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Mechanical alignment of the grains of sintered YBaCuO

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Abstract

It is shown that the combination of deformation and sintering gives rise to a pronounced alignment of the grains of high T_C 123 superconducting ceramics. The procedure (we call it creep sintering), was thorougly optimized varying the numerous parameters of the temperature and load run one at a time. As a result of a detailed microstructural characterization, it is concluded that several mechanisms interfer to build up the texture, the relative importance of them depends on the temperature and the deformation. In addition, it is shown that starting from a J_C of 150 A/cm^2 at 77 K for the untextured material , the procedure allowed to reach 650 A/cm^2. Moreover adding 2.5 wt% of Pb substituted Bi 2223 in order to modify the properties of the liquid phase present during creep sintering, we have increased further the J_C of the material up to 1010 A/cm^2 at 77k and 1950 A/cm^2 at 63 K .

1. Introduction

Alignment of the (ab) planes of the various grains of polycrystalline high-T_C superconducting ceramics is expected to increase their transport critical current density, J_C, for two reasons. First, since the Jc of polycrystals is severely limited by grain boundary disorder, alignment of the (ab) plane should give rise to a huge increase in Jc via the reduction of the misorientation of the grains. Second, because in single crystals of these materials, J_C is between 30 to 100 times higher in the (ab) plane than normal to it, this alignment should give a strongly anisotropic polycrystalline material exhibiting a high current density along its average (ab) plane.

2. Creep sintering

It is now well established that the sintering of high Tc superconductor powders occurs in the presence of a liquid phase. Though small in amount, this phase drastically enhances the growth of the grains giving them their platelet shape parallel to the (ab) plane and stimulating the densification of the material. Hence, when the material is sinter forged under a load heavy enough to squeeze it substantially, the grains are more or less mechanically aligned.
To investigate this process, which we call creep sintering to put the stress on the fact that the deformation is quite large, cylinders of a Rhône Poulenc YBaCuO powder of 1μm average grain size, were cold pressed isostatically at 2500 bars. Next they were sliced into pellets which were about 15 mm in height and 10 mm in diameter. Then they were inserted between the two platens of an INSTRON testing facility , as shown in Fig. 1, to be creep sintered.

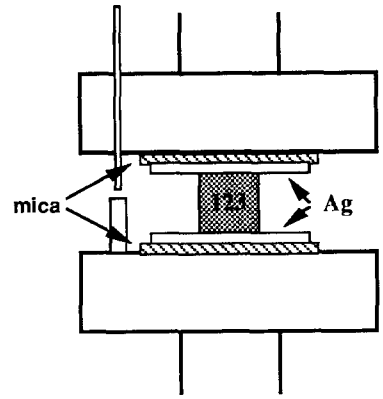

Fig. 1 Schematic view of the set up before deformation of the specimen.

The specimens were creep sintered in air according to the temperature and load run depicted in Fig. 2.

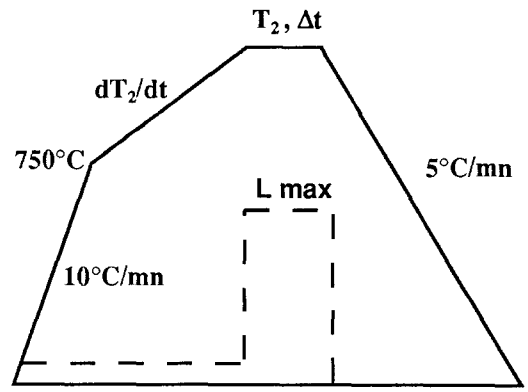

Fig. 2 Temperature and load run.

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2.1 Optimization of the process

It was found that the result depends on numerous parameters [1], namely :
- the second temperature ramp rate
- the temperature of the sintering dwell
- the duration of the sintering dwell
- the rate at which the load is increased
- the maximum value of the load
- the instant at which this value is reached
- the duration of application of the load
- the grain size and the purity of the powder
- the nature and the thickness of the contacting material
- the composition of the surrounding atmosphere
- the re-oxygenation treatment

Most of these parameters were patiently varied one at a time [1], but only essential results will be presented here down.

