

Processing and Property Evaluation of Metal Matrix Superconducting Materials

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ABSTRACT

Metal - superconductor (YBCO) systems have been prepared and characterized by resistivity, ac susceptibility and dc SQUID magnetic moment measurements. The silver composites showed superconducting transition for all the composites processed and the superconducting transition temperature tends to depend upon the concentration of the silver in the composite. Aluminum composites showed an unusual resistivity results with two transitions around 90 K and 120 K. The superconducting property of silver composites can be explained qualitatively in terms of the proximity theory that has been suggested for the low temperature superconductors.

Key Words : Processing, superconductivity, silver , aluminum / YBCO composites

INTRODUCTION

The present day technology of superconducting electrical systems requires cryogenic systems that are operational at liquid helium temperatures (temperature ~ 4 K). The new generation of ceramic superconductors that can superconduct at liquid nitrogen temperatures (temperature ~ 77 K) offer a potential and logistical advantage for both the system reliability and operational cost. Although, few superconducting component systems that can operate at liquid nitrogen temperatures were demonstrated, the full potential of these materials has not been exploited to date. This is essentially due to the fact that the materials are very hard brittle and difficult to form into net shaped components. In the open literature, many attempts were reported to improve the ductility of the high temperature superconducting materials by compositing them with silver or gold [1-2]. However, the phenomenology of the superconductivity in the metal - superconductor composite system has yet to be established. This project was undertaken in an attempt to develop a processing methodology for producing flexible superconducting wires / tapes with different metallic species and to model the mechanism of the superconductivity of these composite systems. In this paper, the experimental results obtained on 0 - 72 wt.% silver or aluminum composites and a possible model to explain the superconducting behavior of the composites is being presented.

EXPERIMENTAL PROCEDURE

The basic superconducting ceramic powder, $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, was prepared by solid state chemical reaction and the details of the powder synthesis were given elsewhere [3]. Although pure $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ powder has good superconducting properties, we found that the presence of excess copper oxide will improve the final composite properties. . Therefore, during the synthesis of the superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ powder, nearly 5 moles of excess copper oxide were added to the precursors. It should be pointed out that any reference in this paper for $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ represent the YBCO with 5 moles of excess CuO. From the micro structural characterization and chemical compositional analysis, it was found that the excess (5 moles) copper oxide remained unreacted with the

final $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ compound. However, a small amount of the excess CuO was reduced to metallic copper.

The as-synthesized $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ powder and commercial silver or aluminum powder were mixed thoroughly in dry state in a ball mill using zirconia balls for one hour. The powder mixture (silver or aluminum powder and $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ powder) was dry pressed into small 2.5 cm diameter discs under an applied pressure of 25,000 psi. The cold pressed discs were placed between two thick silver or aluminum plates and were sintered at 880°C (in the case of silver) and at 400°C (in the case of aluminum) for 30 minutes. During sintering the composite sample was also subjected to a constant axial load of 10,000 psi. The sintered discs were cooled in nitrogen and were cut into small 2 X 2 X 25 mm bars.

The micro structure of all samples was examined under both optical, scanning and transmission electron microscopes. The structural characterization of the superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ particles was carried out using x-ray diffraction. The electrical resistance of all samples was measured as a function of temperature using a dc four probe resistivity measurement unit, ac susceptibility apparatus and dc SQUID magnetometer.

RESULTS

The as-synthesized $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ powder has an average particle size of ~ 10 microns. The morphology of the particles resemble that of small pebbles or rocks. The density of the powder was found to be ~ 6.0 gcm^{-3} . Upon sintering the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ particles tend to sinter to form long elongated rods or plates. The sintered samples show a zero resistance (superconducting) transition and diamagnetic magnetic moment around 86 ± 4 K and has a crystal structure that represents the orthorhombic structure of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ and the detailed analysis of the results are given else where [4-6].

