Chapter 4

Preparation and characterization of different composites for MTG components

Most of the potential applications of bulk YBCO require high critical currents in applied magnetic fields. There are two factors limiting the increase in critical current densities ($J_c$): existence of weak-links at large angle grain boundaries and lack of effective flux pinning centers. Since the concept of the melt-texturing growth (MTG) technology invented by Jin et al. [102], highly textured large YBCO single domains can be prepared and weak-links at large angle grain boundaries have been overcome to a great extent. Various modified editions of MTG, such as the liquid phase processing (LPP) method by Salama et al. [103], the Quenching Melting Growth method (QMG) by Murakami et al.[104] and the powder melting process (PMP/PMG) by Zhou et al.[105], have been developed and substantial increase in high critical current densities has been obtained. On the basis of the elimination of weak-links by these melt growth techniques, further increase in critical current density ($J_c$) needs forceful pinning centers like Y$_2$BaCuO$_5$ (Y-211) has been reported [103] to enhance the flux pinning ability of YBCO dramatically. It is believed [106] that the reduction in Y-211 size will increase Y-123/Y-211 interfacial area and induce many micro-defects around Y-211 particles, which enhance the flux pinning ability and result in a high $J_c$ value. In fact, introducing ultrafine Y-211 (<1 µm) into YBCO is one of the most effective approaches to increase $J_c$ value for every melting growth technology by now, due to different thermal schedules and starting precursors, morphologies and distribution of Y-211 are different for various melting growth technologies. As far as the MTG technology is concerned, Y-211 in a
product of the peritectic decomposition of Y-123 phase at high temperature (usually 1050°C). The phase Y-211 nucleates and grows up during the peritectic decomposition. Owing to the high decomposition temperature, Y-211 particles are very easy to grow up to several tens of microns. In order to suppress the growth of Y-211, several techniques such as optimizing thermal schedules (to lower the decomposition temperature), using additives (Pt, CeO₂) to promote [107] nucleation and restrain the coarsening of Y-211, have been attempted. Although substantial increase in growth has been made, still it is a problem to introduce ultrafine Y-211 into YBCO for practical applications. Different from other melt growth techniques, PMP uses Y₂BaCuO₅, BaCuO₂ and CuO as precursors. The size, morphology and distribution of Y-211 can be conveniently controlled before melting process. During melt growth, if proper processing parameters are employed, the coarsening of Y-211 particles can be suppressed or minimized. Therefore, if the size of Y-211 precursors is fine enough, it is possible to incorporate ultrafine or even nanometer sized Y-211 particles into YBCO. The incorporation of sub-micron Y-211 phase dispersed in YBCO matrix is the objective of this study. Detailed discussion of above processing technique are described in chapter 5.

4.1 Preparation of composite powders for fabrication of components

This chapter describes the preparation and characterization of selected composites for fabrication of components of different shapes by using melt textured growth technique (MTG). The relative stability of solidification growth fronts has been examined by using different varieties of composites given as follows:
<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Sample composites</th>
<th>Composite Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Y-123 + 25 wt % Y-211 (solid state route) + 5 Wt % Ag</td>
<td>A</td>
</tr>
<tr>
<td>2</td>
<td>Y-123 + 25 wt % Y-211 (nitrate decomposition route) + 5 Wt % Ag</td>
<td>B</td>
</tr>
<tr>
<td>3</td>
<td>Y-123 + 25 wt % yttria + 1 wt % Pt</td>
<td>C</td>
</tr>
<tr>
<td>4</td>
<td>Y-123 + 25 wt % yttria + 1 wt % ceria</td>
<td>D</td>
</tr>
</tbody>
</table>

### 4.2 Addition of Y-211 phase

The inclusion of Y-211 particles has several advantages to the growth and properties of bulk Y-123 components, such as:

a) It prevents the liquid flow so as to decrease the amount of pores.

b) It shortens the space between the Y-211 particles to help growth of the Y-123 crystal as well as creating the Y-123/Y-211 boundaries which are effective flux pinning sites [108].

c) Volume fraction of Y-211 particles is approximately constant: the current density ($J_c$), value is an inverse measure of the mean size of Y-211 phase. The high critical density values could be achieved by controlling the volume fraction and particle size of the Y-211 phase [109].

Y-211 is believed to act as reinforcement to the melt due to which the shape of the component is retained.

