Investigation of DyBa$_2$Cu$_3$O$_{7-d}$ superconducting domains grown by the infiltration technique starting with small size Dy-211 particles

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Abstract

An infiltration and growth process is here used as an alternative to the classical top-seeded melt-textured growth process for the production of Dy-123 single-domains with finely dispersed small size Dy-211 particles. The starting materials are the 211-particles and a barium and copper rich liquid phase precursor. The infiltration and growth process allows for controlling both the spatial and size distribution of the 211-particles in the final superconducting 123-single-domain. The main parameters (set-ups, maximum processing temperature with respect to the peritectic temperature, nature of reactant, porosity of the 211 -preform) of the infiltration and growth process are discussed. Moreover, different processes of *chimie douce* are shown in order to produce Dy-211 particles with controlled shape and size, particles that can be used as precursors for the infiltration and growth process.

Introduction

Large superconducting 123-single-domains are of great scientific and technological interest. The control of the 211-particle distribution is an important problem in manufacturing YBCO-type single-domains [1-11]. The usual top-seeded melt-textured growth (TSMTG) process leads to large size samples with heterogeneously dispersed 211-particles of various sizes. Moreover, the morphology of these particles cannot be easily controlled due to the fact that most of the 211-particles directly result from the peritectic decomposition of the 123-phase at high temperature, and the others result from the pro-peritectic 211-particles inserted at the beginning in the green body.

The infiltration and growth process has been proposed by Reddy *et al* [12, 13] to be an alternative technique for single-domain synthesis allowing for controlling the 211-particle distribution. This process is based on the infiltration of a barium and copper rich liquid phase into a 211-preform at a temperature near (below or above) the peritectic temperature of the 123-phase. This technique allows one to obtain high density materials with small size 211-particles well dispersed in the bulk [14].

Moreover, a near-net shape material can be obtained. Indeed, the process leads to a reduced shrinkage which limits cracks and distortions of the matrix [12]. It is thus possible to manufacture samples with complex shapes. For example, Reddy *et al* [15, 16] have used the technique to manufacture YBa$_2$Cu$_3$O$_{7-d}$ superconductor fabrics starting from Y$_2$O$_3$ clothes. This process was also used by the same authors [17] to produce YBCO superconducting foams. In this case, polyurethane foams with controlled porosity were coated with a Y-211 slurry before being burned out. The resulting Y-211 foams were then infiltrated with a Ba- and Cu-rich liquid phase and seeded with an Nd-123 single-crystal in order to produce a new kind of single-domain with controlled high porosity content.

The infiltration and growth process obviously allows for controlling the distribution of 211-particles in the single-domain. The new challenge is thus to produce fine 211-particles with controlled shape and size. In this paper, we propose first some *chimie douce* processes like co-precipitation or sol-gel as techniques to produce Dy-211 particles with controlled shape and size. In the second part of this paper, we discuss different important parameters that influence the infiltration and growth process like set-ups, nature of reactants, and porosity of the 211-preform. The effect of the maximum synthesis temperature being either above or below the peritectic temperature of the 123-phase is also examined. The technique is applied to Dy-123 single-domain growth starting with a Dy$_2$BaCuO$_5$ (Dy-211) preform. In order to evaluate the main parameters controlling the infiltration and growth process, we realized synthesis trials without seeding.

Figure 1. *Scanning electron micrographs of Dy-211 particles obtained by (a) solid-state synthesis, (b) sol-gel process, and (c) co-precipitation synthesis.*
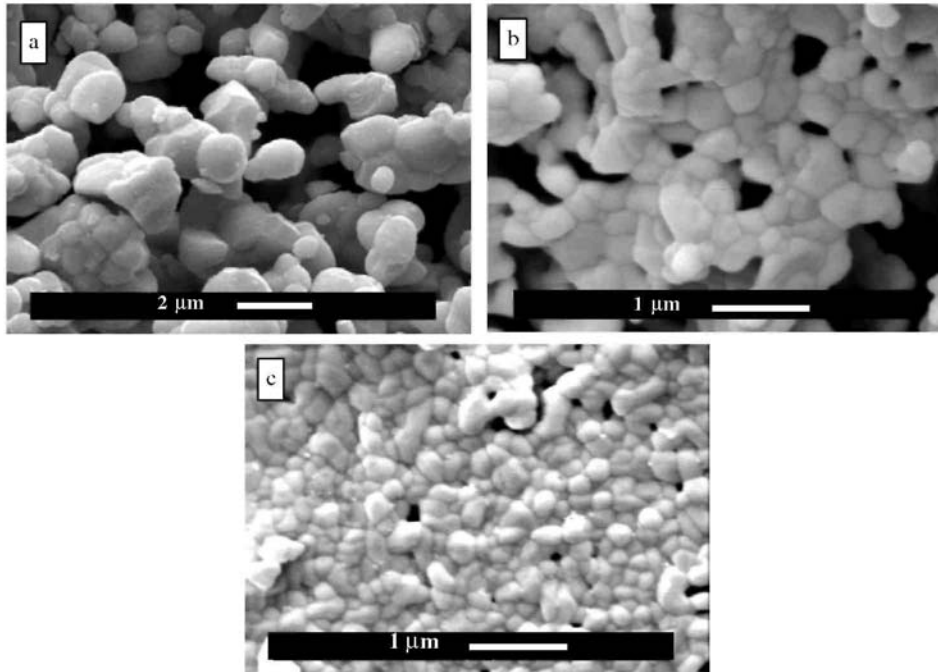
1. 211-particle synthesis