Silver/ $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ Composite System

Figure 1 shows typical electrical resistance versus temperature plots of pure silver and silver/ $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ composites. The zero resistance temperature versus silver concentration in the composites was determined from a number of resistance versus temperature plots similar to those shown in Figure 1 and the results are shown in Table 1. The results indicate that the silver composites show superconducting behavior throughout the entire concentration range investigated (0 - 72 wt.% silver). However, the zero resistance temperature (T_c) tends to decrease with an increase in the concentration of silver in the range 0 - 10 wt.% and 40 - 72 wt.%. The T_c remains nearly independent of silver concentration in the range 10 - 40 wt.%. In addition, the results also suggest that the normal state resistance of the composites decreases with an increase in the silver concentration.

The typical micro structure of silver composites obtained from polished sample surfaces is shown as a function of silver concentration in Figure 2. The results suggest that the distribution of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ in silver matrix is very uniform and the degree of uniformity increases with an increase in the concentration of silver in the composites. In order to model the superconducting property of the composites in terms of the separation distance between two $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ particles, a number of optical photomicrographs representing the micro structure of all composites were obtained. From the micro graphs the average particle size was estimated and the results are given in Table 1. Assuming that the particles are spherical, and are not connected in a 3 dimensional network, the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ particle - particle separation distance was estimated as a function of silver concentration and the results are also shown in Table 1. The results suggest that the particle size of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ increases with an increase in the silver concentration initially in the range 0 - 10 wt.%. For the silver concentration above 10 wt.% this trend is reversed. The results also indicate that the separation distance increases with an increase in the silver concentration.

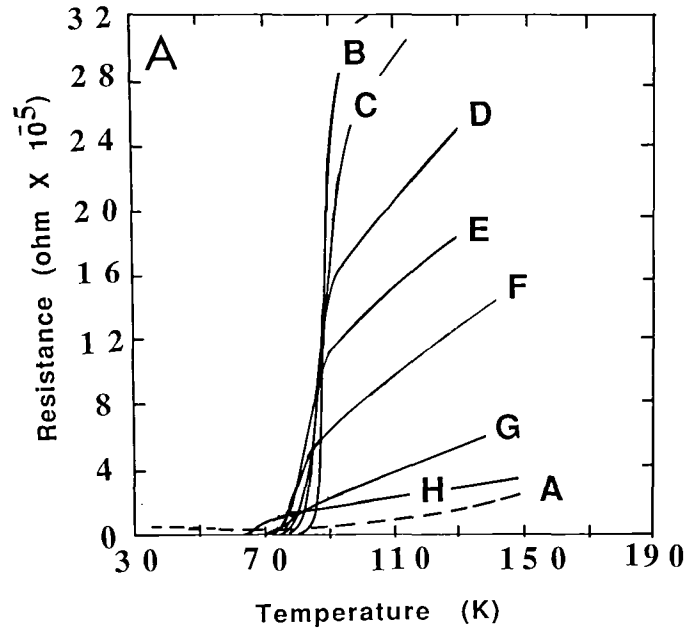


Figure 1. Electrical resistance versus temperature profiles of commercial silver / $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ composites. Silver concentration (A) 100, (B) 10, (C) 20, (D) 30, (E) 40, (F) 50, (G) 60 and (H) 63.6 wt.%. The actual applied current 20 milli amp.

Table 1. The superconducting transition temperature (T_c), the normal state resistance measured at 100 K (R_{100K}), the average $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ particle size and the particle - particle separation distance measured for sintered silver / $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ composites as a function of silver concentration of the composite.

Silver conc. (wt. %)	T_c (K)	R_{100K} (ohm X 10^{-5})	particle size (micron)	separation distance (micron)
0	86 ± 4	2000	35 ± 4	
2	88 ± 4	800	35 ± 4	0.2
5	90 ± 2	300	40 ± 4	0.5
10	82 ± 2	30	45 ± 4	1.0
20	80 ± 2	25	40 ± 4	4.0
30	80 ± 2	16	37 ± 4	8.0
40	82 ± 2	12	25 ± 2	15.0
50	76 ± 2	6	23 ± 2	22.0
55	70 ± 2	4	20 ± 2	26.0
60	68 ± 2	3	18 ± 2	30.0
63.6	62 ± 2	2	16 ± 2	32.0
72.2	62 ± 2	1	14 ± 2	37.0

