Superconducting foams

2002 Supercond. Sci. Technol. 15 L21

(http://iopscience.iop.org/0953-2048/15/8/101)

INSTITUTE OF PHYSICS PUBLISHING SUPERCONDUCTOR SCIENCE AND TECHNOLOGY

Supercond. Sci. Technol. **15** (2002) L21–L24 PII: S0953-2048(02)36338-3

RAPID COMMUNICATION

Superconducting foams

E S Reddy and G J Schmitz

ACCESS e.V. Materials & Processes, Intzestr. 5, D-52072 Aachen, Germany

Received 29 April 2002
Published 28 June 2002
Online at stacks.iop.org/SUST/15/L21

Abstract
The development of foams from a variety of substances such as polymers, glasses, metals and ceramics has led to many important applications of foam structures. A large open porosity, along with a high surface area and good mechanical properties, brings about novel properties and makes foams attractive for various applications. In addition to conventional applications such as filters, shock absorbers, heat exchangers, catalysts or lightweight constructions, porous structures are increasingly being considered for advanced functional materials, such as piezoelectrics revealing novel and improved properties. Until now, superconducting materials have not been processed in foam structures. However, a superconducting foam reveals properties which are highly interesting both for applications such as efficient heat extraction from superconducting components, e.g. in fault current limiters, and for fundamental investigations of e.g. surface pinning. We detail a manufacturing process for superconducting, pseudo-single crystalline foams of $YBa_2Cu_3O_{7-x}$ (Y123) based on a combination of standard ceramic foam processing and an infiltration method.

(Some figures in this article are in colour only in the electronic version)

Materials in foam structures have emerged as a novel class in the categories of bulks, thick films and thin films with specific and promising applications in many areas [1, 2]. Polymer foams have entered everyday life and are used for a host of purposes. Metallic foams are commercially available, under different trade names, for a variety of applications [2]. Most ceramic foams are used for standard applications such as filters or catalysts, and foam structures of advanced functional ceramics such as piezoelectric materials are rapidly evolving, allowing the tailoring of various physical properties [3]. Superconducting ceramic foams may provide solutions for some problems encountered in applications of bulk or film-type superconductors, e.g., by reducing hot-spot formation or by decreasing thermal inertia [4]. Moreover, such foams raise fundamental questions about the morphology of the flux-line lattice in highly porous media and about flux pinning at interfaces, while at the same time they represent suitable objects to study such effects [5, 6].

Although high temperature superconductors are oxide ceramics, the stringent requirement of high critical current densities for many applications makes conventional ceramic foam processing obsolete in the processing of high quality superconducting foams. High critical currents can only be achieved in a biaxially textured microstructure, i.e. a microstructure revealing small misorientations between multiple grains or, ideally, consisting of only a single grain [7]. To achieve a particular microstructure, unique processing techniques for bulk, thin and thick film forms of a 123 material have been developed [8, 9]. Biaxially textured Y123 thin films are realized by epitaxial deposition on single crystalline or textured substrates by various processes [9]. Bulk textured Y123 materials have been realized by solidification processes based on the peritectic reaction occurring slightly below the peritectic temperature T_p

$$Y_2BaCuO_5(211) + \begin{matrix}\text{barium}\\ \text{cuprate}\\ \text{liquids}\end{matrix} \xrightarrow{T_p} YBa_2Cu_3O_{7-x}(123).$$

Variations of the reported melt processing techniques [11] involve the solidification of a mixture of 211 particles and liquid phases obtained either by incongruent melting of 123 or by mixing respective precursor powders at room temperature and heating the resulting powder mixture to a temperature above T_p. Generally, mere solidification of this mixture results in a poly-grain untextured material. However, in

