

Formation of $\text{YBa}_2\text{Cu}_3\text{O}_x$ and the microstructure of melt infiltration processed YBCO superconductors

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Abstract

A YBCO superconductor was prepared in a short time by a melt infiltration process that utilizes melting of $\text{Ba}_3\text{Cu}_5\text{O}_8$ powder and the infiltration into a porous Y_2BaCuO_5 compact. The processing parameters such as a reaction temperature and time, and atmosphere (air and O_2) were controlled to establish the fabrication condition. The formation of a $\text{YBa}_2\text{Cu}_3\text{O}_x$ phase and the developed microstructure are reported.

Keyword : YBCO, Oxide superconductor, Melt process

I. Introduction

It is widely accepted that the melt process is an effective method that can fabricate a large grain YBCO superconductor with a high critical current density (J_c) [1]. The heating cycles of the melt processes are based on the peritectic reaction between solid Y_2BaCuO_5 (211) and a Ba-Cu-O melt. In order to fabricate a large grain YBCO sample, a $\text{YBa}_2\text{Cu}_3\text{O}_x$ (123) powder compact is heated above the peritectic temperature (T_p) and then slowly cooled to the formation temperature of a 123 phase. During slow cooling through T_p , 123 grains grow from the 211-melt mixture [2]. To obtain a homogeneous microstructure, sometimes, the undercooling below T_p replaces the slow cooling [3,4].

The disadvantage of the melt processes is the long processing time. It takes several hundred hours to fabricate a large grain YBCO superconductor of a few cm [3,4]. The long processing time makes it difficult to apply the melt processes to the fabrication

of superconducting wires. Recently, a very simple technique that can fabricate melt textured YBCO samples, was developed by Jee et. al [5,6]. This process consists of the melting of melt-forming powder ($\text{Ba}_3\text{Cu}_5\text{O}_8$) and isothermal holding below T_p . It is a cost-effective method, because of its simple heating cycles and shorter processing time.

In this study, we examined the effects of processing variables such as a reaction temperature and time, and atmospheres (air and O_2) on the phase formation and the microstructure. The details of the melt infiltration process and the resulting microstructure are also reported.

II. Experimental procedure

211 powder (Superconductive Components. Inc. Columbus, Ohio USA) was compacted into a rectangular shape with a size of $40 \times 20 \times 20 \text{ mm}^3$ and then sintered at 950°C for 5 h in air. The sintered 211 compacts involve many open pores which can act as melt channels. Melt-forming powder was prepared by the solid state reaction method using BaCO_3 and CuO

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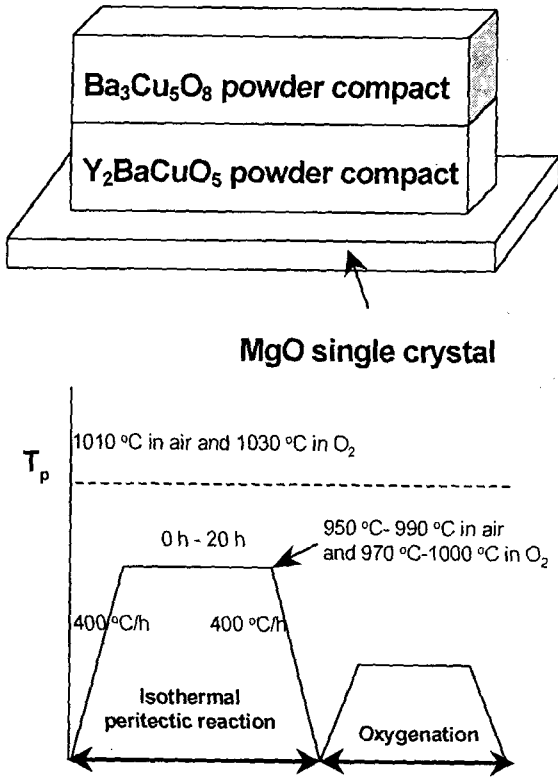
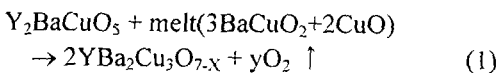


