N92-21606

OXYGEN STABILIZATION INDUCED ENHANCEMENT IN SUPERCONDUCTING CHARACTERISTICS OF HIGH-T_c OXIDES

M.K. Wu*
Department of Physics and Materials Center
National Tsing-Hua University
Hsingchu, Taiwan, Republic of China

J.T. Chen
Department of Physics
Wayne State University
Detroit, Michigan 48202

C.Y. Huang
Lockheed Missiles and Space Company
Research and Development Division
Palo Alto, California 94304

ABSTRACT

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 AgO. The presence of extra oxygen due to the decomposition of AgO at high temperatures is found to stabilize the superconducting 123 phase. Ag is found to serve as a clean flux for grain growth and it precipitates as a pinning center. Consequently, an 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 formulation.

On the other hand, proper oxygen treatment of $Y_5Ba_6Cu_{11}O_y$ was found to possibly stabilize the zero-resistance state near 250 K. I-V, ac susceptibility and electrical resistivity measurements indicate the possible existence of high-temperature zero-resistance state in this compound.

INTRODUCTION

Since the first paper on high-temperature superconductivity reported by Bednorz and Muller [1], several new material systems have been found with their physical properties characterized, and many theoretical models have been proposed. However, no clear understanding of the mechanism responsible for the high-temperature superconductivity has been established. Consequently, there are no science-based guidelines for researchers in the search for new high-T_c materials.

Recently, thermally recycleable zero-resistance states with transition temperatures above 200 K were observed in mixed-phase Y-Ba-Cu-O materials that are treated by a low-temperature oxygenation process and enclosed in an oxygen atmosphere during electrical and magnetic measurements [2]. Although the high-temperature zero-resistance state was verified through careful measurements of the current-voltage characteristics using multiple leads and contact arrangements. Only diamagnetic-like deviations and hysteretic behavior at the same temperature as the resistive transitions were observed in the magnetic measurements.

---

* On leave from Department of Applied Physics, Columbia University, New York, NY 10027, USA.

At the very early stage of the development of high-temperature superconductivity, we observed several interesting phenomena concerning the processing of superconducting oxides. One example is the preparation of Y-Sr-Cu-O [3] superconducting phase which exists only when the material is processed at temperatures higher than 1300°C, quenched, and then submitted to a controlled oxygenation process. The fabrication of RE123/Ag_2O [4] composites, which were found to exhibit strong pinning effect, also requires stringent processing conditions. Our 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 properties of superconducting phase.

On the other hand, there are problems in achieving technological applications of this new class of materials. One difficulty that stands most squarely in the way of the commercialization of the new high-temperature superconductors is the fabrication of bulk materials with high current densities in high magnetic fields [5, 6]. This implies that highly oriented material [7] is required for most applications.

Other experimental results, such as the evidence for intragrain Josephson junctions [8] and the development of a tail in the resistive transition in the presence of even moderate applied fields, indicate that the phenomenology of the high-T_c oxides is significantly different from that of the classical superconductors.

It also creates serious problems when trying to define the upper critical field and the critical current [9, 10]. Several models have been proposed to explain the broadening of the resistive transition under magnetic fields [9, 11, 12, 13]. However, a clear picture of the phenomenology of the transition is yet to come. In addition, there is also a lack of understanding of such important issues as the effect of oxygen stoichiometry and ordering, boundary effects, and formability.

In order to gain more insight into the above-mentioned observations, we have carried out a series of experiments based on the formation of superconducting oxides through the dispersion of fine metal oxide. In this work, we report the results of: the preparation of single-phase superconducting $YSr_2Cu_3O_{6+y}$ compound by the addition of a small amount of MoO_3; the detailed thermal and microscopic studies of the strong flux pinning RE123/AgO composites; and the magnetic and electron microscopic studies of the $Y_5Ba_6Cu_{11}O_y$ (5-6-11) and Sr-doped 5-6-11 compounds. The results suggest that the observed enhancement in the superconducting properties is likely caused by the stabilization of the superconducting phase (or the oxygen contents) through the introduction of extra oxygen from either the decomposition of the silver oxide (for RE123/AgO composites) or the low-temperature oxygenation process (for 5-6-11).

EXPERIMENTAL

The superconductingY-Ba-Cu-O/Ag_2O composites were prepared by mixing properly prepared Y123 compound of different oxygen concentrations of Ag_2O with weight ratio n. 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.

High-T_c YSCO compounds were prepared by mixing appropriate amounts of metal oxides (nominal composition of $YSr_2Cu_{3-x}Mo_xO_{6+y}$ with x in the range of 0.02 to 0.05), pressing it into pellets, heating it at 950°C for 12 hours, and quenching it to room temperature (RT). The material was then reground, pressed, reheated to 1150°C for 6 hours in O_2, and slowly cooled to RT. High-purity alumina crucibles were used in the sample preparation.

