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Synthesis of Bi-based high temperature superconductors using melt technologies

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Abstract.

To obtain high J_c Bi-based superconducting materials melt-texture techniques were applied. Amorphous precursors were prepared by rapid quenching (cooling rate about 10^3 °C/s) of melted powders. Chemical composition and preparing routes of the starting mixtures were varied. The precursor with starting composition $Pb_{0.2}Bi_{1.8}Ca_1Sr_2Cu_2O_8$ was chosen among others for further investigations because of a maximal content of amorphous phase in it. The sample was crystallized by zone melting and gradient treatment. The dependence of texture extent on sample feeding was stated. The transition from isometric to directional crystallization at the cooling rate about 10°C/min was found. The samples demonstrated J_c values about $6 \cdot 10^4$ A/cm^2 (4.2 K, H = 0 T). Some amorphous impurities on grain boundaries were found by TEM in these samples. One can assume that high J_c values were reached due to a good grain alignment but not to a grain boundary purification.

1. Introduction

It is known that Josephson-like weak links are present at the grain boundaries of polycrystalline high-T_c superconductors and lead to the low critical current densities [1]. To reach high J_c values in bulk materials two problems should be overcome: (i) high-angle grain boundaries (grain misalignment) during current path and (ii) disturbing of chemical composition at the grain boundaries [1,2]. There are at least three possible ways to solve these problems for today. The first one is a melt-texture processing [3] based on a directional solidification of high-T_c phases from melt state under temperature gradient. The second - deformation - texture processing, is a texturing under external mechanical stresses. Such kinds of this method as doctor blade casting, cold rolling are described [4,5]. The last one dealing with a texturing under external action of non-mechanical nature (e.g., external magnetic field [6], liquid-phase epitaxy on a perfect monocrystalline substrate [7]) is well known also.

To obtain high-T_c bulk superconducting material Bi-based phases are more friendly than $YBa_2Cu_3O_{7-x}$ phase. Orthorhombic-tetragonal phase transition taking place in 1-2-3 compound leads to microcracking formation in the volume of material [8]. Other words, additional weak links appear. There is no such problem in the case of Bi-superconductors. Morphological and mechanical features of Bi-based phases are also favourable for producing perfect texture. To another hand, Bi-based superconductors have an enormous potential when applied in the helium region of temperature. Only these ones have J_c values higher than 10^5 A/cm^2 at H > 1T [9].

In this paper the effort to produce Bi-based bulk materials using melt-texture processing is undertaken. Particular attention is paid to making and characterisation amorphous oxide precursors for following melt-texture process.

2. Experimental

Nitrates, carbonates and oxides of Bi, Ca, Sr and Cu (purity better than 99%) were used as starting components. Oxide precursors (samples A2, B2 and C2) were obtained using conventional oxide-carbonate and nitrate (including spray-drying step) routes. Besides that, a part of oxide-carbonate and nitrate mixtures was kept untreated at once (samples A1, B1 and C1).

The precursors ascribed above were placed into alumina crucible and heated at 1200°C for 15 min followed by sucking up melt into silica capillary. After cooling the capillary was fractured and a glass-like hard rod with dimensions about 3x50 mm was extracted out of quartz pieces.

The rods of quenched melt were tested by XRD (Guinier camera FR-552, $CuK_{\alpha 1}$-radiation), TEM (platinum-carbon replicas, SAED - Selected Area Electron Diffraction, JEM-200CX equipped with side-entry goniometer operating at 200 kV), DTA and thermodilatometry (original devices operated at the heating rate 10°C/min), chemical analysis, diamond microhardness measurements, high temperature optical microscopy - HTOM (HM-430, "Union", Japan; temperature region 20-850°C, heating rate 10°C/min) and density measurements.

Directional crystallization of amorphous rods were carried out using zone melting (ZM) and gradient treatment

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Table 1. Properties of RQM.

