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HIGH T_c SUPERCONDUCTING $YBa_2Cu_3O_{7-x}$ FILAMENTS: AN IMPROVED THERMAL TREATMENT.

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Abstract.

An Y-Ba-Cu-O suspension was spun into a filament using a phase inversion technique. The flexible "green product" wire needs a high temperature heat treatment and oxygen anneal to form the superconducting $Y Ba_2 Cu_3 O_{7-x}$ phase. The quality of the wire and its superconductive properties are highly dependent on the sinter conditions.
Thermal treatment is optimized to improve the superconductive properties of the wire. To improve sintering, $Y Ba_2 Cu_3 O_{7-x}$ is decomposed peritectically into $Y_2 BaCuO_5$ and a liquid phase at relative low temperature by reducing the pressure in the furnace. Subsequently the pressure is increased and the reaction is reversed; restoring the superconductive phase. A precise activation and deactivation of partial melting can be accomplished in this way.

1. Introduction.

Since the discovery of high temperature ceramic superconductors, with a critical temperature (T_c) above liquid nitrogen temperature[1], there have been extensive attempts to produce high T_c wires and tapes for technological applications. The ceramic material is not easily shaped into the desired fibre geometry and various methods have been proposed. In a previous paper[2] we reported on a low cost suspension spinning method using a phase inversion technique. The critical current density (J_c) of the $Y Ba_2Cu_3O_{7-x}$ wires was in the range of 125 A/cm^2 at 77 K and in zero field and strongly affected by the sinter conditions. A relative high porosity of the wires and a not fully optimized thermal treatment were thought to be responsible for this relative low value. In this paper we describe the optimization of the thermal treatment in order to obtain higher reproducible J_c values. An improved heat treatment is described where, $Y Ba_2Cu_3O_{7-x}$ is decomposed peritecticly into Y_2BaCuO_5 and a liquid phase at relative low temperature by reducing the pressure in the furnace. The incongruent melting of $Y Ba_2Cu_3O_{7-x}$ is used to improve sintering of the wire while its shape is maintained. When the pressure is subsequently increased the reaction is reversed and the superconducting phase is restored.

2. Experimental.

Shaping the ceramic material into a wire was done using a suspension spinning method, where the solvent was removed by a phase inversion technique[2]. A commercially available powder (Hoechst High Chem) was used as a starting material. The phase purity of the powder was checked by X-ray diffraction (XRD). Scanning electron microscopy, equipped with energy dispersive X-ray analysis (SEM/EDX) and inductively coupled plasma mass spectroscopy (ICP/MS) were used to determine the stoichiometry and to check for contamination. No impurities or contamination could be detected and the stoichiometry was found to be Y : Ba : Cu = 1 : 1.98 : 3.04.

For the suspension production, two batches of powder were used: HGr_2, with an average grain size 10μm and H_207, with an average grain size 4μm. The grain size was determined with a Malvern Mastersizer. Polysulfone (PSF) was used as binder, N-methyl-2-pyrrolidone (NMP) as solvent and water as non-solvent. For these experiments, the powder to binder ratio was kept constant at 90 wt% to 10 wt% and the diameter of the wires was about 1 mm. After spinning, the wire is washed in isopropanol, dried and subsequently stored in vacuum until it is used for heat treatment.

2.1 Traditional thermal treatment.

In the heat treatment, three stages are important. A) The PSF binder has to be removed without reacting with the Y-Ba-Cu-O material and without destroying the shape of the wire. B) The filament has to be sintered into a high density ceramic. C) The ceramic material has to be annealed in an oxygen atmosphere to produce the superconductive $Y Ba_2Cu_3O_{7-x}$ phase.

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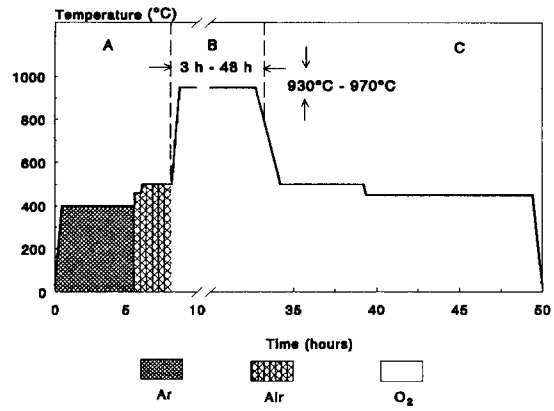

Fig. 1: Traditional thermal treatment sequence of Y-Ba-Cu-O filaments.

