CHAPTER-5

Fabrication of components using MTG technique

The stimulus for the development of melt processing techniques has been the demand for high-quality HTSC materials, i.e. materials combining high current density \( (J_c) \) and large magnetization with high mechanical strength. In recent years it was realized that the attainment of high \( J_c \) and strong magnetization (e.g. for levitation purpose) requires materials in which weak links, involving features such as cracks, voids, high-angle grain boundaries, and insulating phases at grain boundaries, are eliminated. At the same time, a sufficiently high concentration of flux pinning sites (certain defects, impurities or secondary phases) need to be present. The conventional solid state sintering, which was extensively employed during the early development of HTSC materials, yields materials with low \( J_c \) values due to the presence of an excessive number of weak links. These materials also tend to have low density and poor mechanical strength. On the other hand, large, pure and stress-free single crystals of Y-123 cannot be expected to contain enough flux pinning centres. Accordingly, the most promising materials for HTSC applications are polycrystalline materials which can provide, on one hand, high density and a high degree of grain alignment to minimize the number of weak links, and on the other hand, a sufficient number of defects to serve as flux pinning centres. As described subsequently, melt-based techniques can be controlled to produce second phases such as Y-211, which provide effective flux pinning sites.

There are many different types of melt processing techniques such as Mixed-Powder-Partial-Melting (MPPM), Melt-Powder-Melt-Growth (MPMG), Powder Melting Process (PMP, Quench-and-Melt-Growth(QMG), Melt-Texture Growth (MTG) and Top
seed melt texture growth technique (TSMTG) which are described as follows. This chapter describes the design of mould for different shapes, filling the moulds with composites, compaction at varying pressure, temperature, subjecting to TSMTG and prolonged annealing in oxygen atmosphere. Further characterizations of the MTG compacts have also been carried out and will be discussed in the next chapter.

5.1 Melt Processing of YBCO

5.1.1 Melt-Texture Processing

Texture processing was developed as a means to avoid or minimize the effects of many of the weak-link limitations to \( J_c \) in polycrystalline Y-123. By having a microstructure where the current flow can be directed primarily in the basal plane, and by minimizing the occurrence of high-angle grain boundaries, some of the primary causes of weak link behaviour can be considerably minimized, if not eliminated. Formation of texture in bulk Y-123 has been achieved by a number of different techniques, including compaction processes, magnetic alignment of particles and directional solidification.

Numerous groups have shown that compaction, both with and without the use of elevated temperatures, can help develop texture in Y-123. Although textured microstructures have been produced, however, transport properties comparable to those produced by directional solidification processes have not been achieved [122-123].

Magnetic alignment has also been successful for developing texture. Particles of Y-123 have been aligned in epoxy [124] to simulate single crystal-like behaviour and also in organic solvents [125-126]. After the solvent evaporates, the aligned particles can be sintered, resulting in well-textured bulk samples. Transport properties achieved by
this technique, however, are not comparable with those produced through directional solidification (see below) because the alignment produced by the applied field allows for rotation in the nonaligned directions (e.g. a and b directions), producing high-angle twist boundaries between aligned grains. A more effective use of magnetic alignment involves solidification in an applied magnetic field. In this case the Y-123 crystals tend to rotate and become aligned while remaining in the liquid phase. As a result, growth under the influence of the field results in a well-textured sample with excellent grain-to-grain alignment [127].

Texturing by directional solidification from the melt has proven much more successful as a means to achieve texturing from the melt. By this route a microstructure is produced that consists of large grains that are well aligned with respect to each other. Grain boundaries in the direction of current flow can be eliminated by these melt-texturing techniques, so that transport $J_c$ values exceeding $10^4 \text{A/cm}^2$ in applied fields of several Tesla can now be achieved. Since these melt-processing techniques have proven to be so successful, they are the only practical means to achieve high $J_c$ in Y-123, they will be discussed in more details in the following section.

Jin et al. used the term “melt texturing” to describe their pioneering work in this area [128-130]. In the case of Y-123, melt texturing describes directional solidification from the melt or partially melted state. While there are a number of variations of the texturing techniques, as described below, they all involve heating Y-123 above its peritectic decomposition temperature (1015°C in air) and slow cooling to form aligned generally large grains of Y-123. This can be understood upon examination of the section of the ternary phase diagram shown in Fig. 5.1. It can be seen that upon heating above
approximately 1015°C, YBa$_2$Cu$_3$O$_{6+x}$ will decompose to yttrium-rich Y$_2$BaCuO$_5$ (Y-211) and a yttrium-deficient liquid phase consisting of BaCuO$_2$+CuO. Upon slow cooling (e.g., less than 1°C/h) from 1015°C to approximately 900°C, the Y-123 will nucleate and grow.

\[
\text{YBa}_2\text{Cu}_3\text{O}_{6+x} \leftrightarrow \text{Y}_2\text{BaCuO}_5 + \text{L} [\text{BaCuO}_2 + \text{CuO}] \quad \text{(5.1)}
\]

5.1.2 Techniques used for melt processing

5.1.2.1 Mixed-Powder-Partial-Melting (MPPM)

In the MPPM process, Y-211 phase pure powder is mixed with a Y-123 pre-calcined powder. The yttrium content of the YBCO precursor can vary from the stoichiometric Y-123 ratio [131] to about zero [132]. The resulting mixture is first heated above the peritectic reaction temperature and then slowly cooled through the peritectic range to react the Y-211 phase with the liquid phase present to form Y-123 with residual Y-211 providing pinning centers. This method was also studied extensively with varying target concentrations of yttrium in the final product in the present investigation. Again, this method, like all other partial melting techniques, suffers from extensive loss of the liquid phase at high temperatures while fabricating large specimens.

