SUPERCONDUCTING MATERIALS BY DESIGN: BULK WITH ARTIFICIAL THIN WALLS FOR CRYO-MAGNETS

PROJEKTOWANIE MATERIAŁÓW NADPRZEWODZĄCYCH ZE STRUKTURAMI CIENKOŚCIENNYMI WYKORZYSTYWANYCH NA KRIOMAGNESY

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Abstract: From Y_2BaCuO_5 (Y211) foam structure and perforated Y211 bulk with various an artificial array of holes, single domain composites $YBa_2Cu_3O_y$(Y123)/Y_2BaCuO_5 have been prepared by combination of the infiltration and top seed growth (ITSG) process. The process involves the shaping of 211 preforms by conventional ceramic routes such as uniaxial and isostatic pressing. A compact of 123 or 123 rich in liquid phase, acting as a source is placed in contact with the 211 "reservoir", and heated above the peritectic temperature of 123. The liquid source infiltrates the perforated reservoir and the peritectic reaction occurring between the preform 211 and the matrix (liquid phases) during slow cooling from the peritectic temperature results in the growth of 123 with uniformly distributed fine 211 particles.
The goal is to facilitate sample oxygenation and decrease crack formation in order to address the problem of hot spot formation during d.c. transport current characterizations. As-processed samples contain mechanically patterned holes parallel to the mean c-axis interconnected of the textured domain. This makes samples easier to oxygenate and cool.
This approach would allow a better reproducibility in the elaboration of the holes which would make accessible modelled experiments. It will be demonstrated in this work that this latter approach can be used to obtain Y123 bulks exhibiting microstructures, textures and properties under magnetic fields similar to the usual bulks of the literature.
Keywords: superconducting material, Y123 bulk, peritectic reaction, cryomagnet

Streszczenie: Z materiału Y_2BaCuO_5 (Y 211) o strukturze pianki i perforowanego materiału litego z różnym rozkładem porów, w wyniku złożenia procesów infiltracji (wnikania) i rozrostu fazy (ITSG), otrzymano kompozyt $YBa_2Cu_3O_y$ (Y 123) / Y_2BaCuO_5 (Y 211) złożony z pojedynczych domen. Taki proces pozwala na kształtowanie struktury typu Y 211 na drodze konwencjonalnych metod stosowanych w ceramice, takich jak jednoosiowe lub izostatyczne prasowanie. Wypraska z materiału Y 123 lub Y 123 bogatego w fazę ciekłą,

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działająca jako źródło w połączeniu ze „zbiornikiem" Y 211, jest wygrzewana do temperatury powyżej temperatury perytektycznej Y 123. W wyniku czego ciekłe źródło wnika w perforowany materiał i zachodzi reakcja perytektyczna między fazą Y 211 i matrycą (faza ciekła). Podczas powolnego chłodzenia od temperatury perytektycznej zachodzi rozrost fazy Y 123 z jednorodnym rozkładem drobnych cząsteczek Y 211.
Celem pracy jest określenie warunków zwiększonego dotleniania i obniżenia tendencji do powstawania pęknięć w odniesieniu do tworzenia się „gorących punktów" podczas zachodzenia charakterystycznych procesów. Tak otrzymane próbki zawierają mechanicznie modelowane pory równoległe do głównej osi c powiązanej z teksturą domen, co ułatwia dotlenianie i chłodzenie próbek. Takie podejście do eksperymentu pozwala na uzyskanie lepszej powtarzalności wyników w odniesieniu do modelowania rozkładu porów. Praca pokazuje, iż prezentowana tutaj metoda może być stosowana do otrzymywania materiałów typu Y 123 o odpowiedniej mikrostrukturze, teksturze i właściwościach magnetycznych podobnych do typowych materiałów znanych z literatury.
Słowa kluczowe: materiał nadprzewodzący, materiał Y123, reakcja perytektyczna, kriomagnes

