INFLUENCE OF SILVER DOPING ON THE MICROSTRUCTURE AND MAGNETIC PROPERTIES OF $YBa_2Cu_3O_7$/Ag COMPOSITES

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This paper describes the synthesis of a series of bulk samples with different silver content covering the whole range up to very high loadings (0 - 80 wt.%). Although such high loadings are probably less relevant to fundamental phenomena, they may have very high industrial significance. They are for instance required to increase the thermal conductivity of bulk materials used in high power magnetron sputtering deposition techniques. The morphological characteristics of Ag-containing composites are discussed are related to their superconducting properties which have been studied in detail using AC and DC susceptometry at high and low field. The results exemplify the role of silver as synthetic flux at high temperatures and as mediator of oxygen transport at lower temperatures in addition to its role of enhancer of mechanical and thermal properties.

INTRODUCTION

This study forms part of an industrial Brite Euram project BRPR-CT97-0331 dealing with the development of a cost effective flexible YBCO tape, using magnetron sputter deposition of 0.5 – 1 mm thick YBCO films on oriented metallic substrates. For this purpose, the construction of industrially sized cylindrical and rotable sputter targets was developed. The presence of such high loadings of metallic Ag in these targets is deemed very important since it significantly increases the thermal and electrical conductivity as well as improving the mechanical strength of the fabricated composites. Furthermore, the use of such composite material reduces mechanical stresses when it is deposited as thick layers (up to 5 mm) on the surface of stainless steel cylinders 30 cm long and 13 cm diameter, which are used as magnetron targets and its addition certainly does not deteriorate superconducting properties. Furthermore, its potential beneficial effect on increasing critical current densities by promoting the growth of pinning centres has been widely documented. In addition, we think that addition of Ag as a mediator of oxygen, also promotes the formation of the superconducting phase at relatively low synthetic temperatures. If treated at relatively higher temperatures (but still below the melting point of the composites) it may also act as a flux in reducing porosity and improving density.
All these effects are distinctly influenced by the changes in microstructure and grain links in the samples [1]. This report addresses our findings in a study on $YBa_2Cu_3O_7$/Ag composites, where silver was doped in the range of 10 - 80 wt.%. Their microstructure as well as their magnetic and electrical properties, which very finely reflect the inter- and intra- grain properties are described.

EXPERIMENTAL PART

The samples were prepared in a two-step process. Firstly, $YBa_2Cu_3O_7$ powder was prepared from aqueous spray dried solutions of the corresponding nitrates at a concentration of 10 wt.%. These solutions were evaporated in a two fluid, co-current spray dryer (Büchi) at a rate of 4 ml per minute and a flux of drying air of 200 °C and flow of 700 l per hour. After calcining this blue-green powder for 10 hours at 780 °C in air, powdered metallic silver with average grain size 50 μm was admixed to obtain samples with 10, 20, 30, 40 and 80 wt.% of Ag. The compacted pellets were fired at 800 °C for 10 h, sintered subsequently at 940 °C for 40 h and subsequently annealed for 4 h at 400 °C in flowing oxygen.

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The AC and virgin DC volume magnetisation characteristics were measured in the zero-field cooled condition by 2-nd order SQUID gradiometer. All magnetisation characteristics of the samples were measured at 77 K in the range of magnetic fields (10^{-1} - 10^5) A m^{-1}. The applied magnetic field was parallel to sample's thickness (the smallest size). The demagnetising factor was determined from the sample dimension using the ellipsoid approximation. At relatively low magnetisation fields a demagnitisation correction was applied to obtain the values of the applied field H_a and the first penetration field of the samples, H_{p1}^{wl}. For AC magnetisation measurements the frequency of 0.1 Hz was used and the applied field was being gradually increased over five amplitudes. Some characteristic magnetic field values H_{p1}^{wl} (intergrain weak link critical field), H_{p2}^{wl}, H_{p1}^{g} (intra-grain critical field) were determined from the linear behaviour of the virgin DC magnetisation curves in the corresponding regions. The microanalytical characterisation was performed by scanning electron microscopy and WDS microanalytical mapping.

SEM micrographs and WDS-analysis were obtained after careful polishing of the samples using JEOL JXA – 840 instrument.

