Fabrication and properties of BiSrCaCuO superconductors

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Abstract. Fabrication processes for increasing the critical current density J_c in BiSrCaCuO superconductor have been studied. Calcining mixtures of raw material in a reduced oxygen partial pressure or in vacuum after in-air calcination is found to be effective. Intermediate cold work (ICW) i.e. uniaxial pressing, cold flat rolling, etc. incorporated in the sintering Ag-sheathed tape is also effective for raising J_c . From a preliminary experiment on Ag-added tape sample, a combination of both processes appeared to be most effective. The highest J_c obtained is 4.37×10^4 A/cm² at 4.2 K and 12 Tesla. Effects of additional element Ag etc. on J_c have also been described.

Keywords. BiSrCaCuO superconductors; J_c improvement; fabrication process; modification of calcination; silver sheathed tape.

1. Introduction

The BiSrCaCuO superconductor is one of the most important candidate materials for practical use and studies on fabrication processes have intensively continued since its discovery in 1988 (Maeda *et al* 1988). Recently, several technological findings on powder synthesis (Takano *et al* 1988; Endo *et al* 1988) and fabrication process (Asano *et al* 1988) on high- T_c phase enabled one to obtain a high J_c tape which is almost sufficient for practical J_c level in liquid helium temperature (Yamada *et al* 1989; Hikata *et al* 1989). However, if we assume an application in liquid helium, the low- T_c phase as well as the high- T_c phase can be employed because of its high H_{c2} and T_c properties (Enomoto *et al* 1989; Heine *et al* 1989). As for the J_c property, in fact, a small decrease in J_c in increasing the magnetic field for both the low- T_c and high- T_c phases has been reported (Kumakura *et al* 1989; Sekine *et al* 1989). In the present paper, an effective fabrication process consisting of modified calcinations and intermediate cold work during sintering for improvement of the J_c property at 4.2 K is described.

2. Experimental procedures

Pellet and tape samples with initial compositions shown in table 1 were prepared by the processes shown schematically in figure 1. The powder reagents of Bi₂O₃, SrCO₃, CaCO₃, CuO, Pb₃O₄ and NiO were used. Pellet samples were prepared by calcining mixtures in air, pulverized, pressed into a disk and sintered in an atmosphere of Ar:O₂ = 12:1 at 835 ~ 845 °C for 120 ~ 140 hr. Some of them were cold-pressed intermediately during sintering. T_c was measured by the AC magnetization method. The critical current I_c was measured by the four-probe resistive method. Magnetic field was applied parallel to the wide plane of the tape sample. Fractured and polished cross-sections were observed by scanning electron microscopy (SEM). The composition of the phases which appeared in the tape core was analysed by energy dispersion analysis for X-rays (EDAX).

Table 1. Starting compositions for pellet and tape sample

Sample	Bi	Sr	Ca	Cu	M		
					Pb	Ag	Ni
Pellet	0.85	1	1.1	1.6	0.2		
	0.85	1	1.1	1.6	0.2		
Tape A	2	2	1	2			
	2	2	1	2		0.8	
	1	1	1	1			
	1	1	1	1		0.02	
Type B	1	1	1	1		0.8	
	1	1	1	1			0.02
	2	2	1	2			
	0.85	1	1.1	1.6	0.2		

Reagents **Figure 1.** Sample preparation methods.

3. Results and discussion

Figure 2 shows the J_c vs magnetic field, H , for these pellet samples. In order to reduce the Joule-heating damage at the current lead contacts, the samples were shaped in the form of bridge with thinning its middle part as indicated in the inset in figure 2. It is clear that the intermediate cold work followed by sintering is very effective for raising J_c . The sample pressed after initial sintering shows only a very small J_c compared to that of the as-sintered sample. Subsequent sintering after ICW is essential for

Figure 2. SEM micrographs, fractured surface for high- T_c phase pellet sample prepared by (a) conventional sintering and (b) intermediate cold work (ICW) process, respectively.

Figure 3. J_c vs H curves measured at 77 K for high- T_c phase pellet sample prepared by the conventional and ICW process.

completing electric connections within an entire volume of the sample. This is typically observed in the SEM micrographs in figure 3, showing respectively a fractured cross-section of (a) conventional and (b) ICW-processed samples.

Ag-sheathed tape samples were fabricated by the conventional powder-in-tube method. We selected the low- T_c phase because of simpler synthesis, although its T_c is slightly inferior to that of the high- T_c phase. Furthermore, two modifications were tried for enhancing the ICW effect. Figure 4 shows j_c vs B curves for the low- T_c phase Ag-sheathed tape samples. Powders to be encapsulated into Ag tube were made by modified calcinations, in $\text{Ar}:\text{O}_2 = 12:1$ and in-air followed by in-vacuum, besides by conventional in-air calcination. Sintering was carried out in Ar gas atmosphere. It was noticed that addition of Ag resulted in a significant decrease in J_c for in-air calcinated sample.

Figure 5 shows J_c vs B curves for the low- T_c phase Ag-sheathed tape samples, fabricated by the incorporation of ICW, which is the only difference compared to figure 4. In general, ICW raises J_c compared to those prepared without the ICW process. Furthermore, it is interesting that J_c s for the Ag-added tape samples prepared by the modified calcination are larger than those of the conventional calcination. These values are larger than those in figure 4 by about an order of magnitude. However, only the J_c for the Ag-added and calcined in-air sample decreased significantly. This can be

Figure 4. J_c vs H curves measured at 4.2 K for low- T_c phase tape sample fabricated by the conventional powder-in-tube method. The powders were calcined by the quoted c conditions.

Figure 5. J_c vs H curves measured at 4.2 K for low- T_c phase tape sample fabricated by a combined method of ICW with the modified calcination process.

attributed to the difference in microstructures. The microstructure is commonly of a mixture of SrCaCu oxide precipitation embedded in Bi-rich phase and the low- T_c phase. For the Ag-added and in-air calcined samples the SrCaCu oxide precipitations are gross in size as shown in figure 6; the tape sample then has an eventually small effective area for the superconducting current path. On the contrary, when the Ag-added samples are calcined in a reduced oxygen atmosphere or in vacuum, the SrCaCu oxide precipitations disperse finely and play an effective role for improving J_c though the details are not yet known. In figure 7 J_c vs B curves for tape samples prepared by in-air calcination without ICW process are presented. As mentioned above, a combined

Figure 7. J_c vs B curves for tape samples containing a small amount of additional element fabricated by the conventional process.

process of modified calcination and ICW produces high J_c property for both the high- T_c phase and the Ag added low- T_c phase tape sample. Therefore, the J_c values shown in figure 7 are considered not to be the optimized ones. There remains a lot of possibilities that higher J_c on BiSrCaCuO superconductors can be obtained through investigation on items such as suitable composition with additional element, calcination and ICW conditions, etc.

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Figure 6. SEM micrograph on polished surface for low- T_c phase tape core fabricated by the conventional process.