Microstructural and magnetic analysis of a superconducting foam and comparison with IG-processed bulk samples

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Abstract. YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{y} (YBCO) foam samples show an open, porous foam structure, which may have benefits for many applications of high-$T_c$ superconductors. As the basic material of these foams is a pseudo-single crystalline material with the directional growth initiated by a seed crystal similar to standard melt-textured samples, the achieved texture of the YBCO is a very important parameter. We analyzed the local texture and grain orientation of the individual struts forming the foam by means of atomic force microscopy and electron backscatter diffraction (EBSD). Furthermore, the magnetic properties of a foam strut are evaluated by means of SQUID measurements, from which the flux pinning forces were determined. A scaling of the pinning forces in the temperature range between 60 K and 85 K was performed. These data and the details of the microstructure are compared to IG-processed, bulk material.

1. Introduction

For applications of high-$T_c$ superconductors, not only high critical current densities are of importance, but also the weight and the production costs play a significant role. In order to develop new types of superconducting material, Reddy et al. [1,2] developed superconducting foams with an open-cell structure. These materials offer a light weight, the possibility to produce very large sample sizes, as well as an easy oxygenation process. The fabrication of these foams is based on polyurethane foams, which are coated with a slurry of Y\textsubscript{2}BaCuO\textsubscript{5} (211), and then the material is transformed into superconducting YBCO using an infiltration growth (IG) process. The IG process can be applied to the fabrication of large, bulk YBCO samples as well as described in Refs. [3-6]. Therefore, it is interesting to compare the superconducting properties (critical current density, flux pinning) and the achieved microstructure of the foams and the IG-processed samples with each other.
2. Experimental procedure

The foam sample studied here was fabricated at ACCESS, Aachen as described in Refs. [1,2,7]. The IG-processed YBCO samples were produced at SIT, Tokyo according to Refs. [5,6]. A foam strut was broken out of the big piece at a position close to the seed (position (1) in Ref. [7]). For the IG-processed sample, pieces of $1.5 \times 1.5 \times 0.5 \text{ mm}^3$ were cut from the bulk using a diamond saw.

For the characterization of the microstructure, all sample surfaces were mechanically polished prior to scanning, either dry from 12 µm to 0.5 µm 3M diamond paper or wet from 320 grain SiO paper to 4000 grain SiO paper and then from 3 µm diamond polishing solution down to 40 nm colloidal silica suspension [8]. After that, the samples were cleaned for several minutes in acetone in an ultrasonic bath and then for several minutes in an ethanol bath. Both surface preparation methods serve well for the AFM/STM measurements, as well as for the electron backscatter diffraction (EBSD) analysis [8].

![Figure 1](image1.png)

**Figure 1.** Critical current density for the foam (a) and the IG-processed sample (b) and the corresponding flux pinning force scalings (c,d). The currents of the foam sample are much smaller than that of the IG-processed sample, but the pinning force scaling is similar. Note the extremely high peak positions of the scaling for both samples at $h_0 = 0.5$ (foam strut) and 0.52 (IG-processed sample).

AFM scans were performed using Digital Instruments Nanoscope III and IV controllers in contact mode and tapping in ambient conditions. A Q-control unit was used to improve the signal-to-noise ratio in the tapping mode. The magnetic characterization was performed using SQUID magnetometers (QD MPMS 5 and 7XL). The EBSD analysis was carried out on a TSL OIM analysis unit [9] mounted in a JEOL SEM microscope (JSM 7000F).
3. Results and discussion

Flux pinning data ($F_p$) were calculated from the critical current densities, $j_c$, as function of applied field. The irreversibility field, $H_{irr}$, was determined for the IG-processed sample using a criterion of $10^4$ A/cm$^2$; in case of the foam, $H_{irr}$ was determined directly from the $M(H)$ loops. A scaling of the $F_p$ data was performed using the approach of Dew-Hughes [10,11]. The data for $j_c$ and $F_p$ are presented in Figs. 1 (a,c) for the foam strut and in Figs. 1 (b,d) for the IG-processed sample.

