Carderock Division
Naval Surface Warfare Center
Bethesda, MD 20084-5000

CDNSWC-SME-92-11 March 1992
Ship Materials Engineering Department
Research and Development Report

Processing of $YBa_2Cu_3O_x$ Ceramic Materials: Effect of Additives

by
A. Srinivasa Rao

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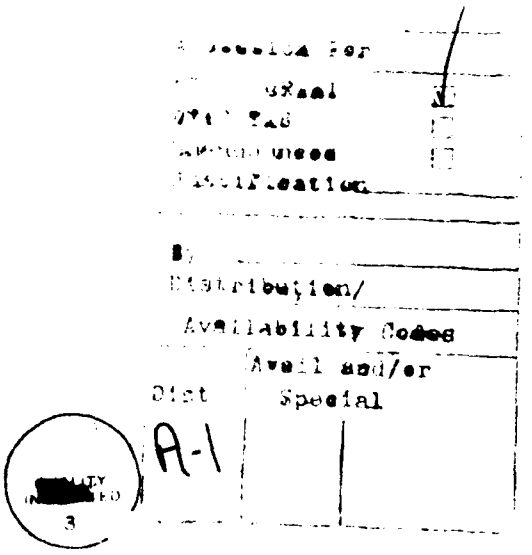

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ABSTRACT

The effect of the addition of Al_2O_3, TiO_2, PbO and Ag_2O, in the concentration range 0 - 30 wt. %, on crystal structure, morphology and superconductivity of $YBa_2Cu_3O_{6+x}$ was investigated. The results suggest that the addition of either Al_2O_3 or TiO_2 or $\geq$ 3wt.% PbO reduces the primary particle size of $YBa_2Cu_3O_{6+x}$. Additives, Al_2O_3, TiO_2 and PbO tend to stabilize the non superconducting tetragonal phase at the expense of superconducting orthorhombic phase. The oxygen from $YBa_2Cu_3O_{6+x}$ tends to migrate towards the additive and this process degrades the superconducting property of $YBa_2Cu_3O_{6+x}$ and increases the resistance. The addition of silver oxide, although, it does not affect the particle size of $YBa_2Cu_3O_{6+x}$, it improves the electrical properties of the composite.

ADMINISTRATIVE INFORMATION

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INTRODUCTION

The new high temperature superconducting ceramic materials are limited in their application as bulk superconductors, because, of the inherent problems that are associated with the processing of brittle ceramic materials. Since, all the ceramic materials show significant plastic deformation at different high temperatures, it is possible that high temperature deformation may intelligently be used in forming these ceramic

superconductors into useful shapes. For maximum superplastic deformation of ceramic materials, it was shown [1,2], that the grain size must be as small as possible (typically 100 - 500 nm). The present study was aimed to investigate methods to produce fine particles of $YBa_2Cu_3O_{6+x}$ by incorporating a few different additives prior to the sintering process without compromising the superconducting properties of the final sintered ceramic. In this paper, some of the results obtained for Al_2O_3,TiO_2, PbO and Ag_2O additions are presented.

EXPERIMENTAL PROCEDURE

The basic superconductor, $YBa_2Cu_3O_{6+x}$, was prepared by solid state chemical reaction of commercial yttrium oxide, copper oxide and barium carbonate. The superconducting Y-Ba-Cu-O ceramic powder was ground into a fine powder. The fine powder was mixed thoroughly with predetermined amounts (in the range 0 - 30 wt.%) of any one of the four additives (Al_2O_3, Ag_2O, PbO and TiO_2) in a ball mill. The mixture was dry pressed into small discs which later were sintered. The general details of the processing of composites are given elsewhere [3].

It has to be pointed out that the selection of additives (Al_2O_3, TiO_2) was based on the fact that both these materials were reported to show superplastic deformation at temperatures above 1000^{o}C [4,5]. The silver oxide was selected because it decomposes on heating to the sintering temperatures and the free silver will be plastic during deformation and may assist the onset of superplasticity. The free oxygen will be taken up by

the frequently oxygen deficient $YBa_2Cu_3O_{6+x}$ structure.

All sintered samples were analyzed using scanning electron microscope, microprobe, x-ray diffractometer and four point electrical resistance measurement apparatus.

RESULTS AND DISCUSSION

The morphology of sintered $YBa_2Cu_3O_{6+x}$ superconducting ceramic material suggests that the as-synthesized $YBa_2Cu_3O_{6+x}$ particles sinter into long elongated rods / plates (Figure 1). The crystal structure is similar to that of orthorhombic $YBa_2Cu_3O_{6+x}$ materials that were reported in the literature.

