Controlled Heterogeneous Nucleation of Melt-Textured YBa$_2$Cu$_3$O$_{6+x}$ by Addition of Al$_2$O$_3$ Particles

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ABSTRACT

The reaction between alumina and yttrium barium cuprate subjected to a melt-texturing heat-treatment was studied. Microstructural examination of quenched, partially transformed samples revealed that at $\sim$ 1050 ºC (which is above the incongruent melting temperature of YBa$_2$Cu$_3$O$_{6+x}$), a reaction layer forms at the alumina interface. The reaction products were identified as Ba$_6$Y$_2$Al$_4$O$_{15}$ and a copper-rich liquid phase. On cooling below the peritectic temperature, aligned domains of YBa$_2$Cu$_3$O$_{6+x}$ (123) were observed to preferentially nucleate at the reaction layer. For samples of melt-textured 123 deliberately seeded with alumina particles, it was found that nucleation and growth of 123 occurred exclusively at the particles. A reaction sequence for the formation of the Ba$_6$Y$_2$Al$_4$O$_{15}$ is put forward, together with a discussion of the possible nucleation mechanisms for the 123. [Key words: yttrium barium copper oxide (YBCO), peritectic, melt-texturing, nucleation, barium yttrium aluminum oxide (Ba$_6$Y$_2$Al$_4$O$_{15}$)].

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I. INTRODUCTION

Melt-texturing or directional solidification of YBa$_2$Cu$_3$O$_{6+x}$ (123) has been regarded as the most viable method of increasing the critical current density ($J_C$) of bulk 123 material. Previous studies have shown that aligned 123 can be formed via a peritectic reaction in the temperature range (950 °C - 1000 °C) during melt-texturing [1,2,3]. Workers at Lehigh postulated that the peritectic transformation involves dissolution of Y$_2$BaCuO$_5$ (211) particles, and subsequent precipitation of 123 from the melt [4]. This model has since been confirmed by other workers [5,6,7]. The significance of the Lehigh solution/precipitation model is that (unlike for the conventional peritectic reaction), the 211 particles are not the preferred nucleation sites. It should be feasible, therefore, to control nucleation via the incorporation of heterogeneous sites. Further, according to the model, the growth rate of 123 will be determined by the slowest of the following processes: dissolution of 211, diffusional transport through the liquid, and precipitation of 123. Since the number and the size of 123 domains will be determined by the relative rates of nucleation and growth of 123, the potential exists to optimize the microstructure through appropriate control of the above parameters.

In the course of preliminary studies on the melt-texturing of 123, pressed pellets of 123 were placed on alumina substrates, heated above the peritectic temperature, annealed at 970 °C for different times, and then quenched to room temperature. In this manner it was possible to study the materials in the partially transformed state. It was observed that the 123 domains always originated from the bottom surface of the samples. At first, this was attributed to heterogeneous nucleation at the substrate surface, but closer examination revealed a distinct reaction layer between the 123 domains and the alumina. It appears, therefore, that preferential nucleation of the 123 occurred at the interface of the aforementioned reaction layer. It should be noted that although chemical reactions between 123 superconductor and alumina substrates have been studied at temperatures below the peritectic temperature (Tp) [8-10]; the corresponding interactions at temperatures $T > T_p$ are not well understood.
involving melt-textured 123, have not been reported. The purpose of this study, therefore, was to carry out a systematic study of the reaction, and hence identify the mechanism(s) underlying the preferential nucleation of 123 domains. In this manner, it was hoped to determine a method of controlling 123 nucleation during melt-texturing, which would be applicable to bulk applications.

II. EXPERIMENTAL

The experimental program involved study of the reaction between melt-textured 123 and alumina for two specimen geometries. In each case, the starting material was YBa2Cu3O6+x powder (Rhone-Poulenc, Princeton, NJ). This was crushed in a mortar and pestle, and then pressed at 180 MPa in a steel die (25x5x4 mm³) to form pressed powder specimens.

i) In the first set of experiments, the preliminary studies involving melt-textured 123 samples supported by alumina substrates were reproduced under more controlled conditions. Accordingly, the green pressed pellets were placed on substrates of either polycrystalline Al2O3 or sapphire, and then heat-treated.

ii) In the second case, to test whether "seeding" of 123 domains could be achieved, individual sintered Al2O3 particles (500 - 1000 µm) were introduced into the pressed powder pellets of 123.

For both sets of specimens, a simple 2-step isothermal heat-treatment schedule was adopted, which is depicted schematically in Fig.1. During step I (T>Tp), incongruent melting of the 123 takes place to form 211 + liquid. On cooling below Tp (step II), the reverse reaction occurs resulting in the formation of melt-textured 123. Because previous work had shown that complete transformation to 123 takes place after 1 hour at 970°C [4], for the purpose of the present study, partially transformed samples were obtained by quenching from step II after time t2, where t2< 1 hr. The specific heat-treatment schedules are listed in Table 1. Note that the initial heating rate to 1050 °C was 10 °C / min, and the
cooling rate between step I and step II was 10 °C/min. Quenching was carried out by rapidly removing the specimens from the furnace, and placing them onto a steel plate. Subsequent microstructural studies and phase identifications were made on polished sections. In the following discussion, samples will be referred to by their heat-treatment schedules (SI-0, SI-30, etc.), where a subscript will be used to distinguish between the substrate supported samples (s), and the particulate containing samples (p).