![AFM topography images of polished surfaces from a foam strut (a) and the IG-processed YBCO sample (b). The inset to (a) shows the stripes filled with tiny secondary phase particles (arrows).](image)

The $j_c(H)$-data of the foam show an exponential decay on increasing $H$, whereas $j_c(H)$ of the IG-processed sample reveals the peak effect. This is a direct consequence of the much easier oxygenation process of the open-cell foam structure. The $F_p(H)$-data of both samples are, however, pretty remarkable. The IG-processed sample reveals a good scaling, and the peak position, $h_0$, is located at a very high value of 0.52. Such a high value is reported in the literature only for the NEG-type 123-superconductors [12,13]. This is a consequence of the strong pinning of the $\delta T_c$-type which is also responsible for the peak effect. Another interesting result is the size of $H_{irr}$ being extremely high for any type of YBCO sample measured so far. The magnetization data for the foam sample reveal homogeneous and symmetric $M(H)$-curves at low temperatures, but exhibit signs of granularity at elevated temperatures. Therefore, $j_c$ reduces quickly at more elevated temperatures, and there is no peak effect. The critical currents determined for the foam sample are quite low as compared to the IG-sample, but similar values were found also previously in Refs. [14,15] at $T = 77$ K. Nevertheless, also for the foam sample the determined irreversibility fields are quite high.

Now, we have a closer look at the respective microstructures. Figure 2 presents AFM topography images of polished surfaces of both samples. The foam sample (a) exhibits many large, densely packed 211 particles embedded in the YBCO matrix. The grain size of the 211 particles ranges from 1 up to 10 $\mu$m. The YBCO matrix reveals characteristics stripes, being between 1 – 15 $\mu$m apart from each other. Topography images with higher magnification (see the inset and Ref. [7]) reveal that the spaces between these stripes are filled with tiny secondary phase particles with dimensions of about 200 nm. The EBSD imaging (Figs. 3,4) and EDX analysis demonstrates that these particles are 211...
particles. In contrast to this, the 211 particles of the IG-processed sample are very small with the majority of them having sizes around 50 - 100 nm, but also some large 211 particles prevail.

Figure 3. SEM images of the two sample types, taken in EBSD configuration (70° inclined to the electron beam). The two images are scaled so that the size of the scale bars is the same. (a) shows the foam strut, and (b) the IG-processed sample. The IG-processed sample exhibits a large number of tiny 211 particles embedded within the YBCO matrix. Note in both cases the smooth sample surface which is free of any scratches, indicating that the tiny 211 particles are formed naturally.

In order to learn more about the texture of the superconducting matrix and the influence of the embedded 211 particles on it, we performed an EBSD analysis on the samples. In this case, a two-phase scan is required. Figures 4 (a) and (b) show the phase maps of both samples; YBCO is denoted in red and the 211 particles in green. Additionally, the EBSD-detected grain boundaries are marked by black lines. In the foam strut large 211 particles dominate, but there are also many tiny 211 particles found within the YBCO matrix, and especially between the characteristic stripes of the YBCO phase as seen already by AFM. In the case of the IG-processed sample, the YBCO matrix is well extended (i.e., the entire section corresponds to one big grain) with 211 particles embedded within. However, there are also small YBCO subgrains formed close to the 211 particles and even within them. Figures 4 (c) and (d) present the IQ+IPF mappings (IQ = image quality parameter (gray scale) and IPF = inverse pole figure (color-coded, see the stereographic triangle)) in (001)-direction for the foam strut (a) and the IG-processed sample (b). In both cases, the 211 particles do not show a preferred orientation. The YBCO matrix of the foam strut (c) shows an orientation (the dominating color is orange, see the stereographic triangle), but also (110)-oriented areas (light blue) do exist. The phase map (a) of the foam strut reveals many small 211 particles being embedded within the stripes of the YBCO phase. However, the IPF map (c) shows that all these particles are randomly oriented. More details on the EBSD analysis of the foam sample are reported in Ref. [7]. The IG-processed sample shows a well-oriented YBCO matrix in (001)-orientation. Also in this case, the 211 particles are randomly oriented and exhibit internal misoriented subgrains.
Figure 3. EBSD phase maps for the foam strut (a) and the IG-processed sample (b). YBCO is shown as red, and the 211 phase in green. In both maps, the detected grain boundaries are marked using black lines. EBSD IQ (gray scale)+IPF (color coded) maps in (001)-orientation for the foam strut are shown in (c) and the same for the IG-processed sample in (d). The arrows in (d) mark tiny 211 particles embedded in the YBCO matrix. The color code for the IPF maps is given in the stereographic triangle, which is the same for both phases.

