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AN INVESTIGATION INTO TEXTURING OF HIGH-Tc SUPERCONDUCTING CERAMICS BY CREEP-SINTERING

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ABSTRACT

The possibility of preparing highly textured samples of $YBa_2Cu_3O_{7-\delta}$, high-Tc ceramics by creep-sintering under an uniaxial stress was investigated in detail. It is shown that the quality of the texture is sharply dependant on : the applied load, the temperature of the sintering dwell, the rate at which this dwell is reached, the exact instant at which the load is applied and the nature of the material in contact with the sample. It is also shown that further annealing without applied stress enhances the texture and considerably increases the grain size. Deformation, which was systematically recorded, occurs within a few minutes after the load is applied and exhibits a stress dependance typical of a viscous flow. Systematic examination by polarized light microscopy has indicated that the texture was homogeneous throughout the whole thickness of all the prepared samples. The resistivity versus temperature curves show that the transition is very sharp and well above 77 K.

KEYWORDS

Superconductivity, superconducting materials, high-Tc superconductors, texturing, ceramics, processing, High-Jc superconductors.

INTRODUCTION

The only practical route to increase the critical current density, Jc, of the new high-Tc superconducting ceramics up to technically usefull values is to align the grains of these materials as well as possible to ensure practical continuity of the superconducting a-b planes. The relevance of this solution has been demonstrated for quasi-single crystal thin films, grown epitaxially on appropriate substrates, for which Jc values of the order of 10^6 A/cm^2 were effectively measured with a permanent direct current (1-3), and also on thin bi-crystal films, where Jc was found to be considerably higher for low angle boundaries than for high angle boundaries (4).

For bulk materials, prepared via the sintering or the melting procedures, although all the usual texturing techniques known to ceramists and metallurgists have been attempted, the situation is considerably less advanced. Nevertheless very encouraging results have been obtained by magnetic alignment of powder grains (5-6), forging-sintering (7-9) and melt-textured growth (10-11). We present here, an investigation into texturing of high-Tc superconducting ceramics by a modified forging-sintering procedure, which has allowed us to prepare extremely textured materials.

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EXPERIMENTAL PROCEDURE

Forging-sintering is a technique well known to ceramists which consists in sintering powders under a uniaxial stress. It is mainly reputed for giving very dense products after a short sintering time only. Usually the green sample is embedded into a rigid matrix closed by a moving piston which restricts to a small extent the deformations, in order to keep the sample dimensions within the accepted uncertainties. To increase the degree of texturing usually achieved by this technique, we have on the contrary let the specimen creep substantially during sintering, and so we call this procedure creep-sintering.

The starting material was an YBaCuO powder from Rhône-Poulenc, which sinters nicely under regular conditions but unfortunately contains a rather high amount of secondary phases. This powder was poured into latex clads and cold pressed to 500 MPa in order to prepare several green product cylinders of 16 mm in diameter and 120 mm in length. The cylinders were sliced into pellets of 10 mm in height which were sandwiched between two metallic foils (Ag, Ag-Pd or Au) and inserted into a hot pressing device.