Fig. 1. schematic of the melt infiltration process using a melt-forming powder and 211 powder compacts and the applied heating cycles.

powders. The two powders were weighed to the ratio of $\text{Ba}:\text{Cu}=3:5$. The powder mixture was ball-milled for 20 h in alcohol with ZrO_2 balls. The ball-milled slurry was dried in air for 10 h. The dried powder mixture was put into an Al_2O_3 crucible and calcined at 870°C for 26 h with intermediate crushing steps for a homogeneous reaction. The calcined powder mixture was compacted into rectangular bar samples. The reaction equation of the melt infiltration process to form a 123 phase is given by



According to eq. (1), the weight ratio of $\text{Ba}_3\text{Cu}_5\text{O}_8:\text{Y}_2\text{BaCuO}_5$ should be 1.87:1 to form a stoichiometric 123 phase. In order to compensate the melt loss during processing, however, the weight ratio of

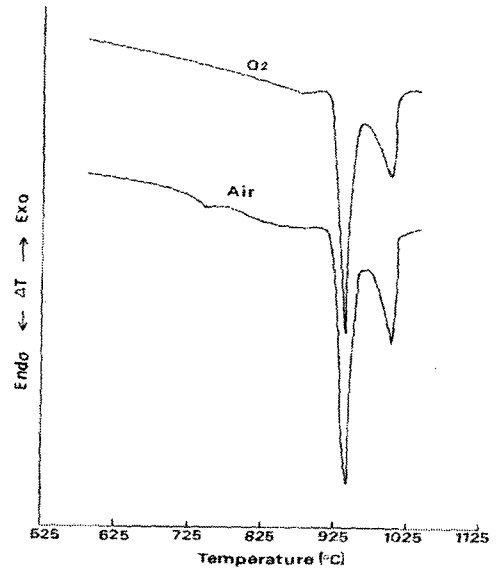


Fig. 2. DSC curves of the melt-forming powder in air and O_2

ratio of this study was modified to a melt-excess ratio of 2:1.

To fabricate a 123 superconductor, melt-forming $\text{Ba}_3\text{Cu}_5\text{O}_8$ powder compact is placed on the top of a 211 compact, and the sample is isothermally heat-treated in a box furnace at a temperature below T_p (Fig. 1). To understand the effects of the atmosphere on phase formation, samples were prepared in both O_2 and air. T_p of a 123 phase was reported to depend on the oxygen partial pressure [7]. T_p s in O_2 and air are 1030°C and 1010°C , respectively. The melting temperatures of melt-forming powder in O_2 and air were checked by Differential Scanning Calorimetric (DSC) analysis.

As can be seen in Fig. 2, the DSC traces show double peaks at about 930°C (partial melting) and 1010°C (complete melting) regardless of atmosphere. Based on the DSC data, the samples were isothermally heated in the temperature range of 950°C - 1010°C for 1 h - 20 h and then were annealed at 500°C for 50 h in flowing oxygen.