The main advantage of various partial melting techniques is that they do not require complete melting, which is normally done in a crucible. Molten Y-123 is very reactive and dissolves almost any crucible materials with which it comes in contact, even noble metals such as platinum and rhodium. Accordingly, the use of partial melting procedures, with the liquid largely confined within the solid structure of the Y-123 material,
minimizes the problem of attack by the reactive melt on the crucible and the resulting contamination of the melt by dissolved crucible material.

5.1.2.2 Melt-Powder-Melt-Growth (MPMG) Process

The MPMG process is similar to the QMG process described latter, being usually practiced with a starting powder stoichiometry that is Y-211 rich [133-134]. The key to this variation on QMG is that the quenched material is powdered before further processing to ensure a homogeneous distribution of Y₂O₃ (which then converts to Y-211) in both the melt and the final melt textured microstructure. The resulting acicular Y-211 particles are less than 1μm in length. Murakami [134] has reported that the properties of MPMG processed material improve with increasing Y-211 content and has suggested that Y-211 acts directly as flux pinning site.

5.1.2.3 Powder Melting Process (PMP)

The PMP process was developed by Lian and his coworkers [135]. This method uses a starting mixture of Y-211/BaCuO₂/CuO powders to secure a uniform distribution of fine Y-211 in the melt without having to employ a melt-quenching process. The pressed samples are processed either by the MTG or modified MTG thermal profile, which yield microstructures identical to those obtained when comparable premixed YBCO stoichiometries are similarly processed. The advantage of this process is that the initial particles size of the Y-211 can be controlled, for example, by milling or using a sol-gel route to produce the Y-211. In MTG by comparison, there is less well defined control over the Y-211 size. Although not mentioned explicitly temperatures because of
the precursors used, since the liquid phase melts below this temperature and begin reacting with the Y-211.

5.1.2.4 Quench and Melt-Growth (QMG) Process

The QMG process was first reported by Murakami and his coworkers [136-138]. This method involves using the Y-211 peritectic reaction to refine the size of the starting Y-211 particles. First, a sintered sample (or a mixture of calcined powders of the required stoichiometry) is quickly heated above the Y-211 decomposition temperature (1270°C) in a platinum crucible. The material is held at 1400°C for 20 minutes and then quenched using cold copper plates. The quenched sample consists of Y₂O₃ particles and an amorphous liquid phase. The quenched material is then processed by the modified MTG process described earlier. When heated above 1015°C, the Y₂O₃ reacts with the liquid to form Y-211, which in turn reacts with the liquid melt on cooling to form Y-123. The distribution of Y-211 in the melt is controlled by the distribution of Y₂O₃ in the quenched material. For stoichiometric Y-123, the QMG process results in a textured material that has little residual Y-211 phase and J_c values on the order of 2 x 10⁴ A/cm² in zero applied field. The Y-211 refinement which leads to near complete reaction with the applied field. The Y-211 refinement which leads to near complete reaction with the liquid to form Y-123 has subsequently been attributed to the presence of platinum in the melt (dissolved from the sample crucible).
5.1.2.5 Melt-Texture Growth (MTG) technique

The MTG process first demonstrated the feasibility of using melt processing to align grains to overcome the electrical anisotropy in Y-123 materials. With this technique, sintered Y-123 was partially melted at about 1150°C and then slowly cooled in a thermal gradient. The resulting microstructure showed preferred orientation for grain growth in the a-b plane and large, non-uniformly distributed spherical Y-211 particles up to 40 microns in length. The connectivity of the Y-123 plates was not good and was attributed to non-uniform growth conditions associated with the Y-211 particle distribution. Although the properties were much improved over those of sintered materials, the \( J_c \) was found to drop precipitously in magnetic fields, indicating the absence of adequate flux-pinning sites in the Y-123 matrix. Jin’s initial success with the MTG process [139-141], which enhanced \( J_c \) two or three orders of magnitude over that of sintered materials (with significantly less field dependence) led to a variety of melt-texturing methods which were developed in an effort to further improve properties and facilitate processing.

5.1.2.6 MTG Process

The modified MTG process was developed to homogenize the Y-211 distribution and minimize the Y-211 coarsening observed during the MTG process [142]. Here, samples are again quickly heated to approximately 1100°C, but rather than being slow cooled, they are held for only 20 minutes at the maximum temperature before being quickly cooled to the peritectic temperature. The samples are then slowly cooled from the peritectic temperature to about 950°C. The initial heating and thermal hold at 1100°C is
designed to ensure adequate sample melting (required to minimize pore formation), while the quick cooling to the peritectic temperature minimized Y-211 coarsening. The final microstructure shows improved Y-123 connectivity and a more uniform distribution of fine Y-211 particles ranging from 1 to 5\(\mu\)m size. The bulk textured material can be produced using the Melt-textured growth (MTG) technique.