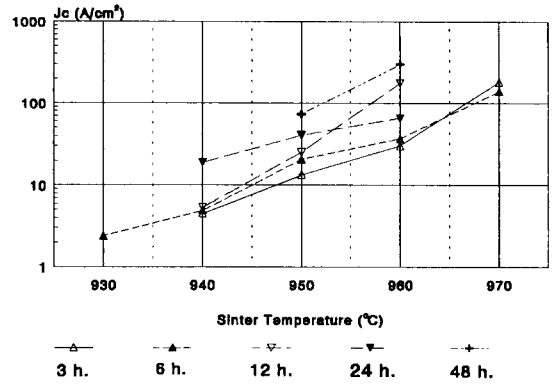

Fig. 2: Critical current density at 77 K in zero field for superconducting $YBa_2Cu_3O_{7-x}$ wires sintered for 3 to 48 hours at 930 °C to 970 °C.

A traditional thermal treatment sequence is shown in fig. 1. After removing the polymer binder (A), the wires were sintered for 3 to 48 hours in flowing oxygen (at atmospheric pressure) at different temperatures (930 °C to 970 °C) (B), followed by an oxygen annealing at 500 °C and at 450 °C for several hours, to restore the right oxygen content (C).

The critical temperature (T_c) and critical current density (J_c) are determined in zero field by the four-probe DC technique. Resistivity measurements as a function of temperature of all samples show a T_c^{onset} above 90 K. The transition width and T_c^{zero} are slightly influenced by the sinter procedure, but zero resistivity is reached well above liquid nitrogen temperature in all samples.

Fig. 2 shows J_c at 77 K in zero field for samples made with the HGr_2 powder sintered at different temperatures and for different times. The results using H_207 powder (average grain size 4 μm) remain approximately the same. From this figure it is seen that both longer sinter times and higher sinter temperatures improve the critical current. The better sintering at higher temperatures is also proven by the SEM micrographs of figure 3. They show images of the cross section of superconducting wires sintered for 3 hours at 940 °C (a), 950 °C (b), 960 °C (c) and 970 °C (d). The sample sintered at the highest temperature seems to be very well sintered and very good intergrain connections are formed. It appears that the grains are melted together. The wires with the highest J_c values (larger than 100 A/cm^2) show similar morphology.

At 970 °C the wire can be sintered for maximum 6 hours. For longer sinter times the wire starts melting (demixing) and looses its shape. At this temperature the obtained J_c values are not reproducible.

The best wires showed J_c values in the range of 100 A/cm^2. Altering the heating and/or cooling rates did not result in higher J_c values.

When bulk samples of the Hoechst powder were prepared (pressed at 200 kPa/m^2) and heat treated in the same way, J_c values in the same range were obtained. The density of those samples was only about 60 % of the theoretical value while in bulk samples prepared from powder made by the solid state reaction method, densities larger than 95 % can be obtained.

2.2 "Peritectic" melt process.

In the search for higher J_c values, several heat treatment procedures have been developed which involve (partial) melting of the sample in order to sinter the material into a high density ceramic and reduce the "weak links". Melt growth[3-5] (MG), quench and melt growth[6] (QMG) and rapid thermal processing [7-9] (RTP) are just some of the names given to such procedures in which the sample is heated up to temperatures higher than the melting point (> 1000 °C) for a "short" time.

By including a short high temperature peak in the thermal treatment (up to 1050 °C for maximum 5 minutes), J_c did increase. The main problem however is that it is very difficult to control the high temperature treatment in this way. This results in J_c values that are not reproducible. Moreover, the wire starts loosing its shape. In order to preserve the wire shape of the sample, only partial melting should take place.