#### 4.2.1 Addition of silver

In order to improve the mechanical and fracture properties of the Y-123 superconductors, different types of superconducting composites have been investigated [110-112]. Among these, the Y-123/Ag composites [113-119] appear to be one of the
most promising choices. Silver has been observed to be one of the few materials that does not degrade the superconducting properties of the Y-123 [113] material. In addition, the presence of Ag lowers the normal-state resistivity and the contact resistance of the composite [114], and facilitates oxygen diffusion into the bulk material [115]. The degree of sintering in Y-123 is also enhanced by the Ag addition, resulting in decreased porosity as the Ag content is increased. Consequently, mechanical properties like Young’s modulus and fracture strength increase with the Ag addition [115-116].

4.2.2 Addition of platinum and ceria

Platinum and cerium oxide powders have been reported to be added for suppressing the coarsening of Y-211 particles during melt texture processing.[120-121].

4.2.3 Preparation of composites

To avoid shrinkage during fabrication using melt texture growth technique, Y-123 powder was first calcined at higher temperature i.e. below sintering temperature at about 900°C, the chunks were then crushed in vibratory mill and passed through 70 # sieve. The high temperature calcined powder was used for fabrication of components.

4.2.3.1 Preparation of sample composite A

400 g of pre-calcined Y-123 powder and 125 g of Y-211 powder (synthesized by solid state route) and 25 g of silver powder (99%) were mixed in a nylon bowl using zirconia balls in a planetary ball mill for 30 min in acetone media. The powders were dried in an oven at 100 °C.
4.2.3.2 Preparation of sample composite B

400 g of pre-calcined Y-123 powder and 125 g of Y-211 powder (synthesized by nitrate decomposition route) and 25 g of silver powder (99%) were mixed in a nylon bowl using zirconia in a planetary ball mill for 30 min in acetone media. The powders were dried in an oven at 100 °C.

4.2.3.3 Preparation of sample composite C

400 g of pre-calcined Y-123 powder, 125 g of yttria (99.9 %) and 4g platinum (99%) powder were mixed in a nylon bowl using zirconia balls in a planetary ball mill for 30 min in acetone media. The powders were dried in an oven at 100 °C.

4.2.3.4 Preparation of sample composite D

400 g of pre calcined Y-123 powder, 125 g of yttria (99.9 % , -325 mesh size) and 4g ceria (99.9%) powder were mixed in a nylon bowl using zirconia balls in a planetary ball mill for 30 min in acetone media. The powders were dried in an oven at 100 °C.

4.3 Granulation of composite powders

High density can be obtained if free flowing powder is available. To obtain free flowing powder it is necessary to granulate the composite powders. The mixed powders were filled in flexible latex bag, vacuum sealed and pressed in cold isostatic press at
1000-1200 bar pressure. These compacts were then crushed in vibratory mill and sieved to obtain -70 # powder.

4.4 Sintering of composites

Composite A, B, C, D and pure Y-123 powders were pelletized using 10 mm dia SS die and sintered in tubular kanthal furnace at 930°C at a heating rate of 3°C/min for about 10 h and then cooled at the rate of 3°C/min to 400 °C and held for 15 h in a flowing oxygen atmosphere.

Composites B,C and D were pelletized, heated to 1010°C and then quenched in liquid nitrogen.

4.5 Characterization of sintered and quenched composites

4.5.1 X-ray diffraction studies

4.5.1.1 XRD of sintered Y-123

X-ray diffraction pattern of sintered Y-123 is depicted in Fig.4.1. Orthorhombic splitting was observed at 32.8° and 58.6° which clearly indicates the single phase orthorhombic structure. No other phase was detected in the X-ray diffraction pattern.

4.5.1.2 XRD of composite B

Fig.4.2 shows the X-ray diffraction pattern of composite B. XRD pattern of the as mixed powder (B1) showed the presence of Y-123 and Y-211 phases as expected. XRD pattern of sintered powder (B2) showed peaks of orthorhombic Y-123 phase along with small peaks of Y-211. XRD pattern of quenched composite (B3) showed mixed phase of
tetragonal Y-123 and Y-211. The Y-211 peaks observed in the (B3), is due to the decomposition of Y-123 at this temperature to form Y-211.