5.1.2.7 Modified MTG Process

Top-seeded melt texture growth (TSMTG) is known as the most effective process to fabricate block-type samples used for example in energy storage applications, such as superconducting flywheel system and others. In this technique, too long isothermal step and large processing times is regarded as one of the most significant weak points. In the case of melt texturing with a temperature gradient, processing time is shorter, but the sample shape and size are restricted.

The TSMTG technique has been widely used to grow YBa₂Cu₃Oₓ crystals as large as several centimetres [143], but these crystals were intended for application like magnetic levitation. The size of single-domain is generally about several centimetres in diameter and limited to about 10 cm for high quality YBCO bulk up to now, because of the grains mis-orientation during the melt growth process [144]. The resulting cubic centimetre-size YBCO crystals are further annealed to obtain the oxygen-ordered orthorhombic phase (x=6.5).

Uniquely, the TSMTG process yields large, single grains of approximately the dimensions of the green body [145-147]. The TSMTG technique has become the preferred method for the fabrication of bulk Rare earth (RE)-123 superconductors and is
used routinely in the processing of single-grain cylindrical/square shape samples of up to 50 mm in diameter [148].

TSMTG processing is classified into two types by seeding method; cold seeding and hot seeding. Cold and hot seeding are named for the moment when the seed crystal is placed on the powder compact. In case of sample handling, the cold seeding method is easier than hot seeding, because the seeding is performed at room temperature [149]. In this study the seeding method used is cold seeding has been employed for TSMTG.

In order to obtain large-domain-sized YBCO and to control the growth orientation, seeding affects should be taken into consideration sufficiently [150]. The seed should not only have a similar structure and lattice constant of similar order to those of as-grown YBCO bulks, but also control the orientation and ensure single-domain growth [151]. The seed crystal initiates the nucleation and growth of the Y-123 phase in the incongruent melt, which subsequently solidifies into single large grain during controlled cooling.

A variety of seeds have so far been applied for the melt-textured (MT) growth of YBCO bulks [150], can be classified into three major categories:

i. Non-superconductors, such as MgO.

ii. Bulk superconductors, such as RE-123 Melt texture bulks or single crystal, such as Nd-123, Sm-123, and others.

iii. RE-123 thin films (RE-Rare-earths) [152].

In principle, the seed material should not melt during the texture process, because the maximum process temperature should be below their melting points. However, the seed crystals were observed to dissolve frequently when they were in contact with the Ba-Cu-
O liquid that was formed as a result of the incongruent melting of Y-123 compact during a high temperature holding period [153]. As the seed dissolves during processing, it no longer acts as a seed for growth of textured Y-123 crystal. In the case of dissolution formed, decreasing the levitation force and trapped magnetic field by reducing the size of the shield current loop has been observed. For this reason, the growth mode of Y-123 grains is critically dependent on seed thickness [154].

This chapter describes, in details, the TSMTG process and fabrication of bulk textured components using cold isostatic pressing (CIP) for preparing green compacts.

5.2 The Y-123 Pseudo-Binary Phase Diagram

The Y$_2$O$_3$-CuO-BaO phase diagram has been the subject of many investigations. Recently a summary of existing phase diagrams for all high-temperature superconductors has been published [155]. Aselage and Keefer [156] identified eleven invariant points on the Y$_2$O$_3$-CuO-BaO phase diagram, including the incongruent melting temperature of Y-123 and Y-211. They found that Y-123 decomposed in air at 1015°C and resulted in the formation of Y-211 and a barium-rich liquid according to the following relation:

\[ 2 \text{ Y-123} \rightarrow \text{ Y-211} + \text{ L (3 BaCuO$_2$ + 2 CuO)} \]  \hspace{1cm} (5.1)

On further heating the decomposition of the Y-211 phase was found to occur at 1270°C and produced Y$_2$O$_3$ and a liquid as follows:

\[ \text{ Y-211} \rightarrow \text{ Y$_2$O$_3$ + L (BaCuO$_2$)} \]  \hspace{1cm} (5.2)
Subsequently, these two sets of peritectic reactions have formed the basis for all YBCO melt-texturing techniques aimed at eliminating the problems associated with both the weak-link character and the poor pinning properties of sintered YBCO. All the significant melt-processing strategies to date ultimately involve slow cooling from the partial melt (above 1015°C) to below 960°C (either isothermally or in a temperature gradient) to form Y-123. As with other (metallic) peritectic systems, the reaction of the primary phase (Y-211) with the liquid to form the peritectic product (Y-123) is extremely slow and rarely proceeds to completion to yield phase-pure Y-123 under normal melt-processing thermal cycles.