We have found that it is possible to control the particle morphology and obtain a narrow size distribution by considering some *chimie douce* processes like sol-gel or co-precipitation, hereby described and briefly discussed. The usual solid-state reaction route is first recalled.

Solid-state reaction

The solid-state reaction is the most often used process for the synthesis of Dy-211 particles, starting from Dy_2O_3, $BaCO_3$ and CuO in stoichiometric ratios [18]. After prolonged milling, particles with irregular shape and large size distribution (1-10 μm) can be obtained. See the scanning electron micrograph shown in figure 1(a).

Sol-gel

The sol-gel process can also be applied to obtain well controlled shape and size 211-particles. Different kinds of sol-gel processes are described in the literature [19-24]. Usually, organic salts, e.g. acetate or citrate, of barium, copper and dysprosium are dissolved in water. A mono- or multi-amino compound, e.g. ammonia, ethanolamine or ethylenediamine, is added in order to create a three-dimensional network trapping the cations. Most of the time, the pH must be adjusted for network formation. The solvent is then slowly removed by heating the stirred solution between 40 and 100 °C depending on the synthesis conditions. A gel is then obtained. It is necessary to burn out the organic phase and calcine the powder in order to obtain the Dy-211 phase. In so doing, we were able to produce small size (about 0.3 μm) Dy-211 particles. See the scanning electron micrograph shown in figure 1(b).

Co-precipitation

The following co-precipitation process has been adapted in order to obtain Dy-211 particles from the synthesis method proposed by Ochsenkühn-Petropoulou *et al* [25] for Y-123 (co-precipitation of oxalic salts). In this process, an oxalic acid solution is rapidly added to a solution containing dysprosium, barium and copper nitrate salts. The pH is then adjusted to 4.5 thanks to an ammonia solution in order to co-precipitate the three ions and to avoid hydroxide formation. The system is stirred for 10 min and next centrifuged in order to recover the solid phase that is washed twice with cold water. After a quick drying of the co-precipitate in an oven at 100 °C, the powder is calcined to obtain the Dy-211 phase.

In order to induce a complete precipitation of the cations, some 10% excess oxalic acid is used. The solubility of the different oxalate salts is not exactly the same. Thus in order to obtain the required 2:1:1 ratio, it was determined that the optimumratio of the different nitrate salts Dy:Ba:Cu in solution must be 2:1.1:1.1. Figure 1(c) shows the scanning electron micrograph of the obtained Dy-211 particles. They have a mean size of about

0.2 μm.

These three processes allow us to produce Dy-211 powders with good purity and crystallinity. Figure 2 shows a comparative x-ray diffractogram of the as-obtained powders. Let us note that co-precipitation is probably the best process to synthesize a large amount of 211-particles because of the short time necessary for such a synthesis. Nevertheless, stoichiometric deficiencies are found due to the difference in solubility between the co-precipitants. This problem can be avoided in the sol-gel synthesis, but the processing time is longer and large solution volumes are required in order to obtain only a small quantity of the final product. Nevertheless, synthesis parameters and calcination conditions can still be improved to control more carefully the size and shape of the Dy-211 particles.

