Effect of additives on the morphology and superconductivity of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ ceramic materials

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Abstract. The effect of the addition of 0–15 wt.% alumina powder on the grain size, morphology and superconducting properties of sintered $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ was investigated as a function of alumina concentration in the composites. The results suggest that the grain size of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ decreases with an increase in the additive concentration. Some surface erosion of the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ grains was also noticeable in $\text{Al}_2\text{O}_3/\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ composites. The results also indicate that the additive tends to stabilize the nonsuperconducting tetragonal phase of the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ at the expense of the superconducting orthorhombic crystal phase.

Keywords. Additive; grain size; morphology; superconductivity.

1. Introduction

After the initial announcement of Bednorz and Muller (1986) that certain ceramic materials possibly show superconducting properties well above the liquid helium temperatures, and subsequently by Wu *et al* (1987), a major scientific effort is being made to understand these materials (Nelson *et al* 1987; Rao *et al* 1987; Rao 1988). However, the engineering problems such as the forming of these brittle ceramics into viable components of different shapes and sizes, have yet to be solved. Since the ceramic process variables control the microstructure and the properties of the final components, it is important to understand and optimize the ceramic processing. This project was undertaken in order to extrude long and thin wires of superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ using the superplastic deformation technology. For superplastic deformation, the important requirement is that the grain size of the ceramic to be deformed has to be as small as possible (typically 100–500 nm). Since, it is very difficult to retain the original particle size of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, after sintering, some additives were added to the superconducting ceramic powder prior to the sintering process. In this paper, some of the results obtained on the grain size, morphology and superconducting transition temperature of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ as a function of additive concentration are presented.

2. Experimental procedure

Yttrium, barium and copper oxide powder was synthesized from Y_2O_3 , BaCO_3 and CuO using the solid-state reaction method. Alumina in the concentration range 0–15 wt.% was added to the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ powder. The mixture was ball-milled in distilled water and dried. The dry powder was sintered at 920°C for 6 h and annealed at 600°C for 6 h in oxygen.

3. Results and discussion

Figure 1 shows the typical microstructure of $\text{Al}_2\text{O}_3/\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ composites as a function of alumina concentration. The corresponding elemental map of aluminum

distribution in the matrix is also shown in figure 1. The results suggest that the additive is uniformly distributed throughout the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ matrix, and even 1 wt.% additive has a significant effect on the surface topography of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ particles in the composite (i.e. the eroded "pit-like" morphology). In order to obtain some semi-quantitative results on the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ particle size as a function of alumina concentration, some samples were polished and these were examined under a

Figure 1. Secondary electron images and the corresponding aluminum X-ray scan images of as-sintered alumina/ $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ composites. Concentration of alumina in the composites (A, B) 0, (C, D) 1, (E, F) 5 and (G, H) 15 wt.%.

Figure 2. Grain size distribution of superconducting yttrium, barium and copper oxide ceramic as a function of additive concentration.

microscope. Figure 2 shows a typical particle size distribution of the superconducting ceramics and the results suggest that the particle size decreases with an increase in the additive concentration. The results also suggest that as the additive concentration increases, the broadness in the particle size distribution also decreases. Although the present experimental results cannot suggest that the observed changes in the morphological features are due to poor grain growth during sintering or that the additive (alumina) has chemically reacted with $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ to produce such surface features, it has to be recognized that some interaction between the additive and $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ occurs during sintering.

The crystal structure of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ in $\text{Al}_2\text{O}_3/\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ composites was determined using wide angle X-ray diffraction method. From a number of X-ray diffractograms, the orthorhombic/tetragonal crystal phase ratio of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ was estimated (figure 3). The results indicate that the superconducting orthorhombic phase of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ decreases (while the nonsuperconducting tetragonal phase increases) with increase in the additive concentration.

The electrical resistivity of all composite samples measured is shown in figure 4. The results suggest that the superconducting transition temperature (T_c) of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ decreases with increase in the additive concentration. However, once a critical T_c value is reached (approximately 50 K), it appears that the effect of alumina concentration is not very significant. It has to be pointed out that a similar but reverse trend is noticeable for the normal state resistivity of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ in the composites.

For superplastic deformation of ceramic materials, the important requirements are (i) very small particle or grain size, and (ii) the retention of the original crystal structure after deformation (Carry and Mocellin 1983; Nieh *et al* 1988). However, the superconducting ceramic materials have to satisfy two more additional requirements for any superplastic deformation; namely, (iii) the superconducting transition

Figure 3. % Orthorhombic and % tetragonal crystal phase versus the additive concentration of alumina/(YBaCu) oxide composites.

Figure 4. Electrical resistivity of sintered $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}/\text{Al}_2\text{O}_3$ ceramic composites. Alumina concentration ($\circ$) 0, ($\square$) 1, ($\triangle$) 2, (∇) 5 and ($\diamond$) 10 wt. %.

temperature and (iv) the critical current have to be unaffected by the deformation process. The present results suggest that although the selected additive (alumina) can fulfil the first requirement for superplastic deformation, it has degraded the superconducting transition temperature and altered the crystal structure of the superconducting ceramic. However, our results provide an important information that has to be considered for the selection of another suitable additive.

It has to be emphasized that although, at present, we cannot provide a suitable explanation for the degradation of superconducting transition due to the addition of

alumina, the tetragonal phase enhancement due to the addition of alumina may be the root cause for the observed lowering of the superconducting transition temperature.

4. Conclusions

From the present investigation the following conclusions can be derived

(i) Sintered $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ superconducting ceramics with small grains can be produced by the solid-state reaction method with the addition of alumina as an additive.

(ii) The addition of Al_2O_3 to $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ not only lowers the superconducting transition temperature (T_c) sintered $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, but also alters the crystal structure (i.e. the superconducting orthorhombic phase decreases while the nonsuperconducting tetragonal phase increases with increase in the additive concentration).

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