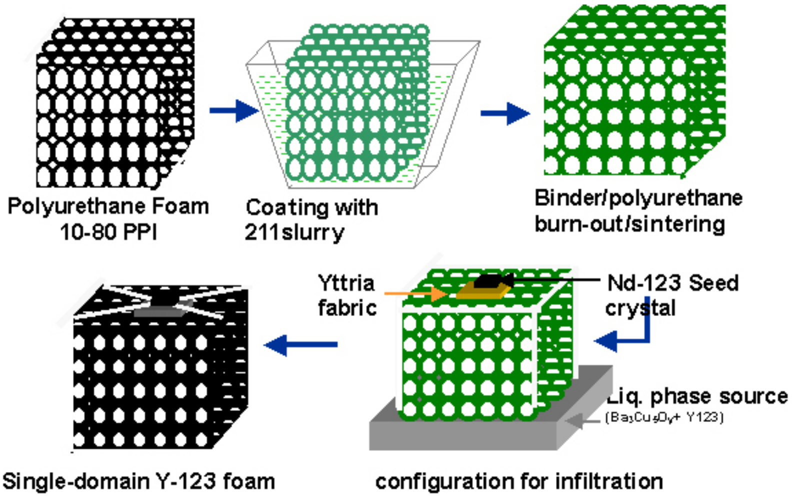


Figure 1. Schematic diagram showing the processing of a single domain $YBa_2Cu_3O_{7-x}$ foam. In the first stage the Y_2BaCuO_5 foam is processed as a replica of a commercial polyurethane foam by standard ceramic foam processing method, which is subsequently converted into a single domain 123 foam by infiltration process [8].

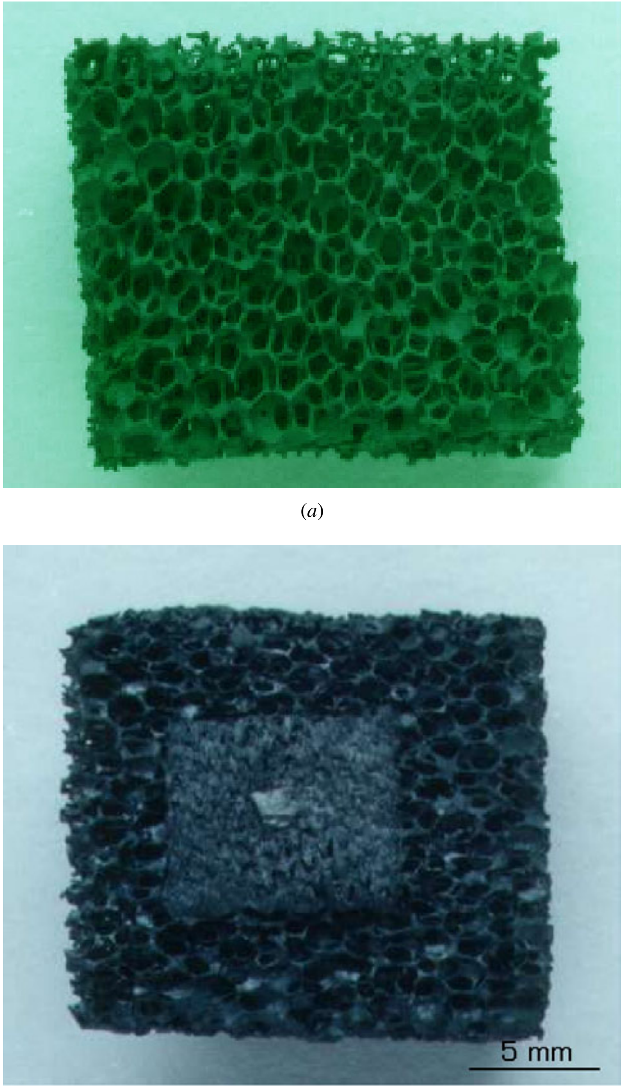
an external temperature gradient or in the presence of a higher melting seed crystal, such as $NdBa_2Cu_3O_{7-x}$, the entire superconductor body solidifies as a single grain. Some intrinsic drawbacks such as large amounts of low viscous liquids and distortions due to large and anisotropic shrinkage do not allow the manufacturing of complex shaped bodies such as foam structures by present melt processing techniques. Single domain superconducting 123 foams can, thus, only be realized by using those methods that avoid shrinkage and distortions during the solidification process.