4.5.1.3 XRD of composite C

Fig.4.3 shows the X-ray diffraction pattern of Composite C. XRD pattern of the as mixed powder (C1) shows mixed Y-123 and yttria phases. The sintered (C2) powder showed presence of orthorhombic Y-123 phase along with small quantity of yttria and Y-211 phase. Y-211 phase observed is due to the reaction between Y-123 and excess yttria added in the composite. XRD pattern of quenched composite (C3) showed mixed phase of tetragonal Y-123 phase along with Y-211 and yttria phase. The Y-123 starts to decompose above 960°C and converts partially to Y-211 phase, hence Y-211 phase is seen in (C3). No platinum peaks were observed due to the presence of low amounts.

4.5.1.4 XRD of composite D

XRD pattern of composite D are shown in Fig 4.4. XRD pattern of the as mixed powder (D1) shows mixed phase of Y-123 and yttria phase and the sintered powder showed (D2) mixed phase of orthorhombic Y-123 phase along with small phase of yttria and Y-211 phase. The Y-211 phase observed in the XRD pattern is due to the reaction of Y-123 with excess yttria in the composite. XRD of quenched material (D3) shows mixed phase of tetragonal Y-123, yttria and secondary phase of Y-211. The Y-211 phase observed in (D3) is due to decomposition of Y-123 above 960°C.
The XRD patterns of quenched samples of all the composites indicate the presence of the tetragonal Y-123 phase. Retention of the high temperature (>1010 °C) tetragonal phase at room temperature is feasible only due to the high quenching rates in all the samples.

**Fig. 4.1** XRD pattern of sintered Y-123 powder

**Fig. 4.2** XRD patterns of composite B, (B1)-as mixed powder, (B2)- sintered powder, (B3)-Quenched powder
Fig.4.3 XRD patterns of composite C. (C1)-as mixed powder, (C2)-sintered powder, (C3)-Quenched powder

Fig.4.4 XRD patterns of composite D. (D1)-as mixed powder, (D2)-sintered powder, (D3)-Quenched powder
4.5.2. Scanning electron microscopy

The fractured surface, as investigated by SEM, of Y-123 sintered at 930°C for 10h followed by an annealing at 400°C for 10 h in oxygen atmosphere is shown in Fig.4.5. The fractograph revealed presence of a highly porous structure. The grain size distribution was fairly broad and mostly towards a multimodal distribution. The fracture mode is found to be inter-granular in nature.

The fractograph of sintered composite A (Y-123 + 25 wt % Y-211 + 5 wt % Ag) is shown in Fig.4.6a. Like Y-123 sample, this sample was also subjected to sintering at 930°C for 10h followed by an annealing at 400°C for 10 h in an oxygen atmosphere. The composite material attained a relatively higher density as compared to pure Y-123, although the sample was porous in nature. The micrograph reveals the presence of intra-granular fracture.

The fractograph of sintered composite B (Y-123 + 25 wt % Y-211 + 5 wt % Ag) is shown in Fig.4.6b. Like Y-123 sample, this sample was also subjected to sintering 930°C for 10h followed by an annealing at 400°C for 10 h in oxygen atmosphere. The composite material attended a relatively higher density as compared to pure Y-123, although the sample was porous in nature. The micrograph reveals the presence of intra-granular fracture with smaller grain size particles as compared to composite A.

The SEM micrograph of composite C and D, which were subjected to similar heat treatment as mentioned above for pure Y-123 and composite B, is shown in Fig.4.7 and Fig. 4.8, respectively. The microscopic feature of these samples were similar to that of composite B. Like composite B, composite C and D also showed presence of predominantly intra-granular fracture mode.
All the samples composite B (Fig.4.9), composite C (Fig. 4.10 and composite D (Fig.4.11) were heated to 1010°C, soaked for one hour and quenched into the liquid nitrogen bath, have shown open pore free highly dense structure. Predominantly, intra-granular fracture mode was observed in the samples. The evidence of randomly distributed elongated grain can be seen in the micrograph. The structure was monotonous and it is difficult to conclude from the micrographs whether there was any secondary phase present along the grain boundary or within the matrix.