For all the samples studied, kerosene (Fisher Scientific, class III A) was used as the lubricant for specimen polishing, since aqueous-based lubricants resulted in serious reaction of the (prior) liquid phase with water. It was found that exposure of the polished surfaces to the atmosphere for even short times resulted in severe reaction. For this reason, quantitative analysis was always carried out immediately following polishing. Although generally inconvenient, the reactivity of the prior liquid was useful in one respect; namely that specimens which were etched by deliberate exposure to the atmosphere exhibited sharp phase contrast between the prior liquid and 123 domains (see for example Figure 6). Compositional analysis of the phases was performed by electron-probe micro-analysis (EPMA) (JEOL 733); Y2BaCuO5 (present in the sample) and Al2O3 (internal standard in JEOL 733) were selected as standards. For unknown compositions, five regions were randomly selected to be analyzed.

III. RESULTS AND DISCUSSION
i) Microstructure Development and Phase Identification

Optical microstructure studies on polished cross-sections of the substrate-supported samples revealed that they consisted of three distinct regions. This is illustrated in Figure 2, which shows the microstructure of sample SII-30(s). A reaction layer "R" (thickness ~ 600 µm) was clearly visible between the Al2O3 substrate and 123 sample. Adjacent to this, preferential nucleation/growth of 123 domains had taken place, resulting in a layer of 123 grains and Y2BaCuO5 (211) inclusions. The third and uppermost region was observed
to consist of a mixture of (prior) liquid phase and 211 particles. Upon examination of the reaction layer "R" at higher magnification (see Figure 3), it was found that it consisted of a prior liquid phase (which was composed of an intimate mixture of two phases), and elongated grains of an unknown phase. Identical results were obtained for samples supported on sapphire substrates.

The EPMA results revealed that the unknown phase consisted of the elements Ba, Y, Al, and O, the atomic ratio of Ba : Y : Al being 3 : 1 : 2 (Table II). A survey of the literature revealed that only two compounds consisting of Ba, Y, Al, and O have been reported [11], namely Ba$_2$YAlO$_5$ and Ba$_6$Y$_2$Al$_4$O$_{15}$. Given the measured Ba : Y : Al ratio, the elongated grains were deduced to be Ba$_6$Y$_2$Al$_4$O$_{15}$. Chemical analysis of the prior liquid phase in the reaction zone revealed it to be a mixture of CuO and BaCuO$_2$; it is assumed that this phase separation occurred on quenching to room temperature. Interestingly, 211 particles were not found within the reaction layer.

ii) Reaction Sequence

Having identified the unknown phase within the reaction layer, it is possible to put forward a sequence of reactions as follows. Firstly, it is known that 123 melts incongruently at ~ 1005 °C via the following reaction:

$$2\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x} \rightarrow \text{Y}_2\text{BaCuO}_5 + L \quad (1)$$

Since the liquid phase can be considered to be composed of BaCuO$_2$ and CuO, equation (1) can be also expressed as:

$$2\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x} \rightarrow \text{Y}_2\text{BaCuO}_5 + 3\text{BaCuO}_2 + 2\text{CuO} + x\text{O}_2 \quad (2)$$

Next, we need to consider the reaction with alumina. Due to the high yttrium content of the Ba$_6$Y$_2$Al$_4$O$_{15}$, it is clear that this phase cannot have formed solely by
reaction with the peritectic liquid (BaCuO2/CuO). However, two possible reactions which would result in the formation of this phase may be postulated:

\[ 3\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x} + 2\text{Al}_2\text{O}_3 \rightarrow \text{Ba}_6\text{Y}_2\text{Al}_4\text{O}_{15} + 0.5\text{Y}_2\text{O}_3 + 9\text{CuO} + 1.5\text{xO}_2 \quad (3A) \]

\[ \text{Y}_2\text{BaCuO}_5 + 5\text{BaCuO}_2 + 2\text{Al}_2\text{O}_3 \rightarrow \text{Ba}_6\text{Y}_2\text{Al}_4\text{O}_{15} + 6\text{CuO} \quad (3A') \]

In the first case (Eqn. 3A), the barium yttrium aluminate phase is formed by direct reaction between alumina and the 123. In the second case, the alumina reacts selectively with some of the reaction products of the 123 decomposition (Eqn. 3A'). To distinguish between the two cases, we need to consider the results obtained from the samples seeded with alumina particles.

The microstructural development in partially transformed samples containing Al2O3 particles is shown in Figures 4-7. As shown in Figure 4, sample SI-0(p) (which was heated to 1050 °C and then immediately quenched), consists of alumina particles and a mixture of 211 and liquid phase. On closer examination, however, it can be seen that a very thin reacted layer has formed around the Al2O3 particle. For samples where the annealing time at T > Tp was longer, the reaction layer became more extensive, and the smaller Al2O3 particles were found to have reacted completely. This is illustrated in Figures 5(a) and (b) respectively, which depict the microstructure of sample SI-30(p) (annealed for 30 min. at 1050 °C prior to quenching). The above observations demonstrate clearly that the reaction layer develops only after decomposition of the 123, i.e. during the first stage heat-treatment. For this reason, we can conclude that reaction 3A' is the more feasible.

