

Oxygen Stabilization Induced Enhancement in J_c of High Temperature Superconducting Composites

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In an attempt to enhance the electrical and mechanical properties of the high temperature superconducting oxides, we have prepared high T_c composites composed of the **123** compounds and Ag_2O . The presence of extra oxygen due to the decomposition of Ag_2O at high temperature is found to stabilize the superconducting 123 phase. Ag may also serve as clean flux for grain growth and precipitate as pinning centers. Consequently, almost two orders of magnitude enhancement in critical current densities has also been observed in these composites. In addition, these composites also show much improvement in workability and shape formation.

I. INTRODUCTION

At the very early stage of the development of high temperature superconductivity, there were several interesting observations concerning the processing of superconducting oxides. One is the relative short time required for preparing the mixed phase Y-Ba-Cu-O' compound which was treated at a relatively higher temperature. Another case is the preparation of Y-Sr-Cu-O² superconducting phase which can only be achieved when the material is treated at temperature higher than 1300° C and quenched to room temperature, and then gone through a well controlled oxygenation process. The fabrication of RE123/ Ag_2O^3 composites which were found to exhibit strongly flux trapping also requires a stringent processing condition. These observations suggested that the phase formation of high T_c oxides is more favorable in a non-equilibrium state plus a proper oxygenation process. It seems that the presence of a second phase, whether metal or non-metal, and oxide or non-oxide, is useful in enhancing the formation of superconducting phase. However, for better understanding the underlying mechanism for these observations requires more detailed thermal studies.

Our studies on the REBa₂Cu₃O_{7-x}Ag₂O (RE123/AgO, RE = Rare Earth) composites which exhibit unusual magnetic suspension effect showed that the processing conditions are critical for the formation of these high T_c composites. Magnetization measurements of

these composites show extremely large residual magnetization, indicating strong pinning effect. From the hysteresis loops, the estimated critical current density at 77K is in the order of $5 \times 10^6 \text{ A/cm}^2$.⁵ The resistance near T_c at high field reveals that the phase slippage is responsible for the transition. Recent HIP (Hot Isostatic Pressing)⁶ study indicates that the silver oxide speeds densification and promotes oxygen transport within the dense material. Most of the densification of the silver particles is believed to be due to yielding.

In order to gain more insight into the above mentioned observations, we have carried a series of experiments including the detailed thermal analyses of the Y 123/ Ag_2O system, and the correlation among the observed properties and the processing conditions. The results suggested that the observed enhancement in the superconducting properties likely is due to the stabilization of the superconducting phase (or the oxygen contents) through the introduction of extra oxygen from the decomposition of the silver oxide. The precipitated silver metal may serve as clean flux for the large grain growth and disperse in the superconducting grain as proper flux pinning center.

II. EXPERIMENTALS

The superconducting Y123/ Ag_2O composites were prepared by mixing properly prepared Y 123 compound of different oxygen concentrations and Ag_2O with a fix weight ratio of 3: 1, All annealing processes are performed with a constant oxygen flow rate of 20 cc/min. Detailed processing conditions of composites with different superconducting characteristics will be discussed later. Electrical resistivity measurements were made with the conventional 4-probe technique. The DC magnetic moment measurements were made with a Quantum Design MPMS SQUID magnetometer. A standard 4-probe using pulse current was used to determine critical current density at zero field. Structural and phase determinations were made by x-ray diffraction. A Cambridge SEM, equipped with a KeveX EDS system was employed for microstructure study. Thermal studies were carried out using ULVAC Multi-TAS-7000 thermal analyzer with DTA and TGA capabilities.

