Chapter-VI

Summary and Conclusions

The present thesis discusses the introduction of nanoparticles of ceria, zirconia and Ba-Ce-O into Infiltration Growth processed YBCO superconductor composites and its effect on the final microstructure and superconducting properties.

A method is developed for the introduction of nanoparticles separate from one another and without agglomeration into the Y-211 preforms used for IG processing. A certain amount of reaction between the preform and the nanoparticles keeps the particles anchored to the Y-211 grains during the infiltration of liquid phases and further texturing stages. Using the Infiltration Growth process, and introducing the nanoparticles as separate entities into the preform, has the advantage that the agglomeration and flow-tracks formed by accumulated particles due to their movement along with liquid phases can be avoided: such tracks have been reported in melt growth experiments [1].

The main motivation for the above work is the reported observation that very high current densities can be obtained in melt processed samples containing large concentrations of nanometer-sized additives. For instance, the best current densities reported till today in any superconductor bulk has been in the melt processed NEG-123 with 35mol. % of nanometer-sized (70 nm) Gd-211 and 0.1 mol. % of nanometer-sized NbO$_3$ it showed a zero field current density of $\sim$600 kA/cm$^2$, and a current density of $\sim$200 kA/cm$^2$ at 4 T [2].
IG process offers advantages of near net shape processing. The process used in the present thesis to disperse nanoparticles in Y-211 preforms, starting with a colloidal solution of the required nano-material and mixing it intimately into a stable Y-211 slurry, has the advantage that it can be combined with the gelcasting process developed in this study. The gelcasting process involves the preparation of a stable suspension of the Y-211 powder using a suitable dispersant in water, along with small amount monomer and cross liners. The dispersant was identified in the present study. The slurry is set in a mould. The mould can be fabricated by the rapid prototyping technique which can potentially allow the formation of extremely complex-shaped superconductor components, if needed. The preform of Y-211 thus prepared is dried, debinded and sintered. It is used in IGP to make superconductor parts with a microstructure that supports high current densities. We have demonstrated the fabrication of a superconductor hollow cylinder by the gelcasting process and have studied its microstructure, and have measured the current densities supported by it.

The NDS process developed for the introduction of nanoparticles separate from one another and without agglomeration into the Y-211 preforms has the potential to yield high current densities in IG processed samples, just as it was obtained in the melt processed samples. However, the nano-materials that we worked with did not help increasing the current density much due to a variety of reasons. A basic problem observed was the lowering of $T_c$ of the Y-123 material by the dissolution of the additives in the Y-123 phase. There were earlier reports of such lowering of $T_c$ [3], and we have confirmed that it occurred in our materials by measurements of electrical resistivity and ac magnetic susceptibility as function of temperature. Another problem was the enormous grain growth of the Y-211
grains in the preforms in most cases, even at low levels of doping. The particle size refinement due to the added material was not sufficient in most cases to reverse this large grain growth and the $J_c$'s observed in those materials were very low. An added effect was the reduction in continuous porosity in the Y-211 preform due to the reactivity of the nano-materials with the Y-211 grains of the preform resulting in Y-211 grain growth. This would affect the liquid phase inflow into the preforms for IGP.

An exception was ceria-doped Y-123. The reaction of ceria with Y-211 preform material was minimal at low concentrations, in the Ce-2 sample. At high concentrations, in the Ce-10 sample, the ceria particles sintered together to form nano-rods. The grain growth Y-211 in the preforms of ceria-added Y-211 was therefore low. Easy infiltration of liquid phases into the preforms was facilitated by the porosity available in their preforms; in the case of the Ce-10 sample, the nano-rods separated the individual Y-211 grains. As a result, the microstructures obtained in those materials, especially in the Ce-10 sample, were very attractive. The IG process, without any doping, inherently gives substantial grain refinement in comparison with the melt growth process; the addition of ceria in IGP lowers the Y-211 grain size even further and narrows the particle size distribution (Fig. 3.12 in Chapter III, reproduced below as Fig. 6.1). The average Y-211 particle size is around 500 nanometers, which we believe is unprecedented.