Examination of the microstructures of specimens which were also subjected to a second stage annealing treatment (SII-15(p) and SII-30(p)), showed that the 123 domains nucleated preferentially at the outer surface of the reaction layer (see Figures 6(a) and (b)). As would be expected, the volume fraction of transformed 123 increased with annealing time at 970 °C.
iii) Nucleation Mechanism

Two possible explanations may be put forward for the preferential nucleation of 123 at the alumina reaction layer. One possibility, is that the grains of the Ba$_6$Y$_2$Al$_4$O$_{15}$ phase behave as heterogeneous nucleation sites for the 123. If so, it should be possible to test this independently by use of Ba$_6$Y$_2$Al$_4$O$_{15}$ particles as seeds during melt-texturing of 123.

Another possible explanation involves the local change in melt composition in the region of the reaction zone. Comparison of the reactions represented by Eqns. 1 and 3A' reveals that of the phases formed by the peritectic decomposition of 123, the reaction of alumina to form Ba$_6$Y$_2$Al$_4$O$_{15}$ involves a relatively higher proportion of the yttrium and barium rich components. For this reason, one would expect relative enrichment of copper in the liquid phase in the region of the reaction layer. It is possible that this may lead to enhanced nucleation of 123 due to more rapid dissolution of 211 particles and/or diffusional transport through the liquid. This hypothesis is supported by some recent work by Shin et al. [12], who observed that for sintering studies carried out at 990 °C, an excess of CuO resulted in directional growth of 123 grains in the direction of the CuO compositional gradient.

Clearly more research is required to clarify the role of the alumina reaction products in enhancing nucleation of 123 from the melt, and this is the subject of ongoing research. What is significant, however, is that this effect can be exploited to control the microstructure of melt-textured 123. This is illustrated in Figure 7, which shows clearly that for the given heat-treatment conditions, 123 nucleation occurred exclusively in the region of the alumina particles. Another important finding of this study, is that the phase Ba$_6$Y$_2$Al$_4$O$_{15}$ does not react with either 123, or the peritectic liquid. This result is highly pertinent to applications where high temperature processing of 123 is required, since Ba$_6$Y$_2$Al$_4$O$_{15}$ may be useful as a relatively inert substrate/crucible material.
IV. CONCLUSIONS

(1) The reaction between alumina and YBaCuO at ~ 1050 °C leads to the formation of a reaction layer consisting of Ba$_6$Y$_2$Al$_4$O$_{15}$ and liquid phase.

(2) On cooling below the peritectic temperature, aligned domains of YBa$_2$Cu$_3$O$_{6+x}$ were found to preferentially nucleate at the interface with the reaction layer.

(3) The nucleation of 123 can be controlled in the melt-textured process by introduction of Al$_2$O$_3$ particles.
REFERENCE:


### Table I. Heat-treatment schedules.

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<th>Heat-treatment code</th>
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- $T_1$ -- first stage heat-treatment temperature
- $t_1$ -- time at $T_1$
- $T_2$ -- second stage heat-treatment temperature
- $t_2$ -- time at $T_2$

### Table II. The result of EPMA analysis of elongated grains in reaction zone.

<table>
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<th>Element (Atom %)</th>
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Figure Captions:

Fig. 1. Schematic representation of 2-step isothermal heat-treatment schedules.

Fig. 2. Optical micrograph of specimen SII-30(s) showing the reaction layer (R) between the 123 and Al₂O₃ substrate (A). Note that a layer of 123 domains has formed preferentially above the reaction layer. (Sample etched by exposure to the atmosphere).

Fig. 3. Optical micrograph showing the interface between the reaction layer and the 123. The elongated grains were subsequently identified as Ba₅Y₂Al₄O₁₅, and the (prior) liquid phase as a mixture of BaCuO₂ and CuO. (Unetched).

Fig. 4. Optical micrograph of specimen SI-O(p). Note thin reaction layer (R) surrounding the alumina particle. (Unetched).

Fig. 5. a) Optical micrograph of specimen SI-30(p). The reaction zone around the alumina particle is now more extensive (compare Fig. 4). b) Same specimen as a), but in region of relatively smaller alumina particle. The reaction has progressed sufficiently that the particle has almost completely dissolved. (Unetched).

Fig. 6. Optical micrographs of a) Specimen SII-15(p), and b) SII-30(p). It can be seen that the 123 domains nucleate and grow preferentially at the outer surface of the reaction layer during the second stage heat treatment. (Samples etched by exposure to the atmosphere).

Fig. 7. Optical micrograph showing that the 123 domains nucleate and grow exclusively at the alumina particles. (Specimen SII-30(p), etched by exposure to the atmosphere).
Step I (1050 °C)
Step II (970 °C)

SI-0  SI-30  SII-15  SII-30