Study on properties and microstructure of $YBa_2Cu_3O_{7-\delta}$-Ag_x composite superconductors prepared by sol–gel method

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The relation between the microstructure and properties of $YBa_2Cu_3O_{7-\delta}$–Ag_x composite superconductors prepared via sol–gel processing has been studied. Optical microscopy, SEM and TEM analyses indicated that Ag-doped samples were dense, with small and regular grains and narrow spaces between grains. Ag particles were distributed homogeneously in samples and these could increase their J_0 values. The mechanisms of the effect of Ag doping on the superconducting properties and microstructure of samples were hindrance of the movements of grain boundaries and metallization of grain boundaries. However, too much Ag doping would weaken the coupling among superconducting grains and induce J_0 to decrease. The experimental results confirmed these ideas.

1. Introduction

The study of $YBa_2Cu_3O_{7-\delta}$ superconductors has been very active since the oxide ceramic superconductors whose T_c values are above liquid nitrogen temperature (77 K) were discovered [1–4] because of their possibly great application in industry, instruments etc. Bulk, wire and film are the main forms in which people utilize these high-T_c superconductors. Now, the properties of superconducting film are satisfactory [5] but for the other forms this is not so. New methods such as MTG [6], QMG [7] and PMP [8] have been used to prepare bulk $YBa_2Cu_3O_{7-\delta}$ superconductors and some progress, especially in getting high J_c, has been made [6–8]. However, these processes are very complicated and expensive, and it is difficult to prepare large or long bulk and wire samples. At the same time, the relationship between the properties and microstructure has not been understood very well. Great efforts have to be made in order to realize these high-T_c superconductors' practical use.

The influences of material microstructure on superconducting property are great [9]. It is an important task to study the relationship between the properties and microstructure of superconductors, so as to find an effective method to obtain a better microstructure possessing good properties. Sol–gel processing can yield superconductors with better properties [10]. At the same time, the superconducting properties can be improved greatly by adding silver to the $YBa_2Cu_3O_7$ phase [11].

In this paper, we studied the relationship between the properties and microstructure of $YBa_2Cu_3O_{7-\delta}$–Ag_x composite superconductors prepared by the sol–gel method. The mechanisms of the effect of Ag addition on the superconducting properties and microstructure of the composite are also discussed.

2. Experimental procedure

Fig. 1 is the flow-chart for preparation of $YBa_2Cu_3O_{7-\delta}$–Ag_x composites. High-purity nitrate salts of yttrium, barium, copper and silver were used as starting materials. The required amount of each nitrate salt was dissolved in distilled water. The individual nitrate solutions were mixed, then mixed with citric acid in a uniform solution. One gram-equivalent of citric acid was used for each gram-equivalent of metal. This was the minimum amount of citric acid needed to bind all the metal ions. A little ethylene glycol was used to increase the viscosity of the solution and accelerate the change of the mixed solution to a sol. Ammonia was used to adjust the solution to pH $\simeq$ 6.8, so as to ensure that no precipitation occurred. The water was evaporated from the solution on a hotplate at about 75 °C. The solution became viscous after 8 to 12 h. The viscous liquid was then heated in a vacuum oven at 85 °C. An amorphous solid was obtained after 4 to 6 h. The solid precursors were then fired to 300 °C to form the ultrafine powder precursors of the desired compound. The powders became $YBa_2Cu_3O_{7-\delta}$–Ag_x upon further pyrolysis at about 900 °C. The $YBa_2Cu_3O_{7-\delta}$–Ag_x powders were pressed at 60, 100 and 200 MPa, respectively, into pellets 12 mm in diameter, then annealed for 10 h at 950 °C in air, followed by slow cooling to room temperature.