1. INTRODUCTION

Since the discovery of the high temperature superconductivity in BaLaCuO [1], the YBCO oxide ceramics have been considered as one of the promising candidates for superconducting applications. Huge effort has been engaged to the development of the processing techniques to prepare the material with properties suitable for practical applications. The applications of superconductors for different systems require various geometries and forms as pellets, rods, thin and thick films, and complex bulk shapes.
The development of different melt processing methods has led to Y123 ceramics with properties acceptable for many applications [2−5]. However, despite these properties some problems exist for e.g. (i) oxygenating the whole bulk material without inducing any micro-cracks during the tetragonal-to-orthorhombic phase transition [6]. (ii) suppression of hot spots, commonly observed during the transport current application. To overcome these problems, the superconducting material processed as a foam structure or with the artificial drilled holes have been developed [7−11]. Using a combination of standard superconducting ceramic processing and an infiltration technique [12−14], single grain superconductor foams of $YBa_2Cu_3O_y$ (Y123) have been processed. An important feature of this process is that it offers the flexibility to produce large samples of near-net shape without distortions and cracks. In this process the liquid source (barium rich liquid phase and copper oxide) infiltrates into porous preformed Y_2BaCuO_5 (Y211) pellet, above the peritectic temperature (T_p) and reacts to form Y123. This can be expressed by the chemical reaction:

$$Y_2BaCuO_5 + (3BaCuO_2 + 5CuO) \longrightarrow 2\ YBa_2Cu_3O_x$$

The novel morphology of superconducting foam or bulk superconductor with multiple holes material processed seems to be a good candidate for increasing interfacial flux pinning if the pores can be made sufficiently small. Many other prospects are related to this novel structure like e.g.

- more efficient heat transfer

- faster oxygenation and less related micro-cracking, possibility of reinforcement and of interlocking connections etc.

Objectives of the present work are to give an overview of:

- single domain Y123 developed on the foam or artificial patterned holes of Y211
- superconducting properties of the porous materials.

2. EXPERIMENTAL

The Y211 precursor foams of different dimensions were fabricated as replica of commercial polyurethane foam (Fig.1a) with a porosity of 10-100 ppi. Details of $YBa_2Cu_3O_y$ (Y123) foam preparation have been reported elsewhere [7,8]. Figure 2 shows the schematic diagram of different steps involved in the preparation of Y123 foam by an infiltration-growth process.

The liquid phase ($3BaCuO_2 + 5CuO$) or $Ba_3Cu_5O_8$ (Y035) was prepared by solid state milling of stoichiometric amounts of high purity $BaCO_3$ and CuO in the agate bowl of a planetary mill for 2 hours. The mixed powder was then heat-treated at 870°C, 24 hours with intermediate grindings. The preparation of Y211 foams involves the coating/impregnation of polyurethane foam of desired porosity with optimised water based Y211 slurry. This slurry was prepared by mixing commercially available Y211 fine (~2 μm) powder in water with 5 wt% polyvinyl-alcohol (PVA) as binder. The process of coating/impregnation of polyurethane foams involves dipping the foams into the Y211 slurry and drying at room temperature. Repeating the step several times results in a thick Y211 coating. The organic components PVA and polyurethane were burned by slow heating at a rate of 50°C/h to 600°C for 6 hours in air. The final Y211 foam was sintered in air at 1100°C, 20 hours for densification. The final green Y211 pre-form was transformed into single-grain Y123 superconducting foam by infiltration growth process reported elsewhere[7,12−14] in using the configuration shown in Figure 2. The sample was rapidly heated to 1050°C for 30 min. At this stage the liquid phase infiltrate into the interstitial spaces between Y211 particles due to the capillary action. The peritectic reaction occurring between the green Y211 reservoir and the liquid phase source Y035 during slow cooling stage (1010°C to 980°C at 0.3°C/h) from the peritectic temperature results in the growth of Y123 grain. The samples, after grain growth, from 980°C were cooled to room temperature in 6 hours. The nucleation and orientation of Y123 phase is controlled by placing a *c*-axis oriented seed- either $NdBa_2Cu_3O_y$ (Nd123)/$SmBa_2Cu_3O_y$ (Sm123) or MgO-on top of the foam with a Y_2O_3 cloth [15] as support for the seed and to facilitate a homogeneous grain growth into the foam. On the other hand, the details of infiltration and top seed growth (ITSG) and multiple holes process of $YBa_2Cu_3O_y$ (Y123) are reported elsewhere [9,10,13]. The holes into the preform were realised by drilling cylindrical cavities with diameter 0.5–2 mm through the circular or square shaped sample. The holes are arranged in a regular network in the plane of the samples (Fig. 1b).