III. Results and discussion

3.1. Melt infiltration

Figures 3(a)-3(d) are photos of samples infil-

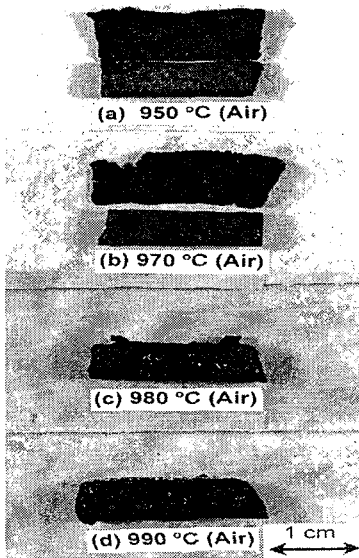


Fig. 3. Photos of the melt-211 compacts after melt infiltration process in air

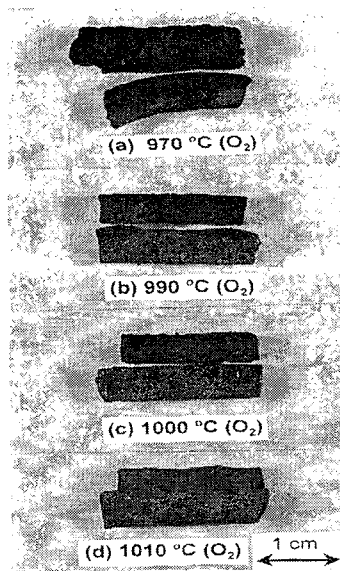


Fig. 4. Photos of the melt-211 compacts after melt infiltration process in O₂

trated in air at various processing temperatures. It can be seen that melt remains at lower processing temperatures due to incomplete melting of the melt-

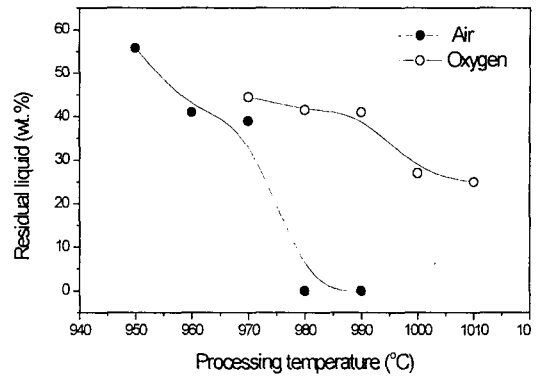


Fig. 5. Amount of the residual melt versus processing temperature in air and O₂

forming powder. As the processing temperature increased, the melt-forming powder melted completely and then infiltrated into the 211 compact easily due to the relatively lower viscosity at the higher temperature. Above 980°C, no melt remains due to complete melting of the melt-forming powder.

In the case of O₂ atmosphere, however, the melt-forming powder did infiltrate into the 211 compact completely even at 1010°C (Fig. 4). This is may be due to the higher viscosity of the melt in O₂ atmosphere. Figure 5 shows the amounts of residual melts after infiltration in air and O₂. At 960°C in air, the amount of the residual melt is 40%, while at 980°C in air no melt remains. On the other hand, at 990°C and 1010°C in O₂, the amount of the residual melt is about 40% and 25%, respectively.

3. 2. Formation of a 123 phase

Figure 6 shows the volume fraction of a 123 phase as a function of processing time and temperature of the samples prepared in air. The volume fraction of the 123 phase increases with increasing processing time to 20 h and temperature to 980°C. After 20 h holding at the various temperatures of 950°C, 960°C, 970°C and 980°C, the volume fractions of the 123 phase are 81%, 83%, 90% and 95%, respectively. The formation reaction of the 123 phase seems to be very fast due to the fast diffusion of solute atoms in a melt. The 123 formation was more enhanced at higher temperatures because of the rapid infiltration of the

melt into the 211 compact due to its low viscosity at the temperatures. The formation kinetics of the 123 phase in O₂ atmosphere shows a manner similar to that in air atmosphere (Fig. 7).

The volume fraction of the 123 phase is also a function of a processing temperature and time. More than 85 % of the sample was transformed into a 123 phase at 1000°C.

The superconducting transition temperature (T_c, R=0) of samples prepared in both atmospheres are summarized in Table I. The T_c of samples ranges from 83 K to 92 K and does not depend on the processing temperature and atmosphere. The value of T_c seems to be related to the microstructure of the grain boundary of the samples, which will be discussed later.