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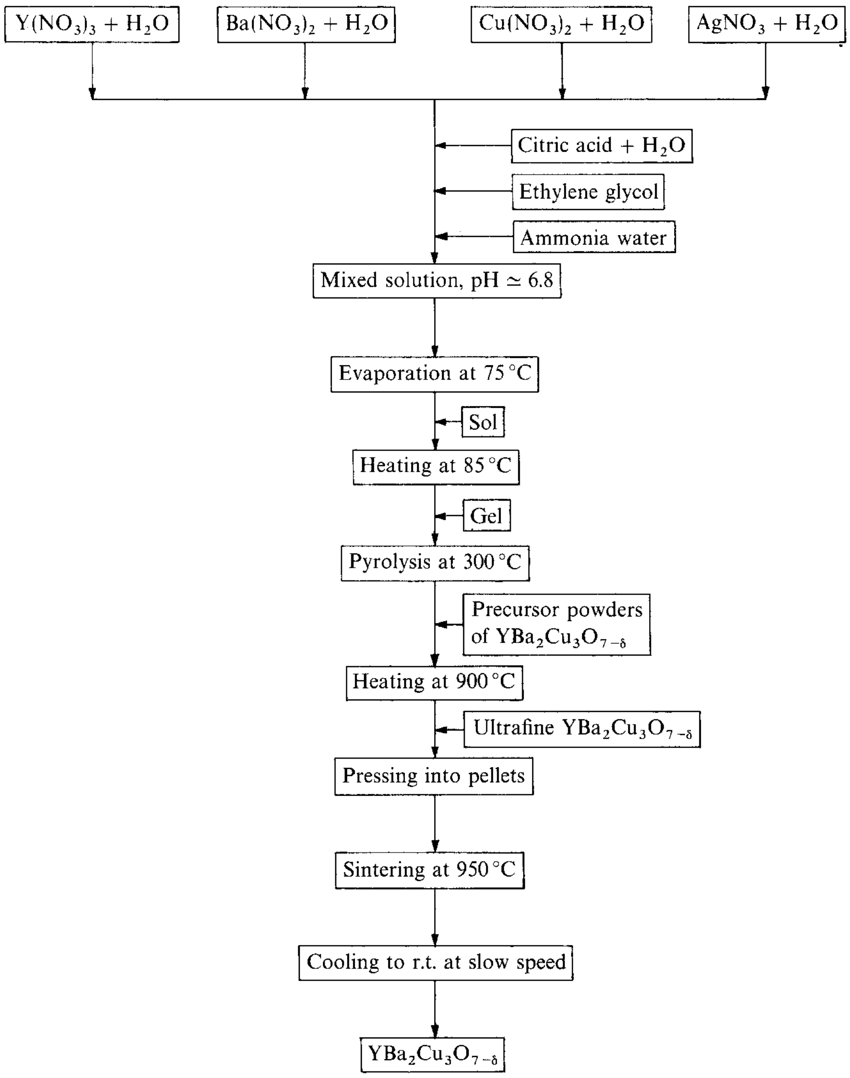


Figure 1 Flow-chart for preparation of $YBa_2Cu_3O_{7-\delta}$–Ag_x composite.

For T_c and J_c measurement the sintered pellets were sectioned into pieces of I form. The four-probe standard method was used to measure T_c and J_c (zero magnetic field, 77 K). The bulk density was measured according to the Archimedes principle. For microstructural analysis, the newly developed pellets were sectioned into small pieces which were mounted in a cold-setting resin and subsequently ground and polished using standard techniques. Microstructural characterization of the polished surfaces was performed by optical microscopy (OM) (Zeiss Neophot 21) using transmissed light. The fracture surfaces of samples were examined with scanning electron microscopy (SEM) (Akashiseisakusho SX-40) using back-scatteral electron imaging. Thin specimens obtained by argon-ion sputtering were observed by transmission electron microscopy (TEM) (Hitachi H-600SEM/EDX), and elemental analysis was performed on selected areas with an energy-dispersive X-ray analyser (EDX).

3. Results and discussion

Measurement of T_c showed that the sample containing 70 vol % Ag showed a superconducting transition (to zero resistance), but the specimen containing 80 vol % Ag did not. So long as the superconducting phase $YBa_2Cu_3O_{7-\delta}$ can form a continuous superconducting network, the influence of Ag content on the T_c of $YBa_2Cu_3O_{7-\delta}$ is not obvious. Fig. 2 gives the T_c values for specimens containing different amounts of Ag. The changes of J_c (zero magnetic field, 77 K) with Ag content are given in Fig. 3. J_c values of all specimens containing Ag were higher than for "pure" $YBa_2Cu_3O_{7-\delta}$ in our experimental range. The specimen containing 20 vol % Ag had the highest J_c. When the Ag content was more than 20 vol %, J_c decreased as the Ag content increased. Fig. 4 shows the change of relative density of samples shaped at different pressures and Ag content (the theoretical