Sample	Density, % from theor.	Relative dilation at 480°C, %	Relative heat evolving at 480°C, %	Micro-hardness, kg/mm^2	Main phase at 800°C	Chemical composition
A1	76.7	58.0	90.1	340	2201	$Bi_{1.9}Sr_{1.8}Ca_{0.8}Cu_{1.7}O_x$
A2	94.6	2.6	11.9	400	2212	$Bi_{1.8}Sr_{1.9}Ca_{0.8}Cu_{1.6}O_x$
B1	85.9	3.2	57.8	400	2212 2201	$Bi_{1.9}Sr_{2.0}Ca_{0.9}Cu_{1.8}O_x$
B2	83.2	5.6	41.3	420	2212 2201	$Bi_{1.7}Sr_{1.9}Ca_{0.9}Cu_{1.8}O_x$
C1	72.1	82.0	100.0	370	2201	$Bi_{1.6}Pb_{0.2}Sr_{1.9}Ca_{0.8}Cu_{1.9}O_x$
C2	79.9	3.3	37.4	400	2212 2201	$Bi_{1.7}Pb_{0.19}Sr_{1.8}Ca_{1.0}Cu_{2.0}O_x$

(GT) techniques. Sample feeding was varied from 2 to 30 mm/hr with the constant temperature of hot zone in ZM-experiment. On the contrary, the temperature of hot zone was varied from 750 to 830°C with the constant sample feeding (v=8 mm/hr) in GT-experiment. Measured temperature gradient was about 20°C/cm in the case of GT, it was not so in the case of ZM. Temperature gradient during ZM-experiment was estimated as 12°C/cm.

The textured rods were examined by XRD and TEM. Texture extent was determined by SEM (REM-100U, images from polished surface coated by gold film) using stereological methods [10].

Critical current density was determined by surface impedance technique [11] at 4.2 K in magnetic field up to 2.5 T in axial and perpendicular to the current path directions.

3. Results and discussion.

The results of the investigation the rods of quenched melt (RQM) are presented in the Table 1. It is necessary to point out some difference between the chemical composition of precursors and RQM as result of loss of PbO and Bi_2O_3. The changes in the chemical composition of the samples without PbO were not established.

The densities of the samples A1 and C1 are less than that of others and are comparable to each other. Relative changes of these samples dimensions at 480°C also differ about ten times from the others. From this we draw a conclusion, that RQM from oxides and carbonate subdued to amorphization to a greater extent than other investigated samples.

This is also proved by the fact. For the samples A1 and C1 was found out double exothermic peak on the DTA-curve in 510°C-region. This temperature is passed the first crystalline phase - $Bi_2Sr_2CuO_6$ was determinated by X-ray analysis, so this peak was interpreted as the end of the first stage of crystallization. However, if in the case of samples A2, B1, B2, C2 this exo-peak is not substantial, for the samples A1 and C1 it is predominant.

Crystalline inclusions into RQM A2, B1, B2 and C2 can be easily determinated by the TEM-replicas method. The size of these inclusions is about 0.5-1 mm.

Samples C1 and A1 do not exhibit dot reflexes on SADP. At every observation the only one amorphous phase with the spacing d_1=1.6 A and d_2=2.4 A was fixed (see Fig.1).

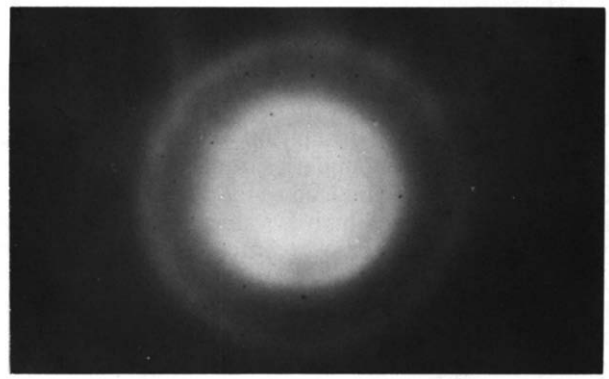

Fig.1. SADP for the sample C1.

The sample C1 was chosen among others for further investigations because of a maximum content of amorphous phase.

The sample was crystallized by ZM- and GT-techniques. The rods with a high axial texture (up to 84%) were obtained. The dependence of grain alignment on crystallization rate in ZM-experiments can be written as follows:

$$P = (83.9\pm1.8) - (1.7\pm0.1)\ v, \qquad (1)$$

where P - texture extent by SEM (%),
v - feeding speed in ZM-process (mm/hr)
(Fig.2).