Samples with nominal compositions of $Y_5Ba_6Cu_{11}O_y$ and $Y_5Ba_4Sr_2Cu_{11}O_y$ were synthesized by ceramic techniques from Y_2O_3, $BaCO_3$ and CuO powders. The first step was to repeatedly calcine the unreacted powders at 930°C for 10 hours in either an oxygen atmosphere or in air until a dark black powder and a fine crystalline texture was obtained. The reacted powders were pressed into pellets and sintered at ≅850°C for 2 days (with one intermediate grinding). A last step used a high-pressure vessel filled up to at least 130 bars for the low-temperature oxygenation. Electrical resistivity measurements were made with the conventional 4-probe technique. AC-magnetic moment measurements were made with a home-made magnetic susceptometer. Structural and phase determinations were made by x-ray diffraction. A Cambridge Scanning Electron Micrograph (SEM) equipped with a Kevex EDX system was employed for microstructural study. Thermal studies were carried out using an ULVAC Multi-TAS-7000 thermal analyzer with DTA and TGA capabilities.

RESULTS

A. Electrical and Magnetic Characterization

The temperature dependence of the resistivity of YSCO with a small amount of Mo is shown in Figure 1. The superconducting onset temperature is about 80 K, which is in agreement with that of the magnetic measurement, as shown in the inset of Figure 1. A linear temperature dependence of R before the onset of superconductivity was observed. Based on the magnetic signal, it was estimated that the superconducting phase is about 60 percent in volume. Without the addition of MoO_3, the 80-K superconducting phase does not manifest itself when the samples are prepared at a temperature lower than 1300°C. This indicates that the 80-K phase in the YSCO compound is thermodynamically stable only at higher temperatures. The addition of MoO_3 resulted in the reduction of the reacting temperature.

A typical M-H hysteretic loop of the nY123/Ag_2O (where n=3) composite is plotted in Figure 2. Similar results are also observed in samples with different values for n. The temperature dependence of the residual magnetization increases with decreasing temperature [14, 15]. Such universal behavior was observed for all the composites which show strong pinning.

AC magnetic susceptibility (with a frequency of 37 Hz and a field <2 G) of the mixed-phase Y-Ba-Cu-O (5-6-11) compound is shown in Figure 3. A superconducting transition near 90 K corresponding to the Y123 phase is observed. In addition, a much smaller diamagnetic-like anomaly with the onset near 270 K is also observed, as shown in the inset of Figure 3. Using the 90-K transition as a reference, it is estimated that the volume fraction of the high-temperature signal has an upper limit of 5 percent. Figure 4 is the field-cooled ac susceptibility of two Sr-doped 5-6-11 samples, one of which has been treated in high-pressure oxygen. It is clear that these samples exhibit similar diamagnetic deviation with the onset temperature near 200 K. A hysteretic behavior is also present in the Sr-doped sample.

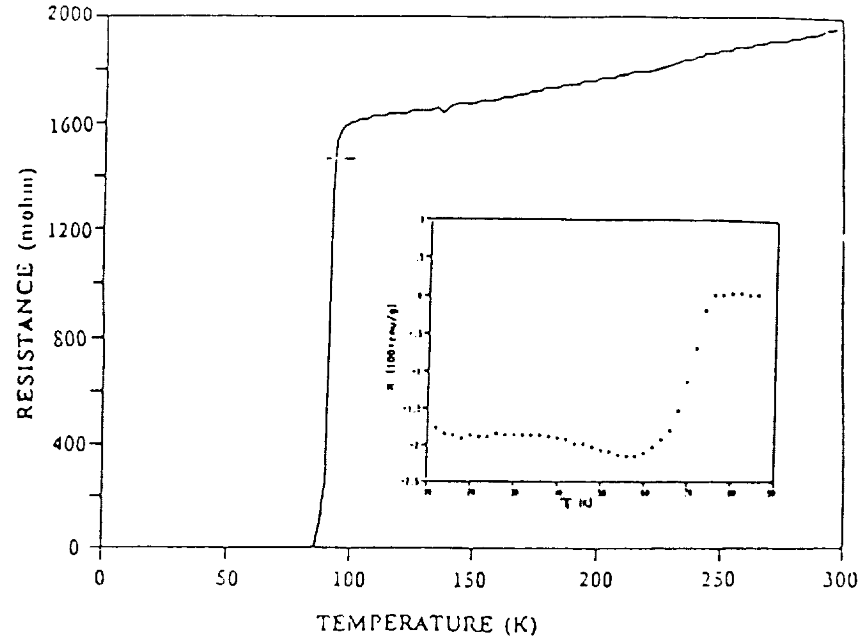

Figure 1. Temperature dependence of resistance of $YSr_2Cu_3O_{6+y}$. Inset: the temperature dependence of the magnetic susceptibility of $YSr_2Cu_3O_{6+y}$.