For stoichiometric Y-123 samples, this incomplete reaction can be exacerbated by a combination of inadequately slow cooling rates and / or liquid phase segregation (i.e., to the sample surface or grain boundaries), which results in a shift in composition to a more 211-rich stoichiometry. Even under optimal conditions, however, the reaction
usually will not go to completion because growing Y-123 will trap unreacted Y-211, eliminating its further reaction, as the growing Y-123 traps unreached Y-211, eliminating its further reaction with the liquid. Consequently, on cooling the reaction is more accurately represented as

\[
Y-211 + 3\text{BaCuO}_2 + 2\text{CuO} \rightarrow (2-x)Y-123 + (x/2)\text{Y-211} + (x/2) [3\text{BaCuO}_2 + (x/2)2\text{CuO}] \rightarrow (5.3)
\]

If the growth of Y-123 were to proceed by the conventional peritectic mechanism, the primary solid (which would be Y-211 in this case) would react with the liquid to form a shell of peritectic product (Y-123) around itself. The reaction would proceed by the diffusion of species through this shell and would result in a microstructure containing randomly oriented (Y-123) grains which could have undissolved primary solid (Y-211) cores. The fact that melt-processed YBCO does not result in this cored microstructure indicates that its growth from the melt is not by the conventional peritectic mechanism.

### 5.2.1 The Y-123 peritectic reaction

Although a desirable microstructure has been indentified that yields high $J_c$ values, generating such structures so far has necessitated extremely slow cooling rates (0.1-0.3°C/h). The slow cooling rate (and therefore the long processing time), which is necessitated by the kinetics of the peritectic reaction, is the greatest disadvantage of the directional solidification processes as currently practiced.

Much of the early literature concerning the melt texturing of Y-123 assumed that the formation of Y-123 from the melt occurs by the traditional peritectic reaction in which the Y-123 forms a shell around a Y-211 particle and thus separates the Y-211 from
direct contact with the Ba- and Cu-rich liquid. This Y-123 envelope would then slow down any further growth of Y-123, since it would depend on the solid-sate diffusion of the reactants through the Y-123 layer. The existence of such a shell is, however, not seen in melt-textured Y-123.

It has been postulated that in most peritectic systems, the peritectic reaction does not occur because crystallization of the peritectic phase occurs directly from the liquid. In peritectic systems in which the liquidus lines of the properitectic and peritectic phases coincide, however, a peritectic reaction can occur at some temperature below the peritectic temperature. St. John has examined the peritectic reaction [157]. In this work he distinguishes between the peritectic transformation and the peritectic reaction. The peritectic reaction is the formation of the peritectic or secondary phase (Y-123, in this case) by reaction of the primary phase (Y-211 in this case) with the liquid at the peritectic temperature. This is the reaction between Y-211 and liquid Y-123. The peritectic transformation, distinct from this, is the growth of the secondary phase (Y-123), which occurs by diffusion through the already-formed secondary phase coating the primary phase. The work by St. John and a number of other groups has shown that a competition exists between the peritectic transformation, which occurs relatively slowly because of the rate limiting solid-state diffusion, and nucleation of the secondary phase directly from the melt. The extent to which the peritectic product grows by the peritectic transformation as opposed to nucleation from the melt will depend on the rate of solid-state diffusion step, and nucleation of the secondary phase directly from the melt. The extent to which the peritectic product grows by the peritectic transformation as opposed to nucleation from the melt will depend on the rate of solid-sate diffusion through the...
peritectic product. In all of the systems in which secondary-phase nucleation from the melt have been reported the secondary phase is not a line compound, as is the case for Y-123. In other work [158] St. John has classified peritectic systems into three types depending on the slopes of the $\alpha$ solidus and the solvus line between the $\alpha$ and $\alpha+\beta$ regions. In Type C systems, in which line compounds form, the extent of the peritectic transformation is only marginally observed. This suggests that during the formation of Y-123, the main mode of formation can be expected to be a growth directly from the melt.

5.2.2 Mechanism of Y diffusion growth model

In 1992, Izumi [159], Cima [160] and Mori [161] reported a Y-123 growth model based on yttrium diffusion. They assumed that the Y-123 crystal growth rate is limited by the yttrium diffusion. In a classical peritectic reaction, once the Y-123 formation occurred, the Y-211 particles would be wrapped by Y-123 phase and yttrium would have to diffuse through the Y-123 solid towards the liquid phase. As the Y-123 becomes larger, it would become more difficult for yttrium to reach the Y-123 solid–liquid interface. The resulting microstructure would be an assembly of Y-123 grains with a Y-211 core. This is not what is experimentally observed. On the contrary large Y-123 grains are obtained trapping many Y-211 particles.
To solve this inconsistency, a new mechanism has been proposed which is illustrated in Fig. 5.2. In this model, the Y-211 particle dissolves partially in the melt and the yttrium is transported to the growing Y-123 interface by diffusion in melt. Once the Y-123 nucleation occurs, the required amount of yttrium necessary for the Y-123 growth front is provided by the neighboring Y-211 particles. As the liquid phase is depleted in yttrium by the growth front, these particles partially melt to compensate the yttrium depletion. The dissolved yttrium ions travel across the liquid to the Y-123 growth interface front- driven by the yttrium gradient for feeding the Y-123 crystal continuous growth. Thus, the growth rate is controlled by the yttrium diffusion rate.

5.3 Compaction of composites

Unlike metals, ceramics are generally shaped using different techniques like cold isostatic pressing, hot isostatic pressing etc. Prior to heating, it is essential to have a preform with shape and dimensions close to the final geometry. This is not only due to
their brittle nature which makes them difficult to machine, but also because pressure is
normally required before subjecting them to thermal cycle so as to ensure large areas of
surface contact between the grains. Such large areas of surface contact not only increase
reaction rates, but also tend to increase the density and strength of the components.