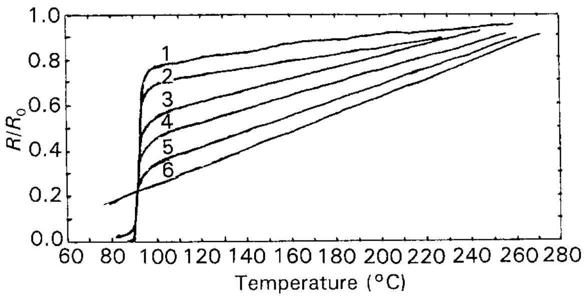


Figure 2 R–T curves of specimens of $YBa_2Cu_3O_{7-\delta}$–Ag_x: volume percentage of Ag (1) 0, (2) 10, (3) 30, (4) 50, (5) 70, (6) 80.

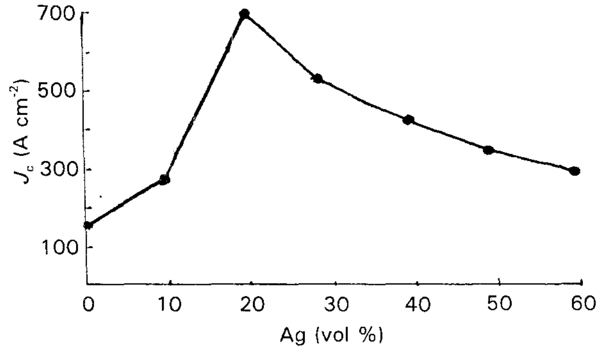


Figure 3 Dependence of J_c on amount of Ag for specimens of $YBa_2Cu_3O_{7-\delta}-Ag_x$.

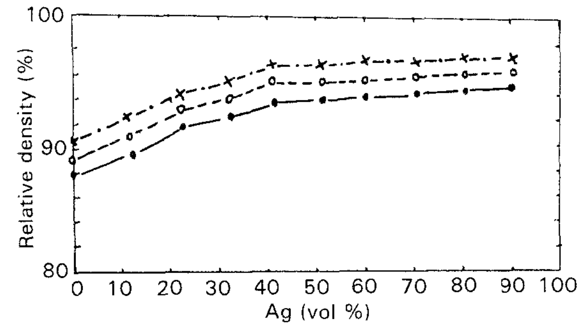


Figure 4 Dependence of relative density on amount of Ag of samples pressed at (●) 60 MPa, (○) 100 MPa, (×) 200 MPa.