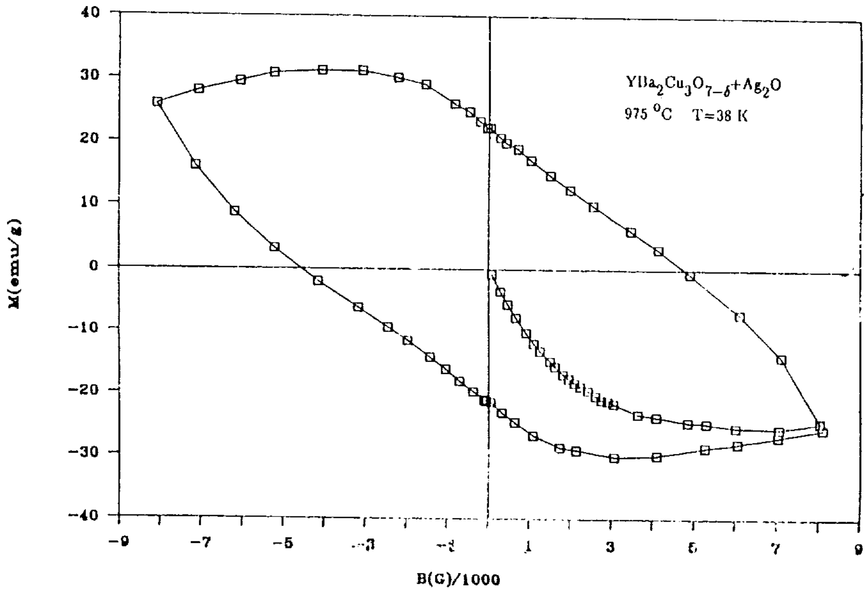

Figure 2. The M-H hysteresis loop of $3Y123/Ag_2O$ at 38 K.

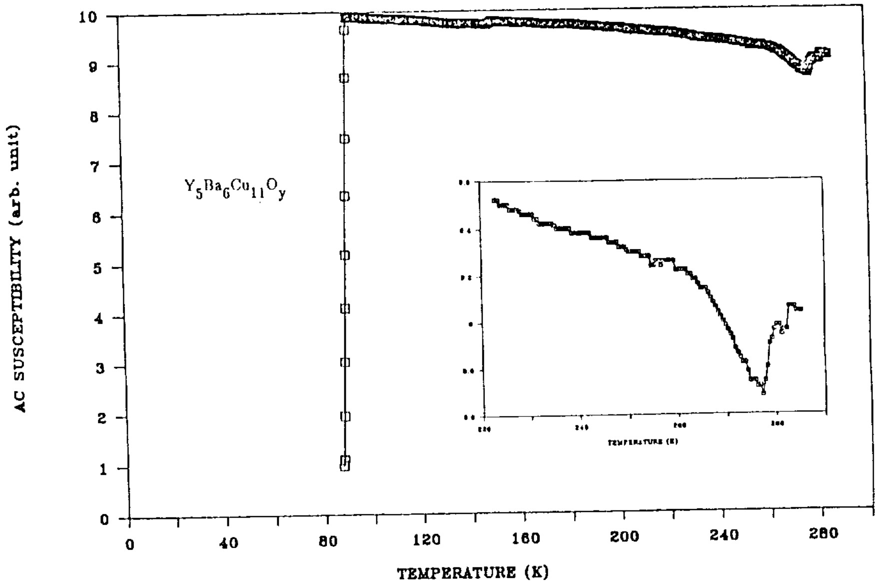

Figure 3. Temperature dependence of ac magnetic susceptibility for $Y_5Ba_4Cu_{11}O_y$.

