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Bridgman growth and enhanced critical currents in textured $YBa_2Cu_3O_7$ - Y_2BaCuO_5 composites

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Abstract

A new method of melt textured growth of monolithic $YBa_2Cu_3O_7$ superconductors has been developed based on a vertical Bridgman method . Long bar samples have been prepared having typical sizes of 100 x 3 x 2 mm^3 and the growth conditions were typically R = 1mm/h and G = 20 °C/cm . The microstructure of the samples was investigated by means of polarized optical microscopy . Single domain textured ceramics having different concentration and size of Y_2BaCuO_5 (211) precipitates have been obtained . We show that our method allows preparation of monolithic conductors having a very homogeneous distribution of micronic or submicronic precipitates while the growth front is maintained along several cm . Critical currents of single domain samples have been measured with a SQUID magnetometer and we have found J_c^c values as high as 6 x 10^4 A/cm^2 at 77 K . We show also that the enhancement effect of critical currents by 211 precipitates is strongly field dependent , being effective only at low magnetic fields . This field dependent effect encompasses a saturation effect in the displacement of the irreversibility line towards higher fields . The mechanisms leading to the observed complex behavior are analyzed .

1.Introduction

It is already well known that the development of practical large scale - high critical current applications of high temperature superconducting materials involves a processing step leading to textured materials . The necessity of this complex processing procedure arises from the weak link nature of the grain boundaries existing in polycrystalline ceramics even if the exact nature of this weak link behavior is still under discussion [1] .

Several methods have been proposed by different authors to overcome the grain boundary problem in 123 superconductors [2-4] . All these methods are based on the peritectic reaction of Y_2BaCuO_5 (211) solid particles with a Ba-Cu-O liquid when the sample is slowly cooled through the peritectic temperature . The directional solidification necessary to obtain bulk textured samples may be achieved either with a temperature gradient [2] or a magnetic field [5] . However , as we will comment later in this paper the exact mechanism leading to misorientation of grains with respect to the vertical direction in Bridgman growth is still an open question which must be further addressed .

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The achievement of high critical currents in $YBa_2Cu_3O_7$ ceramics not only requires to eliminate the formation of high angle grain boundaries , there is also an urgent need for creating new pinning centers which would allow to extend the use of superconductors at high temperatures and at high fields . It has been suggested by several groups [3,6,7] that the 211 precipitates remaining imbeded in the 123 matrix after an incomplete peritectic reaction are acting as pinning centers and so they enhance the critical currents . The observation of higher critical currents when the concentration of these precipitates is increased has been used as an evidence of this pinning behavior , however this interpretation may be misleading because there exists also strong modifications of the microstructure (cracks, dislocations , twin boundary concentration , etc.) accompassing the doping process . There is a need then for a systematic investigation of the correlation between microstructure and the irreversible behavior of these superconducting materials . It must also be stressed that definitive conclusions may be obtained only when a full examination of the whole H - T phase diagram is carried out because the crossover between pinning regimes (single vortex to collective) may shift as a consequence of the enhanced critical currents [8].

In this paper we report first on the preparation of monolithic melt textured bars through a simple procedure which do not involve any special thermal treatment of the 123 precursor , as it is often

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carried out by other authors . We show that different concentrations of 211 precipitates may be achieved when we prepare ceramic precursors having different 123 to 211 ratios . As a consequence of the modified conditions for the peritectic reactions we find a systematic reduction of the size of 211 precipitates .

2. Experimental

Initial preparation of ceramic samples was achieved trough a mixing process with an agata mortar of commercial 123 superconductor and 211 ceramics prepared by solid state reaction . Semicylindrical bars up to 12 cm in length and 0.3 cm in diameter were sintered in a constant temperature furnace . The initial composition of the ceramic composite was varied from 0 % to 30 % in weight of 211 phase . These bars were then suspended vertically in a Bridgman furnace working in air . The furnace was heated up to a maximum temperature never surpassing 1.050 °C and finally the bars were displaced at a constant rate of 1 mm/h in a region having a longitudinal gradient of 20 °C/cm until the full bar has been cooled down to 900 °C . Finally , the bars were oxygenated at 450 °C during typically 72 hours . It is important to stress that within our experimental resolution we have not detected any lateral temperature gradient in the furnace when we look at the space reserved to the sample , in the absence of the growing bar .