A typical morphology of sintered $YBa_2Cu_3O_{6+x}$ ceramic materials containing additives (Al_2O_3, TiO_2, Ag_2O and PbO) is shown in Figures 2 - 3. The results suggest that the addition of Al_2O_3 and TiO_2 to the superconducting ceramic material significantly alter both the particle surface topography and the particle size. In addition, some diffusion of TiO_2 into $YBa_2Cu_3O_{6+x}$ grains was also noticed (partial $YBa_2Cu_3O_{6+x}$) grain color change after sintering above 920^{o}C. However, additives Ag_2O and PbO did not produce any physical changes in the superconductor. In order to quantify the effect of the additives on particle size, a number of both optical and scanning electron micrographs (representing different areas of the whole sample) were taken from polished samples as a function of additive concentration. From the micrographs, histograms were plotted in order to obtain the average particle size of the superconducting ceramic materials. Figure 4 shows

the average particle size of $YBa_2Cu_3O_{6+x}$ in different composites. The results suggest that both additives Al_2O_3 and TiO_2 are very effective in reducing the particle size of $YBa_2Cu_3O_{6+x}$, and the degree of grain size reduction tends to increase with an increase in the additive concentration. However, no such particle size reduction trends are discernible for composites containing Ag_2O. The additive PbO shows a similar behavior as Ag_2O at lower concentrations (below 3 wt.%), but at higher concentrations (above 3 wt.%), the additive appears to reduce the particle size of $YBa_2Cu_3O_{6+x}$.

The interesting observation that was noticed in samples containing Ag_2O is that the particles of $YBa_2Cu_3O_{6+x}$ tend to line up and orient in the direction of pores. Figures 5 shows typical particle morphology of 5 wt % Ag_2O / $YBa_2Cu_3O_{6+x}$ composites. Since, Ag_2O decomposes above 230^oC to metallic silver, it is possible that during the calcination and sintering at 920^oC (well above the decomposition temperature), the metallic silver (decomposition product of Ag_2O) flows towards the nearest pore and accumulates at the pores. Such a free flow of silver in liquid state would serve to orient the grains of $YBa_2Cu_3O_{6+x}$ and produce dense packing (Figure 6).

The structure of all $YBa_2Cu_3O_{6+x}$ samples containing the additives was determined as a function of superconducting (orthorhombic) or non superconducting (tetragonal) phase content of the superconductor and the detailed analysis is given elsewhere [3]. The results suggest that the superconducting orthorhombic phase of the $YBa_2Cu_3O_{6+x}$ material decreases with an

increasing Al_2O_3 or TiO_2 or PbO content. However Ag_2O stabilizes the orthorhombic phase of $YBa_2Cu_3O_{6+x}$. In addition, it was also found that the oxygen liberated as the by product during (i) the decomposition of the additive (viz. Ag_2O to metallic Ag) tend to decrease the concentration of the impurities at the grain boundaries (i.e. between the metallic silver and superconducting $YBa_2Cu_3O_{6+x}$), and, (ii) the transformation of $YBa_2Cu_3O_{6+x}$ to Y_2BaCuO_y was taken up by the additives, and as a result, the additives tend to partially transform into a higher oxide.

Figure 7 shows typical electrical resistivity versus sample temperature plots of PbO / $YBa_2Cu_3O_{6+x}$ composites as a function of additive concentration. From a number of such electrical resistivity versus sample temperature measurements, the superconducting onset temperature (zero resistance temperature) for all samples was measured as a function of additive concentration and the results are shown in Figure 8. The results suggest that the superconducting transition temperature (T_c) of samples containing Al_2O_3, PbO and TiO_2 decreases very sharply with an increase in the additive concentration. Once a critical T_c value (approximately 50 K for Al_2O_3 and 40 K for PbO) is reached, it appears that the effect of the addition of the additive (within the concentration range investigated) on T_c is not significant. However, the studies with TiO_2 as an additive (for the reduction of particle size) have suggested that the additive TiO_2 has a very adverse effect on the T_c of the composite. In addition, it was also noticed that the normal

state resistance (measured at a given temperature) of all the above three composites increase with an increase in the additive concentration.

$YBa_2Cu_3O_{6+x}$ / Ag_2O composites show completely opposite behavior to the above system. For example the superconducting transition temperature (zero resistance), T_c, as was measured by four point resistance method, of pure $YBa_2Cu_3O_{6+x}$ showed an increase from 88 - 90 K to 92 - 94 K with the addition of Ag_2O (Figure 9). The ac susceptibility measurements indicate that this increase can be as high as 97 K. In addition the electrical resistivity verses temperature results also showed that the superconducting transition is very sharp (transition range $\pm$ 2K) and remain independent of the applied frequency indicating that the grain boundaries in Ag_2O / $YBa_2Cu_3O_{6+x}$ composites are nearly free from impurities.