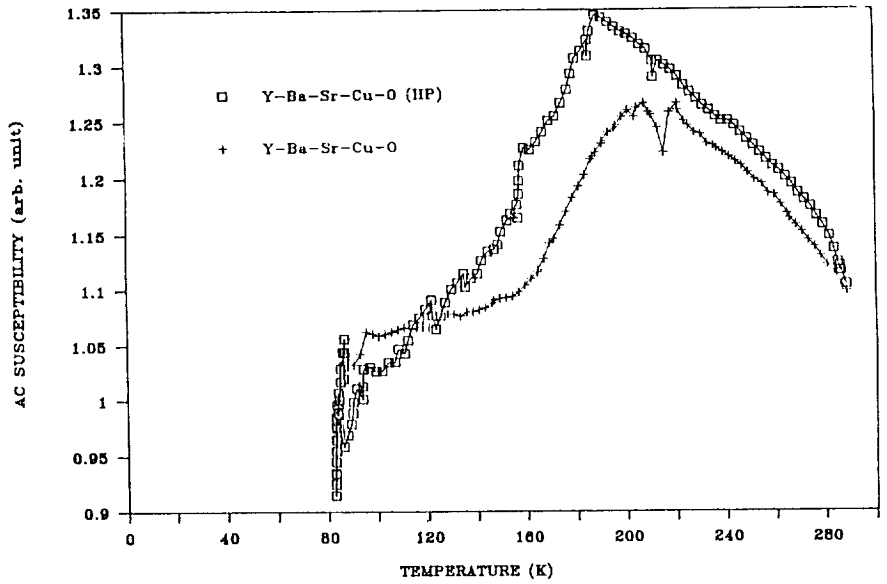

Figure 4. Temperature dependence of ac magnetic susceptibility for $Y_5Ba_4Sr_2Cu_{11}O_y$.

B. Structural Characterizations

The detailed x-ray diffraction pattern of the Y-Sr-Cu-O is shown in Figure 5. A tetragonal structure with lattice constants of a=3.818 A and c=11.555 A was determined using the TREOR program (16). The atomic positions of space group P4/mmm and the isotropic Debye Waller factors listed in Table I were determined with a program based on the stoichiometry of $YSr_2Cu_3O_{6+y}$, where the values of the Debye Waller factors were confined between 0.3 and 4.0 (the corresponding atomic rms displacements are 0.05 A and 0.25 A). The final R factor is 12.6 percent. Atoms O(3) and Cu(1) on the basal plane can be considered relatively unstable due to their large Debye Waller factors. Cu(1) was dragged along by the unstable O(3). The distance between the CuO_2 planes is determined to be 3.305 A, which is smaller than that of the $YBa_2Cu_3O_{6+y}$, which is 3.388 A. It should be noted that a tetragonal phase and an orthorhombic structure for the Y-Sr-Cu-O system [17-20] have been proposed in the literature.

X-ray diffraction patterns of the Ag_2O-added composite show strong c-orientation in the Y123/Ag_2O composites with traces of Ag metal, as shown in Figure 6. The lattice parameters are identical with those of the starting Y123 compound. Figure 7 is the scanning electron micrograph for a 3Y123/Ag_2O composite. EDX has identified the presence of Y123 phase, silver particles, and voids. It shows a microstructure of dispersed silver in the matrix of the Y123 phase. Intergranular silver was observed in some areas and some voids have been filled up by silver, resulting in the reduction of the normal resistivity. More interesting is the observation of large, single crystals in the Ag-dispersed composite. As displayed in Figure 7, the size of the Y123 crystal can be as large as ≅ 0.5mm. Similar results are also observed in other composites exhibiting large flux pinning effects.

The high-resolution transmission microscope view of the 5-6-11 sample exhibiting the high-temperature, diamagnetic-like anomaly is shown in Figure 8. While the x-ray diffraction pattern shows the majority of 123 phase, the TEM picture indicates the presence of a glass-like phase. Detailed structural and composition analyses suggest that this glass-like phase may be caused by the intergrowth of the Y123 and Y248 phases.

C. Thermal Characterizations

The heat treatment conditions for the formation of strong pinning RE-123/AgO composites are shown in Table II. In general, the temperatures required are higher than those needed to form the corresponding RE123 compounds, and they do not depend on the weight ratio of RE123 to AgO. It is found that these strong flux pinning RE123/AgO composites form only in a narrow annealing temperature range. The optimum conditions for the formation of strongly pinned superconducting composites can be summarized as: 1) the annealing temperature is ≅ 980°C; 2) the cooling rate is ≅ 5°C per minute; and 3) there is ≅ 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), a particle size ratio of about 5:1 between the Y123 and the Ag_2O powder seems to give the best result.

