Magnetic properties of superconducting $YBa_2Cu_3O_{7-\delta}$/Ag composites prepared by various techniques

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Abstract

The AC magnetisation measurements and scanning electron microscopy show that the percolation threshold of silver metal in the $YBa_2Cu_3O_{7-\delta}$/Ag composites is crucially dependent on the method of the preparation. In the case when the sintering is performed under the conditions of the eutectic melt formation, this threshold is shifted to lower values. At 20 *wt* % Ag addition, the silver layer precipitated on grain boundaries fully interrupts the intergranular superconducting links.

1. Introduction

Silver is a preferred doping element for fabrication of high T_c superconductor composites with metals, since it does not deteriorate their superconducting properties. The formation of $YBa_2Cu_3O_{7-\delta}$/Ag composites increases their thermal conductivity [1] and their electrical conductivity at room and elevated temperatures [1, 2]. The relatively poor mechanical properties of $YBa_2Cu_3O_{7-\delta}$ (YBCO) superconductor are also improved by silver addition [3]. All the above properties are important from the point of view of the fabrication of industrial magnetron sputtering targets with high power throughputs.

In our previous paper the microstructure and magnetic properties of YBCO/Ag composites, which were prepared by the spry drying method, have been reported [4]. An addition of 80 *wt* % of Ag was necessary for complete disturbing of intergranular superconducting paths in YBCO/Ag composites. In this paper the influence of the preparation method on the magnetic properties and microstructure of YBCO/Ag composites containing up to 20 *wt* % Ag is reported.

2. Experimental

2.1. Subject

Four series of samples were prepared. In the first one (series A), the pellets were prepared in a two step process. Firstly, $YBa_2Cu_3O_{7-\delta}$ powder was prepared from aqueous spray dried solutions of the corresponding nitrates at a concentration of 10 mass percent. The precursor powder was calcined at 800 °C for 10 h. Then, powdered metallic silver with average grainsize 50 μm was admixed to obtain samples with 10, 20 and 40 *wt* % of Ag. The precursors were calcined at 800 °C for 10 h, compacted to pellets and sintered at 940 °C for 24 h and subsequently annealed for 24 h at 550 °C in flowing oxygen.

In the second series (B) all nitrates (Y, Ba, Cu, Ag) were spray dried together to obtain precursors corresponding to YBCO/Ag composites with the same amount of Ag admixture as in series A. The precursor powder was calcined at 800 °C for 10 h. The annealing and oxygenation was performed under the same conditions as in series A.

The samples of the series C were prepared by the citrate method. The appropriate amounts of Y_2O_3, $BaCO_3$ CuO and $AgNO_3$ were dissolved in diluted nitric acid, converted to citrates by addition of citric acid and the pH of the solution was adjusted to 7 by ammonia. The obtained solution was slowly evaporated to gel. Then the organic components and nitrates were burned in an intensive self ignition process and the formed precursor was calcined and annealed at the same conditions as in series B.

The fourth series (D) was prepared by a direct solid state reaction of Y_2O_3, $BaCO_3$ CuO and Ag_2O powders, which were mixed together and then treated at the same conditions as the samples in series B and C.

2.2. Methods

The AC and DC virgin volume magnetisation characteristics were measured by the compensation method using 2-nd order SQUID gradiometer with the sample placed outside the helium cryostat. The samples were discs with a diameter of 10.7 to 11.6 mm and a thickness of 1.9 to 2.4 mm. The sample was inserted in the coil set consisting of magnetisation and compensation coils [5]. All magnetisation characteristics of the samples were measured at 77.3 K after the zero-field cooling in the magnetic fields ranging from 10^{-1} to 10^5 A m^{-1}. For AC magnetisation measurements a frequency of 0.1 Hz has been used. We scanned M vs. H_a dependency for different amplitudes of applied magnetic field H_a in steps of five amplitudes for each chosen range in order to see more details, such as: the effective magnetic susceptibility in the case of Meissner shielding of the whole volume sample, the penetration magnetic fields characterising the onset of the penetration of the magnetic flux into the intergrain weak links and into the intragrains. For both AC and DC magnetisation the applied magnetic field was parallel to axis of the sample. The demagnetising factor was determined from the dimensions of the cylindrical pellet samples [6].

Scanning electron microphotographs of the polished cross sections of the prepared pellets were taken on a Jeol JXA – 840A device.