Fig.4.5 SEM micrograph of fractured surface of sintered pure Y-123 pellet

Fig.4.6a SEM micrograph of fractured surface of sintered pellet of composite A
Fig. 4.6b SEM micrograph of fractured surface of sintered pellet of composite B

Fig. 4.7 SEM micrograph of fractured surface of sintered pellet of composite C

Fig. 4.8 SEM micrograph of fractured surface of sintered pellet of composite D
Fig. 4.9 SEM micrograph of fractured surface of quenched pellet of composite B

Fig. 4.10 SEM micrograph of fractured surface of quenched pellet of composite C

Fig. 4.11 SEM micrograph of fractured surface of quenched pellet of composite D
4.5.3 EPMA analysis

Sintered samples of the composites B, C and D were subjected to electron probe micro analysis (EPMA). The back scattered electron images and corresponding X-ray mapping for the elements are recorded.

It is observed from the Fig.4.12 that the BSE image has the dark region due to the presence of porosity in the sintered pellet of composite B. The X-ray mapping of Y clearly shows presence of larger concentration of Y (green colour) in Y-211 phase and relatively smaller concentration of Y in Y-123 phase. The concentration of Cu is more in Y-123 therefore the reddish regions are more and at the same time it can be seen that Y is less at reddish regions. The regions where Y is more, but the Cu concentration is less represents Y-211. The X-ray mapping of Ag shows homogeneous distribution of silver in the matrix. This shows the evidence that Y-123, Y-211 and Ag are uniformly distributed.

It is observed from the Fig.4.13 that the BSE image has also dark region due to the presence of porosity in sintered pellet of composite B. The X-ray mapping of Y shows presence of larger concentration of Y, this is due to addition of excess amount of yttria in the composite. The x-ray mapping of Ba and Cu shows the uniform distribution of Ba and Cu. The X-ray mapping of Pt shows uniform distribution. Thus it is concluded that Y-123, yttria and Pt are uniformly distributed in the composite.

It is observed from the Fig.4.14 that the BSE image has the dark region due presence of porosity in sintered pellet of composite D. The X-ray mapping of Y shows presence of larger concentration of Y, which is due to addition of excess amount of yttria in the composite. The X-ray mapping of Ba and Cu shows the uniform distribution
of Ba and Cu. The X-ray mapping of Ce shows uniform distribution of Ce. This
concludes that uniform distribution of Y-123, yttria and CeO$_2$.

![Fig.4.12 BSE image and corresponding X-ray mapping of sintered composite B](image-url)
Fig. 4.13 BSE image and corresponding X-ray mapping of sintered composite C

Fig. 4.14 BSE image and corresponding X-ray mapping of sintered composite D
4.5.4 Critical transition temperature measurement

All the samples (B2, C2 and D2) were sintered at 930°C for 10 h followed by an annealing at 400°C for 10 h in oxygen atmosphere. Critical temperature measurements on the different types of sintered samples were carried out using the equipment specially designed for this purpose and described earlier in Chapter 2. Resistance vs Temperature (R vs T) plot of B2, C2 and D2 showed onset drop at 94 K, there was no superconducting behavior till 77K liquid nitrogen temperature. The R Vs T data of all the quenched samples B3, C3 and D3 showed semiconducting behavior.

4.6 Conclusion

Four types of composites were prepared i.e. (i) Y-123 + Y-211 + Ag (solid state route), (ii) Y-123 + Y 211 + Ag (Nitrate Decomposition Route) (iii) Y-123 + Y₂O₃ + Pt and (iv) Y-123 + Y₂O₃ + CeO₂. The samples from pure Y-123 and these composites were (a) sintered at 930°C/10 hours and annealed at 400°C for 15 hours in oxygen atmosphere and (b) Quenched from 1010°C into liquid nitrogen bath. The samples have been characterised by X-ray diffraction, scanning electron microscopy, Electron Probe Micro Analysis (EPMA) and critical temperature measurements (Tc). XRD patterns reveal the phase composition while SEM shows the microstructural features. EPMA revealed homogenous elemental distribution confirming uniform mixing during preparation of samples. Tc measurement of pure samples showed a drop at 94 K and there was no superconducting behaviour upto liquid nitrogen temperature, this is because of 25 wt % addition of non-superconducting phase like yttria and Y-211 phase
which destroys the superconducting properties and all quenched samples showed semiconducting behaviour.

The compacts using all the above four composites were fabricated in hollow cylindrical and plate shapes. These compacts were then subjected to MTG, followed by prolonged annealing in oxygen atmosphere. Their detailed characterization is discussed in the next chapter.