The fabrication of components of different shapes follow various steps sequential
such as :

i. Densification by using Cold Isostatic Press (CIP)

ii. Sintering

iii. Subjecting to thermal cycle through melt texture growth (MTG) technique

Compaction study has been carried out to achieve maximum green density by
varying the pressure in CIP. The effects of pressure are :

(i) To reduce pore size

(ii) To break up particles at surfaces in contact

(iii) To introduce strain and plastic flow to achieve maximum green density.

5.3.1 Preparation of preform and densification

Since the components are of larger size, uniaxial pressing is not possible, where
L/D ratio cannot be maintained. This leads to variation in density in the entire sample and
also complex shapes cannot be pressed using uni-axial pressing. Therefore, for higher
L/D ratio and to achieve uniform density throughout the sample, cold isostatic pressing
(CIP) was used. The compacts using CIP are generally more homogeneous i.e. a uniform
density is maintained in the entire compact shape and it is free of microcracks compared
to the axially pressed counterparts. During cold isostatic pressing, the pressure is applied hydrostatically, resulting in a uniform pressure on all points of the mould.

5.3.1.1 Designing of rubber mould for fabricating different shapes

The required final dimensions to be used in various application are mentioned in Table 5.1. The components as mentioned in Table, at Sr. nos. 1, 2 and 3 have been used to fabricate HTSC prototype motors and fault current limiters and component 4 have been used to study the effect of ceria and Pt on superconducting properties. The fabricated component sr. no 5 was cut into two halves horizontally and their critical density has been measured. The result of both halves will ensure that the $J_c$ value is uniform in both halves. These results will be discussed in subsequent sections.

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Shapes of the components</th>
<th>Final size of MTG components required for applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hollow cylinder</td>
<td>36mm ID x 46mm OD x 50 mm height</td>
</tr>
<tr>
<td>2</td>
<td>Plates</td>
<td>25mm width x 50mm height x 3.5mm thick</td>
</tr>
<tr>
<td>3</td>
<td>Pins</td>
<td>8 mm OD x 25 mm height</td>
</tr>
<tr>
<td>4</td>
<td>Hollow cylinders for studying the effect of additives like ceria and Pt on HTSC properties.</td>
<td>~29 mm OD x ~19mm ID x ~32mm</td>
</tr>
<tr>
<td>5</td>
<td>Hollow cylinders for studying transport property in top and bottom portion.</td>
<td>____</td>
</tr>
</tbody>
</table>

Table 5.1 Required final dimensions of MTG components
To obtain the required final dimensions in MTG components, silicon rubber moulds were designed. Some of the moulds along with corresponding dimensions are shown in Fig.5.3 and the corresponding dimensions in Table 5.2. Moulds were designed in order to account for the shrinkage during compaction and sintering as well as before subjecting to melt texture growth technique (MTG). The anticipated reduction in dimension at all the three stages has to be computed for design of the moulds. Hardness of mould was optimized, so that the pressed compact is easily removed from the mould after releasing the pressure. The optimized hardness of the silicone rubber mould was optimized at 55-60, and pressure varies from shape and size of the component to be pressed.

5.3.2 Densification of composites using CIP

The granulated composites prepared as the procedure described in the previous chapter were filled in the respective moulds as shown in Table 5.2. Filling and vibrating of moulds on a vibrating mill is done simultaneously as shown in Fig.5.4. Vibration is carried out to ensure that the powder is uniformly filled in the mould to ensure pore free, and to achieve compact with maximum packing green density. The type of the composite, size of the mould used to fill and corresponding name of the component are mentioned in Table 5.3 along with the applied pressures which were optimized for different size to achieve maximum green density without lamellar cracks in the compacts. Maximum shrinkage is observed during compaction in CIP (see Table 5.4).
Fig. 5.3 Picture of moulds for fabricating components: (1)- Mould for hollow cylinder 1, (2)- Mould for Plates, (3)- Moulds for PINS, (4)- Moulds for hollow cylinder 2, (5)- Mould for hollow cylinder 3

Fig. 5.4 Typical picture of mould and filling composite powder in mould with vibrating
<table>
<thead>
<tr>
<th>Sr. No (photograph)</th>
<th>Mould shape</th>
<th>OD (mm)</th>
<th>ID (mm)</th>
<th>Height (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Hollow cylinder 1</td>
<td>75</td>
<td>56</td>
<td>70</td>
</tr>
<tr>
<td>2.</td>
<td>Plate 1</td>
<td>45 width (W)</td>
<td>6 thick (T)</td>
<td>70</td>
</tr>
<tr>
<td>3</td>
<td>Pins 1</td>
<td>20</td>
<td>13</td>
<td>35</td>
</tr>
<tr>
<td>4</td>
<td>Hollow cylinder 2</td>
<td>35</td>
<td>23</td>
<td>38</td>
</tr>
<tr>
<td>5</td>
<td>Hollow cylinder 3</td>
<td>75</td>
<td>24</td>
<td>25</td>
</tr>
</tbody>
</table>

Table 5.2 Various moulds with shapes and sizes designed for fabricating components with corresponding photographs

