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The study of microstructure of Bi, Pb–Sr–Ca–Cu–O superconductors prepared by multiple intermediate processing

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The influence of a multistep intermediate pressing and sintering process on microstructure and the relation between microstructure and values of critical current density, J_c, in Bi, Pb–Sr–Ca–Cu–O high-T_c polycrystalline superconductors was studied. The J_c values increased with increasing number of pressing and sintering steps, n, only up to a certain value of n. The increase of J_c was reached by improvement of connections between grains due to compacting and by the alignment of superconducting grains in the c-axis direction. The maximal value of J_c was found for $n = 5$. The crack development is responsible for decreasing J_c for a higher number of steps.

1. Introduction

Since the discovery of the Bi–Sr–Ca–Cu–O system [1], it is well known that one of the most serious problems of bismuth-based copper oxide superconducting ceramics is the multiple-phase character. Furthermore, due to strong anisotropic properties of high-T_c superconductors, their electrical and magnetic properties would depend very much on the microstructure of the sample. One of the main problems associated with technical application of the high-T_c oxide superconductors is increasing the critical current density, J_c. Critical current density in Bi, Pb–Sr–Ca–Cu–O high-T_c polycrystalline superconductors depends on their microstructure which can be characterized by size and orientation of grains, density or porosity, and by the presence and distribution of impurities. The usual structure of high-T_c oxide polycrystalline ceramics is that of irregularly shaped crystalline grains. The grain orientation is random, and the interfaces usually contain some impurities, so it is important to know their composition, size, distribution and volume fraction. Polarization optical microscopy and scanning electron microscopy (SEM) with the possibility of energy-dispersive X-ray (EDX)

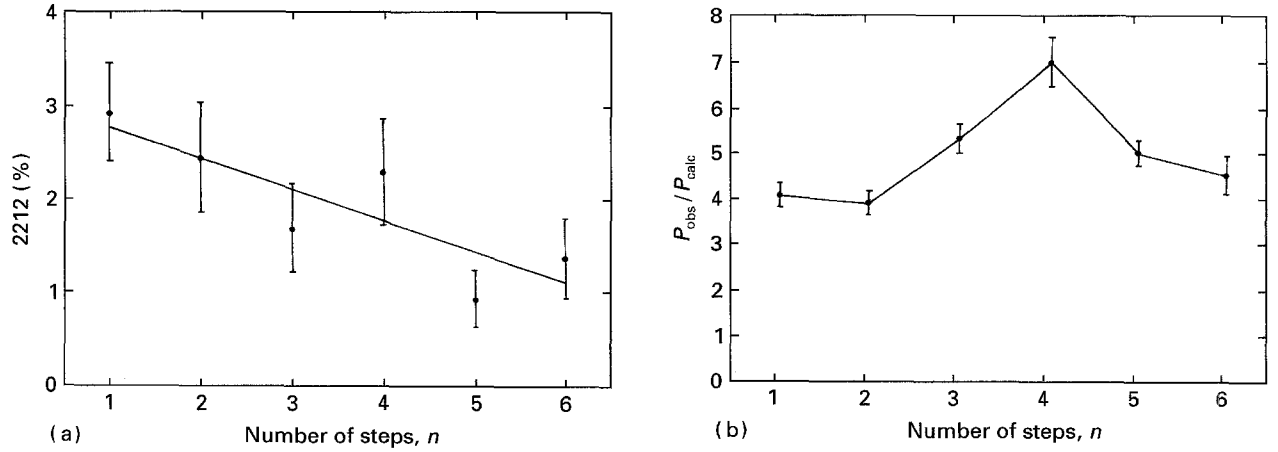

Figure 1 (a) The molar fractions of 2212 phase calculated using the diffraction peaks integral intensities, I (0 0 2), compared to the value obtained from the 2212 + 2223 1:1 molar mixture. (b) The degree of preferred orientation quantified as P_{obs}/P_{calc} using the ratio of diffraction peaks integral intensities $P = I$ (0 0 1 0)/I (1 1 5), where P_{obs} is a value obtained from the surface of a sample and P_{calc} is a calculated value for a disordered sample.