Figure 2. *Comparative x-ray diffractogram of the Dy-211 powders obtained by the solid-state route, sol-gel and co-precipitation. These three processes allow us to produce Dy-211 powders with good purity and crystallinity. ◊ : Dy-211 reference pattern from JCPDF database [No. 39-1479].*
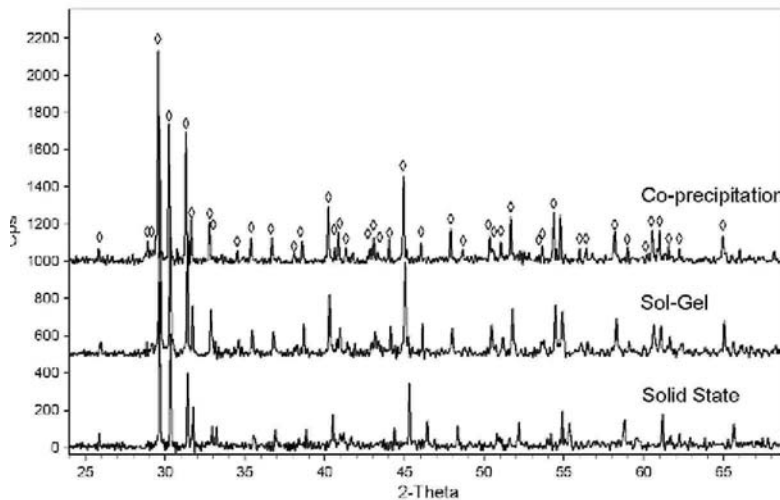
2. Infiltration and growth process

In the infiltration and growth process, the starting materials are the 211-particles and a Ba- and Cu-rich liquid phase precursor. The chemical reaction between the Dy-211 particles and the liquid phase can take place well below the peritectic temperature, T_p, of the Dy-123 phase. Thus the maximum processing temperature could be above or below T_p. This parameter role should be examined (see below).

The 211-particles used for the infiltration and growth process can be produced as recalled above (section 1) by solid-state or by *chimie douce* processes, i.e. sol-gel and co-precipitation. Also, in the Ba- and Cu-rich liquid phase precursor, it is important to respect the 5:3 Ba:Cu ratio, in order to keep a correct stoichiometry for the peritectic recombination reaction:

$$Dy_2BaCuO_5 + 5CuO + 3BaO \rightarrow 2DyBa_2Cu_3O_{7-d}.$$
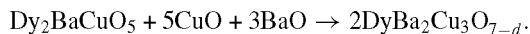
Nevertheless, the nature of the precursor can be a mixing of $BaCO_3$ and CuO or $BaCuO_2$ andCuO. Dy-123 can also be used as a flux precursor [26]. In this case, the maximum processing temperature must be above the peritectic temperature of the Dy-123 phase and the as-obtained flux will contain some dissolved dysprosium ions.

Experiments

In order to evaluate the main parameters controlling the infiltration and growth process, we realized synthesis trials without seeding. Polycrystalline samples are thus expected and were obtained. Different set-ups can be used [13, 26-28], We have studied two of these. In the first case, 211-particles and flux precursors are fully mixed together and uniaxially pressed to form the green body (figure 3(a)). In the other studied case, called the layered system (figure 3(b)), 211-particles and flux precursors are uniaxially pressed separately and then piled up. The liquid phase formed at high temperature penetrates into the 211-bulk by capillarity.

In order to evaluate the effect of the maximum processing temperature, two kinds of thermal cycles were applied. After a rapid heating up to 970 °C (for processing below T_p) or 1050 °C (for processing above T_p) and a

dwell of 2 h, samples were cooled down at 50 °C h^{-1} to 900 °C, then furnace cooled down to room temperature. BaCO$_3$ and CuO, BaCuO$_2$ and CuO, and Dy-123 were all tried as liquid phase precursor.