Figure 9 shows the results of the differential thermal analysis (DTA) and the unreacted Y123, Y123/Ag_2O and Ag_2O, respectively. Data are taken by either heating the samples in air or with a constant oxygen flow. Three reactions are clearly seen in the Ag_2O-added composite. A low-temperature reaction at ≅375°C is related to the decomposition of Ag_2O, as clearly seen in

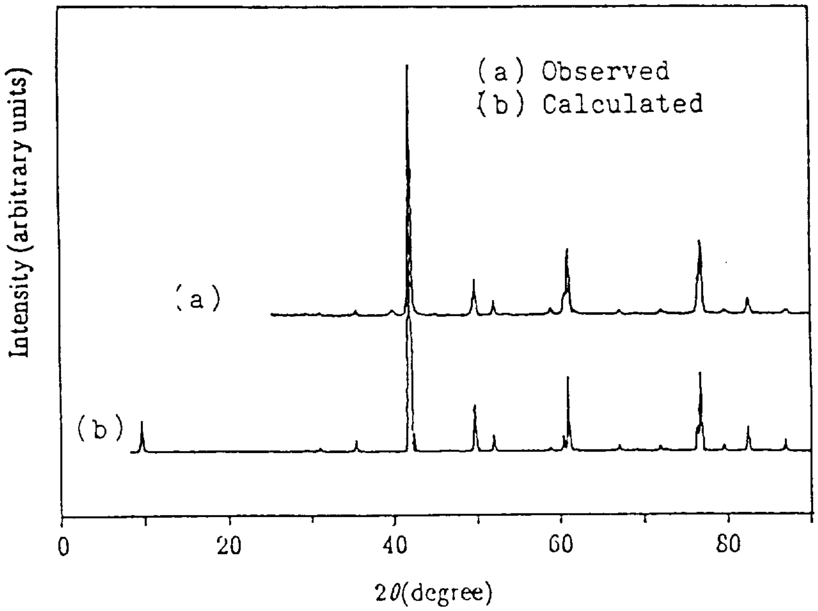

Figure 5. X-ray diffraction pattern of YSCO.

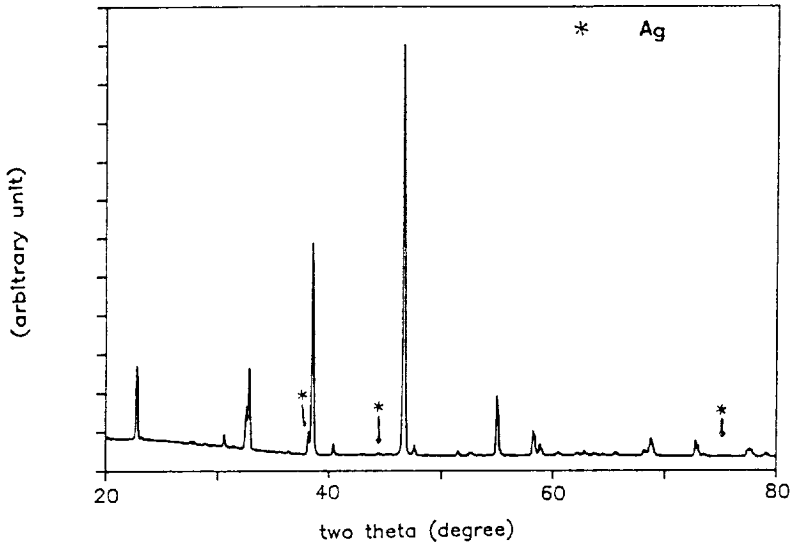

Figure 6. X-ray diffraction pattern of 3Y123/Ag_2O.

TABLE I. Positional parameters and isotropic Debye-Waller factor for the tetragonal structure of $YSr_2Cu_3O_{6+y}$ based on space group P4/mmm and a = 3.818 A, and c = 11.555 A.

Atoms	Wyckoff	x	y	z	B	Occupancy notation
Y	1d	0.5	0.5	0.5	0.3	1
Sr	2h	0.5	0.5	0.197	0.7	1
Cu 1	1a	0	0	0	2.6	1
Cu 2	2g	0	0	0.357	1.3	1
O 1	2f	0	0	0.148	1.1	1
O 2	4i	0	0.5	0.372	4.0	1
O 3	2g	0	0.5	0	4.0	0.6

Table II. Processing Parameters for $Y123/Ag_2O$ Composites

Anneal temp.	$Y_{123}O_x$ x=	Cooling rate	Pinning effect	Grain size	Ag precipitate	Tc* (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
980	6.98	3C/min	weak	s	No	93
980	6.98	5C/min	strong	L	Yes	91.3
980	6.72	5C/min	weak	m	Yes	91.3
980	6.98	10C/min	medium	L	No	92.5
980	6.72	10C/min	weak	m	Yes	91.3
980	6.98	20C/min	weak	m	No	92.5
980	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.

that of the Ag_2O data. The reaction occurring at ≅ 935°C is identified as the melting of pure silver by comparing the anomaly observed at ≅ 960°C to the Ag_2O DTA result. TGA results of these compounds which were measured at ambient pressure (as displayed in Figure 10) show a prominent oxygen loss at 375°C in the Ag_2O-addition Y123, which corresponds to the dissociation of oxygen in Ag_2O. By correcting the 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 temperatures up to 980°C. The same oxygen losses are also observed in samples reacted in flowing oxygen environments, but their values are only about 25 percent lower in comparison with that of the pure Y123. These results support the suggestion that extra oxygen from Ag_2O serves as an oxygen stabilizer of the superconducting Y123 phase.