3. Results and discussion

Scanning electron microphotographs show that all investigated methods lead to polycrystalline YBCO with most metallic silver precipitated in the intergranular space and partly covering the surface of the grains. The presence of YBCO and metallic silver was proven also by X ray diffraction measurements. The sintering temperature is very close to the melting temperature of silver in YBCO/Ag composite, which has been reported to be 944 °C [7]. If the silver addition in the series A, B, C was increased from 20 to 40 *wt* % Ag or above, a part of admixed silver segregated on the outer surface of the pellets in form of droplets. On the other hand, no remarkable formation of liquid silver was observed in the case of series D, which was prepared by direct solid state reaction of Y, Cu, Ag oxides and $BaCO_3$. The prepared samples differ also in porosity, where the most porous pellets were formed in the series D.

The analysis of magnetisation loops can be done in the two separated steps, namely at the magnetisation field values close to zero and the field values which are relatively higher. In the zero field range the central peak in magnetisation loops can be identified. This peak usually accompanies sintered sample and is related to intergrain properties. Next magnetisation peak (local maximum) can be related to grain shielding currents. The grain critical current density is maximum when the value of the average magnetic flux density inside the sample achieves the minimum.

The effects silver doping on the magnetisation hysteresis loops for series (A-D) of YBCO/Ag sintered samples are shown in Figures 1-4, respectively. In the first approximation we consider the same sizes of all the samples. The silver doping levels $x = 10$ and 20 *wt* % Ag decrease the intergrain weak links. This holds for all investigated samples, Figures 1-4, however at a different rate. Relatively sharp zero peak points to the strong field dependency of intergrain critical current density and/or the absence of clusters of strong superconductively connected grains already in the parent samples without silver.

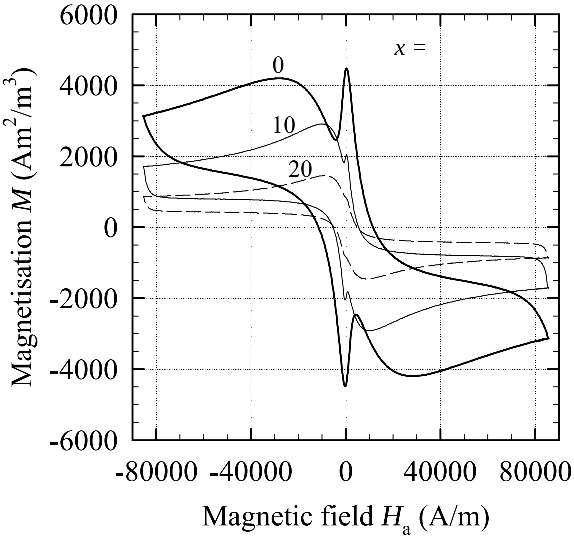

Figure 1. Effects of the silver doping levels on the magnetisation hysteresis loops M vs. H_a of the $YBa_2Cu_3O_{7-\delta}$/Ag sintered samples prepared from aqueous spray dried solutions of the corresponding nitrates, (series A). x denotes the doping level in *wt* % Ag.

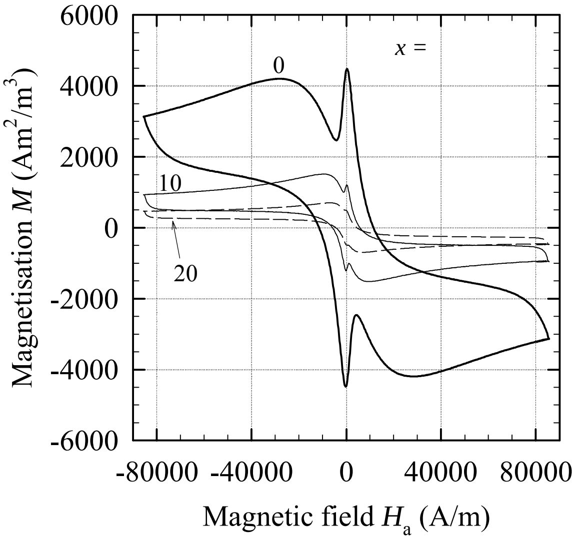

Figure 2. Effects of the silver doping levels on the magnetisation hysteresis loops M vs. H_a of the $YBa_2Cu_3O_{7-\delta}$/Ag sintered samples prepared from aqueous spray dried solutions of the corresponding nitrates including Ag, (series B). x denotes the doping level in *wt* % Ag.