In addition, the as-processed samples were oxygenated at 450°C for 150 hours in flowing oxygen. For microstructural examination, the samples were mounted using cold resin and polished on a rotating machine (Tegrapol-31, Struers Inc.) using varying grades of diamond particle solution until ¼ μm as a final. The polished surfaces were examined using an optical microscope (Olympus, BH2-UMA) and scanning electron microscope, SEM (Philips XL 30 FEG) with EDX.

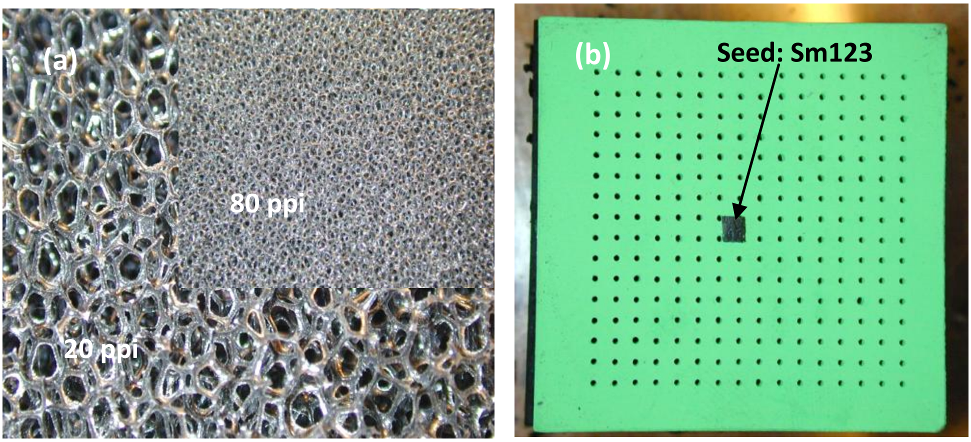

Figure 1. (a) Commercial polyurethane foams of various pore sizes,
(b) artificially patterned Y211 with multiple holes

Resistivity measurements were performed using the standard four-point contact method. Contacts between the sample and the current leads have been fabricated by painting silver paste (4929 Dupont Inc.) and subsequent annealing at 900°C for half an hour to ensure a good silver diffusion followed by oxygenation at low temperatures. A commercial PPMS (Magnet Power Supply) apparatus and a SQUID (Quantum Design) magnetometer were used for resistivity and magnetization measurements.

3. RESULTS AND DISCUSSION

The macroscopic top of the Y123 foams view are presented in Figure 2a. We can observe that, the resulting Y123 foam sample is single domain. The sample has an open porosity of 20 ppi (pores per inch) with a strut thickness of about 300 μm (Fig. 3a). Various number of single-grain Y123 foams of pore size between 10 to 100 ppi were reported elsewhere[7]. Polished surface (Fig. 3b) of the struts reveal the typical microstructural features known from melt processed bulk materials, with parallel platelet gaps and trapped Y211 particles in a Y123 matrix. From the microstructures the volume content of Y211 particles is estimated to be around 40 volume percent with an average particle size around 2–5 μm. The similar microstructure has been observed from multiple holes bulk sample. No specific efforts like doping [16,17] or irradiation [18] have been made to optimize the Y211 particle size and defect density with respect to high critical current densities.

The homogeneous distribution of Y211 inclusions in the infiltration-process can be explained as due to the small Y211 particles in starting Y211 pre-form. In this process, the Y211 particles are further dissolved in the liquid phase to form Y123 phase resulting in finer spherical 211 particles, in contrast to larger acicular size Y211 and their inhomogeneous distribution in the sample processed conventionally without any dopants [14].