DISCUSSIONS

The existence of high-temperature superconducting phase ($T_c > 77$ K) with tetragonal "123" structure in YSCO is rather unusual, since in the YBCO system high-T_c (> 70 K) phase may be related to the enhancement of the phase stability through the dispersion of fine metallic oxide as usually observed in the oxide dispersion strengthening alloys [21]. It is interesting to note that similar results have been observed in the bismuth- and thallium-based superconductors [22] with the addition of lead oxide. The results of the enhancement in electrical and magnetic properties in the 123/AgO composites, which is to be discussed later, may also come from the same origin.

Several conclusions can be drawn from the results compiled in Table II. These include: 1) superconducting composites with $T_c \cong 90$ K are formed independent of the quality of the starting Y123 compounds (i.e., irrelevant to the oxygen contents); 2) samples that 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. Our observations show that the pinning is independent of the weight ratio n. The superconducting transition temperature, T_c, of the composite remains almost unchanged compared with that of the starting RE-123 compound. The decrease in the normal-state resistivity with the addition of silver oxide suggests a lowering of contact resistances between grains. Nearly identical T_c's suggest that grain interiors experienced little change from the starting RE-123 compounds. One important advantage derived from these RE-123/AgO composites is the reduction of overall contact resistance.

To study in detail the resistive transition of the $Y123/Ag_2O$ composite, we analyzed our data of the $RE\text{-}123/Ag_2O$ composites using the model proposed by Tinkham [12]. All of them show that $T_c H^{2/3}$ within our experimental errors. From this result, we estimated that $J_{co}(0)$ 9×10^6 A/cm^2, which is a reasonable value for the 123 superconductor. A particularly significant result is the unusually large pinning effect in these composites, as evidenced by the still-zero resistance state of several samples at about 80 Kwhile under a magnetic field of 8 T [24].

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 grain boundaries. The importance of Ag_2O particle size and Y123 grain size suggests the interdiffusion of Ag is, indeed, essential.

ORIGINAL PAGE
BLACK AND WHITE PHOTOGRAPH

Figure 7. Scanning electron micrograph of 3Y123/Ag_2O.

Figure 8. Transmission electron micrograph of $Y_5Ba_4Cu_{11}O_y$.

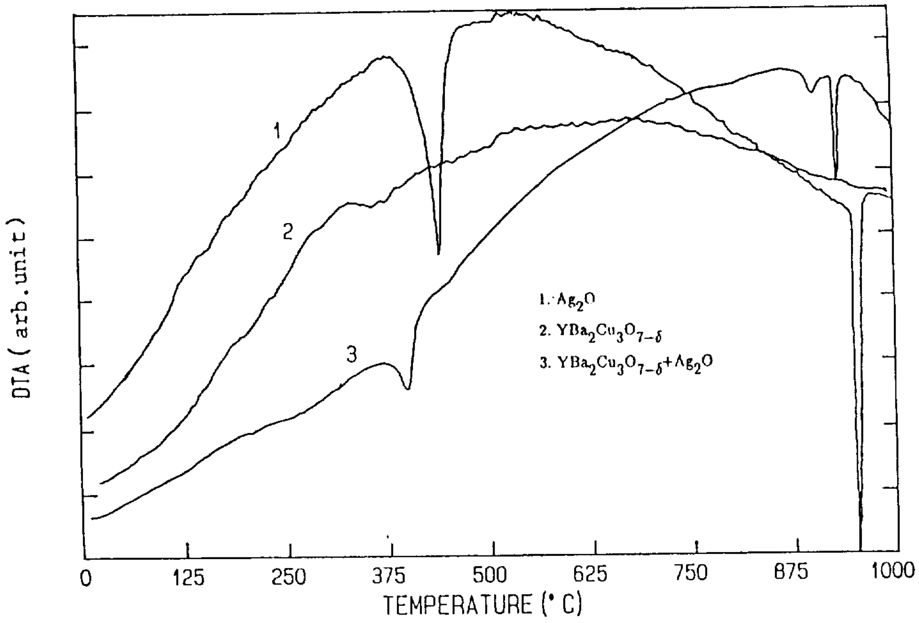

Figure 9. Differential thermal analysis (DTA) of Ag_2O (1), Y123 (2), and Y123/AgO (3). The heating rate is 5°C per minute.