Figure 3. *Some processing set-ups for the infiltration and growth process: (a) fully mixed system in which precursors are mixed and pressed into a green body pressed binary, (b) layered system.*
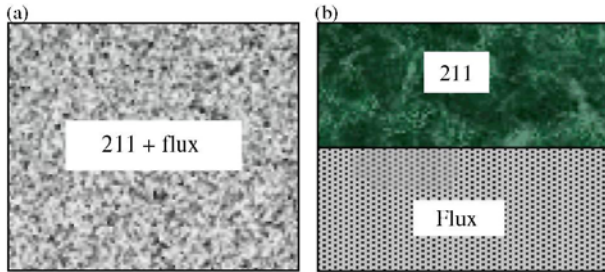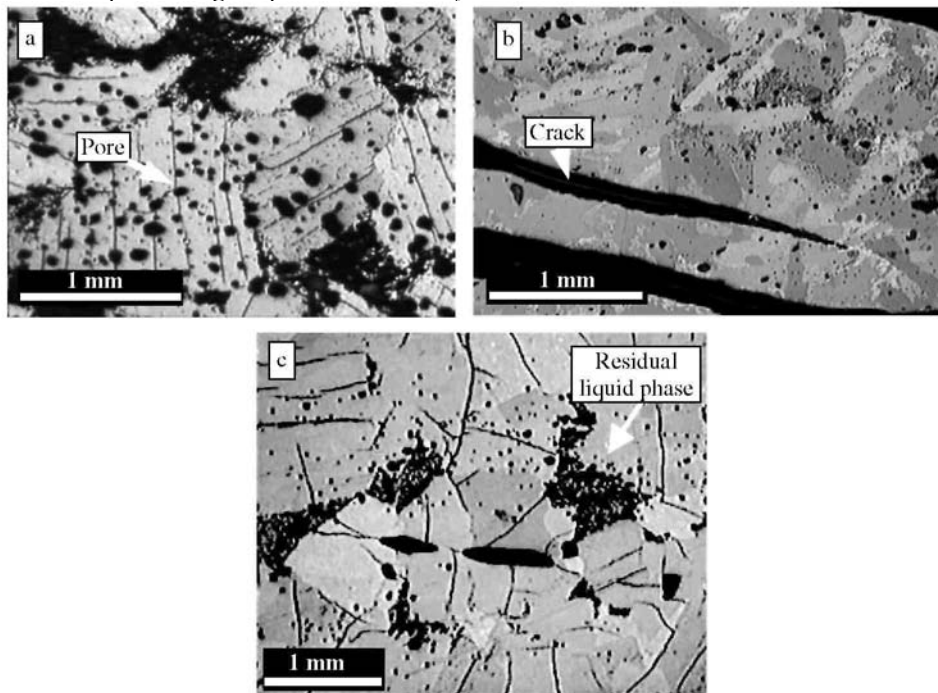

Figure 4. *Polycrystalline samples obtained (a) by mixing the Dy-211 particles and the liquid phase precursor; (b) by 'layered processing' with a maximum processing temperature below T_p; (c) by 'layered processing' with a maximum processing temperature above T_p.*

Results and discussions

Whatever the maximum synthesis temperature (above or below T_p), proceeding by mixing the precursors before synthesis leads to a high porosity material (figure 4(a)). In fact, the liquid phase reacts with the 211-particles and leads to lots of free space in the bulk. This important residual porosity can be avoided by using the 'layered system' with two superposed different bulks: one (above) for 211-particles and one (below) for liquid phase precursors. The capillarity forces are enough to suck the liquid phase into the above Dy-211 pellet. Hence, this set-up gives a high density material with nearly no shrinkage (figures 4(b) and (c)). Notice that this configuration is interesting for the seeding route, because the seed is not in direct contact with the liquid phase (which could dissolve the seed).

Even if the reaction between the Dy-211 particles and the liquid phase can take place well below the peritectic temperature of the Dy-123 phase, polycrystalline samples with smaller domains are obtained when the maximum processing temperature is below rather than above T_p (figures 4(b) and (c) respectively). In fact, when the temperature is below T_p, nucleation of Dy-123 can start everywhere in the bulk, and this induces plenty of small domains. This is noticeably a source of problems for the growth of single-domains. For this reason, we suggest

inserting the initial sample with a top seed in a preheated furnace at a temperature above the peritectic temperature of the Dy-123 phase, in order to grow from the seed and limit secondary nucleation elsewhere in the pellet.

In figure 4(c), some residual liquid phases can be observed at the grain boundaries of the domains. This secondary phase is due to the too high cooling rate in our processing (see above). Hence, all the liquid phase had no time to react with the Dy-211 particles to form the Dy-123 phase.

Important microstructure differences are noticed depending on the nature of the liquid source: 211-particles are larger and the 123:211 volume ratio is lower when Dy-123 is used as liquid source precursor rather than $BaCuO_2$ and CuO (see figures 5(a) and (b) respectively). This can be understood by considering that the liquid phase provided by the peritectic decomposition of Dy-123 is already saturated in dysprosium, whereas the liquid phase from the $BaCuO_2$/CuO mix does not contain any rare-earth element. In this latter case, Dy-211 particles are more dissolved, thereby providing the rare-earth element for Dy-123 formation.