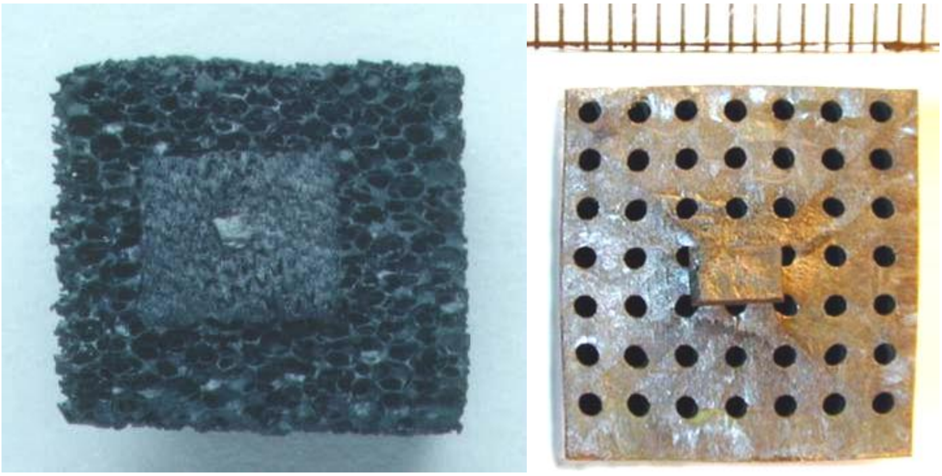

Figure 2. Photograph of a single domain Y123 (a) foam with a porosity of 20 ppi (pores per inch) and (b) bulk with multiple holes

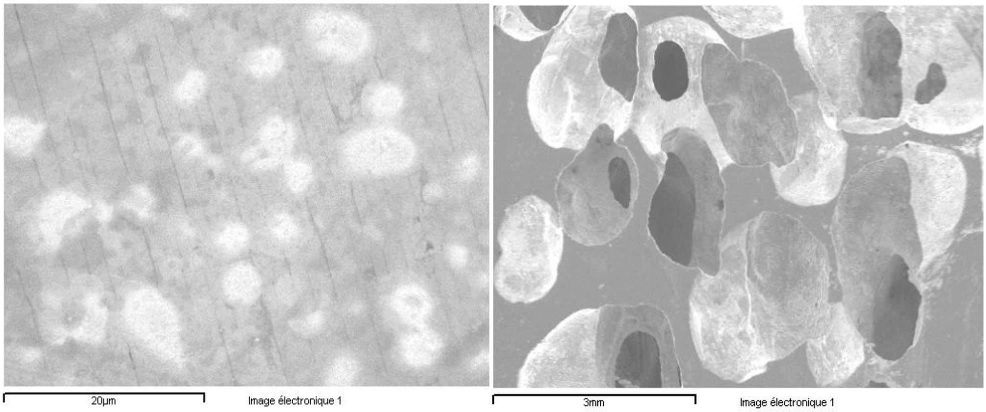

Figure 3. SEM picture, (a) of a fractured surface of superconducting Y123 foam, (b) of the polished surface of the struts reveals residual Y211 particle (white) inclusions in the 123 matrix

The Y123 foam was analyzed using XRD to check the grain alignment and the final sample composition. The diffraction spectrum of the polished surface of the sample is shown in Figure 4. The single-grain signature of the material, presence of only $\{00\ell\}$ peaks, can be evidenced from X-ray diffraction pattern. The XRD pattern also shows that the sample is a single phase with no observable impurities e.g extra liquid phase. Probably during infiltration process, according to the chemical reaction give in the introduction part and after the liquid saturation, the extra liquid is rejected like commonly observed on the sample supports after melt processing.