<table>
<thead>
<tr>
<th>Name of the composite used</th>
<th>Shape of the rubber mould used as mentioned in Table 5.2</th>
<th>Component name</th>
<th>Pressure applied (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composite A</td>
<td>Hollow cylinder (1)</td>
<td>SSR-CY-1</td>
<td>3000</td>
</tr>
<tr>
<td>Composite A</td>
<td>Plate 1</td>
<td>SSR-PL-1</td>
<td>3000</td>
</tr>
<tr>
<td>Composite B</td>
<td>Hollow cylinder (1)</td>
<td>NDR-CY-2</td>
<td>3000</td>
</tr>
<tr>
<td>Composite B</td>
<td>Hollow cylinder (3)</td>
<td>NDR-CY-3</td>
<td>3000</td>
</tr>
<tr>
<td>Composite B</td>
<td>Plate 1</td>
<td>NDR-PL-2</td>
<td>2500</td>
</tr>
<tr>
<td>Composite B</td>
<td>Pin 1</td>
<td>NDR-PI-1</td>
<td>2000</td>
</tr>
<tr>
<td>Composite C</td>
<td>Hollow cylinder (2)</td>
<td>Pt-CY-5</td>
<td>2500</td>
</tr>
<tr>
<td>Composite D</td>
<td>Hollow cylinder (2)</td>
<td>Ce-CY-6</td>
<td>2500</td>
</tr>
</tbody>
</table>

Table 5.3 Components fabricated using composites in rubber moulds

(Abbreviations used are as follows: NDR- nitrate decomposition route, SSR- solid state route, CY- cylinder shape, PI- pins shape, Pl-plate shape)
5.4 Solidification of compacts using MTG and TSMTG technique:

In bulk material, weak links that affect current transport arise from a combination of several features, including

a) High angle grain boundaries.

b) Anisotropic current flow resulting in circuitous paths.

c) Chemical or structural variations at grain boundaries.

d) Insulating intergranular phases, and

e) Microcraking due to thermal stresses arising partly from phase transformations and partly from anisotropic expansion coefficients.

A major goal in processing HTSC material for applications requiring high currents lies in texturing the grains. The procedure for obtaining textured Y-123 grains using MTG technique is described as follows. The texturing occurs as a result of growth of new Y-123 grains from the slowly cooled Y-211 and yttrium deficient liquid below the peritectic temperature. A typical schedule employed by the MTG is indicated in Fig. 5.4. If the temperature of the materials is kept within a few degrees of the melting temperature, the pre-sintered material remains rigid during processing, though densification and shrinkage occur. The grain growth is slow as this diffusion controls texturing, so the process is time consuming.
5.4.1 Sintering of compacts

During MTG process the compact attains higher temperature than the peritectic temperature 1010°C, the upper portion partially melts and shrinks. The lower portion of the compact also partially melts, reacts with the container/base support due to which the shape is distorted at the bottom where the sample is in contact with base material. The lower part of the compact has to be cut and discarded. Therefore in order to decrease the loss of material and to retain optimum shape of the compact, a pre-sintering step is introduced to all the green compacts before it is subjected to MTG in which the compact is slowly heated to 930 °C at rate of 2°C/min and soaked for 5-10 h depending on the size, shape of samples and cooled to room temperature at the rate of 6°C/min to avoid
thermal shock due to which cracks may be generated in the sample to near melting point. It ensures the maximum shrinkage in the components while sintering.

5.4.2 Melt texture growth technique (MTG) of compacts

The typical flow chart of heat treatment pattern followed in this study is shown in Fig. 5.6. The optimization of the temperature profile is crucial for the production of large YBCO components. Depending upon the shape and size of the compacts the temperature varies. The cylindrical and pins shape compacts were heated up to 1060°C at a rate of 300 °C/h, and held for 6-10 h for homogenous melting. The hold time varies depending upon the shape and size of the samples. At this temperature Y-123 dissociates into solid Y-211 and liquid of Ba and Cu oxides. After that, the samples were cooled to about 1010°C at a rate of 180°C/h, and further cooled to 960°C at a rate of about 0.3-0.5°C/h. During slow cooling from 1010-940 °C (peritectic temperature) the Y-123 nucleates from undercooled mixture of Y-211 particles and melt consisting of BaCuO2 and CuO. Thus to facilitate the growth of Y-123, the dissolution of Y-211/yttria is essential so that additional Y³⁺ ions are supplied to Y-123 solidification front. The solidification front will engulf Y-211/yttria particles, this depends upon the particle size of Y-211, velocity of the growth front and interface energies between Y-123, Y-211 and the melt. Therefore it was decided to add 25 wt % of Y-211 in all NDR-X-X and SSR-X-X samples, and 25 wt% yttria to Y-123 in Pt-Cy-4 and Ce-Cy-5 samples before melt processing [samples decoding given in Table 5.3]. This ensures the formation of defects, which are necessary for pinning, as well as enough supply of Y³⁺ so that loss of liquid during melting is minimized. Y-211 recombines with BaCuO2 liquid to form Y-123. Then the samples
were cooled to room temperature at a rate of 300°C/h. All the TSMTG was performed in the indigenously fabricated furnace, the compacts were kept on an alumina crucible, since the sample reacts and sticks with the alumina base after MTG process, it becomes difficult to remove from the alumina crucible, to avoid this, 1-2 mm bed of Y-211 course powder was spread in between compact and the alumina crucible, which helps in easily removing the sample from the crucible. To maintain the circularity of the hollow cylinders and pins, the compacts were kept in alumina cylinder. A gap between the compact OD and the ID of alumina cylinder is 5-7 mm. This arrangement helps in maintaining the constant temperature of the compacts.