For the sake of optimization of the process, the degree of texture of the creep sintered specimens was estimated with the Lotgering factor [2], F, which varies from 0 for randomly oriented grains to 1 for perfectly aligned (ab) grains. $F = \frac{P-P_0}{1-P_0}$ $P = \frac{\Sigma I_{(00l)}}{\Sigma I_{(hkl)}}$;

$I_{(hkl)}$= intensity of (hkl) peak on the X-ray diagram

The influence of the sintering temperature on the texture is shown in Fig.3. In good agreement with a sintering stimulated by the presence of a liquid phase, this graph shows that the influence of the temperature is marked above 890°C, the temperature at which the liquid phase appears.

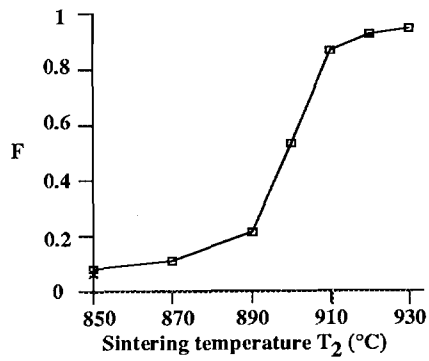

Fig. 3 Influence of the sintering temperature on the degree of texture defined by the Lotgering factor F

As shown in Fig.4, the heavier is the load the stronger is the texture . But more than the load, the deformation induced by the load is the parameter of relevance. In fact, the initial thickness of the specimens has to be reduced by a factor of at least 10 to get a strong texture. The time during which the load is applied is also of great importance. As emphasized by Fig.5, the kinetics of texturing is rapid during the few first minutes when the load is increased up to its fixed value and then slower and slower under constant load.

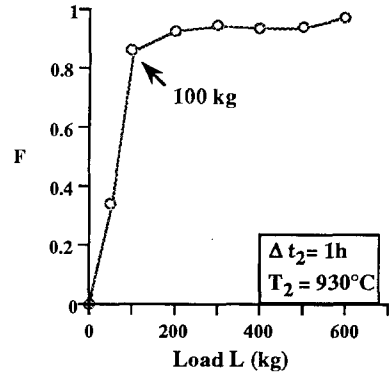

Fig. 4 Influence of the applied load on the degree of texture.

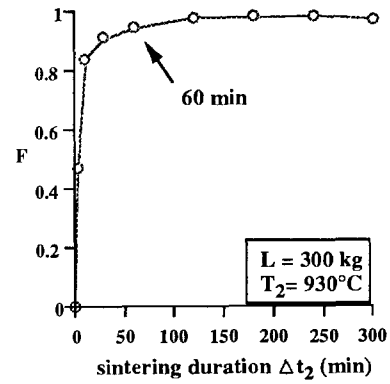

Fig. 5 Kinetics of texture formation.

3.2 Microstructural characterization

The prepared pellets were ground to remove their silver envelop and their degree of texture was estimated on a more physical ground via the (006) rocking curves performed on the faces normal to the applied load. Since the half height width of these curves is a measure of the average misorientation of the (ab) planes, the most peaked curve of the Fig. 6 shows that we finally succeded in reducing this average misorientation down to about 8° .

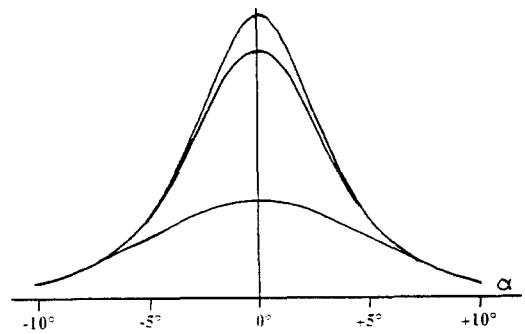

Fig. 6 (006) rocking curves of variously textured samples. Intensity in arbitrary units

In agreement with this, it was observed on diamond polished and etched cross sections that the grains were flat and rather well aligned (Fig . 7).