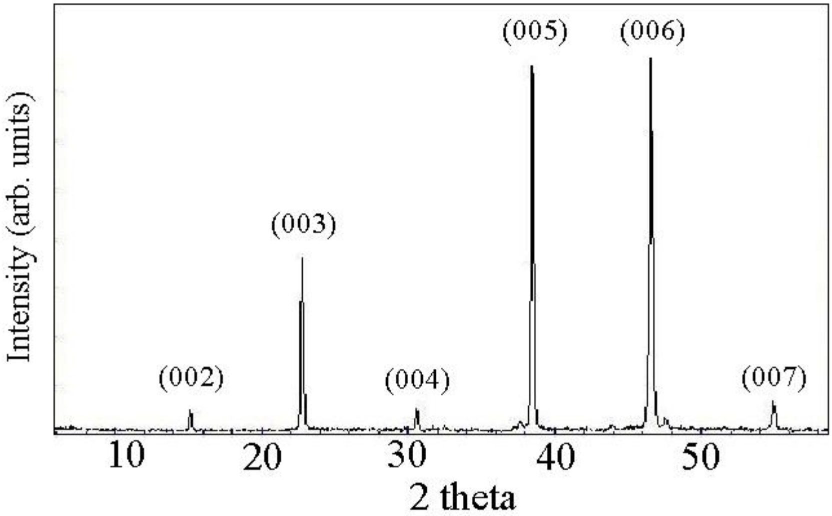

Figure 4. X-ray diffraction pattern recording of the single domain YBa2Cu3O7−*x* foam achieved from foams embedded in epoxy resin, a polished surface parallel to the seed crystal is used for x-ray characterization, the intense {00ℓ} peaks indicate the c-axis texture

The temperature dependence of the resistivities of various bars was measured. The bars were cut parallel and perpendicular to the surface of the seeded plane in agreement with the microstructure. Suitable contacts allowed the current to be passed either in the (*ab*) planes or parallel to the c-axis. Figure 5a shows the resistive transition of a typical Y123 foam sample. Both configurations exhibited a narrow superconducting transition ($\Delta T \approx 1.5$ K) with T_c (onset) ≈ 91.5 K and T_c ($\rho = 0$) ≈ 90 K. The room temperature resistivities along the ab-planes and along the c-axis are 2 and 16 mΩ.cm respectively. The resistivity ratio of about 8 for the parallel and perpendicular configuration confirms the texture/single grain nature of the foam superconductor.

The zero field cooled magnetization curve, Figure 5b, shows a very narrow transition with an onset at 92 K, comparable to values taken from above resistivity R (T) curves. The steep transition characterizes an essentially pure Y123 phase and indicates no substantial contaminations originating from the initial polyurethane foam and organic compounds being burnt to form Y211 precursor foam.

In order to correlate sample texture and magnetic anisotropy, hysteresis cycles with magnetic fields applied parallel and perpendicular to the direction of the single domain surface have been performed at 77 K on a 2 x 2 x 2 mm^3 sample, Figure 6a. The magnetic J_c values are estimated for both directions from M-H cycles on the basis of the Bean model taking $J_c = 30\Delta M/d$, where *d* is the sample size in cm and ΔM in emu/cm^3 is the hysteresis of the magnetization. Figure 6b presents the J_c (H) determined from the width of hysteresis loops at two configurations. J_c^{ab} corresponds to the average critical current density in the ab-planes under magnetic field and J_c^{c}, the critical current density along the c-axis.