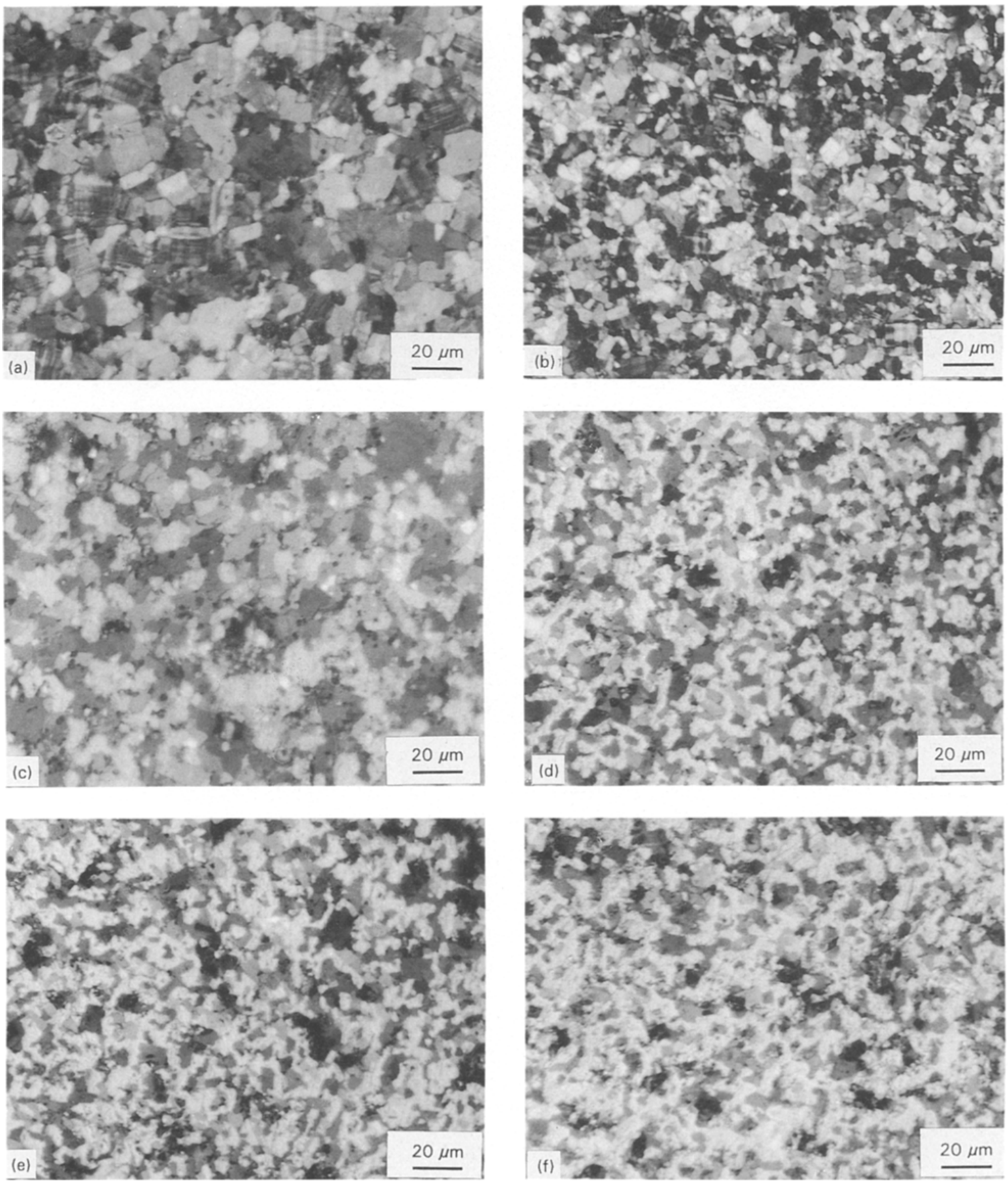


Figure 5 OM photographs of polished surfaces of samples: volume percentage of Ag (a) 0, (b) 10, (c) 20, (d) 30, (e) 40, (f) 60.

densities of silver and $YBa_2Cu_3O_{7-\delta}$ are 10.5 and 6.3 $g\,cm^{-3}$, respectively). It is clearly in Fig. 3 that the relative density of all samples containing Ag increased in different ranges, but this effect became less and less obvious as the Ag content reached a higher volume ratio. At the same time, the higher the shaping pressure was, the denser the samples. It is easy to understand this phenomenon.

Fig. 5 shows OM photographs of $YBa_2Cu_3O_{7-\delta}$–Ag_x. For a "pure" sample (Fig. 5a) the plate-like grains (high-T_c superconducting phase) grew very well in irregular forms; the grain sizes covered a wide range, the grain junctions were compact, and the grains were strongly twinned without obvious orientation along the c axis of the orthorhombic structure phase. A few pores existed in the sample. The overall morphology of this specimen seemed loose. As for $YBa_2Cu_3O_{7-\delta}$–Ag_x samples (Fig. 5b–d), on the contrary, the grains were smaller and monodisperse, and the edges of grains were not obvious. The overall morphologies of specimens containing Ag were denser than that of the sample containing $YBa_2Cu_3O_{7-\delta}$ phase alone. Changes of grain size, form and density of specimens were obvious with the change of Ag content. When the Ag content was less than 30 vol% the $YBa_2Cu_3O_{7-\delta}$ phase grew nearly perfectly. When the Ag content was more than 30 vol% it did not grow well and there were some embryo crystals of $YBYBa_2Cu_3O_{7-\delta}$ phase, but the density increased. Metallic silver was located homogeneously in grain