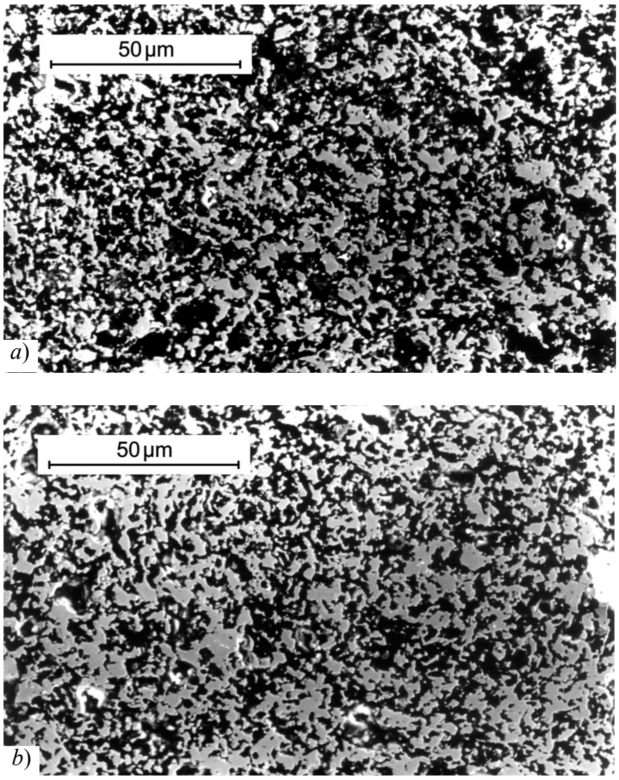

Figure 1. SEM granular sample with 0 (*a*) or 10 (*b*) wt.% Ag.

RESULTS AND DISCUSSION

The results of magnetisation measurements are in accordance with the insights provided by the microstructural investigations. SEM pictures confirm the highly granular character of the samples up to the content of 10 wt.% Ag. We were surprised that no Ag was detected by WDS mapping at the 10 wt.% doping level. This can be explained by the fact that the dopant is surrounded by the grains well dissolved in a superconducting matrix. At this concentration, the presence of the silver is only evidenced by a slight increase of the size of the grains. In contrast, the concentrations of the dopant above 10 wt.% lead to growing areas of precipitated silver. At higher Ag content, a dramatic increase in the grainsize of the superconducting phase can be observed. The Ag dopant acts as a flux, which leads to some degree of texture of the $YBa_2Cu_3O_7$ matrix (figure 1, 2).

The magnetisation M vs. applied field H_a for some Ag-doped YBCO samples without silver, 40 wt.% Ag and 80 *wt* % Ag are shown in figures 3, 4 and 5. The samples where silver is absent and with 10 wt.% of Ag show similar magnetisation loops (figure 3). Poor intergrain properties can be inferred from their magnetisation hysteresis loops in the nearly zero field range. This agrees with lower DC-volume-susceptibility values χ of the samples (χ = -0.83 - 0.84) at relatively low applied fields. It means that the shielded volume is less than volume of the samples even at very low applied fields. The poor magnetic properties are caused by the fact that the oxygenation reaction was performed at relatively low temperature of 400 °C. Further increase of the silver content up to 20 wt.% results to a marked increase of superconducting magnetisation. As can be derived from the plot in figure 4, the samples with higher silver content show significantly better intergrain connects and also improved intragrain / intradomain properties. H_{p1}^{wl} for the samples is 2-3 times higher than that of the samples with with 0 or 10 wt.% of Ag. Their magnetisation is more than twice higher compared to the magnetisation of samples with 0 or 10 wt.% of Ag. The magnetisation of the sample with 80 wt.% Ag content decreases significantly below the starting values (figure 5), indicating a breaking up of the percolative path at these very high Ag-doses.

Similar findings were reported by A. Dwir et al. [2] i.e. the $YBa_2Cu_3O_7$ grains can form an infinite superconducting cluster (flakes, domains) in the samples even when Ag nominal doping level is ranging from 20 wt.% up to 40 wt.% Ag. This correlates with our SEM analyses of the microstructure and it is also supported by the high values of susceptibility of the samples *c* and also by their almost identical magnetisation hysteresis loops. The susceptibility of the samples *c* is close to -1, which corresponds to the full Meissner shielding of the whole volume of the samples.

