Superconducting Au-$YBa_2Cu_3O_7$ composites

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Superconducting Au-$YBa_2Cu_3O_7$ composites have been fabricated over a Au volume fraction range of 0–100%. Microstructure measurement indicates that Au and $YBa_2Cu_3O_7$ form well-separated phases. The superconducting transition temperature T_c was found unaffected by the presence of Au. The composites exhibit low normal state resistivity and much improved ductility. The results suggest that Au is an excellent metal host for making ultrafine $YBa_2Cu_3O_7$ granular solids.

The newly discovered high T_c superconducting ceramic oxide ($YBa_2Cu_3O_7$) has attracted unprecedented research activities worldwide.[1] However, $YBa_2Cu_3O_7$ granular composite solids, in which small superconducting particles are embedded in either a metal or an insulator host, have not yet been successfully fabricated. Superconducting granular solids[2] are a very useful medium in the studies of finite-size effects on superconductivity, thermal fluctuation effects, etc. Technologically, metallic superconductor composites offer the attractive features of a current shunt, reduced resistivity, improved mechanical properties, and environmental resistance. However, the fabrication of high T_c superconducting composites faces a major obstacle. The superconducting properties depend critically on the composition, structure, and proper oxygen content.[3,4] The oxides need to be processed above 900 °C in an oxygen atmosphere in order to achieve these properties. Almost all metal hosts would oxidize severely if subjected to such an adverse environment. In addition, the superconducting oxide will itself react with most metals or insulators, resulting in deteriorated superconducting properties or loss of superconductivity all together.[5]

In this work we will describe the fabrication of a high T_c superconducting gold-$YBa_2Cu_3O_7$ composite system that can survive all of the stringent processing conditions. In this system a much lower normal-state resistivity and improved ductility have been achieved, while the high T_c superconducting properties have been retained. The presence of Au increases the lattice parameters substantially, but is not seen to compromise the superconducting properties notably. The realization of this composite system opens the way to make ultrafine $YBa_2Cu_3O_7$ granules useful for fundamental studies. Our study also suggests the suitability of using Au buffer layers for $YBa_2Cu_3O_7$ thin-film devices.

Composite samples were prepared by mixing the $YBa_2Cu_3O_7$ powder with desired quantities of fine gold powder (99.9%, 325 mesh). The mixture was cold pressed into a thin disk and fired at 950 °C in flowing O_2 for at least 15 h before slow cooling at a rate less than 2 °C/min. The resulting disks were much less brittle than the pure superconducting material.

Figure 1 displays a few representative scanning electron micrographs; the dark regions are $YBa_2Cu_3O_7$ grains and the white regions the Au grains. It is obvious that separated phases of Au and $YBa_2Cu_3O_7$ have been formed. The Au at low Au volume fraction is seen to form isolated grains averaging from 1 to 3 μm in size in a continuous medium of $YBa_2Cu_3O_7$. At higher Au volume fractions, the situation is reversed; the Au is seen to coalesce into a continuous medium with inclusions of $YBa_2Cu_3O_7$. The superconducting oxide now forms isolated grains, with grain sizes ranging from <0.1 to about 5 μm.

Resistivity and magnetization measurements, sensitive to different aspects of the microstructures, were used to determine the superconducting properties. In resistivity measurements the temperature at which the resistivity becomes zero (T_c^{zero}) is dependent on the macroscopic connectivity of the superconducting material. Magnetic measurements, being contactless in nature, are not sensitive to the sample macrostructure; they provide information that is intrinsic to the material under study. The superconducting transition temperature T_c^{SQUID} is marked by the appearance of the Meissner effect.

Standard four-probe resistivity measurements were performed on samples of regular geometry. Magnetization mea-

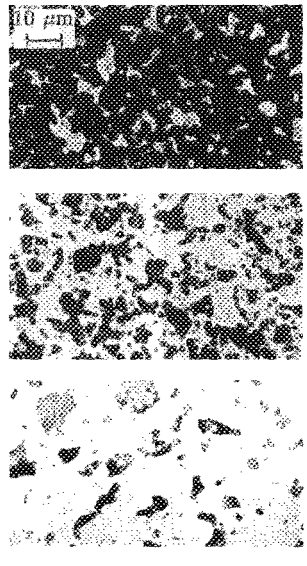

FIG. 1. SEM micrographs of Au-$YBa_2Cu_3O_7$ composites with Au volume fractions x_{Au} = 22.2% (top), 55.0% (middle), and 82.2% (bottom). The dark regions are $YBa_2Cu_3O_7$ grains and the white regions the Au grains.

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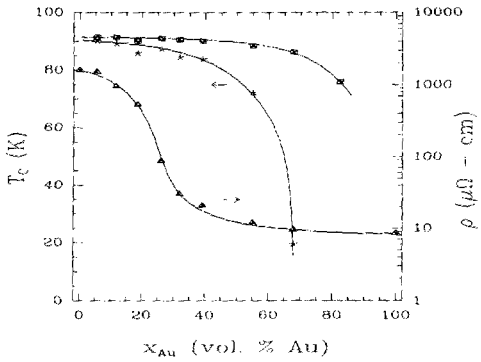

FIG. 2. Superconducting transition temperatures T_c^{SQUID} (squares) and T_c^{zero} (stars) as functions of Au volume fraction x_{Au}. T_c^{zero} remains greater than 85 K until the superconducting material no longer percolates. The room-temperature resistivity ρ (297 K) (triangles) drops to 1/100 of its original value at the Au percolation concentration ($x_{Au} = 23\%$), well before T_c^{zero} is reduced.