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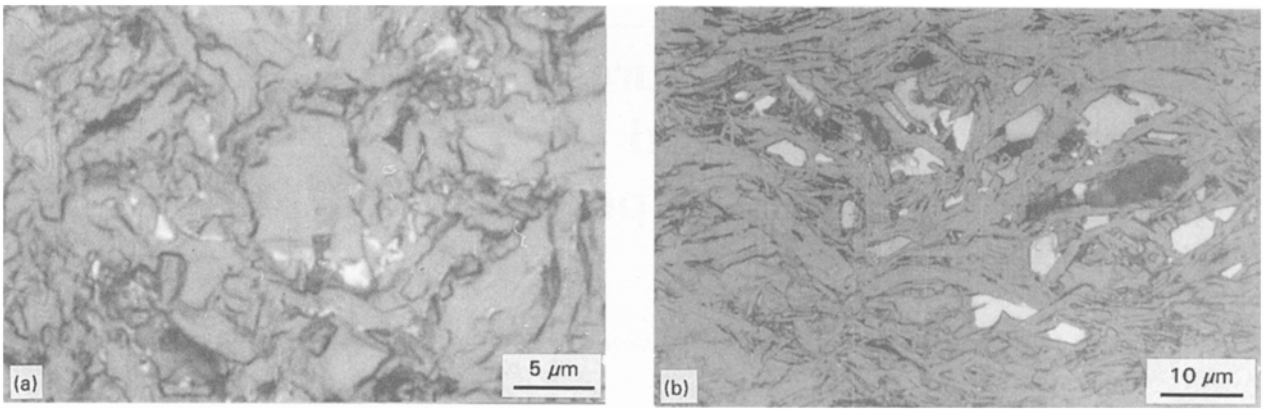

Figure 2 (a) Optical micrograph showing the distribution of phases $(Ca,Sr)_2CuO_3$, $(Sr,Ca)_{14}Cu_{22}O_x$ and CuO on the grain surface. (b) Optical micrograph showing the distribution of the grains of $(Ca,Sr)_2CuO_3$ and $(Sr,Ca)_{14}Cu_{22}O_x$ phases (small white islands) between the grains of Bi, Pb–Sr–Cu–Ca–O.