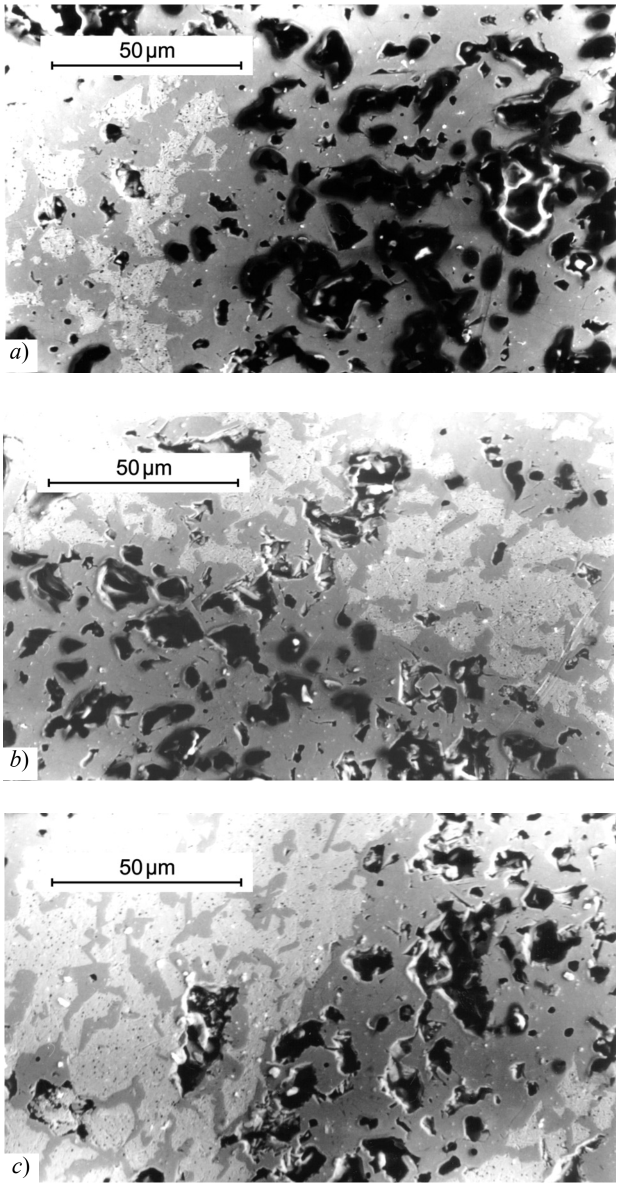

Figure 2. SEM of sample with 20 (*a*), 30 (*b*), 40 (c) wt.% Ag.

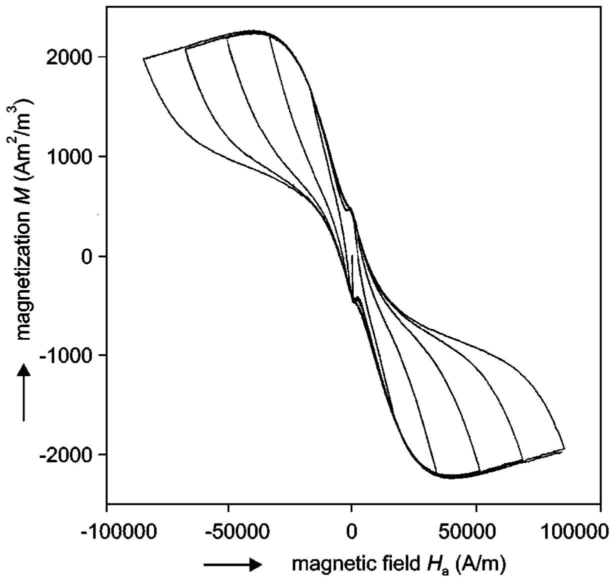

Figure 3. Magnetisation M vs. the applied field H_a for sintered $YBa^2Cu^3O_7$ sample without silver for five field amplitudes.

