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Magnetic Characterization of Hot-Pressed BSCCO (2223) Phase Superconducting Ceramic (*).

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Summary. — BSCCO (2223) phase superconductor, prepared by the traditional solid-state reaction route, was densified by hot pressing, yielding high-density and textured-bulk materials. A correlation between processing parameters and inter-, intra-granular properties of the sample was performed through the evaluation of microstructural features and the study of electrical resistivity and magnetization behaviour as a function of different temperature and magnetic field.

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1. – Introduction.

A control of the microstructure in the polycrystalline $(\mathrm{Bi,\,Pb})_2\mathrm{Sr}_2\mathrm{Ca}_2\mathrm{Cu}_3\mathrm{O}_x$ (2223 phase) high-temperature superconductors has been repeatedly demonstrated to be essential for high bulk intergranular critical-current density. Among the various microstructural parameters, the degrees of grain alignment and grain connectivity seem to be of prime importance [1-3]. The significance of fabricating dense grain-aligned bulk materials is that they appear to be the only ones that enable a systematic study of the intergranular properties of this compound, given that attempts to grow single-crystal samples have so far proved unsuccessful. Indeed BiSCCO (2223) superconductor can be considered a multiconnected system consisting of granules coupled to each other with weak links that can be responsible either for the

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critical-temperature degradation or for the flux creep origin. Actually flux creep seems really enhanced at grain boundaries compared to the interior of the grains in multigranular samples, and strictly related to the microstructural characteristics of the material.

In this paper microstructural, electrical and magnetic properties of dense bulk superconductors are systematically evaluated with a particular attention to the different nature of grain and grain-boundary properties.

2. – Experimental.

The starting superconducting powders, with the nominal composition $Bi_{1.84}Pb_{0.34}Sr_{1.91}Ca_{2.03}Cu_{3.06}O_x$ for the preparation of bulk material were obtained by solid-state reaction from oxides and carbonates.

Powder was uniaxially pressed at 1500 kg/cm^2 and the obtained pellets were hot-pressed using an «Instron» apparatus adequately fitted for the experiments. The alumina die and plungers were sputtered with silver in order to prevent the reaction of superconductor with alumina. The constant pressure of 7 MPa was applied before heating. The hot-pressing temperature was reached with a heating rate of 10 °C/min. Different sintering temperatures and times were used in the range 790–810 °C and 2–6 h, respectively. Details on powder preparation, hot-pressing technique and relative theories were described in previous papers [4, 5].

X-ray diffraction (XRD) data were taken at room temperature with graphite monochromatized Cu$K\alpha$ radiation. From experimentally recorded powder patterns structural characteristics were deduced. Using the ratio of the intensities of the principal peaks falling in similar angular ranges, relative amounts of different phases belonging to BiSCCO system (2201, 2212 and 2223) were evaluated. The degree of grain orientation in axial direction «F» was determined by means of XRD analysis from the Lotgering relationship, using for comparison randomly oriented powder XRD pattern.

The bulk density was measured by Archimedes' method. Morphology of the samples was investigated by means of scanning electron microscopy (Leica Cambridge Ltd.) Energy dispersion analysis X-ray (EDAX) system was also employed on the polished surfaces of sintered samples; electron probe microanalysis was conducted to determine the composition of the superconducting phases and of the impurity phases. Samples were prepared by grinding on SiC abrasive paper and subsequent polishing with diamond paste up to 0.5 μm.

The superconducting properties were investigated by means of transport and magnetic measurements. The resistivity was measured by means of the four-probe method, with Ag-paste contacts and with a maximum feeding current of 1 mA perpendicular to the hot-pressing directions. The critical temperature was extracted from the ρ *vs.* T curves. Two critical values are deduced (table I), *i.e.* the onset superconducting temperature T_c and the zero-resistivity temperature $T_c(0)$. Transport critical current (J_{ct}) was determined by I-V measurements at 77 K and zero magnetic field with voltage criterion of 1 μV/cm.

Magnetization measurements were performed by a vibrating-sample magnetometer ($77 < T < 300$ K); $H_{max} = 1.0$ T and a SQUID magnetometer ($2 < T < 400$ K; $H_{max} = 5.5$ T). The magnetic critical current (J_{cm}) was estimated at 5 K and 77 K from the hysteresis cycles by using the Bean critical-state model.

3. – Results and discussion.

As can be deduced by table I, the density of the hot-pressed samples increases with sintering temperature and time; on the other hand, time shows also a deep influence on orientation factor: indeed samples fired at 810 °C for a time longer than 2 hours show an increase in the F value up to $F = 62\%$. As regards 2212 phase content, it must be mentioned that the starting powder had an average 2212 volume fraction around 5%, while the hot-pressing treatments cause an increase in such a value up to a maximum of 10%; on the contrary, by increasing the sintering time, the amount of this phase decreases, reaching values lower than the starting ones. From a more detailed discussion of microstructural features of the tested samples, see [6].