The process described here involves two distinct stages. In the first stage (figure 1) a porous Y211 foam is fabricated by established ceramic foam manufacturing processes [10]. The second stage involves the infiltration of this 211 foam by molten barium cuprates and copper oxides followed by a controlled peritectic growth of the 123 phase. In the presence of a seed crystal during the process, the resulting 123 superconductor foam grows as a single grain.

The fabrication of 211 foams involves the impregnation of a reticulated polyurethane foam of desired porosity (measured in 'PPI' (pores per inch)) with a 211 slurry, followed by a heat treatment to burn off the polymer and, subsequently, sintering the 211 ceramic foam. The slurry for impregnation is prepared by mixing a commercially available 1–5 μm sized '211' powder in a water based solution with 5 wt% polyvinyl alcohol as binder in a 1:2 ratio. The organic components—polyvinyl alcohol and polyurethane—are burnt by slow heating at 50 K h^{-1} to 600 °C and dwelling for 6 h. For densification of the resulting 211 ceramic foam, further heat treatment comprises heating at a rate of 100 K h^{-1} to 1150 °C and dwelling for 10 h. The cooling back to room temperature proceeds at a rate of 150 K h^{-1}. The resulting 211 foam preform, figure 2(*a*), reveals a sufficient handling strength and its struts reveal sufficient porosity for further infiltration.

The method used to convert these 211 foams into single domain 123 foams is similar to the infiltration process used for the fabrication of superconducting fabrics [11] and near-net shaped bulk components or materials [12]. The process involves the infiltration of liquid phases into the body of the 211 foam from a liquid phase source. The liquid phase source is a mixture (1:1 ratio) of barium and copper oxides (CuO) with an overall stochiometry corresponding to $Ba_3Cu_5O_y$ and additional 123 powder. This mixture is pressed into a block and placed onto an alumina plate and beneath the 211 foam. Heating of this assembly proceeds in a box-type furnace in ambient atmosphere to temperatures above the peritectic melting temperature (1010 °C) leading to the decomposition of the 123 phase into 211 + liquid phase and eventually results in infiltration of the 211 foam by the liquid phase due to capillary action. This leads to the coexistence of '211' and 'liquid' required for the peritectic solidification, while simultaneously maintaining the foam shape.