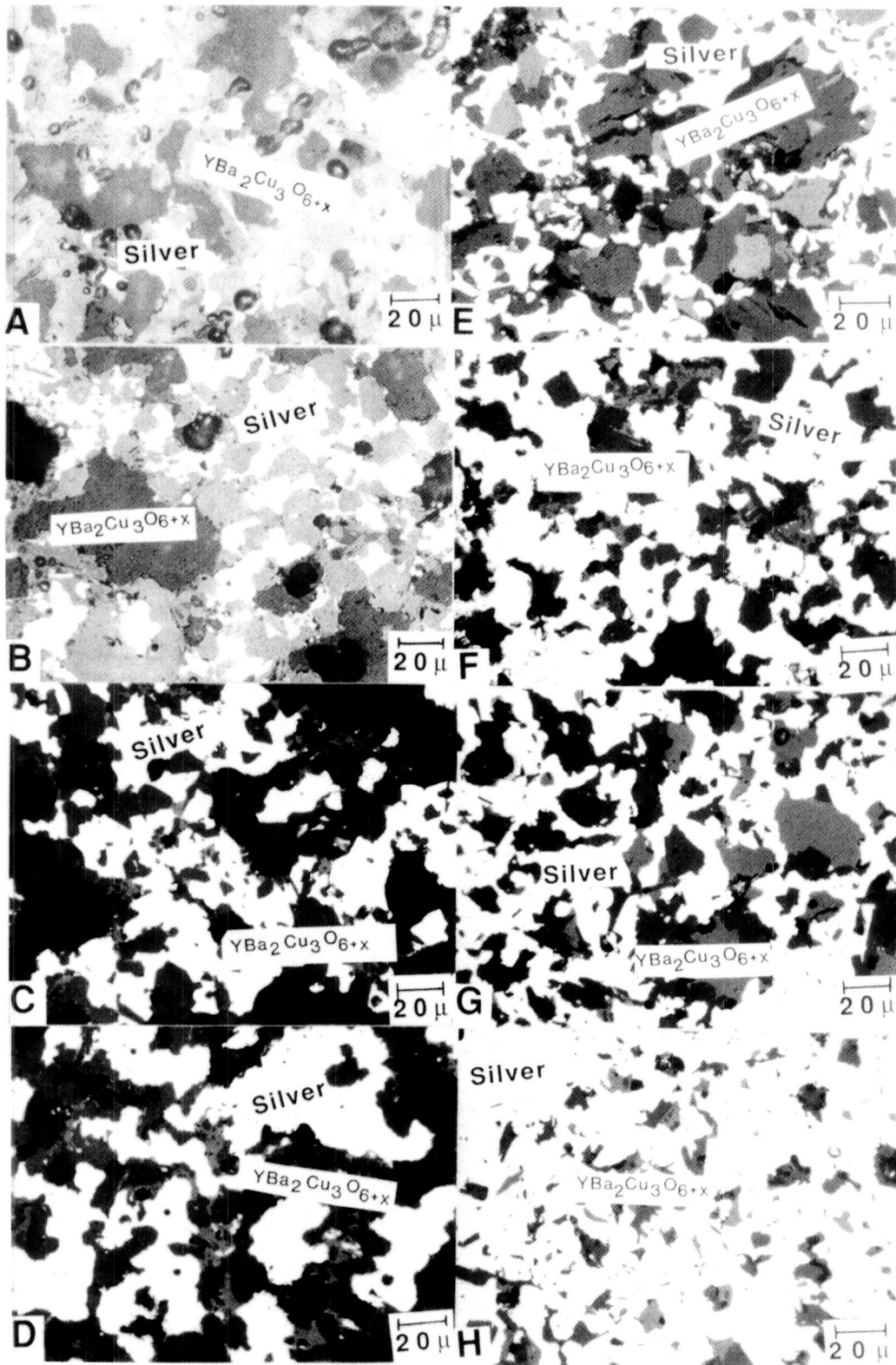


Figure 2. Typical micro structure of polished silver / $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ composites. Silver concentration (A) 10, (B) 20, (C) 30, (D) 40, (E) 50 (F) 60 (G) 63.6 and (H) 72 wt.%.