III. RESULTS AND DISCUSSION

Several conclusions can be drawn from the results compiled in Table I. These include: (1) superconducting composites with T_c 90K are formed independent of the quality of the starting Y 123 compounds (i.e. irrelevant to the oxygen contents); (2) samples exhibit strong pinning are annealed at a temperature higher than the melting temperature of silver metal; and (3) only samples with large grains show strong pinning effect. We have also observed that superconductivity sustains with the weight ratio of Y123 to Ag_2O up to 2: 1. The pinning characteristic of these composites strongly depends on their sample morphologies. The presence of large grain seems to be one of the key factors for the material to show

TABLE I. Processing Parameters for Y 1 23/Ag₂ O Composites

Anneal temp.	Y ₁₂₃ O _x x=	Cooling rate	Pinning effect	Grain size	Ag precipitate	T _c * (K)
1000	6.98	5C/min	medium	L	Yes	88
1000	6.72	5C/min	weak	m	Yes	82
1000	6.98	15C/min	weak	m	No	93
990	6.98	3C/min	weak	s	No	93
990	6.98	5C/min	strong	L	Yes	91.3
990	6.72	5C/min	weak	m	Yes	91.3
990	6.98	10C/min	medium	L	No	92.5
990	6.72	10C/min	weak	m	Yes	91.3
990	6.98	20C/min	weak	m	No	92.5
990	6.72	20C/min	weak	m	Yes	91.3

* T_c is the onset of the resistive transition.

+ Oxygen flow rate is 20 cc/min. for all runs.

unusual magnetic suspension effect. Another factor is the fine dispersion of silver metal particles in the superconducting grains. It is conceivable that these dispersed silver particles serve as pinning center which may then be responsible for the strong flux pinning observed.

The optimum conditions for the formation of strongly pinned superconducting composites can be summarized as: (1) the annealing temperature is -990°C ; (2) the cooling rate is -5°C per minute; and (3) -20 cc/min. oxygen flow during sintering. We also observed that in order to obtain better material morphology (i.e. relatively large grains and fine Ag metal dispersion), it is not necessary to have a uniform mixture of the starting powder (Y 123 and Ag₂O powder). In fact, a particle size ratio of about 5: 1 between the Y 123 and the Ag₂O powder seems to give the best result. The sensitivity of the observed pinning effect to the sintering temperature and cooling rate could be due to the change of the interdiffusion rate of silver metal with the superconducting particles, particle surfaces and particle grain boundaries. The importance of Ag₂O particle size and Y 123 grain size suggested the interdiffusion of Ag indeed is essential.

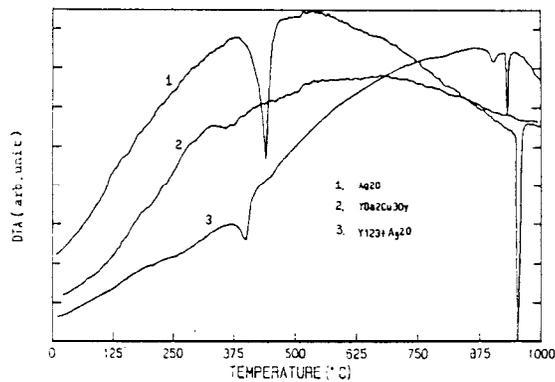


FIG. 1. Differential thermal analysis (DTA) of Ag₂O(1), Y123(2), and Y123/AgO (3). The heating rate is 5°C per minute.

Figure 1. shows the results of the differential thermal analysis (DTA) on the Y 123, Y 123 /Ag₂ O and Ag, O, respectively. Data are taken either heating the samples in air or with a constant oxygen flow. Three reactions are clearly seen in the Ag, O added composite. A low temperature reaction at -375°C is related to the decomposition of Ag₂ O, as clearly seen in that of the Ag₂ O data. The reaction occurs at -935°C is identified as the melting of pure silver by comparing the anomaly observed at -960°C of the Ag₂ O DTA result. The reason for the decrease in melting temperature of the silver metal in the Y123/Ag₂O composite is not well understood at the present time. It should be noted that an opposite result, which show the increase in the liquidus temperature, was observed by Chen et al. in their study of the Yb123/Ag metal composite.⁷ The 895°C reaction observed may be due to the reaction of Ag metal with Y 123. However, x-ray diffraction study shows that the resultant superconducting oxide contains no Ag. Electron microscopy indicates that Ag metal precipitated on the grain boundaries and filled in some voids.⁸