A full inspection of the samples was achieved through polarized optical microscopy of polished samples where it is very easy to identify crystalline domains separated by high angle grain boundaries . Single domains could be easily separated and oriented optically taking advantage of the fact that cracks are mainly oriented parallel to the a-b plane . Finally , we have verified the correctness of our orientation procedure through magnetic measurements which display a pronounced anisotropic behavior . It is also straighforward to note that these low field ac susceptibility measurements or , equivalently , high frequency rf mutual impedance measurements with a microprobe [7] are very sensitive to the existence of any residue of a misoriented domain and hence we may feel very confident on the quality of the samples choosed for inductive critical current measurements.

Isothermal magnetization curves were measured at 77 K with a SQUID magnetometer using short sample scans (2 cm) to avoid any perturbation associated to field inhomogeneities . The typical size of the samples was 2x2x1 mm^3. We have also measured the irreversibility line in some selected samples and compared to a single crystal grown by the flux method and being free from any 211 precipitate . In all the measurements presented in this paper we refer only to the H || c orientation . Finally , because a great discrepancy may exist between the nominal concentration of 211 phase an the actual content after the melt textured growth process we have also measured the paramagnetic susceptibility in all the examined samples up to 300 K . From these measurements a Curie - Weiss component may be detected which arise completely from the 211 phase and hence we may estimate the real concentration in each sample .

3. Results and discussion

The first problem which needs to be carefully analyzed in any directional solidification process is at which point a controlled nucleation and growth front is achieved . In our experimental setup we usually find an initial multiple nucleation process which after some growth competition leads to a single grain extending along the vertical axis. In Fig. 1 we show , for instance a typical bicrystal of a nominally 0 % 211 sample corresponding to two different growth fronts having the a - b planes (parallel to the cracks) forming nearly 45° from the vertical axis . In most samples a unique domain is finally achieved which may lasts up to 3 cm and which is often misaligned from the vertical axis . The origin of this deviation of the a - b planes , which is assumed to be the direction of rapid growth rate , from the thermal gradient axis is controversial at present . It has been recently suggested by Selvamanickan et al [9] that a lateral thermal gradient appears as a consequence of an enhanced effectiveness in the dissipation of the fusion latent heat through the lateral surfaces . This would lead to a plane growth front forming a certain angle from the vertical axis , not particularly 45° . Our experiments show very often that this misorientation may be much higher than 45° , thus supporting the idea that the thermal transfer towards the lateral

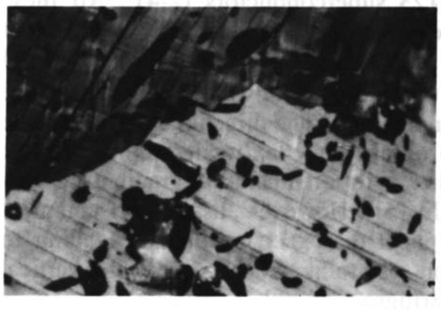
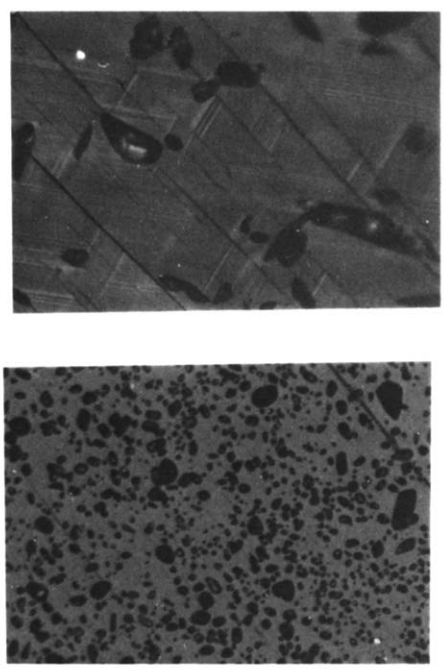