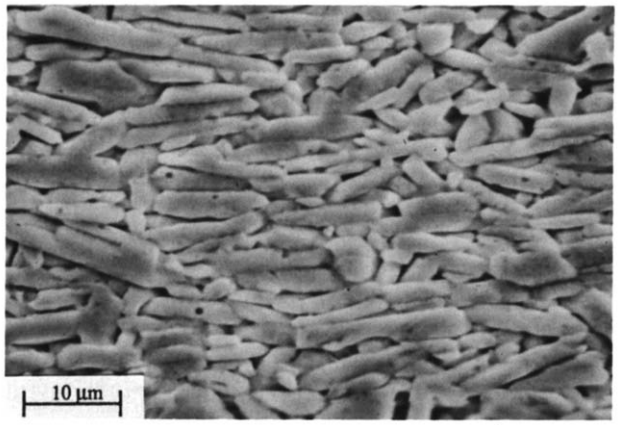

Fig. 7 Aspect of the grains observed in SEM on a cross section normal to the applied load.

Morever, it is worth noting that the specimens were almost perfectly dense after the creep sintering run and only slightly porous after the re-oxygenation treatment, remaining still mechanically strong.

2.3 Texturing mechanism

The texture we observed can be either due to the rotation of the initially randomly oriented grains or to the growth of well oriented grains at the expense of others. The relative importance of these two mechanisms depends on the temperature and on the deformation.
Rotation can be generated by the motion of dislocations into the grains, as in the case of texturing of metallic foils, or by the rolling of the grains one over another.
But, even if plastic deformation of the grains contributes to texturing, it certainly does not control its kinetics since this should lead to a strain rate proportional to the stress at an exponent ranging from 3 to 7, which was not observed.
As for the growth rate, it is considerably enhanced by the faster transport of atoms in the liquid phase. When no load is applied, due to the strong anisotropy of the material, platelet like grains develop at random orientation. Now when a heavy load is applied, the growth is "polarized" by the load as in Herring Nabarro or Coble creep. But these mechanisms, even when stimulated by the liquid phase, do not generate any re-orientation of the grains ; nevertheless, they quickly dissolve badly oriented grains and they re-precipate the removed atoms on the side of well oriented grains. The detailed microstructural characterization we have performed on the creep sintered specimens let us think the texture is mostly built up in that way.

2.4 Electrical characterization

From the electrical point of view, as shown in Fig. 8 , the lower the misorientation between the (ab) planes, the lower the resistivity in the normal state. Moreover, confirming the pronounced texture, the resistivity of our samples was close to that measured along the (ab) planes of single crystals.

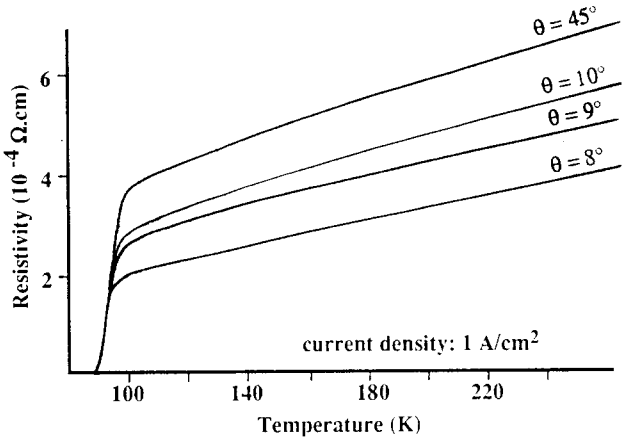

Fig. 8 Resistivity as a function of temperature for various average misorientations of the (ab) planes.

The transport critical current density, Jc, was measured in specimens of 1 mm^2 in cross section., Starting from 150 A/cm^2 for the untextured material, we increased it up to 650 A/cm^2 by reducing the average misorientation between the grains to 8°.
The comparison with the results of Dimos et al. [3] and Chaudhary et al. [4], refering to thin bicrystalline films, indicates that Jc can certainly be increased further by improving the texture, especially by achieving some alignment of the a and b directions.