In order to understand the mechanism of the superconducting behavior of the silver composites, the proximity theory was applied. According to the classical proximity theory of low temperature superconductors, the extrapolated length for the diffusion of "Cooper pairs" from superconductor to the non superconducting metallic conductor is ~ 0.1 microns. However, the measured separation distance for the silver superconductors range from 1 - 37 microns. It is therefore, evident from the measured separation distance data that the proximity theory of low temperature superconductors is not applicable to the high temperature superconducting silver composite system. However, an effort was made to estimate the extrapolated length of diffusion of the superconducting electrons into the silver matrix using the Deutscher and de Gennes model that was suggested for low temperature superconducting materials [7].

Although the high temperature superconducting materials have been established during the past five years, the actual mechanism of the superconducting behavior of these materials, in particular in composite systems, has not been understood. The behavior of composites in low temperature superconductors has been explained in terms of the diffusion of "Cooper pairs" from superconducting material into the non superconducting metallic conductor.

In general it has been suggested by Deutscher and de Gennes that the superconducting transition temperature of the composite system (T_{cc}) can be related to the T_{cs} of the pure superconductor and the extrapolated length of diffusion of superconductivity from superconductor to the metal as

$$T_{cc} = T_{cs} - A (1/D_s + B)^2 \quad \dots\dots\dots(1)$$

where A is a constant, D_s is the thickness of the superconducting layer and B is the extrapolation length for the diffusion of superconductivity from a superconductor to the metal.

As a first attempt to explain the superconductivity of the metal matrix composite system, we assumed that the process of the diffusion of superconducting electrons from the superconductor through the non-superconducting metal matrix is similar to that of the diffusion of the electric charge from a polarized oxide surface into the liquid phase and form an electrical double layer at a solid - liquid interface. To analytically model the superconducting behavior, we also assumed that the penetration of the superconducting electrons into the non-superconducting metal matrix constitutes two different regions. In the first region, the electrons form a fixed boundary which is formed due to the leakage of the "Cooper Pairs", a process similar to that of the diffusion in low temperature superconductors (typical distance ~ 0.1 micron). The second region constitutes the superconducting electron diffusion into the metal. Assuming that the electron distribution in the diffused boundary follows Poisson - Boltzmann equation, the superconductivity of the composite can be represented as a function of concentration of the superconducting phase and the extrapolation length for the diffusion of the superconductivity in the simplified final form as

$$(T_{cc} / T_{cs}) = A \exp (- CB) \quad \dots\dots\dots(2)$$

where A is a constant that represents the "Cooper Pair" leakage distance into the non-superconducting metal

$$C = ((1 - f_v) / f_v) \text{ where}$$

f_v is the volume fraction of the superconducting phase, $(1-f_v)$ is the volume fraction of the non superconducting phase and

B is the diffusional distance for the superconducting electrons into the metal.

The above expressions not only can be applied to test the validity of the proximity theory of low temperature superconductors for high superconducting metal matrix composites, but also can be used for the determination of the extrapolated length of the diffusion of superconductivity from the superconductor

to the metal matrix from the information of the superconducting transition temperature of a composite (T_c) measured as a function of composite composition.

The results of the modeling indicated that the present " T_c versus Silver concentration" data on silver composites can be normalized on the Deutscher and de Gennes's expression (equation 1), over the entire concentration range investigated (i.e. silver concentration range 10 - 72 wt.%). However, the model predicts that the maximum distance that the superconducting electrons can penetrate into the matrix will be ~ 6 microns. A similar analytical treatment of the measured data with the our model reveal that the over all behavior of the silver composites (over the concentration range 10 - 72 wt.%) cannot be normalized into one generalized expression. However, the observed superconducting behavior of silver composites fall into two categories (viz. composites containing 10 - 40 wt.% silver; and $T_c \geq 60$ K) and composites containing 40 - 72 wt.% silver; and $T_c \leq 60$ K). In addition, the present model predicted the diffusional depth for superconducting electrons to range from 0.28 - 2 microns. These results indicate that the predicted extrapolated lengths for the diffusion of superconductivity are too low compared to the measured separation distance (range 1 - 37 micron).