Figure 1. Grain boundary of two domains misoriented by 90° in a nominally 0% sample . The growth axis is horizontal.

surfaces is indeed the key factor in the control of the orientation of the growth front . Further experiments with variable crystallization rates and longitudinal thermal gradients are needed to confirm this assertion

Now focusing our attention in the microstructure of the single domains corresponding to different samples we may easily observe that an increase in the nominal concentration of 211 phase in the initial composite leads to 211 precipitates with a progressively reduced size (Fig. 2) , eventhough the crystallization rate was identical in all the samples . While in the 0% sample the particles have a rod character with mean dimensions 10 μm x 4 μm in the nominal 20 % sample the mean size is reduced to about 1 μm and the shape is more spherical . Simultaneously , the density of cracks running parallel to the a - b planes is strongly diminished (mean distance in 0% about 10 μm , hardly visible in 20 % and 30 %). Finally , an estimation of the volume concentration of 211 precipitates has been achieved either from the optical micrographs or from the paramagnetic susceptibility measurements . We found that the nominal 0 % sample has already about 15 % of 211 phase , and this concentration is progressively increased when the initial concentration of 211 phase in the composite is augmented , finally saturating to about 45 - 50 % in the 30 % sample .



(a)

(b)

10μm

Figure 2. Polarized optical micrographs of single domain samples having nominal 211 phase compositions of (a) 0% and (b) 20%. The actual 211 contents are about 15% and 40% in volume , respectively.

It has already been mentioned above that 211 precipitates remain in the 123 matrix because the peritectic reaction is incomplete , the main limitation for a full exhaustion being the atomic diffusion through the peritectic solid phase (123) and hence we must conclude that the final size is reduced because we have increased the concentration of the nucleation centers (211 particles) . A wide program intending to prepare conductors with controlled size of the precipitates is now in progress . This will allow a systematic comparison of the critical currents in samples having different concentrations of all the defects existing in melt textured ceramics .

Typical hysteresis loops observed in our samples are shown in Fig. 3 where we may note that the width is enhanced at low magnetic fields when the nominal concentration of 211 is increased . The magnetic field dependence of J_c^c for different samples may be observed in Fig.4 where it is straighforward to note that an optimum concentration of 211 phase appears at about 15 - 20 % which corresponds to a real volume concentration of about 40% . An optimum concentration of 211 precipitates has also been recently observed [10] and it may be understood as arising from a competition between two opposing terms . In one hand , if we admit that 211 particles are active interphase pinning centers we must lead to the conclusion that J_c should increase indefinitely . However we must also consider that the volume of

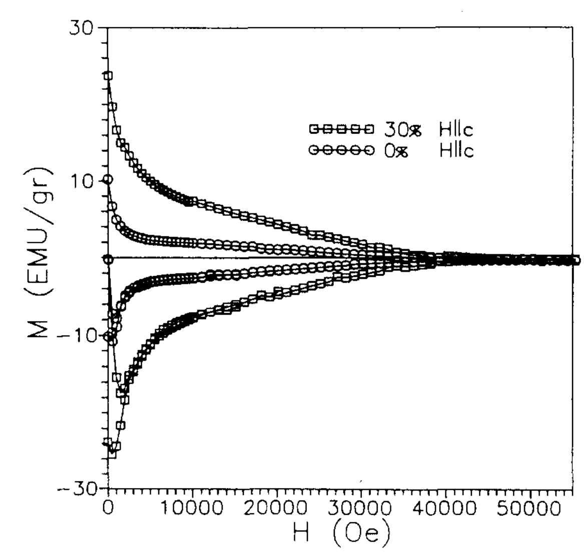


Figure 3. Hysteresis loops measured at 77 K in two $YBa_2Cu_3O_7$ samples having a nominal excess of 211 phase of 0% and 30%.