The current density recorded in the Ce-10 sample decreases only slowly as a function of the applied magnetic field up to 9 T. This is just as in the POIGP (Ce-0) sample; i.e. in a sample prepared from optimized Y-211 preforms just as in the present case, but without the additives [4].
**Fig. 6.1.** The Y-211 size distribution in the Ce-10 sample is below 0.5 μm (bottom row), whereas the Y-211 particles in the Ce-0 sample are sized around 1 μm (top row).

The reasons for the observed high current density to high fields in the Ce-0 sample occur in the Ce-10 sample as well; there is extensive nano-twinning [5] in the Ce-10 sample, and the Y-211 grain size is even smaller (see Fig.6.1). But the observed $J_c$ values are lower in the Ce-10 sample in comparison with the Ce-0 sample (Fig. 6.2). This can be attributed to the dissolution of ceria in the Y-123 matrix and the associated lowering of $T_c$. We have studied the flux entry into the Ce-2 and Ce-10 materials as function of the applied dc field using an ac field of varying amplitude as the probe: we have correlated the observations to the content of lower $T_c$ phases.
Fig. 6.2. Critical currents in both Ce-0 and Ce-10 are sustained up to 9 T due to extensive twinning. But in case of Ce-10 the magnitude of the Jc is lower when compared with Ce-0.

We can also conclude from the above study that Y-211 particle size refinement, though attractive, if brought about by a nano-material that interacts with the matrix and lowers Tc, the benefits to improvement of the current carrying capacity of the material would be limited.

The refinement of the Y-211 particle size in melt processed Y-123 through the introduction of dopants such as Pt, ceria, barium cerate and zirconia has been a matter of intense study. The NDSC process developed in this work enables the deposition of nanoparticles separately without agglomeration on the Y-211 particle surface in the preform, and this enables the study of the reaction taking place between various components of the reaction system more clearly. We observe that the particle size refinement takes place because of the ability of the above materials to draw Ba from the Y-211 material [6]. Other work in the literature also has pointed out that the
reactivity of the above dopants to form stable compounds with Ba is behind the particle size refinement [7-9]. The chemical reactions involved are as follows.

\[
\begin{align*}
Y_2\text{BaCuO}_5 + \text{CeO}_2 & \rightarrow \text{BaCeO}_3 + Y_2\text{O}_3 \\
Y_2\text{BaCuO}_5 + \text{ZrO}_2 & \rightarrow \text{BaZrO}_3 + Y_2\text{O}_3 \\
2\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} + 2\text{PtO}_2 & \rightarrow \text{Ba}_4\text{CuPt}_2\text{O}_4 + Y_2\text{O}_3 + 5\text{CuO}
\end{align*}
\]

Withdrawal of Ba from regions where the nanoparticles are attached forms one or more Y-rich regions within the Y-211 grains. The regions of the Y-211 grains which have not thus become Y-rich react with the liquid phases and develop necks (Fig.3.16 and Fig. 3.27) which can break in cases where the reaction continues. This accounts for the particle size reduction of Y-211 in the presence of the reactive additives like the ones mentioned above. The particles that are residual in the Y-123 matrix after IG processing are mostly Y-rich compositions of the Y-Ba-Cu-O system. In the samples to which ceria nanoparticles were added, there are also very fine, BaCeO_3 particles, with sizes in a few tens of nanometers, which originated from the added ceria nanoparticles.

In the case of samples with Zirconia and Ba-Ce-O nanoparticles, the influence on microstructure and on the field dependence of current density by even small amounts of the dopants was very dramatic. With only 0.1 wt. % Ba-Ce-O added, the microstructure of the IG processed material resembled that of a sintered material and the \(J_c\) values were very small. But increasing the amounts of the dopants refined the Y-211 size, restored the typical melt processed microstructure, and the \(J_c\) (H) improved. This could be attributed to the grain growth of Y-211 in the preform even with small amounts of additives and the effect of more of the additives in refining the Y-211 by
particle division. We have also seen, especially in the case of the Zirconia-doped samples, that the increased grain growth of Y-211 particles in the preform, even with small amounts of the additive, could become a problem in IGP because the continuous porosity needed to allow the infiltration of liquid phases could get closed leading to samples of very poor microstructure and $J_c$. 
Chapter VI
Summary and Conclusions

References

5. N. Devendra Kumar, T. Rajasekharan, Ravi C. Gundakaram, and Vummethala Seshubai, IEEE transactions on applied superconductivity 21 (2011) 3612-3619