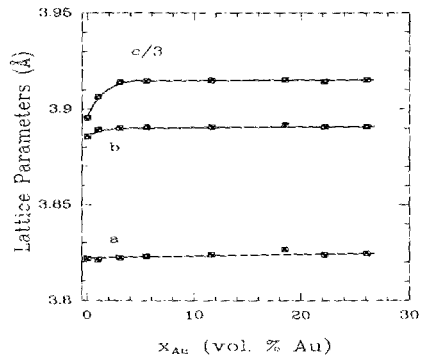

FIG. 4. $YBa_2Cu_3O_7$ lattice parameters as a function of Au volume fraction. The structure is orthorhombic over the entire composition range. The c and b axes expand 0.56% and 0.12%, respectively, in the range $0 < x_{Au} < 3\%$. Error bars are smaller than the symbol size.

surements were performed in a SQUID magnetometer. Figure 2 displays the variation of T_c^{zero} and T_c^{SQUID} with Au volume fraction (x_{Au}). The values of T_c^{SQUID} remain high (> 85 K) for Au volume fractions as high as 70%. Clearly, the presence of Au has a negligible effect on the superconducting transition temperature. The resistive transition temperature T_c^{zero} shows a different behavior. It is above 85 K for Au volume fractions up to $x_{Au} = 40\%$ and then drops toward zero rather abruptly for $x_{Au} \sim 70\%$, which is taken to be the critical volume fraction for connection of the superconducting material (i.e., the superconducting percolation threshold).

Because the resistivity of $YBa_2Cu_3O_7$ is about two orders of magnitude higher than that of Au, the resistivity (ρ) in the normal state is a measure of the connectivity of the Au in the composite system. Consequently, the value of ρ will exhibit percolation behavior. Indeed, as shown in Fig. 2, the room-temperature resistivity ρ (297 K) shows a sharp drop of two orders of magnitude at the Au percolation threshold of $x_{Au} \sim 23\%$.

The hardness of the samples was measured on a TECO M-400 Vickers Microhardness Tester. Figure 3 displays the Vickers hardness number (VHN) of these Au-123 composite materials as a function of Au content. The hardness, which is inversely related to the ductility in most materials, is seen to drop almost two orders of magnitude (from a VHN of ~ 475 to ~ 25) starting at a Au volume fraction of $x_{Au} \sim 20\%$.

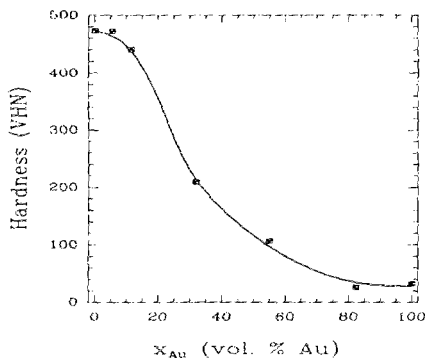

FIG. 3. Vickers hardness number (VHN) for the Au-$YBa_2Cu_3O_7$ composite materials.

For Au concentrations in the range of $20\% < x_{Au} < 60\%$ such that both the Au and $YBa_2Cu_3O_7$ are percolating, the composite material performs as a high T_c superconductor while exhibiting dramatically reduced resistivity and improved ductility. The resistivity and hardness at $x_{Au} = 40\%$ are, respectively, 0.02 and 0.3 times the values for the pure superconducting ceramic oxide; yet T_c^{zero} is 95% of the original value and T_c^{SQUID} is unchanged.

X-ray diffraction spectra were obtained from the samples with a Philips APD 3720 automated x-ray diffractometer. Each of the samples was exactly two phase: Au and orthorhombic $YBa_2Cu_3O_7$. However, as shown in Fig. 4, there is a substantial expansion of 0.56% in the c axis in the region $0 \leqslant x_{Au} \leqslant 3\%$ and a slight expansion of 0.12% in the b axis. The a axis remains essentially unchanged.

There are a few possible explanations for this expansion, but some of them can be immediately eliminated. The stress-induced lattice expansion casued by the unmatched thermal expansion constants of the two materials is unlikely, because the lattice parameters of the Au remain unchanged. Moreover, the lattice expansion observed is too large to be caused by stress. Neither is the expansion caused by the loss of the oxygen content in the orthorhombic structure. Cava *et al.*[4] have shown that in the $YBa_2Cu_3O_{7-\delta}$ system, c expands with increasing δ. The change of c with δ is approximately linear and can be characterized by a slope of $(1/c)/(\Delta c/\Delta\delta) \sim -1.37\%$/O atom. In the composite system, this would correspond to $\delta \simeq 0.4$. Such a level of oxygen removal is not possible if the material is to remain superconducting at temperatures above 85 K.[2,6]

We are therefore led to the conclusion that the lattice-wide expansion is caused by Au entering the orthorhombic structure. As shown in Fig. 4, the c-axis expansion occurs in the region $0 \leqslant x_{Au} \leqslant 3\%$, beyond which it remains unchanged. This phenomenon can be best explained by the existence of a Au solubility region in the $YBa_2Cu_3O_7$ materials, beyond which Au precipitates into separated phases. Further investigation of this anomalous lattice expansion is underway.

Most interesting of all, the superconducting transition

temperature is not affected at all by such a large expansion of the c axis, which is intimately related to the coupling between the Cu-O_2 planes and the Cu-O chains. It is known that the T_c of $YBa_2Cu_3O_7$ is sensitive to external pressure,[7,8] with a rate of $dT_c/dP = 0.043$ K kbar^{-1}. The incorporation of Au, in effect, induces a uniaxial stress along the c axis. The lack of sensitivity of T_c to such stress deserves further study, since it may provide valuable information as to the anisotropic electronic structures and the interlayer couplings.

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