Resistivity curves reported in fig. 1 reveal that long sintering times yield

TABLE I. – *Microstructural, electrical and magnetic properties of dense samples.*

Sample code	Temp./time (°C/h)	Relative density (%)	Orientation factor F(%)	2223/2212 content	2223 c-axis (Å)
HP1	790/2	92	37	92/8	37.14
HP2	800/2	93	43	89/11	37.20
HP3	810/3	96	46	93/7	37.20
HP4	810/6	98	57	95/5	37.24

Sample code	T_c offset (K)	T_c onset (K)	J_{ct} (A cm^{-2})	J_{cm} (10^3 A cm^{-2})	
				$T = 5$ K, $H = 10$ kOe	$T = 77$ K, $H = 0$
HP1	94	108	0.5	12	9
HP2	98	108	6	26	2
HP3	90	108	3	12	2
HP4	88	100	1	7.5	—

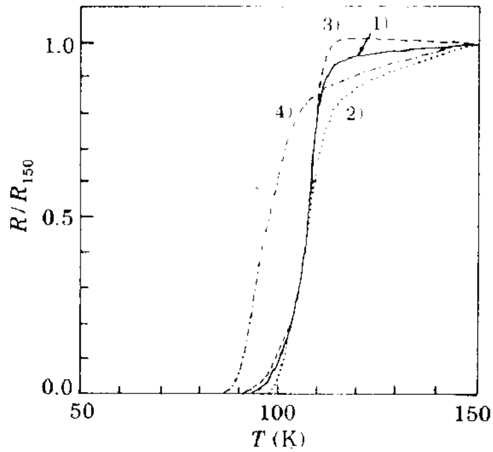

Fig. 1. – Normalized resistivity *vs.* temperature (numbers refer to different samples as reported in table I).

pronounced tailing phenomena attributable to a lower connectivity among grains due to the gradual degradation of superconductive properties of intergranular phases or to the formation of structural defects like cracks or microcracking; the simultaneous degradation of superconductive properties of the grains reflects in a less sharp transition profile. As regards the influence in sintering temperature the resistivity curves reveal the presence of a more pronounced tailing phenomenon in HP1 (790 °C) even if its superconductive transition is sharper in the initial stage with respect to HP2 (800 °C).

3˙1. HP *temperature effect*. – SEM investigation of polished surfaces of HP1 and HP2 together with microprobe analysis reveals the different grain boundary morphology. The first is characterized by very thin, disordered grain boundaries consisting essentially of 2212 phase. The slighter slope of the HP2 curve could be attributed to a larger 2212 content forming a thick grain boundary structure resulting in a broadened transition, but contemporarily higher density and orientation factor reduce the tail giving $T_c(0) = 98$ K.

Similarly, the comparison between the transport critical currents allows to estimate the differences between the actual strength of the intergrain coupling in the different samples to be estimated.

Transport J_c (J_{ct}, $T = 77$ K, $H = 0$) is higher for the sample hot-pressed at higher temperature (HP2), as expected as a consequence of the increase of the relative density and of the degree of texturing (table I). The comparison between the magnetic critical currents allows to gain a direct insight on the differences between the actual intragrain properties.

At $T = 5$ K a slightly higher J_{cm} value is found for the sample HP 2 whereas at 77 K J_{cm} is much higher for the sample HP1, as can be seen in fig. 2. This can be explained taking into account the effect of the densification on the oxygen content and consequently the role of oxygen on pinning energy. It is well established that oxygen vacancies act as pinning centres in high-T_c superconductors but, because of the weakness of the associated pinning potentials, they are effective only at low temperatures [7]. By increasing temperature, the dominant role on pinning is played by the actual dimensionality of the flux line lattice. A decrease of the oxygen content is expected to lower the pinning energy and intragrain critical current, because it determines an increase of the anisotropy of flux lattice (tending to quasi-2D

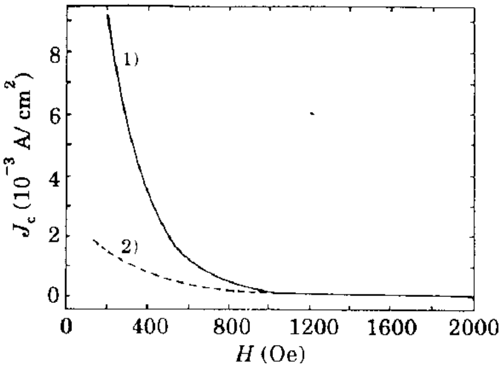

Fig. 2. – Critical-current density *vs.* magnetic field at 77 K for HP1 (curve 1)) and HP2 samples (curve 2)).

behaviour), due to the weakening of the coupling between the superconducting Cu-O layers.