Comparing with the standard sintered $YBa_2Cu_3O_{7-\delta}$, the values of next local maximum (bump) in the magnetisation hysteresis loops of the A-C samples point to worse intragrain shielding current or lower radius of the current paths. Doping by 10 *wt* % of silver significantly decreases the intergrain superconducting links and also the intragrain

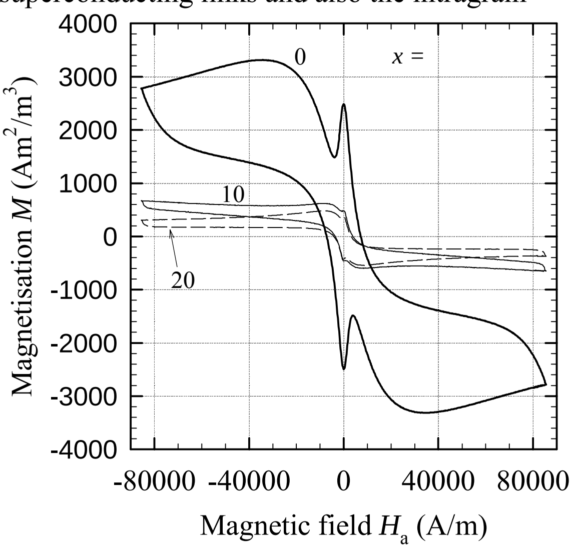

Figure 3. Effects of the silver doping levels on the magnetisation hysteresis loops M vs. H_a of the $YBa_2Cu_3O_{7-\delta}$/Ag sintered samples prepared by the citrate method, (series C). x denotes the doping level in *wt* % Ag.

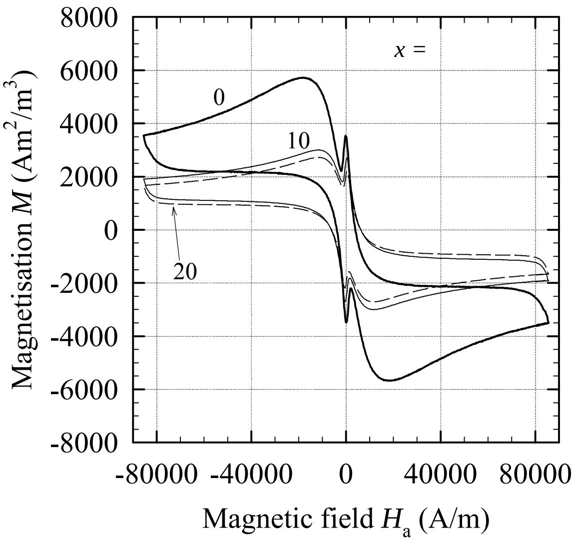

Figure 4. Effects of the silver doping levels on the magnetisation hysteresis loops M vs. H_a of the $YBa_2Cu_3O_{7-\delta}$/Ag sintered samples prepared by a direct solid state reaction of Y_2O_3, $BaCO_3$, CuO and Ag_2O powders, (series D). x denotes the doping level in *wt* % Ag.

shielding current, or the radius paths of the grain shielding current, as can be seen from decreasing of the central magnetisation peak and magnetisation hysteresis of the grains (magnetisation in the higher field range after the second maximum). Doping by silver with the level of 20 *wt* % Ag leads to almost full Ag coating of superconducting grains for A, B, C series of the samples, and this way to significant interrupting of the superconducting links between the grains. All in all, worse superconducting properties were found for the samples of C-series prepared by the citrate method. However, the values of the critical temperature ($T_c \leq 88.9$ K) and also magnetisation loops of the C-samples indicate the presence of a degradation process factor. The increase of the silver amount to 40 *wt* % led in series A – C to samples with bad reproducible properties.

From the above composites with 20 *wt* % Ag only the sample prepared by the direct solid state reaction of Y_2O_3, $BaCO_3$, CuO and Ag_2O powders shows still relatively good intergrain superconducting links. In this series no remarkable liquid phase formation was observed and the silver is precipitated mostly in intergrain voids.

In conclusion the percolation threshold of silver in superconducting YBCO/Ag composites crucially depends on the preparation method. In the cases where significant amount of Ag rich melt was built in eutectic reaction, an addition of 20 *wt* % Ag, which corresponds to a 13.2 % volume fraction of metallic silver in the composite, completely disturbs the intergrain superconducting connections. Very similar values of silver percolation threshold of 12.5 % volume were obtained in [8]. If the YBCO/Ag composites were sintered below the temperature of eutectic formation, the percolation threshold of the metal is shifted to higher values.

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