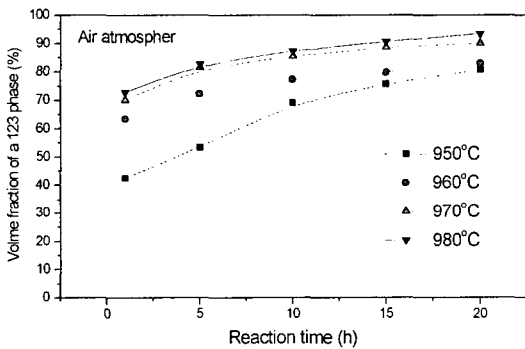


Fig. 6. Volume fraction of the 123 phase as a function of processing temperature and time in air.

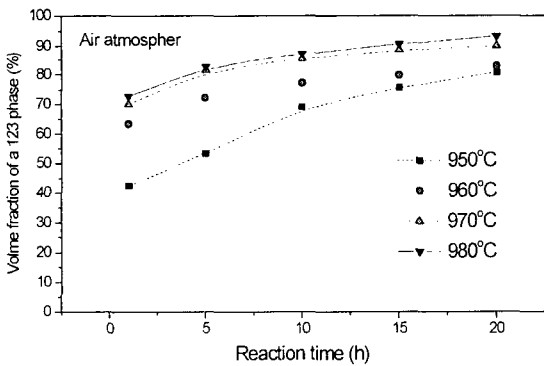


Fig. 7. Volume fraction of the 123 phase as a function of processing temperature and time in O₂

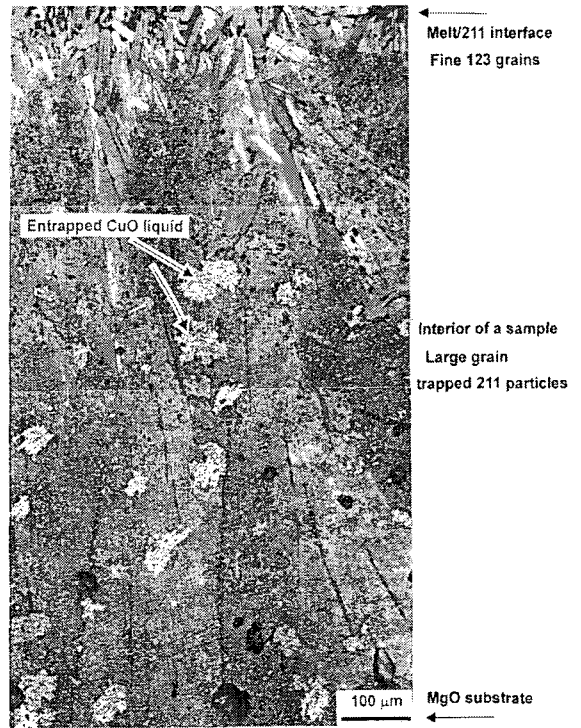


Fig. 8. Microstructure of the melt infiltration –process YBCO sample in O₂

3.3. Microstructure of melt infiltration processed samples

Figure 8 shows the typical microstructure of a sample prepared by a melt infiltration process in O₂ atmosphere, which is quite similar to the reported melt-textured microstructure [8].

The microstructure consists of three different parts. At the melt/211 compact interface, small plate-like 123 grains are observed. The center part consists of the larger 123 grains in which fine 211 particles are trapped. The columnar 123 grains grown normal to the MgO substrate are observed at the region adjacent to the substrate. This is because the MgO substrate acts as heterogeneous nucleation sites for the 123 grains.

Figure 9 shows the microstructures of the interior of the samples prepared in air at various processing temperatures. The grain size of the 123 phase

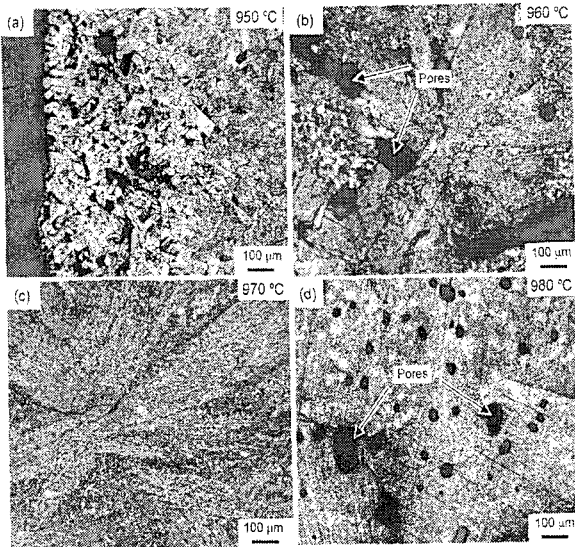


Fig. 9. Microstructure of the interior of the samples prepared in air.