3. Current limitation by amorphous phase

Texture is a necessary requirement for achieving high critical currents but, more than texture, what restricts the Jc of our samples to low values is the presence of thin amorphous bands probably of a complex carbonate, which cross over the grains or decorate some of the grain boundaries [5]. These bands are detrimental for the critical current, since they are insulating. They come from the solidification of the liquid phase which on the other hand is beneficial as it stimulates the densification and the texturing of the material. In a first attempt, we tried to get rid of them by operating under pure flowing oxygen. This led to a material containing less of the secondary phases of the equilibrium diagram of the Y, Ba and Cu oxides. Moreover the transport critical current density of the untextured samples was 2

times higher. But the amorphous bands were still present in the material.

3.1 Proposed solution

To cope with this dilemma, we decided to try to modify the composition of the liquid phase so that it would then dissociate during the subsequent heat treatments. At best, the precipitates would be widely separated or located at grain boundary corners and triple junctions, leaving the faces of the grains clean and properly welded.
Following this strategy, we added 2.5 wt % of Pb substituted Bi 2223 to our YBaCuO powder and creep sintered the mixture at 910°C, a temperature at which the 2223 phase is melted. Due to the abundance of the liquid phase, the pellets so prepared were extremely dense and in addition rather textured, in the X-rary diffraction diagram the (110) peak was 10 times smaller tha the (006) one.

The different phases present were identified in the electron microprobe on diffusion couples of the 2 superconductors as reported elsewhere [6] and It was checked on a coaser grained powder that the YBaCuO grains were really coated after creep sintering [7]. In agreement with the assumption that the grains of our fine grained Rhône Poulenc powder would be coated too with a non superconducting material after the creep sintering run, it was found that the Jc of the specimens was practically zero at this stage. But, confirming our hope, after a 100 h annealing at 850°C followed by our regular re-oxygenation treatment, the Jc measured on a specimen of 1 mm^2 in cross section was boosted up to 1010 A/cm^2 at 77 K and 1950 A/cm^2 at 63 K. These values are about twice those we used to get on specimens prepared with the pure powder and having the same section and exhibiting the same degree of texture [Fig. 9).

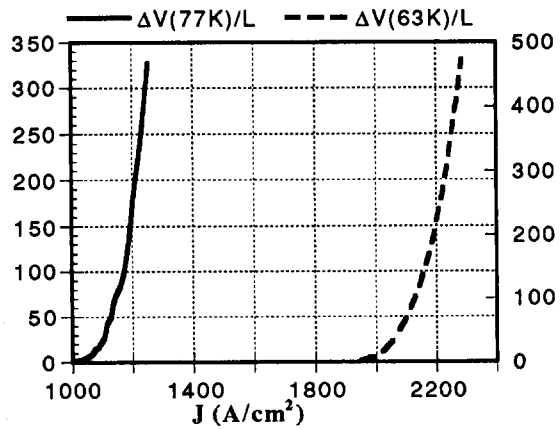

FiG. 9 Voltage drop versus current density of a creep sintered rod of YBaCuO-2.5 wt % Pb sustituted Bi 2223.

This reult is very encouraging since neither the amount of Bi 2223 nor the creep sintering and the post annealing treatments were optimized. Furthermore Pb substituted 2223 is probably not the best liquid phase, but a deeper understanding of its role in the already prepared sample shoul help finding a better one.

4. Conclusion

We have shown that the combination of creep sintering and of an appropriate modification of the liquid phase which stimulates it, allows to increase the transport critical current density of YBaCuO bars, of 1 mm^2 in cross section, from 150 A/cm^2 to more than 1 000 A/cm^2 at 77 K. The mere reduction of the sample thickness should already lead to higher values, since J_c is proportional to the inverse of this parameter. But even more interesting improvements are to be found in optimizing the process.

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