It is well known that $YBa_2Cu_3O_{7-x}$ shows incongruent melting[5,10] and that it decomposes into the Y_2BaCuO_5 phase and a liquid on heating. On cooling the 1:2:3 phase is restored by the following peritectic reaction:

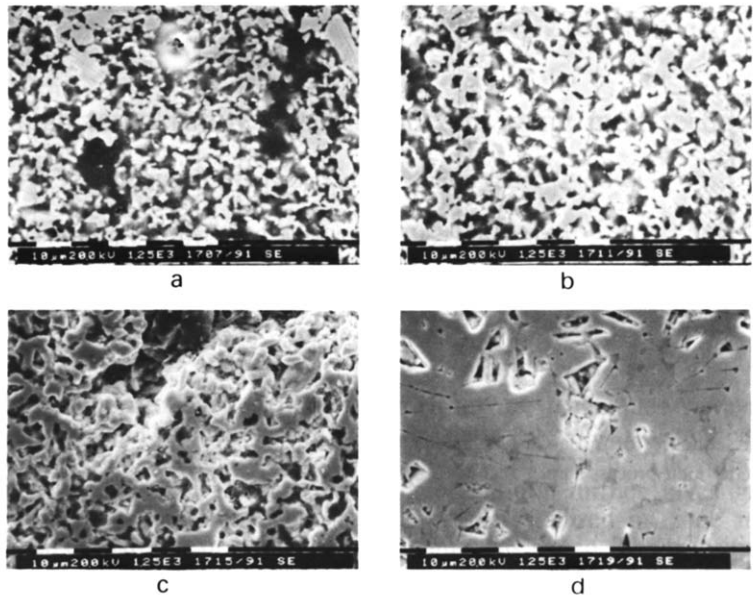

Fig. 3: SEM micrographs of the cross section of $YBa_2Cu_3O_{7-x}$ wires sintered for 3 hours at 940 °C (a), 950 °C (b), 960 °C (c) and at 970 °C (d). Magnification: x 1250.

$$Y_2BaCuO_5 \text{ (solid)} + \text{liquid} \rightarrow Y\,Ba_2Cu_3O_{7-x} \text{ (solid)}$$

It is believed that the oxidation/reduction reaction of Cu in $Y\,Ba_2Cu_3O_{7-x}$ plays an important role in this process.

In fig. 4 a heat treatment sequence is shown where a "peritectic" melt process step is included in the sintering (B). First the PSF polymer is burned out (A) at 500 °C in vacuum or in an inert atmosphere to avoid $BaSO_4$ of being formed by the reaction of the sulphur in PSF with $Y\,Ba_2Cu_3O_{7-x}$. Next the wire is heated to at least 820 °C and maximum 940 °C in an oxygen atmosphere at reduced pressure (500 Pa) to complete the binder removal and start the sintering which gives the wire its firmness. Subsequently the temperature is kept constant for a few hours (compacting plateau). During this period one or more steps are included where the pressure is even lower (150 Pa and/or vacuum (in this case vacuum means smaller than 10 Pa)). As a result of the low (oxygen) pressure, the Cu^{2+} in $Y\,Ba_2Cu_3O_{7-x}$ will be reduced to Cu^{1+} and the 1 : 2 : 3 phase will be decomposed into Y_2BaCuO_5 and a liquid phase at this relative low temperature. From the pseudo-binary phase diagrams[11-12] it can be deduced that the liquid phase consists mainly of $BaCuO_2$ and CuO, where CuO will be reduced to Cu_2O.

When the pressure is raised again to atmospheric pressure (about 100 kPa) by allowing oxygen into the furnace, the $Y\,Ba_2Cu_3O_{7-x}$ phase is restored by the peritectic reaction between Y_2BaCuO_5 and the liquid phase.

Next the temperature is raised again to the actual sinter temperature (930 °C to 1000 °C) at a rate of 6 °C/hour. When the sinter temperature is reached the sample is allowed to cool at 30 °C/hour to about 800 °C (sinter "peak").

When air is used instead of oxygen during the sinter proces, melting starts at even lower temperatures.

After sintering an oxygen annealing at 500 °C and 400 °C at atmospheric pressure is performed.

Many questions about the solid-state chemistry of this sinter process still remain unanswered and a systematic investigation is being carried out.

The advantage of using this kind of sinter process is that the pressure in the furnace can be easily regulated while the temperature is kept constant. This enables a precise and flexible control for activating and deactivating the partial melting of the sample.