A comparison of the phase map and the IPF map reveals that in the close neighborhood of the larger 211 particles also misoriented YBCO particles exist. This is due to a mismatch of the unit cells of the two phases as already observed in Ref. [16]. At some orientations of the 211 phase, the growth of the YBCO phase is altered due to stress/strain, and subgrains are formed. The tiny 211 particles are not detected in this EBSD scan due to the stepsize of 70 nm used for the EBSD mapping. Only some ~100 nm particles were found (marked by arrows) within the YBCO matrix. Therefore, an EBSD scan with a smaller stepsize is required to detect the tiny 211 particles embedded in the matrix. The high image quality of the Kikuchi patterns achieved in the previous scans allows such measurement.
Figures 5 (a,b) present an EBSD measurement on the IG-processed sample with a stepsize of 40 nm. The large number of grain boundaries seen in (a) reveals that the YBCO phase exhibits misoriented grains with sizes ranging between 80 and 800 nm. The grain size of the majority of the 211 particles is between 50 and 100 nm, but also some larger 211 particles (lower right corner) can be observed. The IQ+IPF map (b) shows some interesting features: (i) There are only two orientations of the 211 particles (green, blue) found in the entire scan area and also of the YBCO subgrains, which demonstrates the alignment of the YBCO and 211 particles due to stress/strain as discussed before. (ii) The comparison of the phase map and the IQ+IPF-map reveals that on this scale, there is a large amount of misorientation of the YBCO phase due to the presence of the 211 particles. These misorientations of the YBCO subgrains together with the tiny 211 particles provide an unique flux pinning landscape, which is directly responsible for the large irreversibility fields observed in the magnetic measurements. (iii) The image quality of such a high resolution scan is much lower as compared to Fig. 4. This shows that these measurements are close to the detection limit of the standard EBSD technique on samples with nano-sized structures; a higher resolution can only be achieved employing the transmission EBSD (t-EBSD) technique [17].

Figure 5. EBSD measurements on the IG-processed sample with a stepsize of 40 nm. (a) gives the phase map (YBCO – red, 211 – green) and the detected grain boundaries are marked with black lines. (b) shows the IQ+IPF map in (001)-direction. The color code is the same as in Fig. 3 (d).

To summarize our observations on both types of samples, the microstructure analysis clearly reveals the differences, but also the common features of the two types of materials produced by the IG-technique. While the overall orientation of the YBCO matrix is different in the two samples, the presence of tiny 211 particles is common for both and according to the results presented in Ref. [13], directly responsible for the high irreversibility fields due to the effective flux pinning. The high irreversibility fields and the high peak positions in the pinning force scaling make the IG-processed materials ideal candidates for high-field applications.
Conclusions

The comparison of a YBCO foam sample with an IG-processed YBCO bulk reveals many differences, but also common features due to the similar processing technique. The foam contains many large 211 particles, but also tiny ones which provide additional flux pinning sites. The YBCO matrix is oriented, but not as perfect as in the case of the IG-processed bulk. Here, the 211 particle size is much smaller, and the matrix contains even smaller (~50 nm) 211 particles. EBSD scans with high resolution (stepsize 40 nm) reveal that the 211 particles only show two main orientations, which cause misorientations of the YBCO matrix. This characteristic pinning landscape is essential for the high irreversibility fields observed.

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