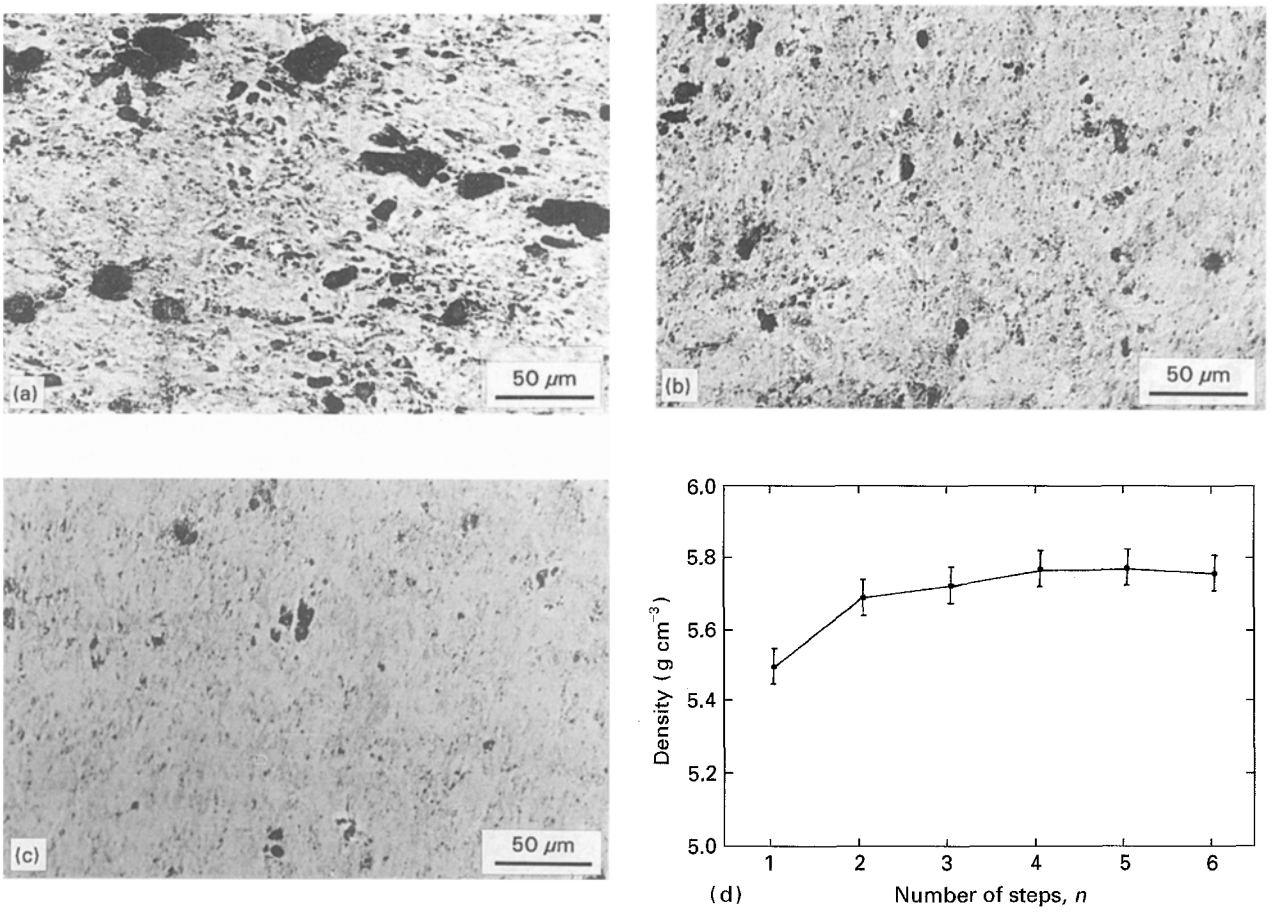

Figure 3 Optical micrographs of the change of density with the number of steps for n = (a) 1, (b) 3 and (c) 6. (d) The dependence of the density of the samples on the number of steps, n.

analysis may be very useful for studying the microstructure of polycrystalline superconductors [2, 3]. These methods provide local information, whereas X-ray analysis provides only average data and resolution is limited by the volume of secondary phases.

Critical current density has already been improved in thick layers at silver substrates and in silver-sheathed tapes [4–7], but much effort must be made to improve it also in the bulk ceramics. Several processes have already been proposed to increase the critical current density, J_c [8–11]. Plechacek [12] reported the influence of multiple intermediate processing on J_c. In the present paper, studies of microstructural development on multiple intermediate processing for Bi, Pb–Sr–Ca–Cu–O polycrystalline superconductors are presented. For each processing step, optical microscopy and the EDX analysis were performed. The X-ray analyses were used to identify the 2223 and 2212 phases.

2. Experimental procedure

Polycrystalline samples with the nominal composition of $Bi_{1.8}Pb_{0.26}Sr_2Ca_2Cu_3O_{10+x}$ were prepared by the common powder metallurgical method from bismuth, lead and copper oxides, and strontium and calcium