The thermal schedule for SSR-CY-1, NDR-CY-1 and NDR-CY-3 is as shown in Fig.5.5. The temperature was raised to 1060°C at the rate of 300 °C/h and held for 10 h were partial melting takes place. Further the sample was cooled to 1010°C at the rate of 600 °C/h. From 1010 °C to 940°C where the nucleation starts, the compacts were slow cooled at the rate of 0.3-5 °C/h. The furnace was cooled to room temperature from 940°C.

In the thermal schedule for SSR-PL-1,NDR-PL-2,NDR-PI-1 and Pt-Cy-5 and Ce-CY-6 temperature was raised to 1060°C at the rate of 300 °C/h and held for 6 h were partial melting takes place, further cooled to 1010°C at the rate of 600 °C/h, and then cooled to 940°C at the rate of 0.3 °C/h. Finally, the compacts were furnace is cooled to room temperature.

The soaking temperature for plates and pins were slightly less i.e. 3-4 h, and for cylinders the soaking time was 10 h at 1060°C. Rest of the thermal schedule remains
same as that for cylinders. Since the wall thickness is around 20mm, to partially melt the whole component, the soaking time higher than pins and plates was required.

Finally, the as-grown MTG specimens were annealed at 400-450 °C in flowing oxygen for 150-300 h (In this step phase transformation from tetragonal to orthorhombic phase occurs as a result of oxygenation).

Top seeded melt texture growth were carried out in Pins and plates samples. A MgO seed crystal of preferred orientation (00l) with a size 1mm x 1 mm was placed on the top portion before commencing MTG process.

Fig. 5.6 Flow chart of typical MTG technique
**Fig. 5.7** Picture of cylinder during stages of fabrication using mould size hollow cylinder size as mentioned in Table 5.1 Sr. No. 1: (1) Compacted cylinder, (2) Sintered cylinder, and (3) MTG cylinder

**Fig. 5.8** Pictures of plate during various stages of fabrication using mould size plate as mentioned in table 5.1 Sr. No.2.: (1) Compacted plates, (2) Sintered plates and (3) TSMTG plates
Fig. 5.9 Pictures of pin during various stages of fabrication using mould size pin as mentioned in Table 5.1 Sr. No. 3: (1) Compacted pin, (2) Sintered pin, and (3) TSMTG pin.

Fig. 5.10 Pictures of cylinder during various stages of fabrication using mould size hollow cylinder as mentioned in Table 5.1, Sr. No. 4: (1) Compacted cylinder, (2) Sintered cylinder, and (3) TSMTG cylinder.

The shrinkage behavior of composites at various stages like pressing, sintering and while subjecting to MTG is shown in Table 5.4 and Figures 5.7, 5.8, 5.9 and 5.10. Here it can be seen that maximum shrinkage occurs while compaction in CIP, but the shrinkage while CIP is maximum in height of the sample i.e. around 10-15 %. Then during sintering the compacts shrink about 2-4 % of CIP pressed compacts and after subjecting to MTG the pre-sintered compacts shrinkage is around 1-2%.
5.5 Machining of MTG compacts

During MTG process the compacts partially melt and the shape gets distorted from the original shape. To apply the compacts in Fault current limiter (FCL) and motors, the compacts have to be machined. Since the compacts are brittle in nature, while machining considerable care is necessary. The lower 5-7% part of the compacts reacts with base material and therefore the lower portion was sliced in high speed cutting machine using diamond cutting wheel. Machining was done in CMC milling machine to the accuracy of ±0.2mm using oil as cooling fluid.

SSR-CY-1 and NDR-CY-2 samples were machined to dimensions 36mm OD x 46mm ID and 50mm H respectively and oxygenated at 400 °C for 200h. The cylinders were surface protected with paraffin wax (as mentioned in section 5.7) and studies on microstructural features and other superconducting properties were carried out. The $J_c$ values were measured at Budapest University Technology and Economics (BUTE), Hungary.

SSR-PL-1 and NDR-PL-2 samples were machined to dimensions 25mm width x 50mm height x 3.5mm thick and oxygenated at 400 °C for 150h. The plates were then surface protected with paraffin wax (as mentioned in section 5.7) and then measurements for trapped magnetic field and levitation force were carried out.

30 Nos Pins were fabricated using composite B (NDR-PI-1) compacted in mould size Sr. no. 3 as mentioned in Table 5.2. Pins were then sintered and subjected to TSMTG and further machined to size 8mm OD x 25 mm H. The pins were then oxygenated at 400 °C for 150h further surface protected with paraffin wax (as mentioned in section 5.7) and then measured for levitation force.
NDR-CY-3 cylinder was fabricated using composite B. The compact was pressed in mould size Sr. no. 5 as mentioned in Table 5.2. The green compact was sintered and subjected to TSMTG and further oxygenated and surface protected by applying paraffin wax. This hollow cylinder was cut into two halves horizontally. These two hollow cylinders were oxygenated and further surface protected by applying paraffin wax. Both the halves were sent to Budapest University of Hungary, Hungary for measuring $J_c$.