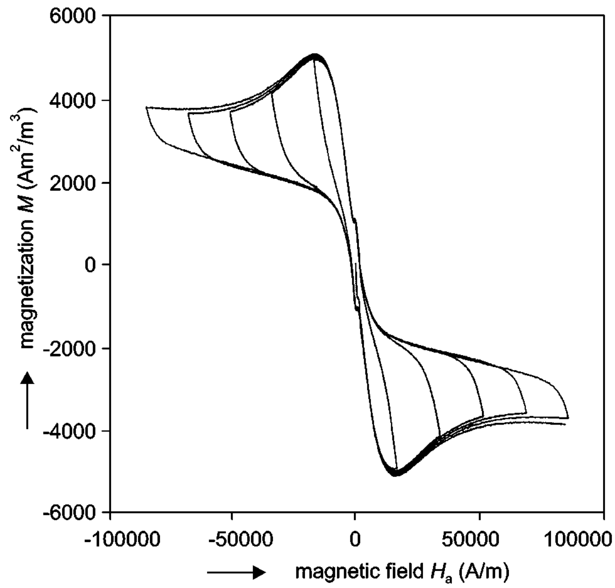

Figure 4. Magnetisation M vs. the applied field Ha for sintered $YBa_2Cu_3O_7$ - Ag composite with 40 wt % silver for five field amplitudes.

At the higher field values, the high level of the magnetisation of the samples with nominal silver content 20 - 40 wt.% Ag can be ascribed to the higher value of radius of circulating superconducting current cluster paths contrary to the samples with nominal silver content 20 - 40 wt.% Ag, where the current path radius is determined by the smaller grain size. Finally, our magnetisation measurements also show a clear decrease of the superconducting properties at the nominal content of 80 wt.% Ag (figure 5). In addition, the shape of magnetisation loops of this sample and the low value of volume - susceptibility ($c \sim 0.5$) suggest a significant loss of bulk superconducting behaviour, probably due to the excess silver which percolates through the superconducting phase.

In order to explore the internal structure of the magnetisation loops at lower fields, we also performed magnetisation measurements at different amplitudes of the magnetising field. The sample with 80 wt.% Ag almost completely lacks the magnetisation kinks near zero field, which are fingerprint characteristics of intergrain or inter-cluster links. This was confirmed up to very low magnetising field. This means, that the probable percolation threshold of the superconducting

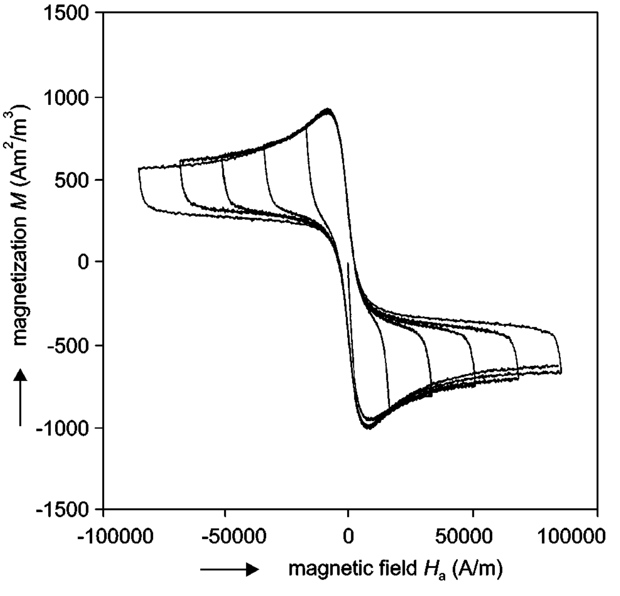

Figure 5. Magnetisation M vs. the applied field H^a for sintered $YBa_2Cu^3O_7$ - Ag composite with 80 wt % silver for five field amplitudes.

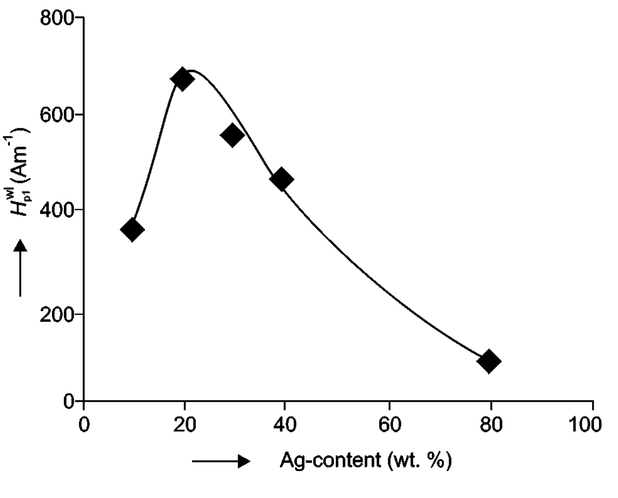

Figure 6. Evolution of H_{p1}^{wl} (intergrain weak link critical field) as a function of Ag-loading in $YBa_2Cu_3O_7$ - Ag composites.