TGA results of these compounds which was measured at ambient pressure, as displayed in Fig. 2. show that a prominent oxygen loss at 375°C in the Ag₂ O addition Y123, which is corresponding to the dissociation of oxygen in Ag₂ O. By correcting the

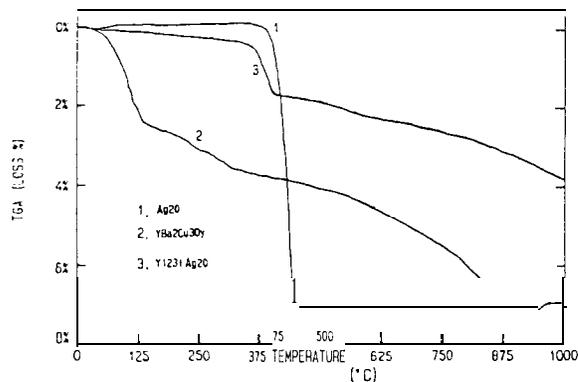


FIG. 2. Weight loss of Ag₂O (1), Y 123 (2), and Y 123/AgO (3) at ambient with a heating rate of 5°C per minute.

oxygen loss due to the silver oxide decomposition, the oxygen loss in the Y123 of the composite is found to be about 50 percent lower than that of the pure Y123 for temperature up to 980°C . The same oxygen losses are also observed in samples reacted at flowing oxygen environment but its value is only about 25 percent lower in comparison with that of the pure Y123. This is because the oxygen loss is reduced for Y 123 annealed under oxygen atmosphere. These results supports the suggestion that extra oxygen from Ag, O serves as an oxygen stabilizer of the superconducting Y 123 phase.

Many oxygen diffusion studies⁹⁻¹¹ have been carried out in high T_c oxides. Most of the studies indicated that the in-and out-diffusion of oxygen in the oxides, particularly in 123, is extremely effective. These studies suggest that the out-diffusion is most likely surface-reaction-limited, while the in-diffusion is diffusion control. The diffusion mechanism are through the defects which include the oxygen vacancies and twinings. In general, several activation energies have been observed corresponding to the out diffusion

and in-diffusion (depending on the oxygen concentrations). The higher activation energy for the out-diffusion process suggested that the surface barrier which can be affected by the grain boundaries and impurity plays an important role in controlling the oxygen concentration. If a good oxygen catalyses (or oxygen inert species, such as Ag metal) were used in contact with the oxide, then better stabilization of the phase might be achieved through the limiting oxygen out diffusion process. This oxygen stabilization process may then be used to explain the stabilization of 123 phase in the Ag-addition composites. The observation of Y 123 phase stabilization in the mixed phase Y-Ba-Cu-O may also be due to similar process attributed to the presence of the insulating 211 phase. In addition, the rather sensitive oxygen condition of the Y-Sr-Cu-O¹² system may also be related to this diffusion control steps.

Very recent work⁶ also revealed that the AgO or Ag is a mechanical processing aide. Hot isostatically pressed (HIP) Y 1 23/AgO^{13,14} is not only 100% dense, but the bulk shapes were also relatively free of microcracks. Silver appears to wet the surfaces of the RE123 quite well, segregating to prior particle boundaries and grain boundaries. A much better workability has also been demonstrated by the inclusion of Ag in RE123.⁶ It is believed that Ag on boundaries enhances oxygen diffusion. This may be a most necessary feature for bulk material since preliminary data have shown oxygen diffusion to be slow in dense oxide superconductors.

IV. SUMMARY

Detailed thermal and microscopic studies of the Ag₂ O-added Y 123 composites, which exhibit an unusually large pinning characteristic, suggested that silver metal serves as the agent to clean out unwanted unclean centers, thus allowing the superconducting "123" grains to grow. It is also found that silver particles, in the order of micron, are present dispersively inside grains. It is conceivable that these dispersed silver particles may serve as pinning center for the strong flux pinning observed. The extra oxygen provided by AgO is believed to enhance the oxygen stability of the superconducting phase, and consequently the superconducting characteristic of the composites.

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