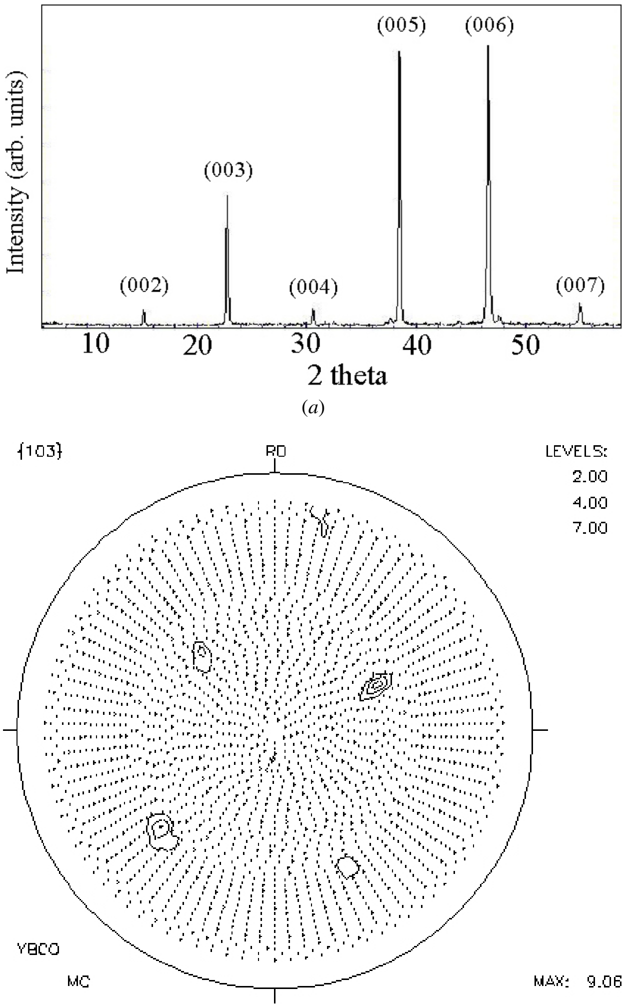
Solidification of the infiltrated 211 foam at a rate of 0.3 K h^{-1} through the peritectic temperature in the presence of a small $NdBa_2Cu_3O_{7-x}$'Nd123' seed crystal—placed at the top centre of the 211 foam prior to the heat treatment—initiates the growth of a single 123 grain starting at this seed. The peritectic reaction between infiltrated liquid phases and the 211 skeleton results in the growth of the 123 phase. If the peritectic solidification process is confined to low undercoolings preventing random nucleation (i.e. to temperatures above 980 °C), the entire foam is converted into a single grain of Y123 (figure 2(*b*)). The possibility of significantly undercooling the Y–Ba–Cu–O system without random nucleation/precipitation of the 123 phase allows us to convert bulk preforms as large as 100 mm in diameter into a single grain [7]. The single grain signature of the foam is evidenced by x-ray diffraction and by the (103) pole figure (figure 3). The polished microstructure (figure 4) of the struts of the foam reveals a microstructure typical of melt textured 123 bulks with parallel platelets including small residual 211 particles, making it ideal for high critical current densities. In the first measurements, the critical currents across



(*a*)

(*b*)

Figure 2. (*a*) Macrograph of a Y_2BaCuO_5 foam processed from a 40 PPI polyurethane foam. (*b*) Single domain $YBa_2Cu_3O_{7-x}$ foam as processed from a Y_2BaCuO_5 foam. The small Nd123 seed crystal used for nucleation of a single grain is supported by an yttria cloth placed on the foam structure.



(*a*)

(*b*)

Figure 3. (*a*) X-ray diffraction pattern and (*b*) 103 pole figure recording of the single domain $YBa_2Cu_3O_{7-x}$ foam achieved from foams embedded in epoxy resin. A polished surface parallel to the seed crystal is used for x-ray characterization. The intense (001) peaks indicate the c-axis texture and the presence of four-fold symmetric poles confirms the single domain nature of the foam.

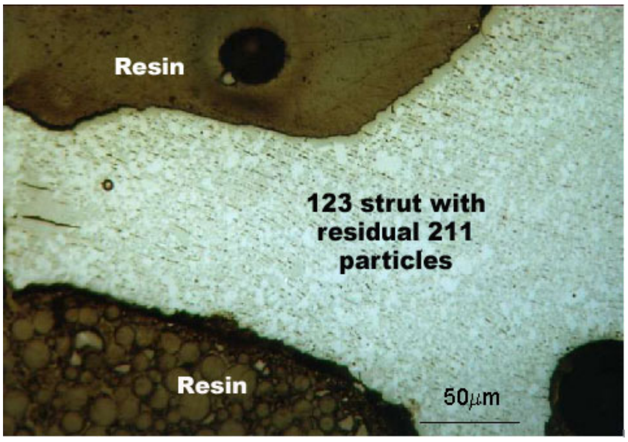


Figure 4. Microstructure of struts (grey) of a single domain $YBa_2Cu_3O_{7-x}$ foam mounted in an epoxy resin (dark) revealing parallel 123 platelets with residual 211 particles (light grey) typical of melt textured microstructures.

a single-grained 123 foam exceeded 1000 A (limited by the current source, pulsed currents of 150 ms duration, 1 μV cm^{-1} criterion, four point method) for a foam cross section of 1×1 cm^2. This corresponds to a superconducting cross section of approximately 0.1 cm^2 and accordingly to a critical transport current density exceeding 10^4 A cm^{-2} at 77 K and 0 T.