The typical temperature and load run used is depicted in figure 1

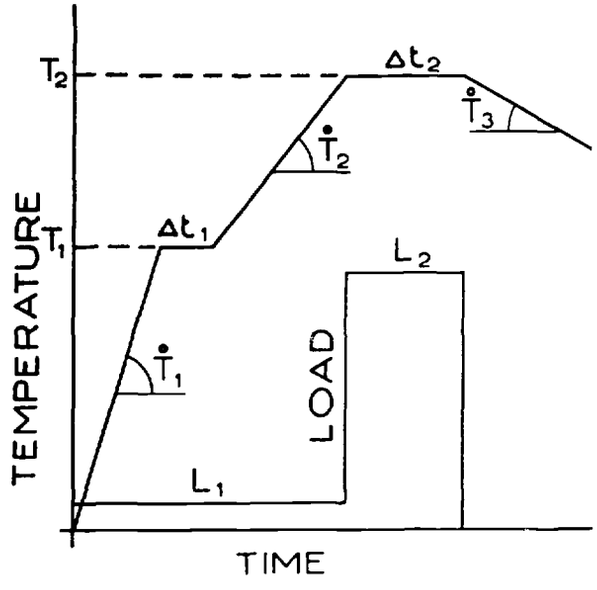

Fig. 1 Temperature and load run

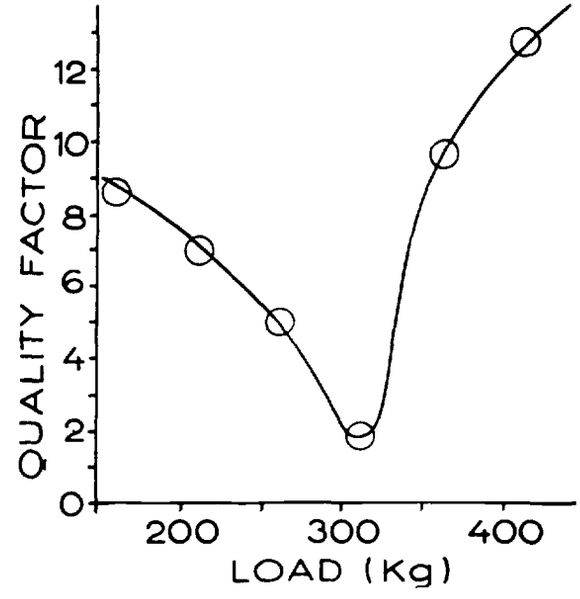

Fig. 2 Influence of the applied load on the texture quality

The temperature is first increased steeply, $\dot{T}_1$ = 600 C/h, up to a first dwell, T_1 = 650 C, Δt_1 = 0,5 h. It was checked that no change was noticeable on the X-ray diffraction diagram after this first part of the run, the usefullness of which is just time saving. The second temperature ramp, $\dot{T}_2$, and the temperature, T_2, of the second dwell were found to be crucial parameters and their influence was therefore systematically investigated. The duration, Δt_2, of the second dwell was not found to be very important, provided it was long enough and thus it was kept constant (Δt_2 = 1 h). However the influence of a further long anneal at T_2 was investigated. The cooling down rate, $\dot{T}_3$, which, if slow enough, has probably little influence, was also kept constant at a low value : 60 C/h.

Since the role of the load L_1 is just to ensure good thermal contact between the specimen and the device, its value was fixed at 10 kg. On the contrary, L_2, which is one of the most sensitive parameter was systematically varied.

At the end of the run, each specimen was sanded and polished to remove one of the metallic foils ; an X-ray diffraction diagram was then taken on the polished face, to look for texturing and secondary phases. The quality of the texture was characterized by the ratio of the intensity of (103)(110) peak to that of the (003) one, a crude but convenient criterion. In addition, the homogeneity of the texture throughout the whole sample thickness was carefully checked by polarized light microscopy.

INFLUENCE OF THE PROCESSING PARAMETERS

Most of the specimens obtained by creep-sintering were tetragonal, hence, to get a reference, a pellet of green product was sintered 24 h at 920 C under flowing nitrogen, cooled down to room temperature and ground into powder for X-ray diffraction. The diagram obtained was in fair agreement with those published in the literature (12) and gave a quality factor Q = 16.5.

Influence of the applied load

To test the influence of the applied load, all the parameters which characterize the temperature run were fixed to the following constant values : $\dot{T}_1$ = 600 C/h, T_1 = 650 C, Δt_1 = 0.5 h, $\dot{T}_2$ = 60 C/h, T_2 = 920 C, Δt_2 = 1 h, $\dot{T}_3$ = 60 C/h. In addition, the pre-load L_1 fixed at 10 kg, and the load L_2 itself was first systematically applied at the beginning of the sintering dwell T_2. Figure 2 highlights the marked influence of the applied load on the texture. The lower the quality factor, the higher the texture. Hence, as expected Q begins to decrease when the load increases, but this trend does not persist at high loads, for secondary phases Y_2BaCuO_5 and $BaCuO_3$, then appear , especially at the periphery of the sample. The creep curves, $\varepsilon = f(t)$, which were systematically recorded show that most of the deformation occurs within a few minutes after the load is applied (Fig. 3). All these informations corroborate the idea that the grains are embedded into a liquid phase of a different composition which enhances the creep and the sintering. However a very dense tangle of dislocations was observed in the specimens, which proves that there is at least a contribution of plastic deformation in texturing.