The effect of the "peritectic" melt process step on the critical current density is shown in fig. 5. Values of up to 500 A/cm^2 at liquid nitrogen temperature and in zero field are obtained. SEM micrographs confirm that the wire is less porous than the ones sintered in a conventional way. Sintering is more effective and good intergrain connections are formed. With the exception of a small amount of the 2 : 1 : 1 phase only the superconductive $Y\,Ba_2Cu_3O_{7-x}$ phase could be detected using X-ray diffraction.

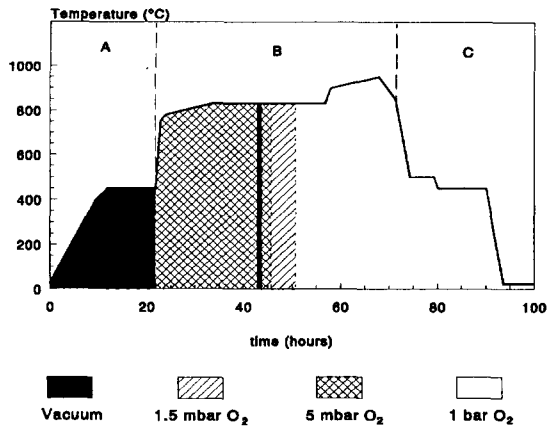

Fig. 4: Thermal treatment sequence for Y-Ba-Cu-O filaments including a "peritectic" melt process step.

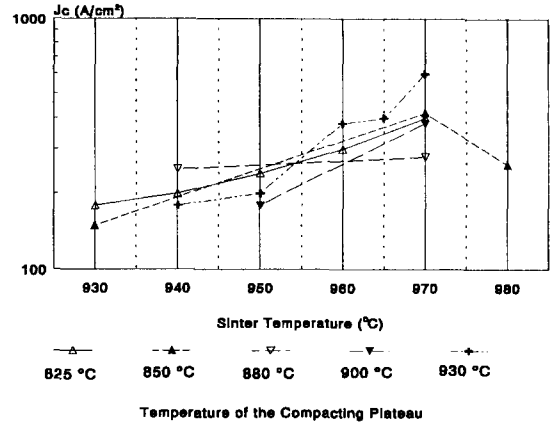

Fig. 5: Critical current density at 77 K for $YBa_2Cu_3O_{7-x}$ wires in zero field which were subjected to a heat treatment sequence including a "peritectic" melt process step.

3. Summary and conclusions.

An optimized thermal treatment was discussed which uses the incongruent melting of $YBa_2Cu_3O_{7-x}$. By using a low pressure in the furnace this melting and decomposition of the 1:2:3 phase into Y_2BaCuO_5 and a liquid phase, occur at relative low temperatures. When the pressure is subsequently increased by allowing oxygen in the furnace, $YBa_2Cu_3O_{7-x}$ cristallizes by a peritectic reaction of Y_2BaCuO_5 and a liquid phase. Experiments which should give a better understanding of the solid-state chemistry responsible for these reactions are being carried out presently. The samples in these experiments were wires produced by a suspension spinning method. Critical current density, at liquid nitrogen temperature, was found to be at least four to five times higher when compared to a traditional heat treatment. Values of up to 500 A/cm^2 were obtained for wires.

The resulting superconductive wires are untextured and polycrystalline. Because the treatment allows for an accurate control of activating and of deactivating the partial melting of the sample, this method could be optimized in order to further improve J_c and be used to develop textured wire.

4. Acknowledgements.

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5. References.