The control of the microstructure is essential for the development of both mechanical and electrical properties of high temperature superconductors. In general for superplastic flow, the important requirements are (1) a very small particle size, and (2) the retention of original crystal structure even after the deformation. Although, chemical coprecipitation methods often produce very fine particles, those methods are very tedious and time consuming. The present investigation clearly demonstrates that the addition of 15 wt. % Al_2O_3 or TiO_2 to $YBa_2Cu_3O_{6+x}$ prior to the sintering process will not only inhibit grain growth (Figure 3), but also decrease the primary particle

size. Although, the present study failed to reveal an additive that will decrease the particle size without degrading the superconducting properties of $YBa_2Cu_3O_{6+x}$, it has given enough evidence to postulate a mechanism for the degeneration of the superconducting properties of $YBa_2Cu_3O_{6+x}$ in the composite. It is therefore possible that a proper selection of the additive on the basis of its chemical inertness towards $YBa_2Cu_3O_{6+x}$, may produce a preform consisting of fine particles of superconducting ceramic that is suitable for superplastic deformation.

CONCLUSION

In conclusion it can be suggested that the addition of Al_2O_3, TiO_2 and ($\geq$3 wt.%) PbO to fine $YBa_2Cu_3O_{6+x}$ powder prior to the sintering process produces composites with fine particle size. However, the superconducting properties of $YBa_2Cu_3O_{6+x}$ degrades with the increased concentration of the above three additives. The addition of silver oxide appears to show no effect on the particle size but it improves the superconducting properties of $YBa_2Cu_3O_{6+x}$.

ACKNOWLEDGMENT

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Figure 1. Morphology of sintered $YBa_2Cu_3O_{6+x}$ superconducting ceramic material. (A) Secondary and (B) back scattered electron image.

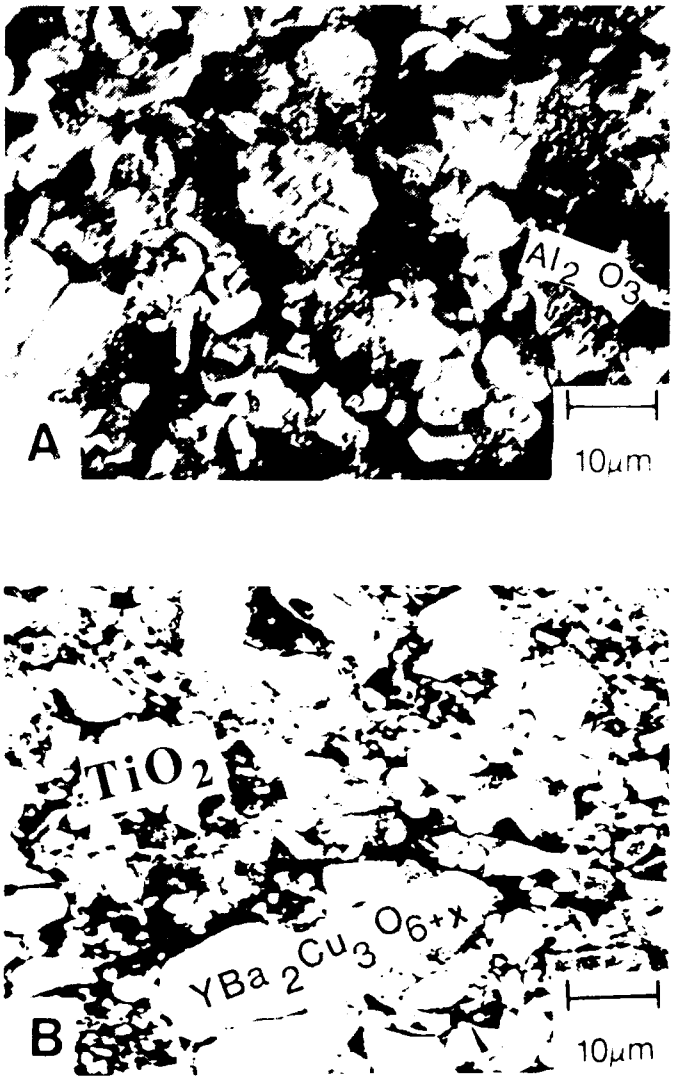

Figure 2. Morphology of sintered $YBa_2Cu_3O_{6+x}$ ceramic composites containing 5 wt. % (A) Al_2O_3 and (B) TiO_2.