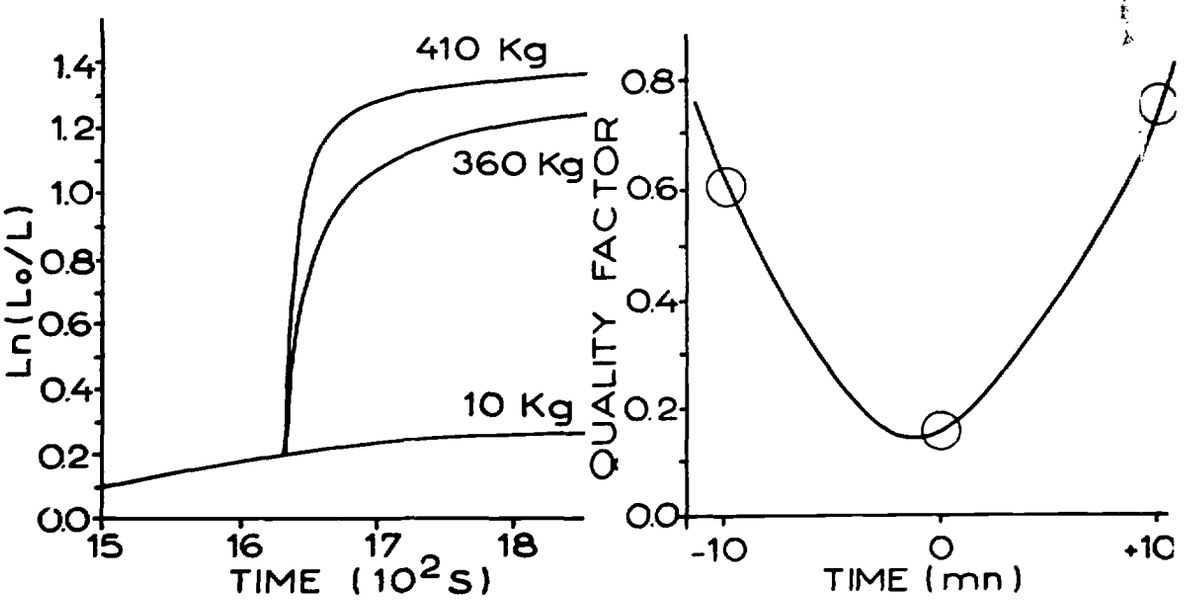

Fig. 3 Deformation as a function of time for various applied loads.

Fig. 4 Influence of the exact instant at which the load is applied on the quality of the texture.

The instant at which the load is applied is also a very sensitive parameter, as shown in figure 4. In this set of experiments, the creep-sintering load L_2 was 310 kg and all the other parameters had their previously defined values. The origin of time is chosen as the instant at which the temperature dwell T_2 is reached. As shown by this plot, this is the best choice for applying the load.
Ten minutes later is worse, probably because sintering of the randomly oriented grains is then too pronounced to allow a maximum alignment. On the other hand, ten minutes earlier the temperature is only of 910 C, i.e. 10 C below the optimal as will be discussed in the next paragraph.

Influence of the creep-sintering temperature

Keeping again L_2 = 310 kg and all the others parameters at their previously defined values, the temperature T_2 of the creep-sintering dwell was systematically varied (Fig. 5)

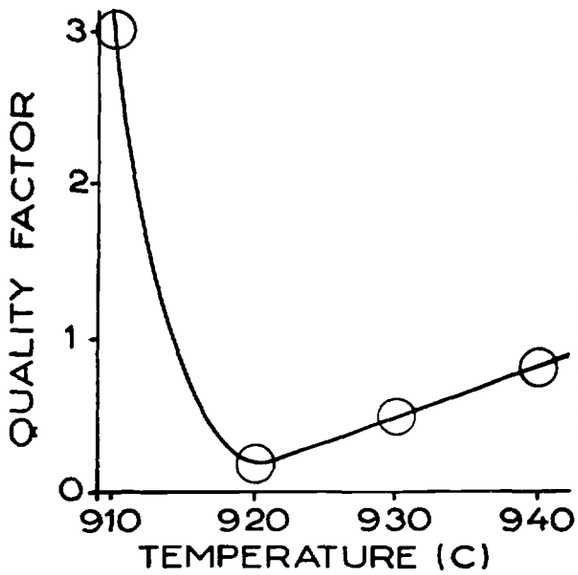

Fig. 5 Influence of the temperature dwell T_2 on the texture quality.