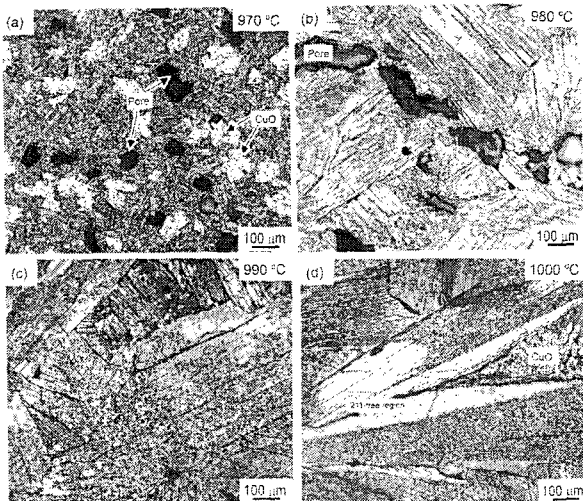


Fig. 10. Microstructure of the interior of the samples prepared in O_2

increases with the increase of a processing temperature. The 211 particles and spherical pores are trapped within the 123 grains. The origin of the spherical pores is different from that of the open pores that were present in the 211 compact prior to infiltration. The spherical pores form due to the evolution of oxygen gas during the melting [9].

Table I. Superconducting transition temperature (T_c) of the sample infiltration-processed in air and O_2 atmosphere.

Processing temperature ($^{\circ}C$)	Superconducting transition temperature (T_c : K)	
	in air atmosphere	in O_2 atmosphere
950	85	
960	89	
970	88	84
980	89	88
990	85	89
1000		92
1010		83

Some of the pores are eliminated by melt filling but others are often trapped within the 123 grains. The sample interior shows higher pore density than the sample surface, due to the easier diffusion of oxygen atoms at the sample surface. The microstructure of the sample prepared in O_2 atmosphere is similar to that prepared in air atmosphere: the large 123 grains including trapped 211 particles (Fig. 10). Unreacted CuO pools are often observed in the sample prepared at lower temperatures (Fig. 10(a)). Compared to the samples prepared at lower temperatures, the sample prepared at higher temperatures shows lower pore density. Furthermore, the pore density of the samples prepared in O_2 atmosphere seems to be much lower than that prepared in air atmosphere. Two possible factors can reduce the pore density. One is the amount of the oxygen gas evolved during melting of the melt-forming powder. If the total amount of the oxygen gas evolved is smaller in O_2 atmosphere, it can reduce the pore density. Another is the higher oxygen diffusion in a melt in O_2 atmosphere. If the oxygen diffusion in a melt in O_2 atmosphere is faster than in air, oxygen atoms can easily diffuse out of the sample, resulting in lower pore density.

IV. Conclusions

The effects of the processing parameters (a reaction temperature, time and atmosphere) on the forma-

tion of a $\text{YBa}_2\text{Cu}_3\text{O}_x$ during a melt infiltration process were studied. 20 h is enough time to form a 123 phase by the reaction between a melt and 211. The microstructures of the samples prepared in both atmospheres were quite similar to the melt-textured microstructure which is characterized by the large 123 grains and the trapped 211 particles. The grain size of the 123 phase increased with an increase of a reaction temperature. Many pores were developed as a result of oxygen evolution during melting and were trapped within the 123 grains. The pore density of the samples prepared in O_2 atmosphere was lower than in air atmosphere.

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