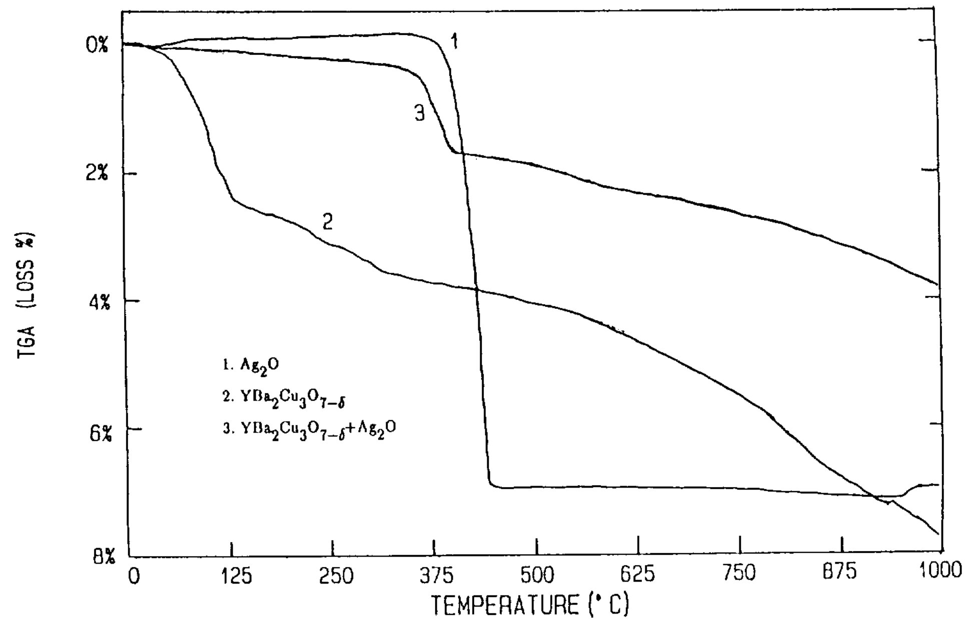

Figure 10. Weight loss of Ag_2O (1), Y123 (2), and Y123/AgO (3) at ambient temperature with a heating rate of 5°C per minute.

The reason for the decrease in melting temperature of the silver metal during the formation of the Y123/Ag_2O composite is not well understood at the present time. It is noted that an opposite result, showing the increase in the liquidus temperature was observed by Chen et al. in their study of the Yb123/Ag metal composite [23]. The 895°C reaction observed may be caused by the reaction of Ag metal with Y123. However, x-ray diffraction studies show that Ag does not permeate the lattice sites of the superconducting oxide. Electron microscopy indicates that Ag metals precipitated on the grain boundaries and filled in some voids [24]. The pinning characteristics of these composites strongly depend on their sample morphologies. The presence of large grains seems to be one of the key factors in the material showing unusual magnetic suspension effects. 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 centers which may then be responsible for the strong flux pinning observed.

Many oxygen diffusion studies [25-27] 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-controlled. The diffusion mechanisms are through the defects, which include the oxygen vacancies and the twinnings. In general, several activation energies have been observed corresponding to the out- and in-diffusions (depending on the oxygen concentrations). The higher activation energy for the out-diffusion process suggests that the surface barrier (which can be affected by the grain boundaries and impurities) plays an importat 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 limiting the oxygen out-diffusion process. This oxygen stabilization process likely may be the reason for the stabilization of 123 phase in the Ag-addition composites. The observation of Y123 phase stabilization in the mixed-phase Y-Ba-Cu-O [28] may also be caused by a similar process attributed to the presence of the insulating 211 phase. The strong oxygen dependence of the Y-Sr-Cu-O [29] system may also be related to this diffusion control step.

Although zero-resistance states under repeated thermal cycles have been observed by one of us (JTC) in the Y-Ba-Cu-O (5-6-11) mixed phase [2], we do not reproduce the same result in this study. On the other hand, diamagnetic-like anomalies are observed in both doped-with-Sr and undoped samples. The relatively small volume percent of the magnetic anomaly may be accountable for the absence of the resistive transitions. However, we do not claim the confirmation of the existence of superconducting phase with transition temperature above 200 K based on our results. More detailed measurements, such as magnetic field dependence, are needed to identify the origin of the observed anomalies.