Likewise Pt-CY-5 and Ce-CY-6 hollow cylinders were also fabricated using composite C and D respectively in mould size Sr. no. 4 as mentioned in Table 5.2., compacted, sintered and subjected to TSMTG, oxygenated and further surface protected. Both the cylinders were also sent to BUTE, Hungary for measuring $J_c$. Followed by characterisation of microstructure and other HTSC properties.

### 5.5.1 Machined MTG components

Some of the HTSC MTG machined products (Fig.5.11, Fig.5.12, and Fig.5.13) which are shown below were applied in HTSC prototype motor used to rotate HTSC motor as rotor (details are given in chapter 8).
<table>
<thead>
<tr>
<th>Compact name</th>
<th>SSR-CY-1 Cylinder (mm)</th>
<th>NDR-PL-1 Plate (mm)</th>
<th>NDR-CY-2 Cylinder (mm)</th>
<th>NDR-CY-3 Cylinder (mm)</th>
<th>NDR-PL-2 Plate (mm)</th>
<th>NDR-PIN-1 Pin (mm)</th>
<th>Pt-CY-4 Cylinder (mm)</th>
<th>Ce-CY-5 Cylinder (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>dimensions</td>
<td>OD  ID  H  W  T  L</td>
<td>OD  ID  H  W  T  L</td>
<td>OD  ID  H  W  T  L</td>
<td>OD  ID  H  W  T  L</td>
<td>OD  H  OD  ID  H</td>
<td>OD  ID  H</td>
<td>OD  ID  H</td>
<td>OD  ID  H</td>
</tr>
<tr>
<td>Inner size of mould</td>
<td>56  35  70  45  6  70</td>
<td>56  35  70  75  24  28</td>
<td>45  6  70  13  -  35</td>
<td>35  23  38</td>
<td>35  23  38</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Size after CIP</td>
<td>52  35  64  41  4.8  65</td>
<td>52  35  64  62  24  26</td>
<td>42  4.7  65.5  12.5  32</td>
<td>32  23  35</td>
<td>32  23  35</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Size after sintering</td>
<td>51  32  62  38  4.4  64</td>
<td>51  32  62  58  23  24</td>
<td>38  4.5  64  12  31  31</td>
<td>21.5  33</td>
<td>31  21.5  33</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shape after MTG</td>
<td>49  34  60  36  4  60</td>
<td>49  34  60  54.8  20.8  21</td>
<td>36  4.1  61  11  29  ~29</td>
<td>~20.5  ~28</td>
<td>~28.5  ~20  ~27</td>
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</tr>
<tr>
<td>Final size after Machining</td>
<td>46  36  50  25  3.5  50</td>
<td>46  36  50  25  3.5  50</td>
<td>8  25</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Table 5.4 Shrinkage in size of the compacts while pressing, after sintering and after subjected to MTG
Fig. 5.11 Machined TSMTG cylinders

Fig. 5.12 Machined TSMTG plates

Fig. 5.13 Machined TSMTG pins using composite B (NDR-PI-1)
5.7 Surface protection

The application of bulk YBCO TSMTG compacts requires on the environmental compatibility and long term stability of the bulk material. The protection against degradation has become a major issue. Humidity, aggressive ambient and thermal cycling can slowly degrade the superconducting properties of the YBCO bulk material. Under environmental conditions, it is mainly the carbonic acid from dissolved atmospheric CO₂ which leads to the long term degradation of YBCO. In order to provide an effective surface protection layer, the sample has to inhibit the contact of water or CO₂ or both. Considering the requirements for the cryogenic use the most important ones are chemical compatibility with the delicate superconducting material, curing, adhesion, thermal expansion mismatch, water absorption and diffusion, dielectric losses, and good insulation. Considering the degradation of the MTG components, all the MTG components were dipped in a molten liquid containing paraffin wax and paraffin liquid in a weight ratio 2:1 respectively for about 15-20 min on a heating mantle whose temperature maintained at 150 °C. Here the liquid enters the open pores and forms a layer of coating on them which protects the samples from environmental attack.
Fig. 5.14 Picture of rubber mould used to fabricate MTG components

5.8 Conclusion

Taking into consideration the shrinkage behaviour at various stages of fabrication i.e. during compaction using CIP, sintering and while subjecting to MTG, rubber moulds were designed and fabricated as per the final required dimensions. The hardness of the moulds was optimised so that the green compact is released from the mould after CIP. The corresponding composites were filled along with in situ vibration in the moulds to achieve maximum green density with minimum pores. The MTG thermal schedules and oxygen annealing time were optimised for various shapes and subjected to MTG schedule. Before subjecting to MTG all the green compacts were sintered.

Various components were fabricated using different composites. In the next chapter the superconducting properties of MTG samples are given. The samples were
studied for $T_c$, microstructure (SEM), composition (EPMA), Texture (OIM), transport properties, trapped magnetic field, levitation force and critical current density. The superconducting properties like $J_c$, levitation force as well as trapped magnetic field of components TSMTG SSR-CY-1, TSMTG SSR-PL-1 were compared with TSMTG NDR-CY-2, TSMTG NDR-PL-2, respectively.