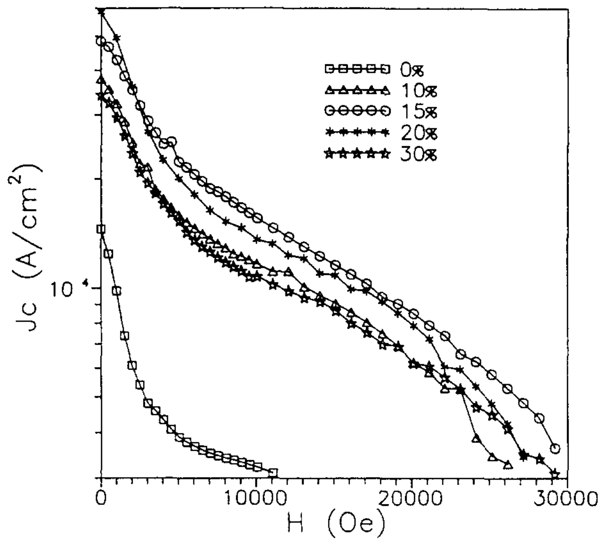


Figure 4. Magnetic field dependence of the critical currents measured at 77 K and H || c in samples having different nominal concentrations of the 211 phase.

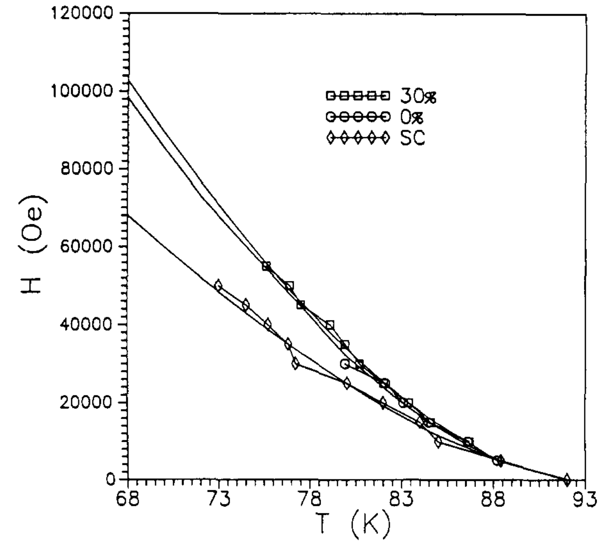


Figure 5. Irreversibility lines corresponding to a $YBa_2Cu_3O_7$ single crystal (SC) and two melt textured samples with nominal 211 compositions of 0% and 30%.

123 phase is also reduced and hence the shielding currents must run through progressivelly narrower channels which will finally limit the total amount of flowing current .We must stress , however , that our optimum concentration is higher than that previously reported by other authors [10], probably indicating that our precipitates are smaller and hence our surface / volume ratio is greater .

The irreversibility line of several samples was measured through zero field cooled - field cooled temperature dependent magnetization protocols in the SQUID magnetometer . Similar temperature scan rates (0.5 K/min) have been used in order to be able to compare the results between different samples . In Fig. 5 we show our results with three different samples . We observe first a shift of H_{irr} (T) towards higher temperatures on going from the single crystal towards the 0% sample . This may indicate that 15% of 211 particles (0% sample) is enough to increase the pinning forces dominating at high fields but after this a saturation effect appears. A similar behavior has been reported in proton irradiated 123 single crystals [11] and neutron irradiated melt textured ceramics [12] where in spite of a strong enhancement of critical currents at low fields , the irreversibility lines remain unchanged . In the case of extended defects ,instead , a clear displacement may be observed [11] . The different behavior of point and extended defects regarding their pinning characteristics at low and high fields may be indicative of a diverging behavior in the single vortex or collective pinning regimes .

In conclusion , we have demonstrated that the Bridgman technique has a very strong potentiality in preparing long single domain $YBa_2Cu_3O_7$ monolithic conductors with high critical currents allowing to develop large scale electrical engineering applications.

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