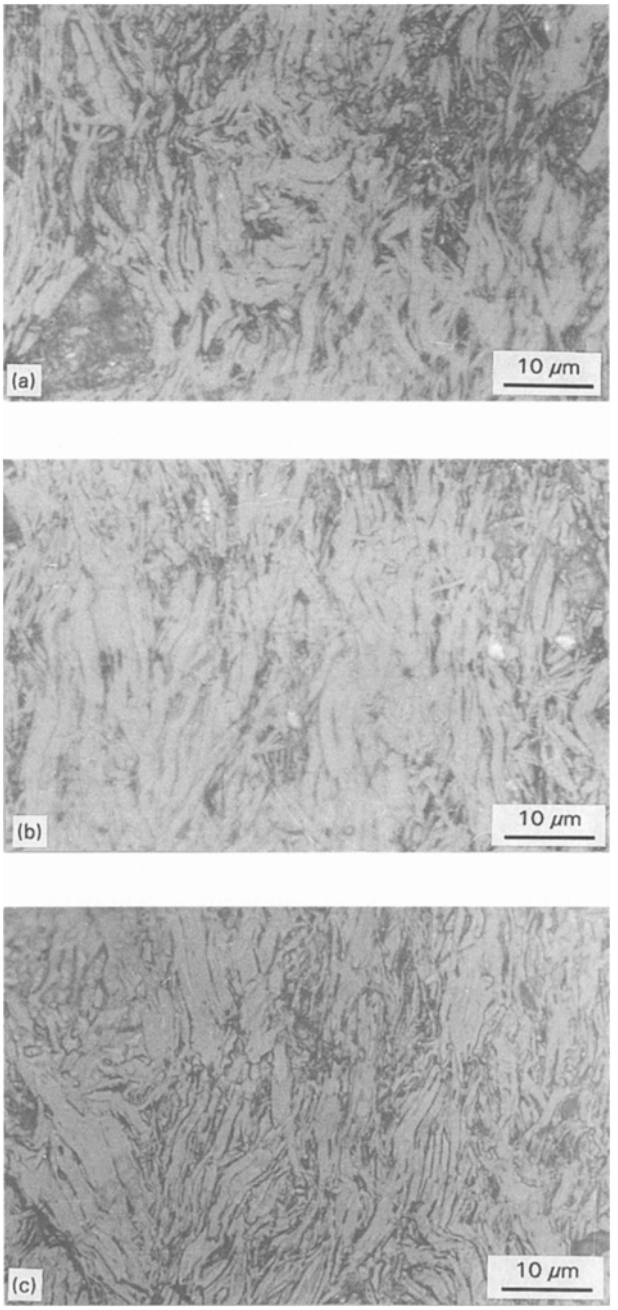

Figure 4 Optical micrographs of the microstructure in the plane parallel to the direction of pressing in samples for (a) $n = 1$, (b) $n = 2$ and (c) $n = 6$.

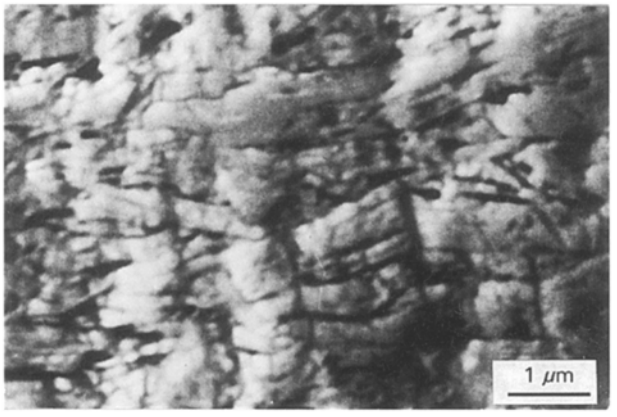

Figure 5 Scanning electron micrograph of the local arrangement of grains in the sample for $n = 6$.