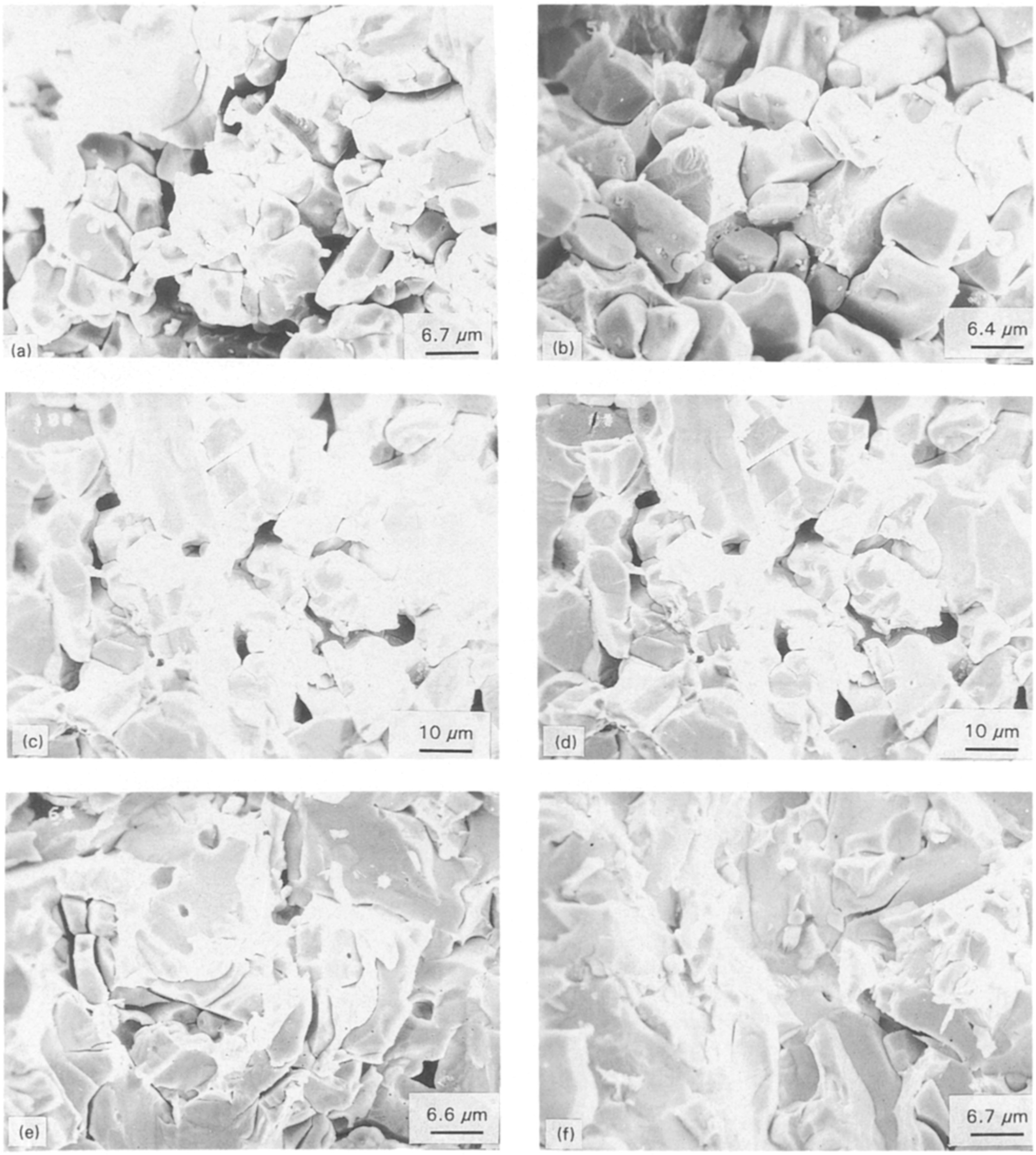
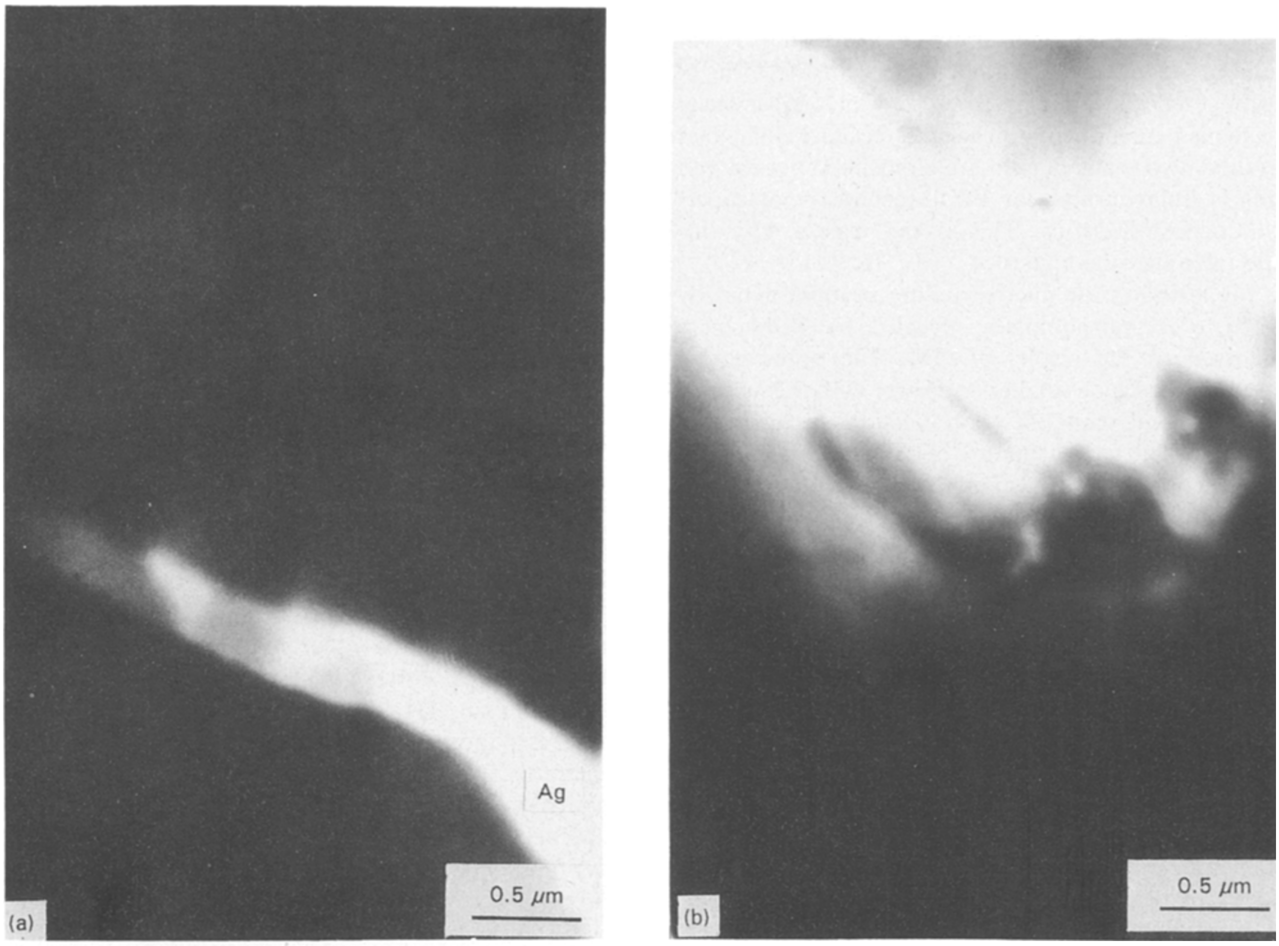