The above disagreement may arise due to several factors. For example, (1) the above models assume that the superconducting phenomena in these materials is similar to that of low temperature (liquid helium temperature) superconductors; (2) the separation distances were estimated taking into consideration only the large superconducting $YBa_2Cu_3O_{6+x}$ particles that were accessible for the estimation of particle size (it is possible that a large fraction of very fine (<0.1 micron) size particles that are often distributed throughout the matrix may account for smaller separation distance between any two adjacent superconducting $YBa_2Cu_3O_{6+x}$ particles); and (3) the model does not take into account the three dimensional effect of the particle - particle separation.

Aluminum/ $YBa_2Cu_3O_{6+x}$ Composite System

The typical electrical resistance versus temperature plots of pure aluminum and aluminum / $YBa_2Cu_3O_{6+x}$ composites indicate that all aluminum composites show typical metallic behavior . However, if the concentration of the aluminum in the composites is ~ 60 wt.%, the composite system shows two transitions of the electrical resistance [4]. Figure 3 shows a typical plot of the electrical resistivity of 60 wt.% aluminum composite represented as a function of temperature. The magnetic moment versus temperature profiles of the same sample measured using dc SQUID magnetometer and ac susceptibility method are given in Figures 4 and 5 respectively. The results suggest that the composite shows two transitions around 90 and 120 K respectively. In addition the results also suggest that the composites behave as diamagnetic below 86-88 K. Although, the magnetic moment data does not suggest the presence of diamagnetism above 88 K, it provides ample evidence that the paramagnetic component of the aluminum matrix is being opposed. Such a lowering of the paramagnetic component of the matrix (aluminum) leads to the speculation that a new and higher temperature superconducting phase may be present in these composites. From micro structural characterization of the composites using high resolution electron microscopy, we found that a thin (thickness 10 - 20 nm) layer of new phase is present at the interface between the aluminum matrix and $YBa_2Cu_3O_{6+x}$. No such interfacial film formation and or growth was observed in the silver composites. The detailed analysis, stoichiometric composition and the structure of this new interfacial phase will be reported in the future.