phase clusters is higher than 40 wt.% Ag and less than 80 wt.% Ag. It is also known that a significant change of critical temperature occurs below a volume fraction YBCO about 0.3. (about 74 - 79 wt.% Ag [3]. According to Ash et al. [4] the samples with the volume superconducting fraction $p < 0.3$ (< ~21 - 20 wt.%) do not exhibit bulk behaviour of the magnetisation characteristics at any temperature less than the critical one. On the other hand it is interesting that the percolation threshold of silver in $YBa_2Cu_3O_7$ - Ag composite is close to 19 wt.% Ag (12.5 % silver volume fraction) as was determined from the electrical resistivity and from the thermal conductivity measurements [6].

It is known that silver additions can accelerate the oxygenation reaction at relatively low temperatures (~ 350 °C), however they do probably retard the reaction at relatively high temperatures (~ 550°C), [5]. This must be related to the endothermic and heterogeneous decomposition reaction of argentous oxide

$$2\ Ag_2O(s) \leftrightarrow 4Ag(s) + O_2(g)$$

On heating this oxide in the pure state, oxygen evolution is rapid up to about 250 °C, but it is known that the thermal stability is much increased in the presence of heavy metal oxides [7]. According Wiessner et.al. [8] this temperature has been reported to be 350 °C in $YBa_2Cu_3O_7$ - Ag composites. We suggest that the mediating role of this oxide as oxygenation catalyst in the increasing of the superconducting phases is intimately related to the annealing temperature. Oxygenation of the samples under investigation was performed at a relatively low temperature of 400 °C for 4 h where the formation of argentous oxide is relatively easy. At the same time, these temperatures enable a high level dynamic equilibrium thus promoting the role of Ag as intermediate for the oxygen diffusion and redistribution throughout the matrix.

We know from literature studies [9] but also from our own investigations [10,11] that Ag doping markedly improves the mechanical properties, thermal properties and room temperature conductivity. The obtained results here show that, in addition, Ag doping also dramatically induces improved superconducting magnetic properties of the samples. It is remarkable that the magnetisation hysteresis loops indicate superconducting intergrain (inter-cluster) links to be present up to the very high doping level of 40 wt.% of Ag. In addition, the intragrain magnetisation loops of the samples with x = 20, 30, 40 wt.% are to a great extent similar to each other in the range of lower magnetic fields. Only in the magnetisation curves of the sample with 80 wt.% Ag does manifest disappearing of the intergrain superconducting links. Further investigations on $YBa_2Cu_3O_7$ - Ag composites prepared at different sintering and oxygenation conditions are in progress [12].

CONCLUSIONS

The results of magnetisation measurements are in accordance with our microstructural investigations. SEM confirms the granular character of the samples up to the content of 10 wt.% Ag. Based on significant differences in microstructure and magnetisation measurements between the YBCO samples doped with increasing amounts of Ag, the percolation thresholds for superconducting and silver path can be evaluated. The role of Ag as oxygenation catalyst could be exemplified in the sensitivity of the systems response to different annealing temperatures. The percolation threshold of the superconducting $YBa_2Cu_3O_7$ - Ag composites phase grain or cluster path in our samples is about nominal 80 wt.% Ag or less.

Acknowledgements

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VLIV PŘÍDAVKU STŘÍBRA NA MIKROSTRUKTURU A MAGNETICKÉ VLASTNOSTI $YBa_2Cu_3O_7$/Ag KOMPOZITŮ

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Článek popisuje přípravu kompozitů $YBa_2Cu_3O_7$/Ag s obsahem 0-80 hmotn. % Ag. Ačkoliv tak vysoké přídavky pravděpodobně nejsou významné pro podstatu materiálu, mohou mít velký průmyslový význam. Jsou například požadovány ke zvýšení teplotní vodivosti objemových materiálů používaných při výkonovém magnetronovém nanášení. Morfologické charakteristiky Ag kompozitů jsou diskutovány vzhledem k jejich supravodivým vlastnostem, které byly podrobně studovány měřením střídavé a stejnosměrné susceptibility v silném a slabém poli. Výsledky dokládají, že kromě zlepšení mechanických a tepelných vlastností plní přídané stříbro úlohu syntetického média při vysokých teplotách a zprostředkovává transport kyslíku.