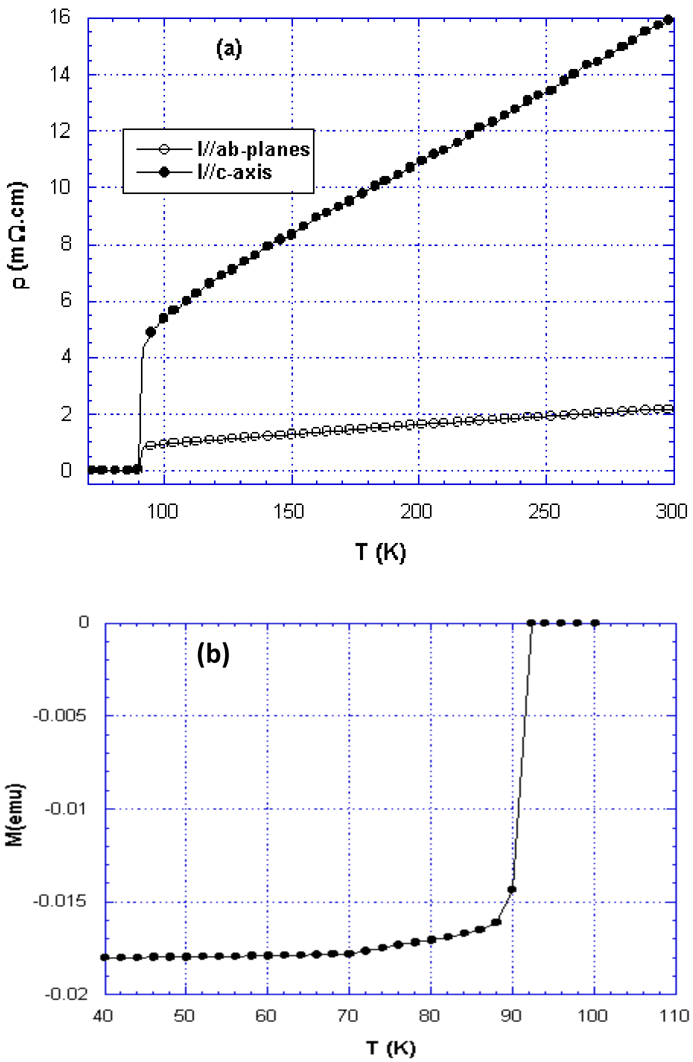

Figure 5. (a) Electrical resistivity versus temperature according to two configurations, the current, I, being injected parallel to the *ab*-planes or parallel to the *c*-axis into bar-shaped foam samples,
(b) magnetization vs. temperature M (T)

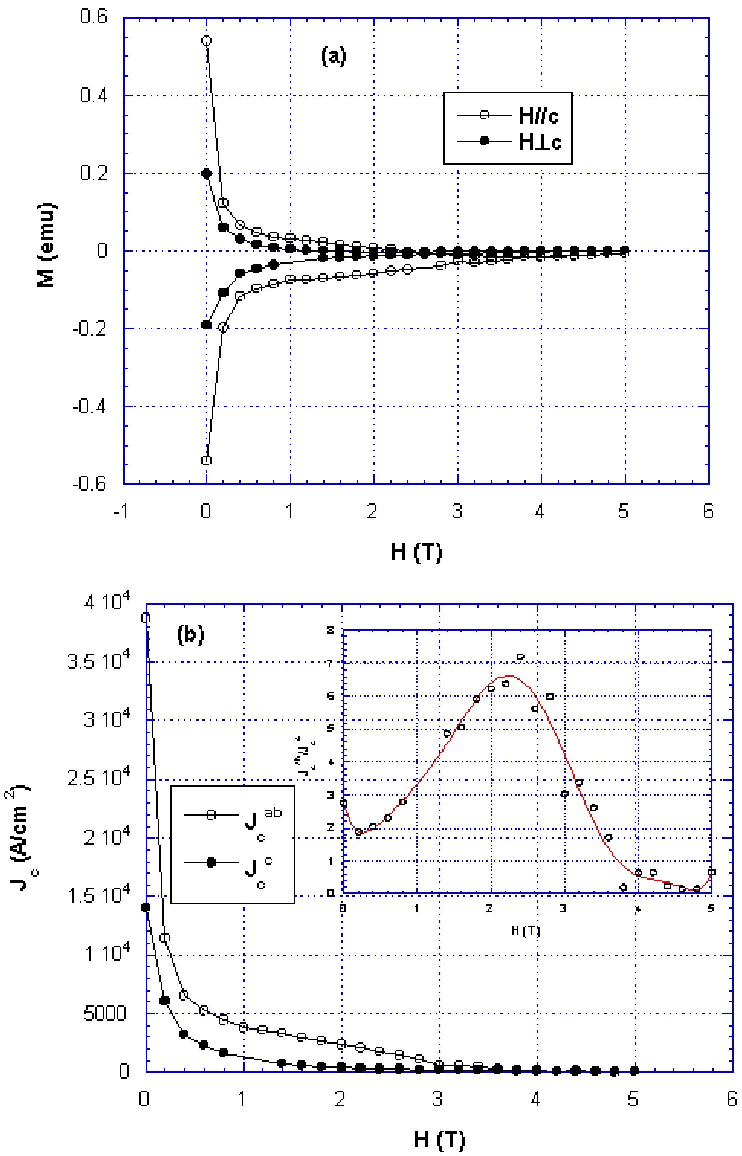

Figure 6. (a) Magnetic hysteresis cycle M (H) at 77 K following two directions of the measuring magnetic field parallel and perpendicular to the c-axis,
(b) field dependence of the critical current density J_c deduced from M (H),
the inset shows the anisotrophy of J_c as a function of the external magnetic field

A critical current density of $J_c^{ab} \approx 40$ kA/cm^2 at 0 T can be deduced for current parallel to the ab-planes. A $J_c^{c} \approx 15$ kA/cm^2 is obtained for currents parallel to the c-axis, inset Figure 6b, leading to an anisotropy factor J_c^{ab}/J_c^{c} of about 7 at 2 T.