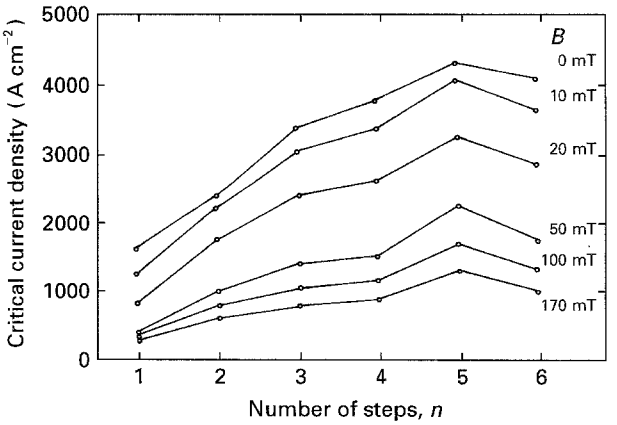

Figure 6 The dependence of J_c at 77.3 K on the number of steps.

carbonates. For more details, see elsewhere [13]. After calcination at 770 °C for 80 in air, subsequent heating at 840 °C for 400 h in a N_2–O_2 atmosphere with oxygen partial pressure of 7 kPa, produced the 2223 phase. The reacted powder was compacted by uniaxial pressing at 1 GPa into disc-shaped pellets of 16 mm diameter and about 1 mm thickness. All the prepared samples were sintered at 830 °C for 32 h in the N_2–O_2 atmosphere with a lowered oxygen partial pressure of 7 kPa. After that, the samples (except a reference single-worked one) were subjected to another pressing process at 1 GPa and sintered at 830 °C for 32 h under the same atmosphere. The maximum number of steps, n, was 6.

Powder X-ray diffraction analysis (CuK_α, DRON3) was used to identify secondary phases and to measure the preferred orientation.

The microstructure was observed using a Neophot 21 polarization optical microscope and a SEM TESLA BS 300 with the possibility of EDX analysis (EDAX 9100/60). Before microstructural observation, the samples were polished and etched in a solution of 1% Br in CH_3CH_2OH [14].

The transport critical current density, J_c, at 77.3 K and at a magnetic flux density up to 170 mT, was measured using the criterion of 1 μV cm^{-1}. The samples were cooled at zero magnetic field and the field was gradually increased during measurement. The direction of the measured current was perpendicular to the direction of the magnetic field and also to the pressing direction.

3. Results and discussion

The results of the X-ray analysis of the prepared Bi, Pb–Sr–Ca–Cu–O samples are shown in Fig. 1a. The 2212 phase content gradually decreases with number of steps, but a small amount is still present. Fig. 1b shows the degree of preferred orientation quantified as P_{obs}/P_{calc}, using the ratio of diffraction peaks integral intensities $P = I\,(0\,0\,1\,0)/I\,(1\,1\,5)$, where P_{obs} is a value obtained from the surface of a ground sample and P_{calc} is a calculated value for a disordered sample as a function of the number of steps, n.

The results of optical microscopy and EDX analysis showed that about 2% of phases $(Ca,Sr)_2CuO_3$,

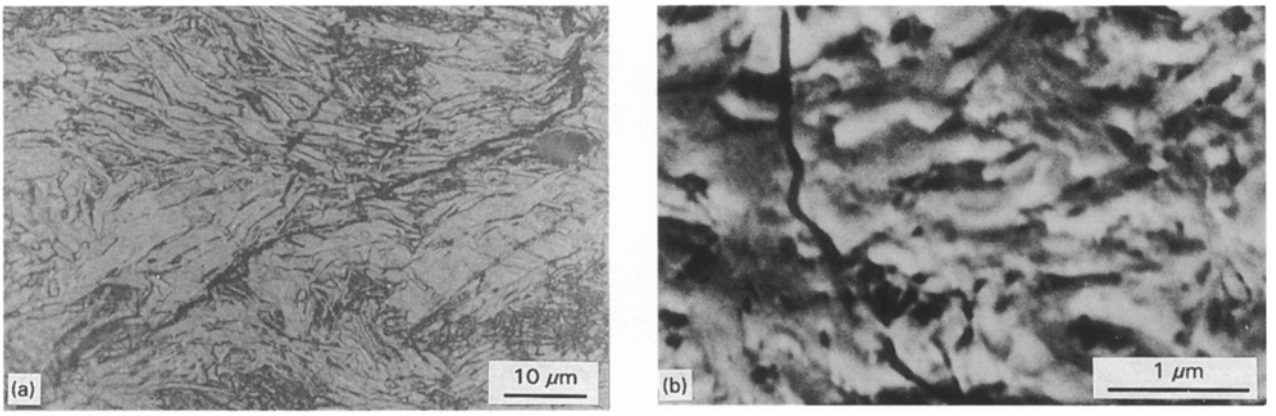

Figure 7 Crack in the sample for $n = 6$: (a) optical micrograph; (b) scanning electron micrograph.