Figure 6 SEM photographs of fracture surfaces of samples: volume percentage of Ag (a) 0, (b) 10, (c) 20, (d) 30, (e) 40, (f) 60.



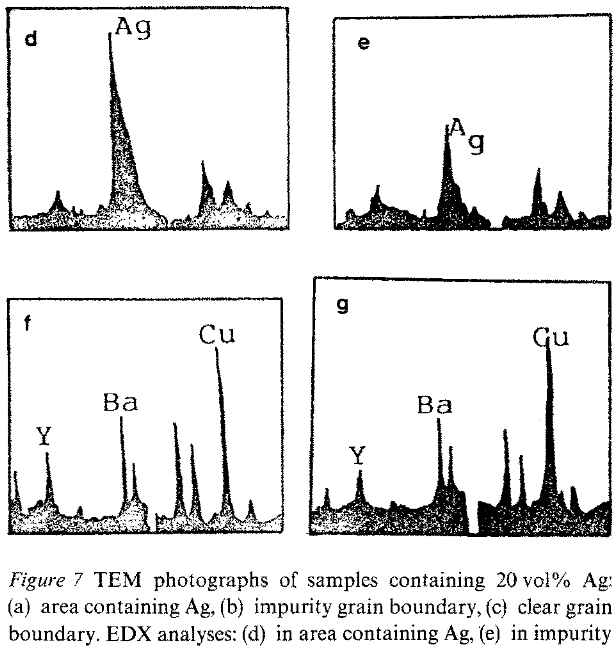


Figure 7 TEM photographs of samples containing 20 vol% Ag: (a) area containing Ag, (b) impurity grain boundary, (c) clear grain boundary. EDX analyses: (d) in area containing Ag, (e) in impurity grain boundary, (f) in clear grain boundary, (g) within one $YBa_2Cu_3O_{7-\delta}$ phase grain.

boundaries in a spherical form. The Ag particles grew bigger as the amount of Ag increased.

