechanical properties can be expected from this result alone. XRD studies show that the generation and texturing of 2223 phase is enhanced in samples that have been explosively consolidated prior to the drawing step of the PIT process.

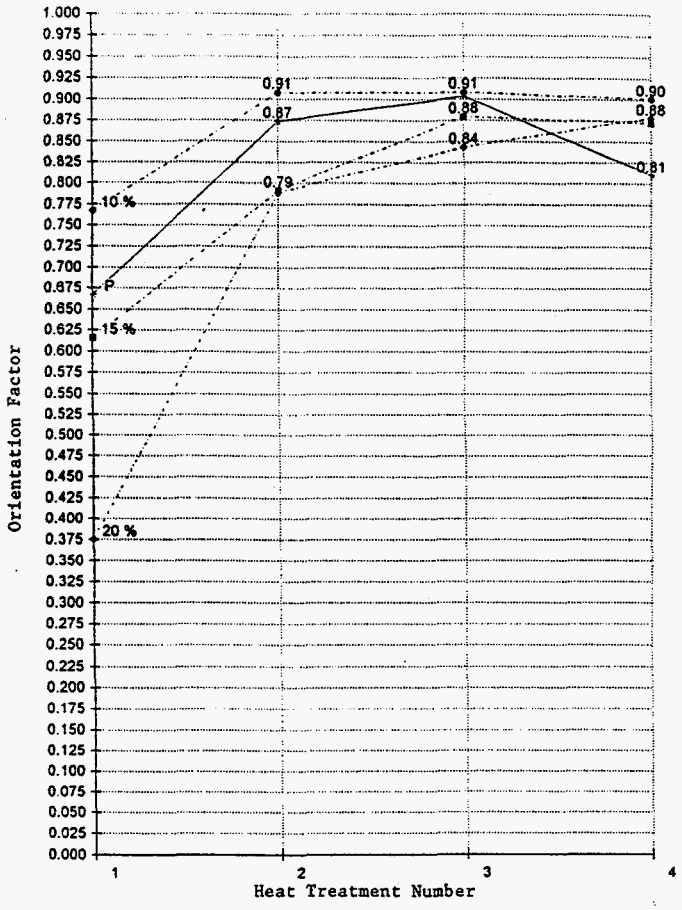


Fig. 11 - Effect of heat treatment on 2223 orientation, using Lotgering orientation factors. Highest orientation occurs with 10 vol.% silver samples.

From this research, we conclude that explosive consolidation is a promising technique for fabricating high-temperature superconductor ceramic tapes. However, further research is necessary to determine the mechanisms underlying the improved properties that we observed.

Acknowledgments

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