Therefore, since the improvement of the densification reduces the diffusion and the oxygen content in the inner part of the sample (producing a small increase of the c lattice parameter), the higher J_{cm} value for HP2 at 5 K is due to a higher oxygen vacancies concentration and its much smaller value at 77 K is determined by a reduced coupling between the Cu-O planes.

3·2. HP *time effect.* – The increase in sintering time from 3 h (HP3) to 6 h (HP4) that involves an increase in relative density and in orientation factor, also reflects on T_{c} onset $T_{\mathrm{c}}(0)$ offset values. Actually HP4 shows a sharp decrease in $T_{\mathrm{c}}(0)$ value in agreement with the detrimental effect caused by the lack of oxygen in a highly dense bulk sample and also evidenced by the increase of c-axis length ($c = 37.24$ Å). It is in fact well known that T_{c} goes through a maximum for a particular oxygen stoichiometry corresponding to an optimum concentration of charge carriers. A decrease of oxygen content should move the charge carrier concentration far from the optimum value.

As far as the critical current is concerned, both J_{ct} and J_{cm} are lower for HP4. The decreases of J_{ct} for longer HP times, although the orientation factor increases, should

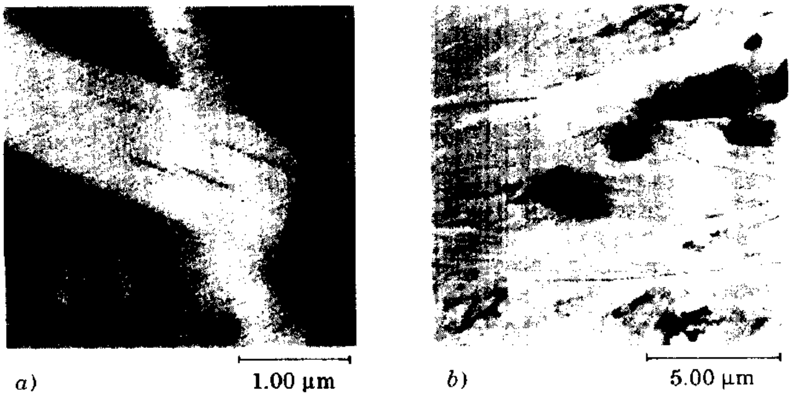

Fig. 3. – Micrographs showing the morphology of *a*) sample HP3 characterized by cracks at grain boundary and *b*) HP4 characterized by microcracks into the grains.

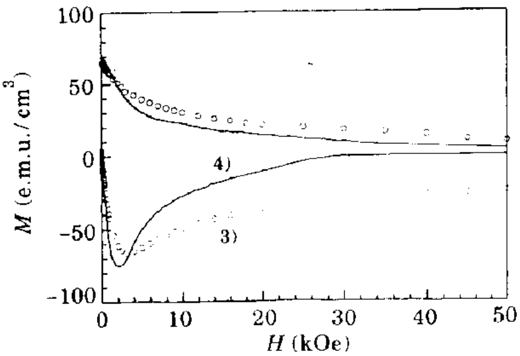

Fig. 4. – Hysteresis cycles at $T = 5$ K for HP3 (curve 3)) and HP4 samples (curve 4)).

be determined not only by the reduction of the oxygen content (that has also an effect on composition and electrical properties of grain boundary phases) but also by long cracks running at grain boundaries clearly evident in fig. 3*a*).

In fig. 3*b*) the morphology of HP4 is also shown characterized by microcracks into the grain.

Magnetization cycles in fig. 4 show a lower width (*i.e.* lower J_{cm}) for HP4 in comparison to HP3. The decrease of J_{cm} for longer HP times (at 5 K as well as at 77 K) is determined by the further weakening of the coupling between the superconducting Cu-O planes.

4. – Conclusions.

The results indicates that the hot-pressing technique is effective in preparing highly dense textured superconducting samples with improved intergrain coupling. However, a very high densification and texturing imply, as a counterbalancing effect, a reduction of oxygen content and cracks formation at grain boundary detrimental for both transport and magnetic critical current.

REFERENCES

[1] Y. Yeshurun and A. P. Malozemoff: *Phys. Rev. Lett.*, **60**, 2202 (1988).
[2] A. Oota, H. Noji and K. Ohba: *Phys. Rev. B*, 43, 10455 (1991).
[3] Wai Lo, D. N. Zheng, B. A. Glowacki and A. M. Campbell: *J. Mat. Sci.*, **29**, 3897 (1994).
[4] A. Tampieri and G. N. Babini: *Jpn. J. Appl. Phys.*, **30**, L1163 (1991).
[5] A. Tampieri, G. Celotti, F. Ricciardiello and G. Russo: *Physica C*, **227**, 300 (1994).
[6] G. Celotti, A. Tampieri, R. Masini and M. C. Malpezzi: *Physica C*, **225**, 346 (1994).
[7] J. Maier and G. Pfundtner: *Advan. Mater.*, 30, 292 (1991).