Among the specimens, the sample containing 20 vol % Ag possessed the most desirable microstructure. Its $YBa_2Cu_3O_{7-\delta}$ phase kept a plate-like form, the limits of grain size were very narrow and it crystallized perfectly. Within one grain, the twins grew very well. Compared with twins growing within specimens not containing Ag, twins growing in the sample containing 20 vol% Ag did not appear in the form of orthogonal and oblique structure, which is beneficial to the superconducting properties because the *c* axes of these two kinds of twin are almost orthogonal and this is unfavourable for the transmission of superconducting electrons. This is the reason why this specimen had the highest J_c.

Fig. 6 shows the microstructure in more detail by SEM. The morphologies revealed by SEM were identical to the results of OM. The pores within specimens became smaller and fewer with the increase of Ag content, while the grain junctions became more compact. The microstructure of the specimen containing 20 vol% Ag was also closest to that desired.

In order to study the relationship between the microstructure and properties of $YBa_2Cu_3O_{7-\delta}$–Ag_x composite further, the microstructure and elemental composition of the specimen containing 20 vol% Ag were resolved by TEM and EDX. The results are given in Fig. 7. The results show that "clean" and impurity grain boundaries existed in specimens. EDX analysis on a clear grain boundary revealed that the ratio Y:Ba:Cu was 1:2:3, while the ratio in an impurity grain boundary was not; excess copper was found. That is to say, a non-superconducting phase other than Ag existed in this kind of grain boundary. The junctions of clean grain boundaries were very compact. Metallic silver existed in grain boundaries and pores in the form of bars or triangles. A lot of dislocations were observed within one grain. The EDX analysis within one $YBa_2Cu_3O_{7-\delta}$ phase grain revealed that no Ag was present.

4. Mechanisms of the effect of Ag on properties and microstructure

The superconducting property of $YBa_2Cu_3O_{7-\delta}$ derives from particle superconduction, so the microstructure of the ceramic, such as the orientation of adjacent grains, relative density, morphology of grain boundaries and impurity content have a great influence on its superconducting properties. As shown above, metallic silver existed in grain boundaries; furthermore, silver existed in the solid form in the course of sintering because the sintering temperature was 950 °C, lower than the melting temperature of silver (968 °C). The equilibrium between solid and liquid states can be adjusted by Ag in the course of sintering. This effect can induce overcooled grains to separate and over-temperature grains to melt. These effects can hinder the movement of grain boundaries, prevent grains from growing unusually, reduce the size of grains, induce air to escape more easily and increase relative density of the specimen. On the other hand silver can change the conducting property by metallization of the grain boundaries, reduce the resistance of grain boundaries and clean grain boundaries. All of these effects can strengthen coupling among the superconducting grains, so that J_c increases. However, this increase of J_c is confined to an amount of Ag within narrow limits, because with increase of Ag the proportion of non-superconducting phase in the sample increases. This induces a decrease of superconducting networks, while at the same time the coupling between the superconducting grains will weaken because a lot of non-superconducting Ag exists in grain boundaries. All of these effects will worsen the superconducting properties, as the results in Fig. 3 demonstrated.

5. Conclusion

$YBa_2Cu_3O_{7-\delta}$–Ag_x composite superconductors can be prepared by the sol–gel method. At first, adding silver to samples can induce the $YBa_2Cu_3O_{7-\delta}$ phase to grow well, decrease the size of grains and densify the sample. On the other hand, adding silver can induce the plate-like $YBa_2Cu_3O_{7-\delta}$ phase grains to strongly twin, clean the grain boundaries and decrease the resistance of grain boundaries. Both the effects mentioned above can strengthen the coupling among superconducting grains and increase the J_c of the specimen. However, the effect of increase of J_c was confined to an amount of Ag added to the $YBa_2Cu_3O_{7-\delta}$ phase within narrow limits.

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