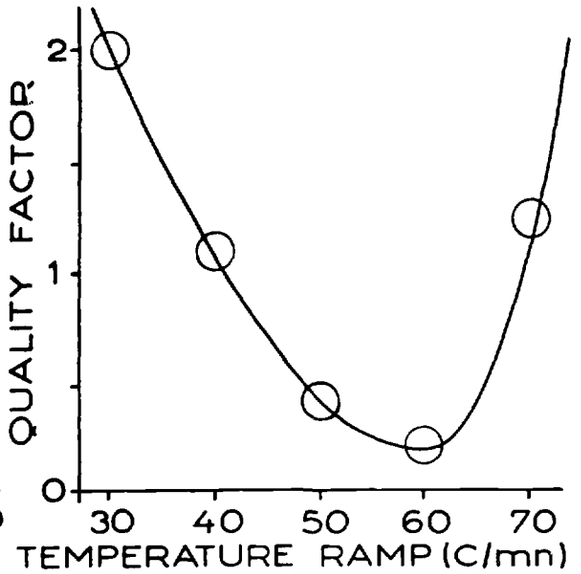

Fig. 6 Influence of the temperature ramp $\dot{T}_2$ on the texture quality.

It was found that for $T_2 \leq 900$ C the degree of texturing was modest and that the amount of secondary phases was nearly the same as that of the green product. Between 920 and 930 C, the texture was more pronounced and no secondary phase was detected on the X-ray diffraction diagram. At higher temperatures : $T_2 \geq 940$ C, secondary phases re-appear in the X-ray diagram and the texture quality was worse. In fact the very narrow temperature range over which no secondary phase can be detected was nearly the same when the specimens were regularly sintered under 0 applied load.

More surprising was the effect of the temperature ramp $\dot{T}_2$ depicted in Figure 6. For low temperature rates : $\dot{T}2 \leq 30$ C/h, the texture was faint and secondary phases were abundant. As soon as $\dot{T}2$ reaches 50 C/h, secondary phases were no longer detected on the X-ray diffraction diagrams and the texture was stronger. However is was much more pronounced for 60 C/h than for 70 C/h.

Influence of the contacting material

The nature of the contacting material was found to have a decisive influence on the texture. When the ceramic is sandwiched between two silver foils, as in all the reported results so far, it creeps abundantly and is textured. On the contrary when silver is replaced by pure gold (the experiment was repeated three times), the specimen neither creeps nor textures. In order to confirm this amazing effect, a specimen was sandwiched between a gold and a silver foil. After processing, it was heavily squeezed and textured on the silver side, whereas it was again neither deformed nor textured on the gold one. This very important result is now under further investigation.

Influence of a long annealing

After the one hour creep-sintering run the average grain size of the specimens ranged between 5and 10 μm, and no or few porosity was present and only minor amount of CuO undected on the X-ray diffraction diagram, were observed as very bright grains randomly distributed in the YBaCuO matrix. Several of the so-produced specimens were subsequently annealed for 200 h at 920 C in air. Whatever the starting level of the texture quality, it was observed that such a long annealing improves it (Q was lowered by a factor of 2) and considerably increases the grain size (for most of the grains it ranged from 30 to 100 μm). Unfortunately this annealing has two drawbacks : first it gives rise to some de-sintering in the form of big secondary pores induced by the stress created by the anisotropic growth of the grains. Second and worse, it leads to segregation of the 211 green phase in grain boundaries. Typical micrographs of the most textured sample produced (Q = 0,07) are presented as figures 7 and 8

