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The influence of the partial Ca substitution on the microstructure of YBCO tapes

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YBCO tapes were obtained by the OPIT (Oxide Powder in Tube) method. As a superconductor two type precursors ($YBa_2Cu_3O_z$ and $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_z$) were used. Calcium substitution increases the number of carriers and pinning centres in the superconducting material. Hot-rolling can provide texturing of the superconducting core. The microstructure was investigated by scanning electron microscopy, X-ray microanalysis and energy dispersive spectroscopy. It was established that hot-rolling increases the critical current density of Ca substituted YBCO tapes.

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1. Introduction

Recently, Y-123 type superconductors with Ca doping have been attracting much attention, because of their strong pinning properties in magnetic field at liquid nitrogen temperature [1,2,3]. From a practical point of view, $YBa_2Cu_3O_z$ (YBCO) is expected to be utilized for the wire material as well as the bulk material. Chemical doping generates substitutional defects and increases the number of the carriers and pinning centres in the superconducting material [3-5]. In our previous reports, it was established that the superconducting properties in $REBa_2Cu_3O_z$ (RE-rare element, briefly REBCO) ceramics with Ca-substitution depend strongly on the phase purity, porosity, alignment of crystallites and properties of the grain-boundaries [3,6,7]. It is well known that the Oxide Powder in Tube (OPIT) method including several cycles of heat treatment and mechanical deformation steps, leads to a higher critical current density (J_c) in Ag- sheathed Bi(Pb)SCCO tapes [8-10]. On the other hand using the hot-rolling leads to a purer crystal structure and better textured superconductors [11]. The YBCO tapes were obtained by the OPIT method and two different regimes of rolling (cold and hot) with two types of precursors ($YBa_2Cu_3O_z$ and $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_z$). The best results were obtained for hot-rolled YBCO tapes with Ca substitution [12]. Additional investigations on the microstructure of such tapes could be very useful to accumulate new knowledge about the processing conditions of superconducting tapes.

In this work, we investigate the influence of hot-rolling and calcium substitution on the phase formation, texture and structure of YBCO tapes.

2. Experimental

2.1. Precursor preparation

$Y_1Ba_2Cu_3O_z$ and $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_z$ samples were synthesized by a optimized ceramic method, including solid-state reaction and sintering [13].

It used the triple heat treatment regime. The first step included the mixing and milling of appropriate amounts of Y_2O_3, CuO, $BaCO_3$, $CaCO_3$ and calcinations in flowing oxygen at 900 °C for 21h. The second step of the heat treatment was at 930 °C for 21h in the same atmosphere, followed by annealing at 450 °C for 2h. The last step started with grindings and pressing the powder into pellets, followed by sintering at 950 °C for 23 h, slow cooling to 450 °C and holding at that temperature for 23 h.

2.2. Tapes preparation by the OPIT method

The tube used was made by pressing and drawing of Ag with 4N purity. The dimensions of the tube were: inner diameter -3.6mm; thickness -1.1mm. The OPIT method including filling up and mechanical packing of the superconducting powder in the silver tube, rolling of the tube until the forming of the tape, thermal treatment and sintering of the 1:2:3 phase – the basic superconducting phase in the YBCO system. For deformation of filled Ag tubes, we chose longitudinal rolling as described in [12]. The rolling was realized in six stages of deformation with equal steps (Fig. 1). The total degree of deformation was 220% for rolled tapes. During "hot rolling" the material was heated in advance up to 825 °C for 1h followed by rolling at room temperature. In this way, obtained tapes were subjected to thermal treatment in oxygen under optimal conditions – heating up to 890 ^{o}C for 21h with isothermal delay, cooling slowly to 450 ^{o}C and keeping at that temperature for 23h.

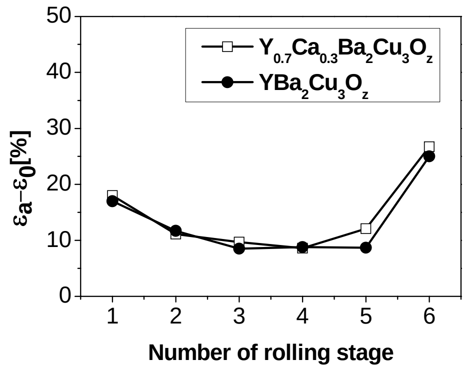

Fig. 1. Difference between the assigned (ε_a) and obtained (ε_o) deformation for each rolling stage.

2.3. Sample analyses

The phase formation of the samples was studied by X-ray powder diffraction analysis using a Bruker D5005 diffractometer with Cu Kα radiation. The microstructure of the tapes was studied with a Jeol JSM-840A scanning electron microscopy (SEM). The chemical composition of the samples was determined by the X-ray microanalyses and using energy dispersive spectroscopy (EDS) on a LINK Analytical AN10000 system. The qualitative and quantitative analyses were carried out at an accelerating voltage of 20 kV. The distribution of the elements inside the superconducting core was visualized by an X-ray mapping technique. Optical images were taken with polarized light, using Nikon, Microphot-FX optical microscopy (OM).

