Microwave sintering of YBa$_2$Cu$_3$O$_x$ superconductors

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Since the discovery of the high-$T_c$ YBa$_2$Cu$_3$O$_x$ superconductor, there has been a tremendous effort to improve the critical current density ($J_c$) of the sintered body. Misalignment of grains, secondary phases at the grain boundaries, microcracks and oxygen deficiency in the sintered body were, among others, considered to be the main causes of the low $J_c$ of the bulk materials [1-5]. Many researchers employed various techniques to circumvent these problems. One way to minimize some of these problems would be to sinter the superconductors to nearly theoretical density at lower temperatures. Sintering at low temperature might be beneficial to the $J_c$ by reducing both the number of microcracks and the amount of impurity segregation at the grain boundaries.

Microwave heating is an attractive method for sintering ceramic materials because of the uniform and rapid heating capability resulting from the direct absorption of energy into the materials [6]. In addition, increases in the densification rate have been observed for some ceramic materials (for example, Al$_2$O$_3$, ZrO$_2$ and TiB$_2$) by sintering in a microwave furnace [7-10]. As a result of the increased densification rates, those materials could be sintered at lower temperatures in a microwave furnace than those in a conventional resistance furnace. Low sintering temperature, coupled with uniform volumetric heating, is potentially very beneficial in improving the mechanical and electrical properties of a sintered body. In this letter we report data on the sintering behaviour of YBa$_2$Cu$_3$O$_x$ superconductors when sintered in a microwave furnace. The effects of microwave heating on the densification rate, microstructure and critical current density of the superconductor were compared with the results obtained by conventional resistance heating.

The superconductor powder used in this experiment was prepared by conventional solid-state reactions. Calcination was repeated three times with an 8 h soak at the highest temperature of 940 °C. The fabricated powder was characterized with the use of an X-ray diffractometer, particle size analyser (Leed and Northrup Instrument) and a scanning electron microscope (SEM). Sintering of the superconductor pellets was performed in a 2.45 GHz microwave furnace. The furnace was composed of a 2.6 kW microwave source (Genesys Systems, Inc.) with continuously variable powder, and a 46 cm diameter × 61 cm long aluminium processing chamber capable of being evacuated and gas backfilled. Superconductor pellets (4 mm diameter × 15 mm long) were sintered in flowing O$_2$ at constant temperatures between 850 and 1000 °C for 10 h by mixed-mode heating. Mixed-mode heating was accomplished by using SiC susceptor rings to re-radiate infrared energy to the sample, as shown schematically in Fig. 1. The susceptors were spaced sparingly to allow microwave energy to propagate to the sample. The thermocouple was separated from the sample by approximately 0.3 cm to avoid chemical reactions and arcing. Without the susceptors, very high microwave fields were required to heat the samples. By not touching the sample with the thermocouple, a low reading of the temperature measurement could be expected. With the susceptor method, however, the error can be minimal. All of the samples were subsequently annealed in the microwave furnace at 500 °C for 7 h in the same atmosphere (flowing O$_2$). Parallel experiments were performed in a conventional resistance furnace for the purpose of comparison. The critical current density ($J_c$) of the as-sintered samples was measured at 77 K at zero magnetic field by the standard four-probe technique. Contacts were attached by means of indium solder.

The average particle size of the superconductor powder was about 5 μm with a standard deviation of 2 μm. This relatively large particle size was apparently due to the long calcination time at elevated temperature. According to the X-ray diffraction pattern, the powder had more than 99% superconductor phase. The relative densities of the superconductors sintered for 10 h in the microwave furnace and in the conventional resistance heating furnace at various temperatures are shown in Fig. 2. The densities of the samples sintered in the microwave furnace exceed those sintered in the conventional furnace.

![Figure 1 Schematic diagram of the experimental set-up for sintering the superconductor in a microwave furnace.](image)
Figure 2 Comparison of the relative densities of the superconductors sintered in a microwave furnace (•) and in a conventional resistance furnace (○). Superconductors with higher densities were obtained by sintering in the microwave furnace.

The densities of the samples sintered in the microwave furnace were consistently higher than that of those sintered in the resistance furnace at the same temperature. Differences in the densities became more significant as the sintering temperature increased. The highest density of the superconductors sintered in the resistance furnace was only 85% theoretical. This relatively low density was apparently due to the large particle size of the starting powders. However, more than 95% theoretical density was readily obtained by sintering the same powder in the microwave furnace. This improvement in densification is believed to be related to the diffusivities of constituent elements in the material. Recently, the effect of the microwave field on the diffusion coefficient of oxygen in oxides was investigated by Janney and Kimrey [11]. They observed a substantial increase in the diffusion coefficient of oxygen in Al₂O₃ under the influence of the microwave field. A similar phenomenon is believed to have occurred for the superconductor in the microwave furnace.

Differences were also observed in the microstructures of the samples sintered by either method. The fracture surface of the superconductors sintered at 1000 °C for 10 h in the microwave and resistance furnaces are shown in Fig. 3a and b, respectively. The difference in density and microstructure of the samples sintered at the same temperature are seen clearly. The density of the sample in Fig. 3a was about 95%, whereas that in Fig. 3b was about 85%. The sintering temperature to obtain the sample with 85% theoretical density in the microwave furnace was about 960 °C (Fig. 2), which is about 40 °C lower than the sintering temperature in the resistance furnace. The effect of lowering the sintering temperature was observed in the average grain sizes of the sintered body. Fig. 3c shows the microstructure of the superconductor (density about 85% theoretical) sintered in the microwave furnace at 960 °C for 10 h. The average grain size of the sample in Fig. 3c is about 10 μm, whereas that in Fig. 3b is larger than 20 μm.

The improvements in the densification behaviours were expected to be beneficial to the Jc of the sintered bodies. However, the Jc values of the superconductors were improved only slightly by sintering in the microwave furnace, as shown in Fig. 4. The data points and error bars represent the average and one standard deviation of three to five samples, respectively. The Jc values obtained in these experiments are relatively low compared with the previously reported optimum values, presumably due to the large sample sizes (4 mm diameter × 15 mm long) employed in this research; however, the Jc of the superconductors increases faster when sintered in the microwave furnace than in the resistance furnace as the relative density of the material increases. Therefore, when the densities were greater than 80% theoretical, the Jc values of the superconductors sintered in the microwave furnace were higher than for those sintered in the resistance furnace. This difference is believed to be due to the difference in the microstructures of the
sintered bodies. Samples sintered in the microwave furnace (Fig. 3c) have a smaller grain size than those sintered in the resistance furnace (Fig. 3b). Therefore, it is easier for the oxygen to diffuse into the grains during annealing because there are more pore channels, resulting in less oxygen deficiency in the sintered body. When the density of the sample was more than 90% theoretical, the \( J_c \) dropped rapidly due to the closure of the open pore channels as observed previously [4].

In conclusion, the YBa\(_2\)Cu\(_3\)O\(_x\) superconductors sintered in a microwave furnace have higher relative density than samples sintered at the same temperatures in a conventional resistance furnace. The enhanced densification was attributed to the increased diffusion coefficient of constituent elements in the microwave field. When samples had similar relative densities, the superconductors sintered in the microwave furnace had a grain size significantly smaller than those sintered in the resistance furnace. These differences in the densification behaviour and microstructure are potentially beneficial in improving the electrical properties of the superconductor.

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**References**


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