[1] M.K. Wu,J.R. Ashburn, C.J. Torng, P.H. Hor, R.L. Meng, L. Gao, Z.J. Huang, Y.Q. Wang and C.W. Chu: Phys. Rev. Lett. **58**(9), (1987), 908.
[2] H. Weyten, W. Adriansens, J. Cornelis and R. Leysen: J. Mat. Science (to be published)
[3] T. Komatsu, K. Imai, K. Matusita, M. Ishii, M. Takatka and T. Yamashita: Jap. J. Appl. Phys. **26**(8), (1987), L1272.
[4] K. Matsuzaki, A. Inoue, H. Kimura, K. Aoki and T. Matumoto: Jap. J. Appl. Phys. **26**(8), (1987), L1310.
[5] S. Jin, T.H. Tiefel, R.C. Sherwood, M.E. Davis, R.B. van Dover, G.W. Kammlott, R.A. Fastnacht and H.D. Keith: Appl. Phys. Lett., **52**(24), (1988), 2074.
[6] M. Murakami, M. Morita and N. Koyama: Jap. J. Appl. Phys. **28**(7), (1989), L1125.
[7] T.O. Sedgwick: Mat. Res. Soc. Symp. Proc., **92**.
[8] M.J. Hart and A.G.R. Evans: Semicond. Sci. Techn., **3**, (1988), 421.
[9] D.S. Ginley, E.L. Venturini, J.F. Kwak, R.J. Baughman, R.J. Bourcier, M.A. Michell, B. Morosin, J.W. Halloran, M.J. Neal and D.W. Capone: Mat. Res. Soc. Symp. Proc., **169**, (1990), 1235.
[10] J. Takada, H. Kitaguchi, A. Osaka, Y. Miura, K. Takahashi, M. Takano, Y. Ikeda , Y. Bando, N. Yamamoto, Y. Oka and Y. Tomii: Jap. J. Appl. Phys. **26**(10), (1987), L1707.
[11] M. Nevriva, E. Pollert, J. Sestak, L. Matejkova and A. Triska: Physica C, **153-155**, (1988), 377
[12] M. Murakami, M. Morita, K.Doi, K. Miyamoto and H. Hamada: Jap. J. Appl. Phys. **28**(3), (1989), L399.

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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).

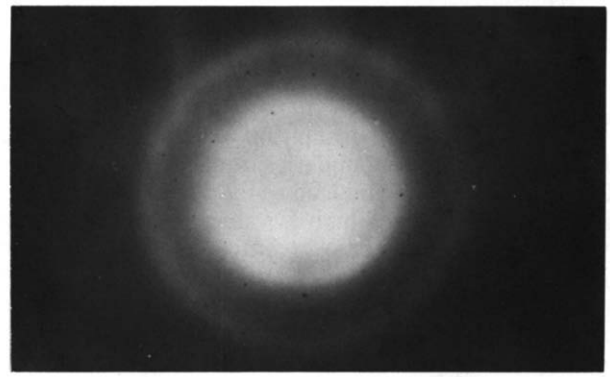

Fig.1. SADP for the sample C1.

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.

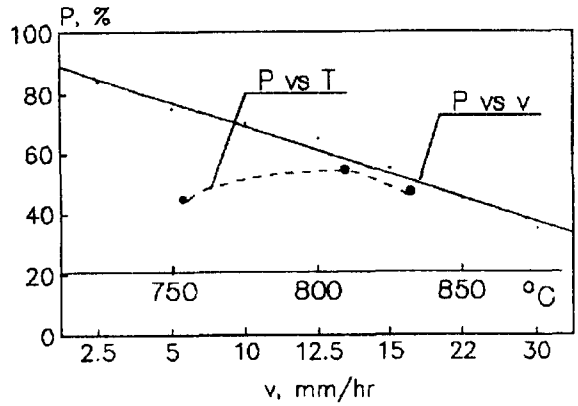

Fig.2. Texture extent vs feeding speed and hot zone temperature plot.

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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References

1 D. Dimos, P. Chaudhari and J. Mannhart, Phys. Rev., B41 (1990) 4038.
2 J. Manhart et al., Phys. Rev. Lett., 61 (1988) 2476.
3 S. Jin et al., Appl. Phys. Lett, 52 (1988) 2074.
4 J. Kase and T. Morimoto, Trans. on Magn., 27 (1991) 1254.
5 T. Nikata, K. Sato and Hitotsuyanagi, Japn. J. Appl. Phys., 28 (1989) 182.
6 D.E. Farrel et al., Phys. Rev., B36 (1987) 4025.
7 T.H. Tiefel et al., Mater. Lett., 7 (1989) 363.
8 A. Goyal et al., Physica C, 182 (1991) 203.
9 Nikkei Superconductors (June 25, 1990).
10 S.A. Saltykov, Stereometrical Metallography, USSR, Moscow, 1976.
11 L.M. Fisher and N.G. Ilyin, Solid State Commun., 76 (1990) 141.