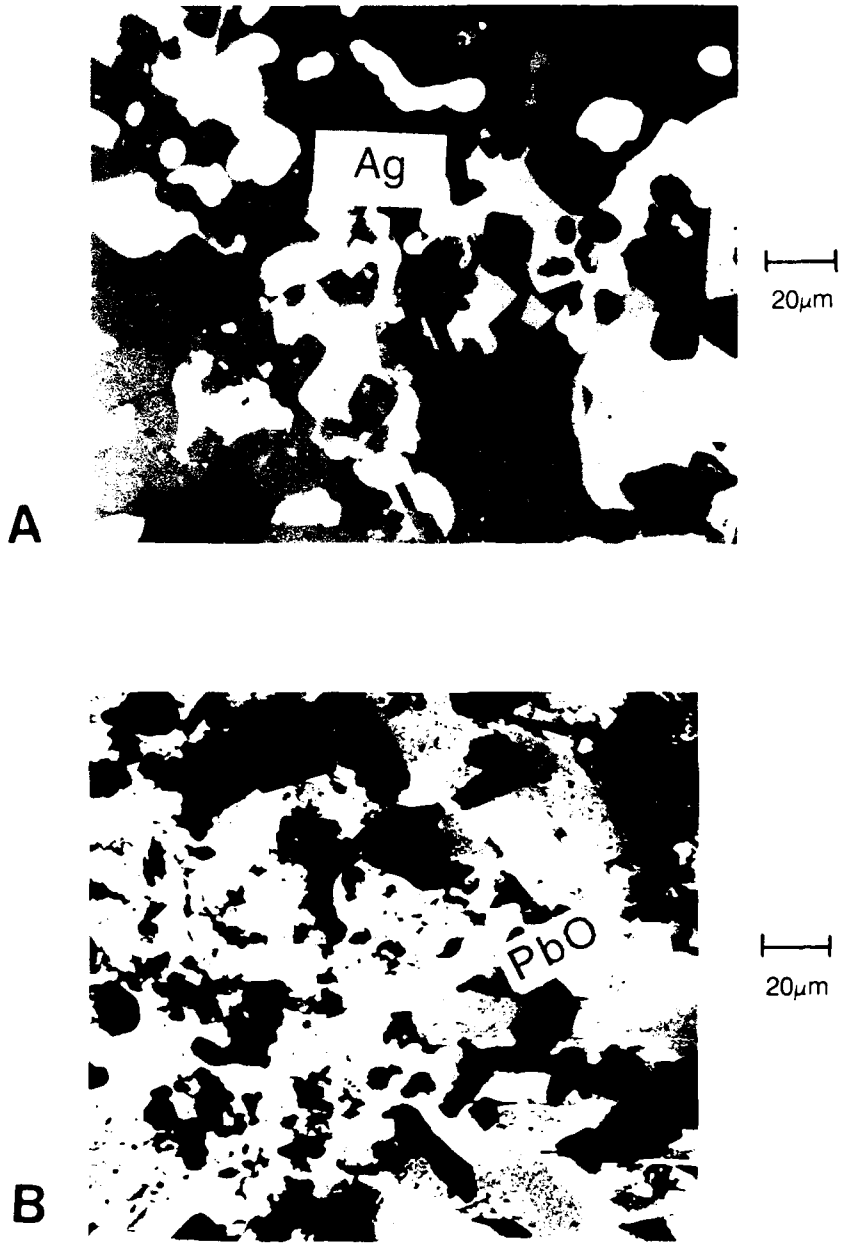

Figure 3. Morphology of sintered $YBa_2Cu_3O_{6+x}$ ceramic composites containing 5 wt. % (A) Ag_2O and (B) PbO.