The single-grained 123 as open porous foam structure may be considered as a solution for many applications with improved performance in place of bulks and thick films. The 123 foams of strut thickness of few 100 μm could effectively be used as resistive elements in the mostly sought superconducting fault current limiters [4]. The small thickness of the struts allows a more efficient heat transfer between superconductor and cryogenic coolant during faults as compared to the bulks. This also minimizes the probability of hot-spot formation. Cooling of superconducting foam structures from room temperature to 77 K proceeds about ten times faster compared to respective bulk materials of the same mass and composition[1]. Superconducting foams with small open porosity can easily be continuously reinforced, e.g. with resins, to improve their mechanical properties and, thus, to overcome the forces encountered in levitation and quasi-permanent magnet applications. The high surface area of the foams—being adjustable by selecting the pore size—makes them interesting objects for studying fundamental aspects of flux pinning as the extent of surface pinning and hence the critical current densities will strongly differ from bulk specimen having similar microstructures.

The present superconducting foams, being a porous pseudo-single crystal realized for the first time, are also assumed to be interesting objects for crystallographers, materials researchers and mathematicians interested in crystal formation and modelling the growth of porous single crystals. In conclusion, crystalline Y123 superconductor foams have been realized with promising novel properties. The process, as a whole or with partial modifications, can be extended to other families of superconductors.

Acknowledgment

This work is supported by the German Federal Ministry of Higher Education and Research (BMBF) under grant no 13N7490.

References

[1] Nettleship I 1996 Applications of porous ceramics *Key Eng. Mater.* **122** 305

[2] Banhart J, Baumeister J and Weber M 1997 Metal foams near commercialisation *Metal Powder Rep.* **53** 38

[3] Marcus H L and Bourell D L 1993 Solid freeform fabrication finds new applications *Adv. Mater. Process.* **9** 28

[4] Tournier R *et al* 2000 Processing of large $YBa_2Cu_3O_{7-x}$ single domains for current limiting applications *Supercond. Sci. Technol.* **13** 886

[5] Burlachkov L 1993 Magnetic-relaxation over the Bean-Livingston surface-barrier *Phys. Rev.* B **47** 8056

[6] Zeng Z Y, Sun A M, Xu X N, Yu Y, Ding S Y and Yao X X 1997 Surface pinning effects in $YBa_2Cu_3O_7$ bulk sample *Physica* C **282** 2139

[7] Picard P G, Chaud X, Beaugnon E, Erruad A and Tournier R 1998 Growth of YBaCuO single domain up to 7 cm *Mater. Sci. Eng.* B **53** 66

[8] Salama K and Lee D F 1994 Progress in melt texturing of $YBa_2Cu_3O_7$ superconductor *Supercond. Sci. Technol.* **7** 177

[9] Driscoll J L M 1998 Recent development in conductor processing of high irreversibility field superconductors *Ann. Rev. Mater. Sci.* **28** 421

[10] Saggio-Woyaansky J and Scott C E *et al* 1992 Processing of porous ceramics *Am. Ceram. Soc. Bull.* **71** 1674

[11] Reddy E S and Rajasekharan T 1998 Fabrication of textured $REBa_2Cu_3O_7/RE_2BaCuO_5$ (RE = Y, Gd) composites by infiltration and growth of RE_2BaCuO_5 preforms by liquid phases *Supercond. Sci. Technol.* **11** 523

[12] Reddy E S, Noudem J G, Tarka M and Schmitz G J 2001 Single-domain $YBa_2Cu_3O_7$ thick films and fabrics prepared by an infiltration and growth process *J. Mater. Res.* **16** 955

---

[1] Video sequences available at webpage http//www.access.rwth aachen.de/superconductivity/cooling