These values are similar to those of single domain bulks with a non-optimized Y211 content and size distribution. There is a lot of scope for further improvement of J_c in the Y123-foams by refining the Y211 distribution in their microstructure using e.g. doping methods known from bulk materials processing [16,17]. The transport current measurements have been performed using pulse current [7]. The current across textured Y123 foam exceeded 1000 A during 150 ms. This corresponds to the current carry through 0.1 cm^2 cross section and critical transport current density exceeding 10^4 A/cm^2 at 77 K in self field.

OUTLOOK

Foams of conventional ceramic materials or porous structures, such as alumina and zirconia, are established components in a number of industrial applications such as filters, structures for catalysts, elements for thermal insulation and flame barriers. The combination of high surface area and low density of YBCO superconducting foams makes them interesting candidates for both a variety of novel applications and for fundamental studies. YBCO foams of strut thickness of a few hundred μm or artificial perforated Y123 bulk into desired structure (Fig. 7), for example, are good candidates for resistive elements in superconducting fault current limiters. In this application, the low thickness of the struts or wall between the holes allows more efficient heat transfer between foam or perforated superconductor and cryogenic coolant during an over-current fault compared to conventional bulk material. Superconducting bulks with artificial array of holes can be reinforced continuously with alloys [5] or high strength resins to improve their mechanical and thermal properties to overcome the forces encountered in levitation and quasi-permanent magnet applications. The high surface area of the foams, which may be adjusted by varying the pore size, makes them interesting candidates for studying fundamental aspects of flux pinning, since the extent of surface pinning, and hence J_c, are expected to differ significantly from bulk YBCO grains of similar microstructure.

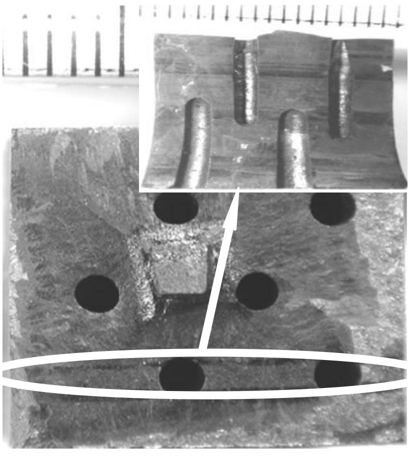

Figure 7. Feasibility of c-axis meander shape (inset) for fault current limiter issue from single domain monolith sample with 2 mm holes

CONCLUSION

The textured YBCO (Y123) foams have been successfully prepared from commercially available polyurethane using infiltration-growth process. In addition, the bulk Y123 with artificial patterned holes has been also processed. The single grain nature and microstructure resulted in properties similar to those of bulk materials.

The properties of the superconducting Y123 foams have been investigated. From R (T) and M (T) measurements, a T_c of 92 K with a (narrow) transition width of 1.5 K has been deduced indicating an uncritical contamination by residuals of the organic raw materials used to manufacture the foams. Magnetic hysteresis curves reveal a critical current density of $J_c^{ab} \approx 40$ kA/cm^2 and a high anisotropy J_c^{ab} /J_c^{c} ~ of up to 7 in an external field of 2 T. Further investigations on oxygenation annealing, optimization of Y211 particle size and distribution as well as on the thermal and mechanical properties of the superconducting foams or multiple holes samples are necessary. The possibility of fabricating high J_c Y123 foam in various structures allows a host of applications using this new form of material, one of these applications being the superconducting element of a resistive fault current limiter. The important property required for a FCL element is the rapid dissipation of thermal energy during fault conditions without burning the superconductor. The use of Y123 foam or multiple holes sample with a large surface area allows us to effectively extract the heat generated in the bulk superconductor.

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