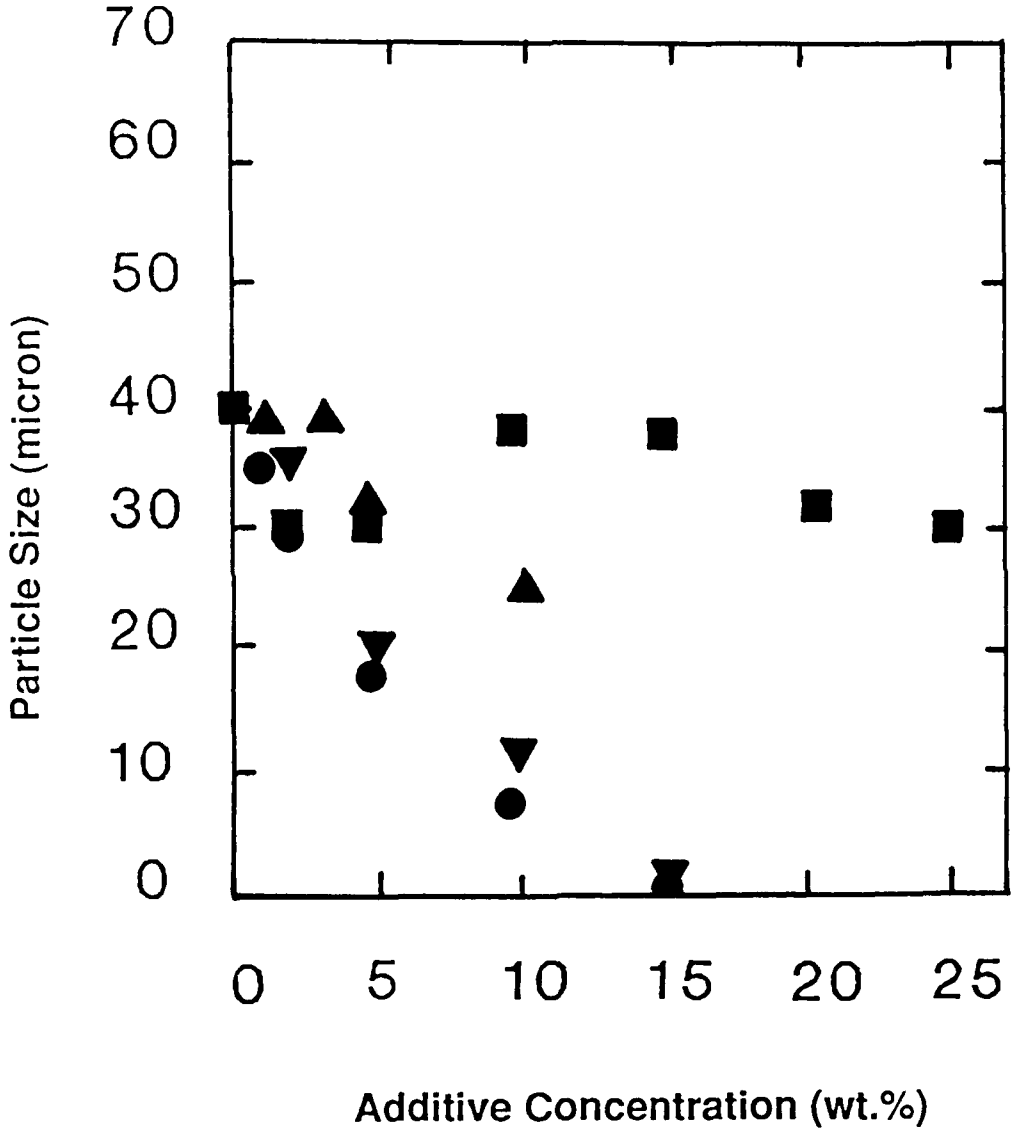

Figure 4. $YBa_2Cu_3O_{6+x}$ particle size distribution versus the additive concentration of sintered composite samples containing (●) Al_2O_3, (■) Ag_2O, (▲) PbO and (▼) TiO_2.