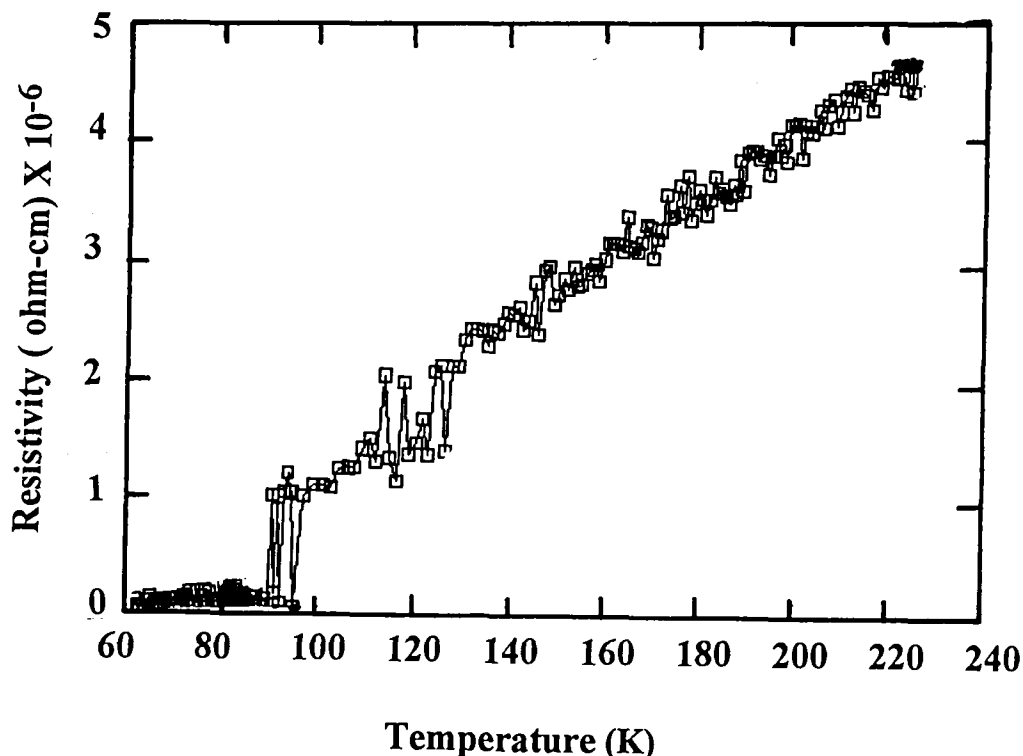


Figure 3. Electrical resistivity versus temperature plot obtained from 60 wt.% aluminum / 40 wt.% $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ composite. Actual applied current 20 milli amp.

DISCUSSION

The high temperature superconducting ceramic materials are expected to provide a suitable and cost effective alternative to the presently used metallic superconductors, such as NbTi and Nb_3Sn that are being operated at liquid helium temperatures (~ 4 K). However, for the large scale processing of the ceramic materials into ductile forms remains unresolved. Although, processing via composite fabrication is the possible practical solution to overcome the brittle nature of the ceramic superconductors, both the superconducting transition temperature (T_c) and the critical current capacity of the ceramic superconductor (J_c) has to be maintained. In addition, the added metallic species should not alter the stoichiometry of the superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ ceramic material. Both silver and gold may satisfy all the above requirements, however, based on the economical criteria for large scale manufacturing the noble metal based composite systems are not very practical. Aluminum is a better substitute for the noble metals. It is because (i) the aluminum is readily available and is very cost effective; (ii) from the present investigation it has demonstrated that the aluminum based YBCO composites also behave as superconductors at liquid nitrogen temperature. However, it has to be recognized from the present investigation, aluminum based superconducting composite material technology requires further refinement of the processing as well as a better understanding of both the macro- and micro- structural properties of the composites.