SUMMARY

We have achieved the preparation of single-phase, high-T_c Y-Sr-Cu-O compound by the addition of a small amount of MoO_3 to the stoichiometry $YSr_2Cu_3O_{6+y}$. The presence of the Mo atom reduces the required reaction temperature to form the high-T_c phase. On the other hand, detailed thermal and microscopic studies of the Ag_2O-added Y123 composites, which exhibit an unusually large pinning characteristic, suggested that silver metal serves as the agent to clean out unwanted nucleation 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 serve as pinning centers 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. Based on this study, inclusion of "proper" metal oxides in the formation of high-T_c oxides will enhance the physical properties of the original compound. Diamagnetic-like anomalies were observed in the mixed-phase Y-Ba-(Sr)-Cu-O which have been treated in a low-temperature oxygenation process. Exact origin of the observed anomaly is yet to be determined.

ACKNOWLEDGEMENTS

The authors wish to acknowledge H. Chou, T.L. Kuo, and C.H. Lin of Columbia University; D.C. Ling, M.J. Wang, J.L. Lin, and K.M. Fan of Tsing-Hua University; and K.R. Ma and Dr. S.P. Chang for their contributions. We also thank Dr. H.C. Ku for his support in the thermal analysis work and Dr. L.J. Chen for the TEM work. The work at Tsing-Hua was supported by ROC National Science Council grants NSC79-0208-M007-95.

REFERENCES

1. Bednorz, J.G. and K.A. Muller, 1986, *Z. Phys.*, **B64**, 189.

2. Chen, J.T. et al., 1989, *Mod. Phys. Lett.*, **B3** (November).

3. Wu, M.K. et al., 1988, *Appl. Phys. Lett.*, **52**, 1915.

4. Peter, P.N. et al., 1988, *Appl. Phys. Lett.*, **52**.

5. Dinger, T.R. et al., 1987, *Phys. Rev. Lett.*, **58**, 2687.

6. Chaudhari, P. et al., 1987, *Phys. Rev. Lett.*, **58**, 2684;
   Jin, S. et al., 1988, *Appl. Phys. Lett.*, **52**, 2074.

7. Larbalestier, D. et al., 1987, *J. Appl. Phys.*, **62**, 3308.

8. Esteve, D. et al., 1987, *Europhys. Lett.*, **3**, 1237.

9. Yeshrun, Y. and A.P. Malozemoff, 1988, *Phys. Rev. Lett.*, **60**, 2202.

10. Palstra, T.T. et al., 1988, *Phys. Rev. Lett.*, **61**, 1662.

11. Muller, K.A. et al., 1987, *Phys. Rev. Lett.*, **58**, 1143.

12. Tinkham, M.K., 1988, *Phys. Rev. Lett.*, **61**, 1658.

13. Yeh, N.C. and C.C. Tsuei, 1989, *Phys. Rev.*, **B39**, 9708.

14. Wu, M.K. et al., 1988, Chemistry of High Temperature Superconductor II, ed. by D.L. Nelson and T.F. George, *ACS Symposium Series*, **377**, p. 181.

15. Huang, C.Y. et al., 1988, *Modern Phys. Lett.*, **B2**, 869.

16. Werner, P.E. et al., 1985, *J. Appl. Crystallogr.*, **18**, 367.

17. Mei, Y. et al., 1987, Novel Mechanisms of High Temperature Superconductors, ed. by V. Kresin and S.A. Wolf, p. 1041.

18. Oda, M. et al., 1987, *Jpa. J. Appl. Phys.*, **26**, L804.

19. Zhang, Q.R. et al., 1987, *Solid State Commun.*, **63**, 535.

20. Wu., M.K. et al., 1988, *Phys. Rev.*, **B37**, 9765.

21. Borofka, J.C. et al., 1989, Superalloys, Supercomposites and Superceramics, ed. by J.K. Tien, Academic Press, Inc., 237 pp.

22. Luo, H.L. et al., 1990, Superconductivity and Applications, ed. by Y.H. Kao and H.S. Kwok, Plenum Publishing Co.

23. Chen, H.S. et al., 1989, *Appl. Phys. Lett.*, **55**, 191.

24. Huang, C.Y. et al., 1989, *Mod. Phys. Lett.*, **B3**, 525.

25. Tu, K.N. et al., 1988, *Phys. Rev.*, **B38**, 772.

26. Fueki, K. et al., 1988, *Rev. Solid State Sci.*, **2**, 219.

27. O'Sullivan, E.J.M. and B.P. Chang, 1988, *Appl. Phys. Lett.*, **52**, 1441.

28. Wu, M.K. et al., 1987, *Phys. Rev. Lett.*, **58**, 908.

29. Chien, F.Z. and M.K. Wu, to be published.