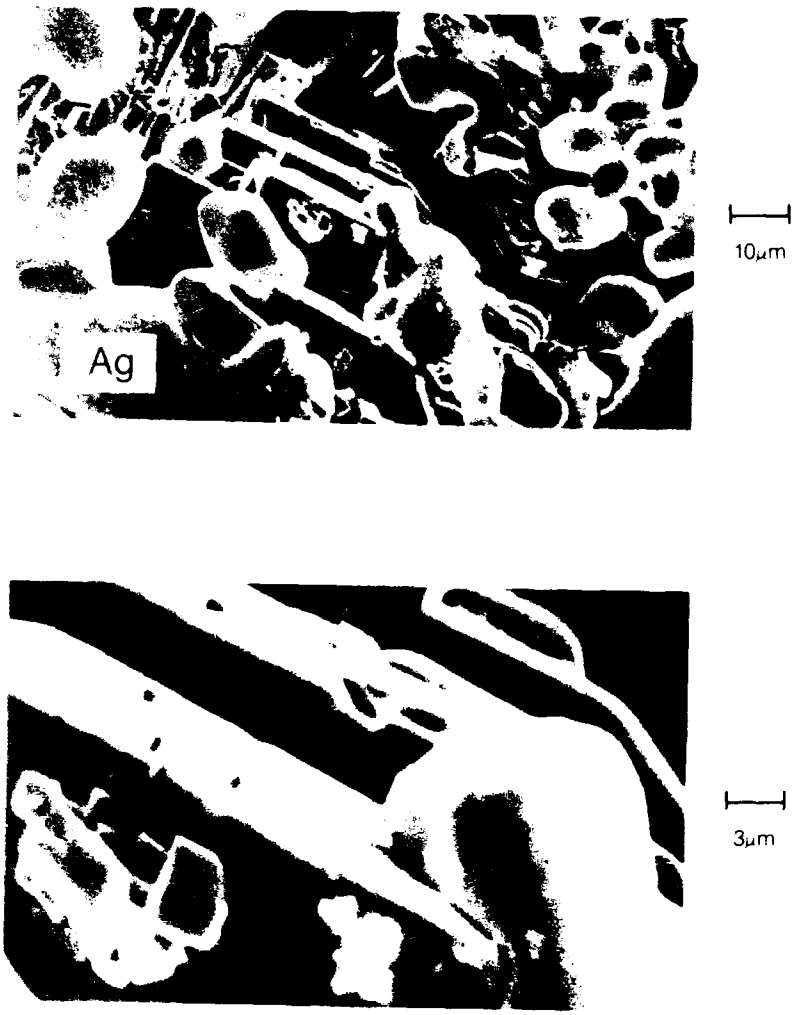

Figure 5. Scanning electron micrograph of aligned $YBa_2Cu_3O_{6+x}$ particles in sintered $YBa_2Cu_3O_{6+x}$ / 5 wt.% Ag_2O composites.