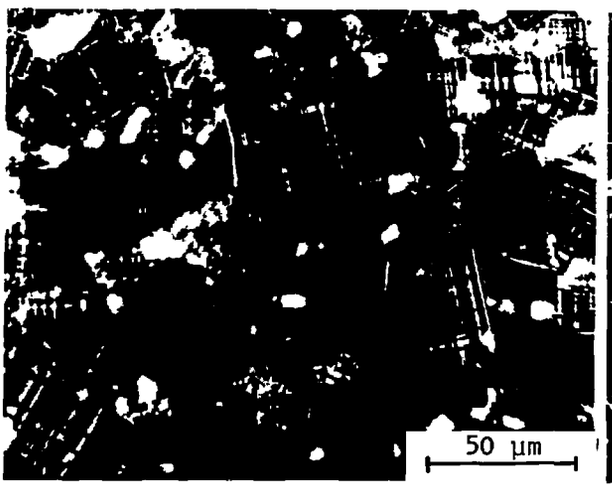

Fig. 7 Micrograph normal to the applied load

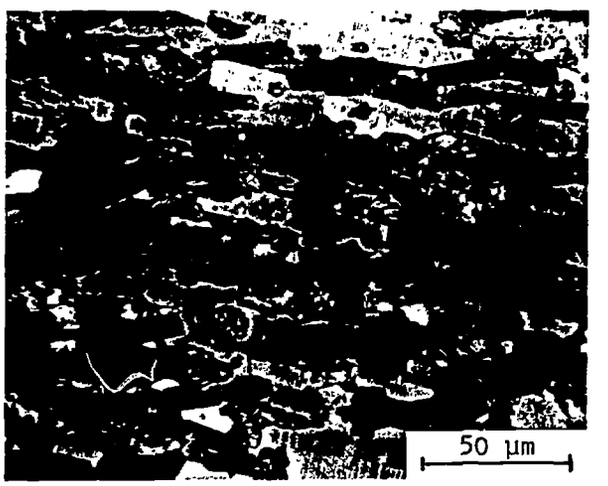

Fig. 8 Micrograph parallel to the applied load

ELECTRICAL CHARACTERIZATION

Some specimens were sliced into rods and the two silver slabs were carefully ground leaving four pads for electrical connections. They were subsequently annealed for 48 h at 400 C under flowing oxygen and their resistivity was measured as a function of the temperature between 77 and 300 K. As shown in figure 9, their resistivity in the normal state was very low : $2,5 \times 10^{-4}$ Ω cm at 90 K, a value quite close to that reported for single crystals. The transition was rather sharp and tailless. Direct measurement of current density Jc is now in progress and will be reported soon.

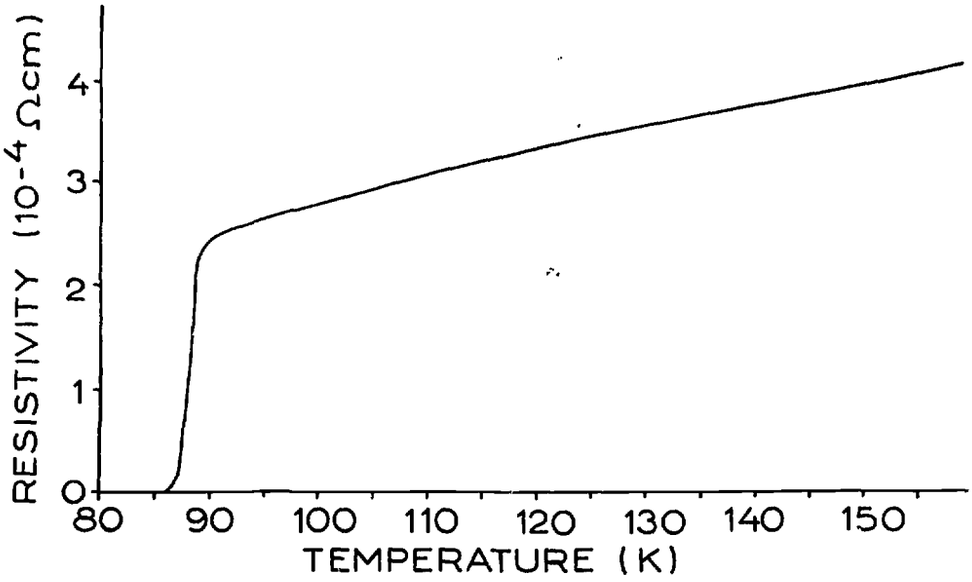

Fig. 9 Resistivity of the most textured sample as a function of temperature

CONCLUSION

It was shown that creep-sintering is a very efficient technique for producing highly textured samples of $YBa_2Cu_3O_7$, but that very careful optimization of numerous parameters is required in order to get good results.

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