The transition from isometric to directional crystallization at the cooling rate of about 10°C/min was estimated using this equation.

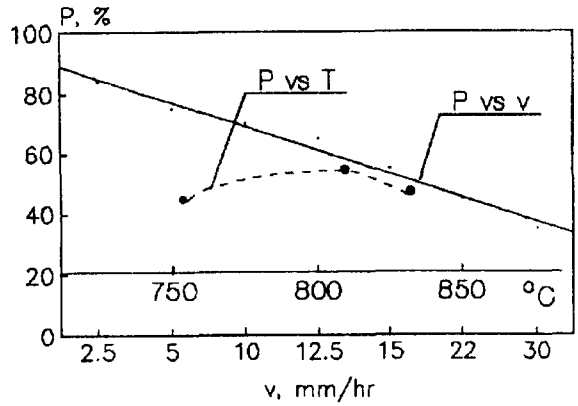

Fig.2. Texture extent vs feeding speed and hot zone temperature plot.

Grain alignment vs feeding speed in the ZM-experiment is shown in Fig.2.

In the case of GT the texture extent has a maximum at 825°C (see Fig.2). It is likely to be connected with crystallization mechanism change. The temperature of sample exceeded 800°C formation of liquid phase was found. This fact was also proved by HTOM-observations.

The intergrain critical current density of the materials decreases with the feeding speed increasing. The materials exhibit a high degree of anisotropy of the critical current. When it goes along the axis of the sample obtained with the feeding speed 11 mm/hr in the ZM-experiment J_c is $5.8 \cdot 10^4$ A/cm^2 in zero field at 4.2 K, and about $3 \cdot 10^4$ A/cm^2 in the field of 2.5 T. Alternative orientation of the sample causes the decreasing J_c to $9 \cdot 10^3$ A/cm^2 in zero field at temperature 4.2 K.

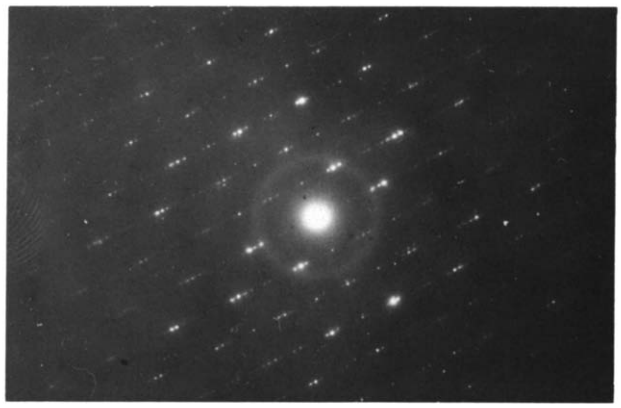

Fig.3. SADP for intergrain space of crystallized material.

According to the TEM-data the material has also a good texture, and SAED image of the grain corresponds to the crystalline phase $Bi_2Sr_2CaCu_2O_8$. Nevertheless, electron diffraction pattern of intergrain space shows the presence of amorphous phase residues causing a characteristic halo (see Fig.3). Consequently, the high values of J_c were obtained thanks to a high mutual orientation of grains along the current path. We are not fully successful in elimination of weak links between the grains of ceramics, since the phase (and, possibly, chemical) composition of the grain boundaries is likely to be a somewhat different from this one of the grain volumes.

4. Conclusion

The presence of crystalline inclusions in amorphous matrix was stated, - the quantity of $Bi_2(Sr,Ca)_2CuO_6$ crystalline inclusions is fewer if Pb-containing component is included into the composition of a precursor and the last one is not a single phase. Much depend on the following crystallization conditions. The critical cooling rate for transferring from isotropic to directional solidification for investigated materials was about 10°C/min. One can assume that the value is applicable not only for ZM- and GT- treatments of Bi containing superconductor but also for another kind of treatment. It was shown that high values of J_c were obtained thanks to high mutual orientation of grains along current path. Nevertheless, deviation in chemistry at the grain boundaries is still present and leads to an additional weak link formation. To eliminate weak links at all the grain purification is necessary.

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