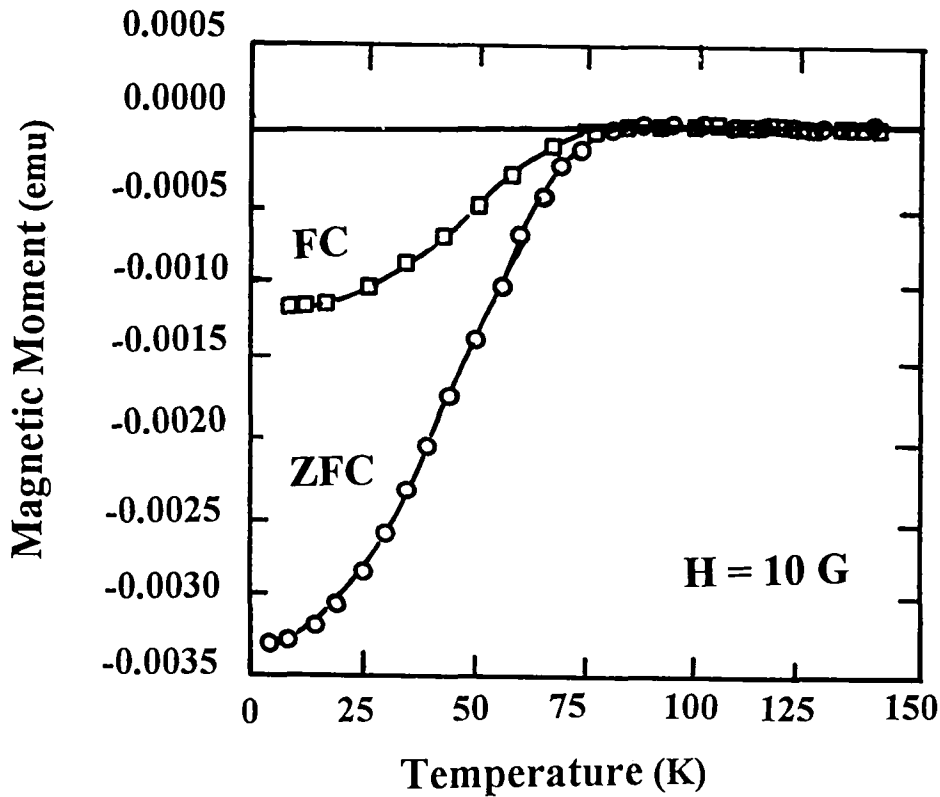


Figure 4. Magnetic moment versus sample temperature profiles of 60 wt.% aluminum / 40 wt.% $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ composites measured using SQUID. FC Field cooling and ZFC zero field cooling.

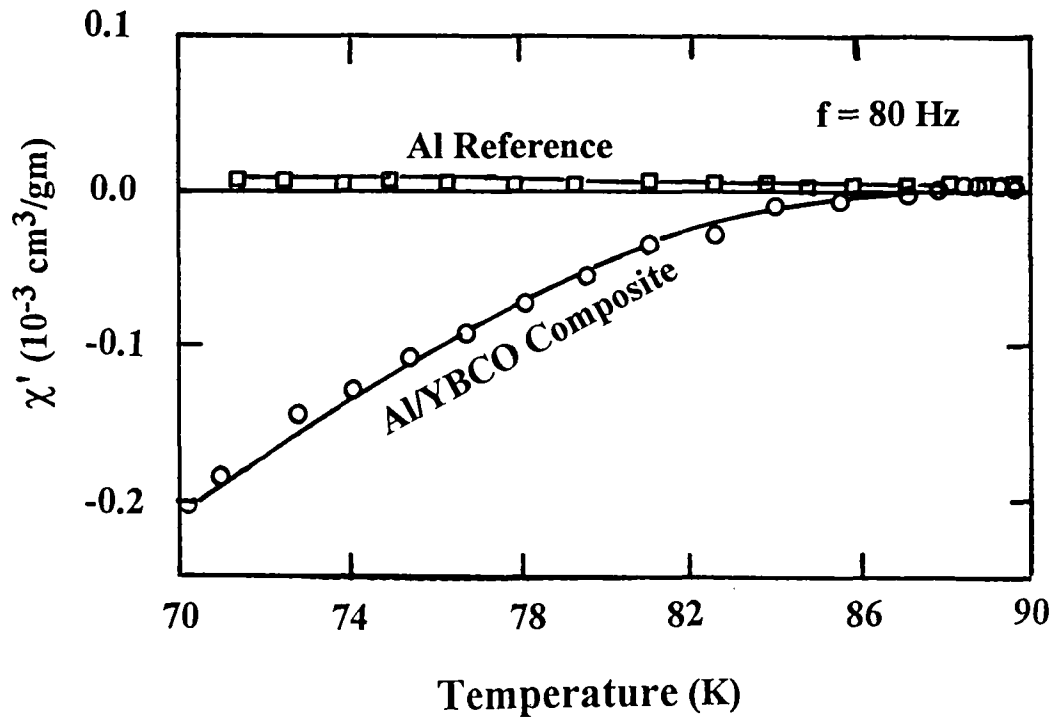


Figure 5. Magnetic moment versus sample temperature profiles of pure aluminum and 60 wt.% aluminum / 40 wt.% $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ composites measured using ac susceptibility apparatus..

CONCLUSION

From the present investigation the following conclusions can be derived :

1. The addition of silver to the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ does not affect the superconducting behavior of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ over the entire concentration range of 10 - 72 wt.% silver. However the T_C decreases from T_C 77 K to 60 K with an increase in the concentration of silver above 40 wt.% to 72 wt.%.
2. Although, the theoretical models based on classical proximity theory of low temperature superconductors can predict the lowering of T_C with the increase in the concentration of silver in the composites, the extrapolated length for the diffusion of superconductivity from $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ into silver matrix predicted from the theory are not agreeable with the experimentally determined superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ particle - particle separation distance.
3. 60 wt. % Aluminum/ $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ composites behave as superconductors and these composites show two transitions around 90 and 120 K respectively.

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