3. Result and discussion

The X-ray diffraction patterns for $Y_1Ba_2Cu_3O_z$ and $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_z$ tapes (Fig. 2) show that they have orthorhombic structures and there are no extra peaks from the impurity phases. Scanning electron and optical micrographs in polished samples of 1:2:3 from a region containing the grain boundary phases was shown in Fig. 3. The micrographs reveal a plate-like structure of the 1:2:3 grains. Their average sizes ranges from 10 µm to 40 µm for the $Y_1Ba_2Cu_3O_z$ tape (Fig. 3A). It can be seen in Fig. 3B that the structure of the superconducting core of the $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_z$ tape has finer grains and both types of tapes are without pores. From the data in Table1, one can see that powders and YBCO tapes have the stoichiometric 1:2:3 superconducting phase.

Table 1. Integral EDX data for elements contents in atomic percentages (at%).

Samples	Y	Ca	Ba	Cu
$Y_1Ba_2Cu_3O_z$ powder	7.2	0	12.4	21.0
$Y_1Ba_2Cu_3O_z$ tape	8.9	0	16.0	22.8
$Y_{0.7}Ca_{0.3}Ba_2Cu_3O_z$ powder	5.7	2.0	12.7	20.8
$Y_{0.7}Ca_{0.3}Ba_2Cu_3O_z$ tape	6.9	2.4	16.5	22.4

The transition temperature (T_c) was defined from AC current magnetic measurements and the critical current density (J_c) was measured by the four contact method. The data from all measurements are given in Table 2. The $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_z$ tape has the highest critical current density.

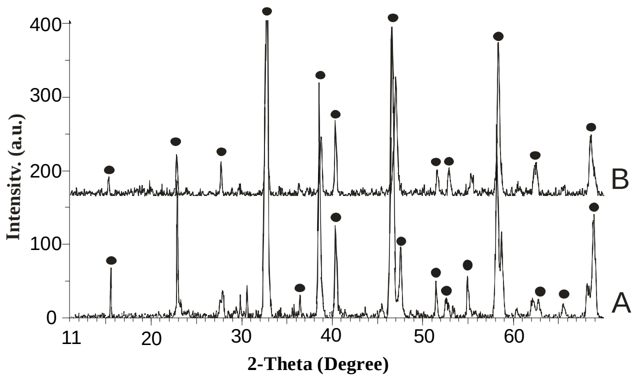

Fig. 2. XRD patterns using Cu-Ka radiation for $Y_1Ba_2Cu_3O_z$ *(A)* and $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_z$ *(B)* tapes. *The symbol (●) indicates the main peaks of the 123 phase.*

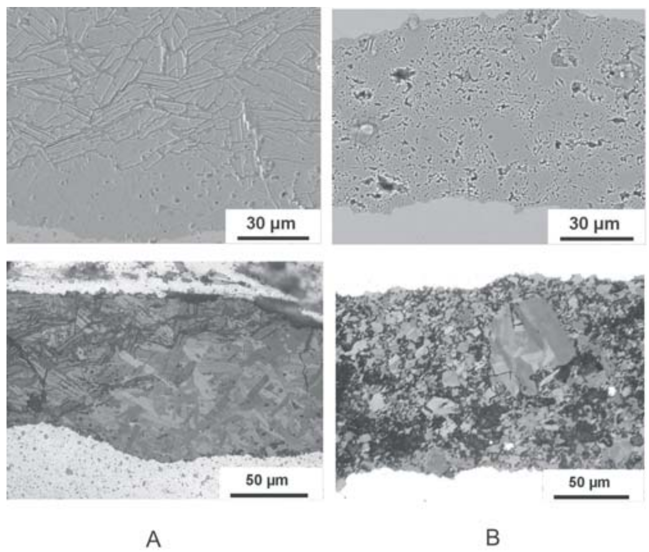

Fig. 3. SEM (up) and optical micrographs (down) of $Y_1Ba_2Cu_3O_z$ *(A)* and $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_z$ *(B)* tapes.

Table 2. The critical temperature (T_c, [K]) and critical current density (J_c, [A/cm^2]) of $Y_1Ba_2Cu_3O_z$ and $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_z$ tapes.

Samples	T_c	J_c	J_c After 3 months
$Y_1Ba_2Cu_3O_z$ bulk sample	91	7.3	7.3
$Y_1Ba_2Cu_3O_z$ hot-rolled tape	90	98.8	144.9
$Y_{0.7}Ca_{0.3}Ba_2Cu_3O_z$ bulk sample	81	6.3	6.3
$Y_{0.7}Ca_{0.3}Ba_2Cu_3O_z$ hot-rolled tape*	81	614.0	733.0

* The J_c of $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_z$ tapes was measured after one year and the value was 965 *A/cm^2*.

4. Conclusion

It is established that hot-rolling technology is suitable for making $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_z$ tapes. The results show that hot-rolled tapes with and without Ca-substitution have orthorhombic 1:2:3 structures with no impurity phases. The superconducting core of the $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_z$ tape has a finer grain structure than the $Y_1Ba_2Cu_3O_z$ tape.

It is shown that the critical current density (J_c) continues to increase with the time, reaching up to 965 A/cm^2 after one year.

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