The use of $BaCuO_2$ is also preferred to a mix of CuO and $BaCO_3$ as components of the liquid phase precursor because of the important gas losses when carbonates are used. Indeed gas emission is known to cause cracks in the bulk.

Figure 6 presents the microstructure of a Dy-123 sample obtained by infiltration of a melt produced by decomposition at 1050 °C for 2 h of a Dy-123 phase (bottom part) into a Dy-211 pellet (upper part). The system was cooled down to 900 °C at a rate of 50 °C h^{-1} and then furnace cooled. A marked difference in the 211-particle distributions in the upper and lower layers can be observed. The morphology, mean size and spatial distribution are finer in the infiltrated part. In the bottompart of the sample, Dy-211 particles nucleated and grew at high temperature due to the peritectic decomposition of the Dy-123 phase. In this case, it is extremely difficult to control the morphology and size of these particles. In contrast, in the upper part of the sample, Dy-211 particles in the bulk are not produced at high temperature but they were nevertheless present in the initial preform. It is thus easier to control the morphology and size of these particles in the upper layer. Moreover, the density of 211-particles in the final bulk can be expected to be controlled by modifying the porosity of the Dy-211 preform.

Figure 5. *SEM micrographs of infiltrated sample using (a) Dy-123 or (b) $BaCuO_2$/CuO mix as liquid phase source. The 211-particles are larger and the 123:211 volume ratio is lower when Dy-123 is used as liquid source precursor rather than $BaCuO_2$ and CuO.*
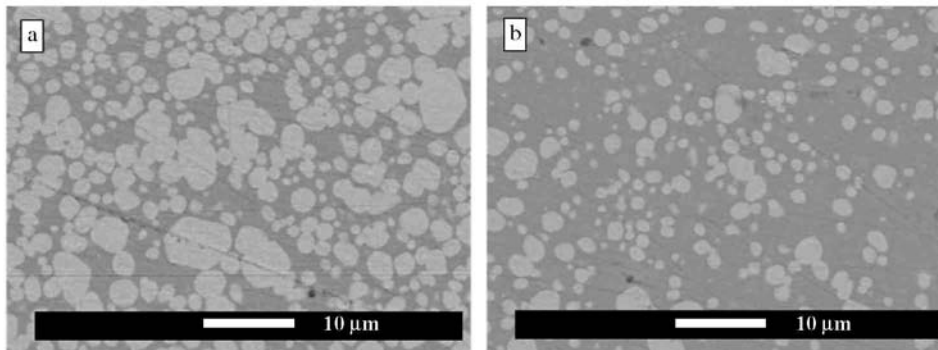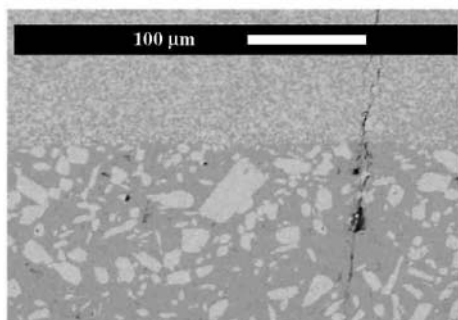

Figure 6. *SEM micrograph near the interface of a 211-bulk (upper part) infiltrated by a liquid phase from a Dy-123 precursor (lower part).*

Conclusions and outlook

The infiltration and growth (IG) process is an interesting alternative to the classical TSMTG process for the synthesis of 123-single-domains. In this process, the 211-particle distribution can be highly controlled, which is not the case in the TSMTG process where 211-particles are formed at high temperature due to the peritectic decomposition of the starting 123-phase. Moreover, in the IG, it is possible to control the Dy-211 size and size distribution by using particles as a precursor, produced by a co-precipitation or a sol-gel process. These two processes have been discussed and results compared to those of the classical solid-state reaction method. The main parameters of the infiltration and growth process, such as the nature of the reactants and set-ups and, in particular, the role of the maximum processing temperature with respect to the peritectic temperature, have been discussed.

Notice that the porosity of the initial Dy-211 bulk has also to be controlled carefully. If the porosity is too low, the final Dy-123 concentration in the sample will be too low. In contrast, if the bulk porosity is too high, on the one hand, capillarity forces for the liquid phase penetration might not be high enough for infiltration; on the other hand, residual porosity could remain in the final 123-single-domain. An optimum of porosity for the Dy-211 preform has thus to be found.

Acknowledgments

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