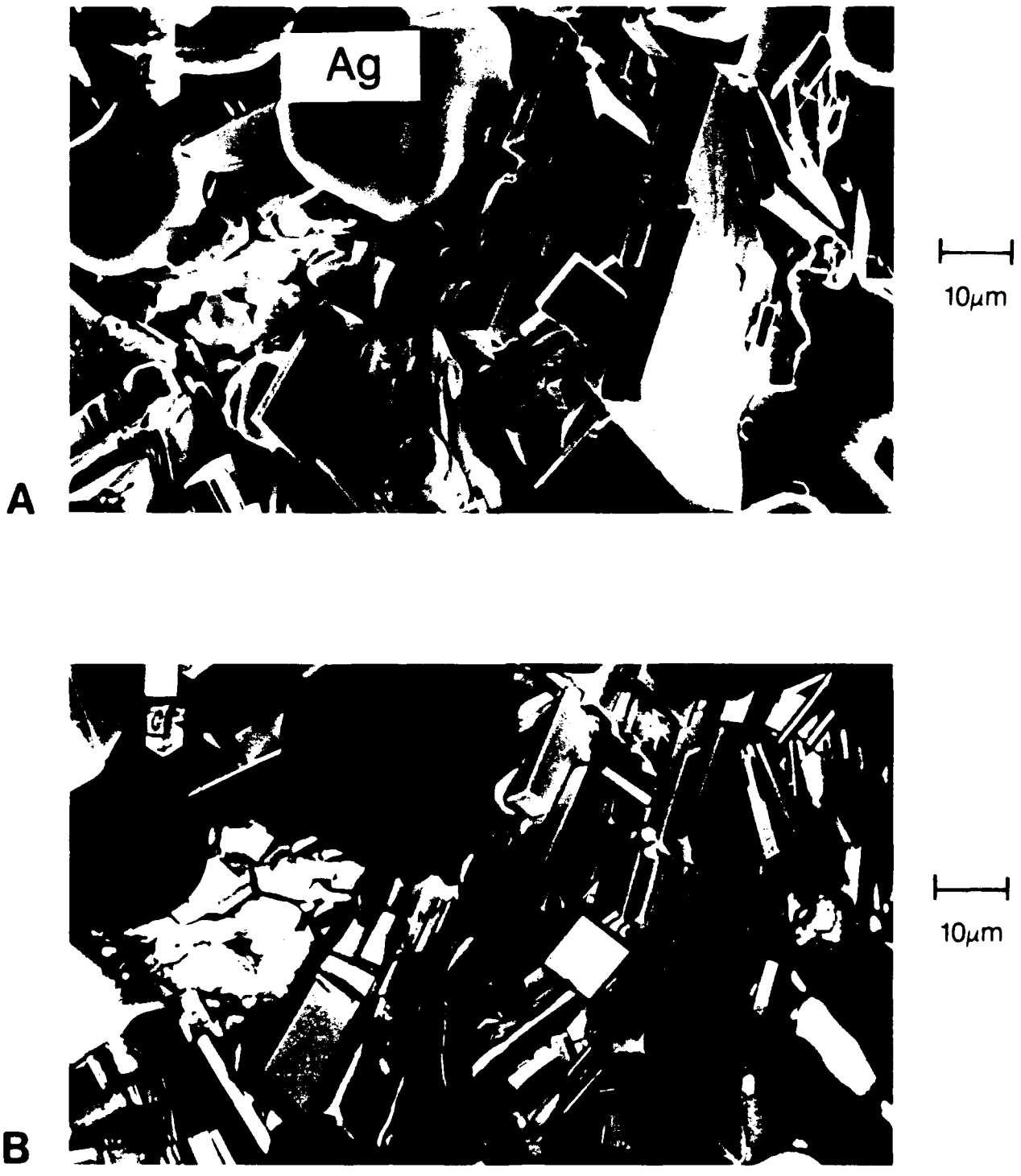

Figure 6. Scanning electron micrograph of aligned $YBa_2Cu_3O_{6+x}$ particles in sintered $YBa_2Cu_3O_{6+x}$ / 5 wt.% Ag_2O composites. (A) Secondary and (B) back scattered electron image.

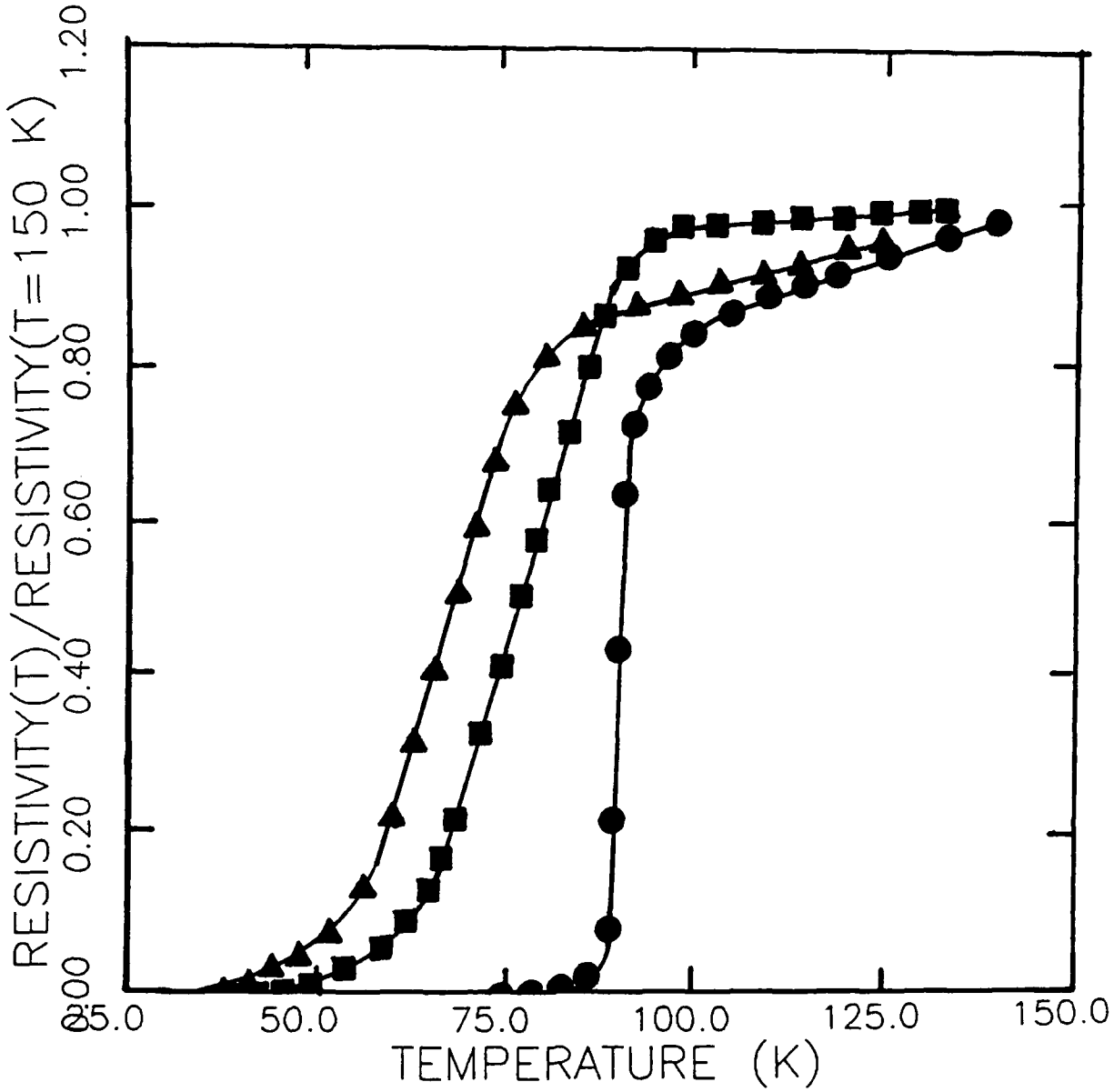

Figure 7. Electrical resistivity versus temperature profiles of PbO / $YBa_2Cu_3O_{6+x}$ composites containing (●) 0, (■) 1 and (▲) 10 wt.% PbO.