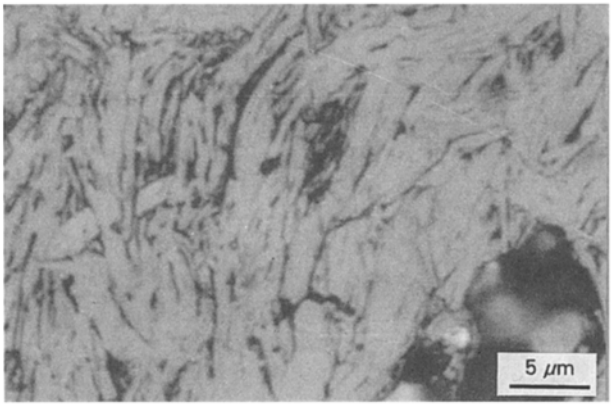

Figure 8 Optical micrograph of microcracks in the sample for $n = 5$.

$(Sr,Ca)_{14}Cu_{22}O_x$ and CuO is present in all samples. Fig. 2a shows the distribution of these phases on the surface of the grains. Some small grains of the phases $(Ca,Sr)_2CuO_3$ and $(Sr,Ca)_{14}Cu_{22}O_x$ are also randomly distributed in all samples (Fig. 2b).

The bulk density increases if several pressing and sintering steps are used. Fig. 3a–c shows changes in density of samples for $n = 1$, 3 and 6. The size and density of pores decrease with the number of steps. Fig. 3d shows the dependence of the density, calculated from the weight and dimensions of the samples, on the number of steps, n. The size and thickness of the grains is about 20 and 5 μm, respectively. No dependence of grain size or thickness on the number of steps was found.

Fig. 4a–c shows the microstructure of plane parallel to the direction of pressing in samples for $n = 1$, 2 and 6. If we compare the microstructure for $n = 1$, 2 and 6, some steps of preferred grain orientation for $n > 1$ are observed. Fig. 5 shows a scanning electron micrograph of the local arrangement of grains in a sample for $n = 6$.

It can be supposed that J_c will still increase with increasing bulk density because of improvement of the connections between grains. The dependence of J_c at 77.3 K and at magnetic fields up to 170 mT is shown in Fig. 6. The maximal J_c was determined to be at $n = 5$. This result is in agreement with the microstructural observation, because of the presence of cracks in the sample for $n = 6$ (Fig. 7). Some microcracks were also observed in the sample for $n = 5$ (Fig. 8). At the beginning of microcrack development, these microcracks could serve, because of their very low dimensions, as effective pinning centres [15] and, because of their high density (it is not, however, obviously fulfilled), they could favourably influence the critical current density. During further pressing, the microcracks can, however, grow into cracks and break the superconducting paths in the sample. We suppose that the growth of the cracks is responsible for the decrease in J_c in the sample for $n = 6$. An improvement of the J_c of the 2223 phase Bi, Pb–Sr–Ca–Cu–O polycrystalline bulk superconductors depends on further local improvement of the coupling of the 2223 phase grains and on a limitation or even on control of crack development.

4. Conclusion

The dependence of the microstructure of $Bi_{1.8}Pb_{0.26}Sr_2Ca_2Cu_3O_{10+x}$ on the number of pressing and sintering steps, and its influence on the critical current density, were studied. Improvement of J_c depends on the further local improvement of the coupling of the grains of the 2223 phase. The crack development is responsible for decreasing J_c in samples subjected to a higher number of steps.

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