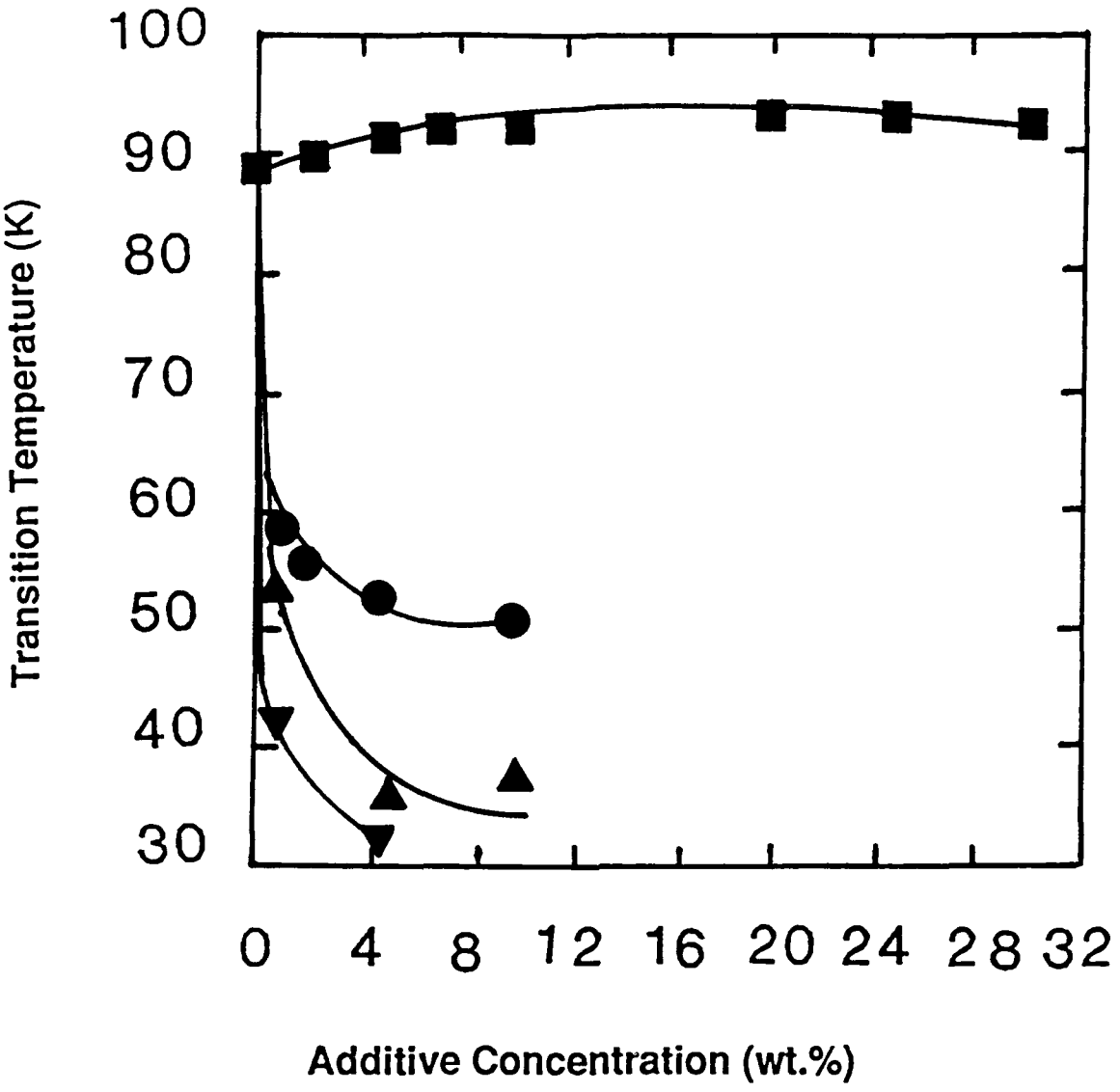

Figure 8. Superconducting transition temperature versus additive concentration of sintered $YBa_2Cu_3O_{6+x}$ composite samples containing (●) Al_2O_3, (■) Ag_2O, (▲) PbO and (▼) TiO_2.

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13. ABSTRACT *(Maximum 200 words)*

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