Dependence of the microstructure of Ag/BSCCO composites on filler content

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Abstract. In order to obtain high Tc superconducting materials with improved mechanical properties, $Bi_{1,5}Pb_{0,5}Sr_2Ca_2Cu_3O_x$ / Ag-composites with 3 different filler morphologies were successfully synthesised. It is shown that Ag-addition improves Bi-2223 grain growth and reduces sample-porosity. An alignment of the ceramic phase along the surface of the Ag was observed and the results of TEM, SEM, DTA and EDX mapping are discussed. Conclusions concerning the alignation-mechanisms based upon these observations are compared with popular models described in literature.

Composites exhibit increased ductility and isostrain conditions are met. Little effect on the mechanical strength is observed but the mismatch in thermal expansion coefficient induces a residual stress field at the filler matrix interface and allows toughening mechanisms to appear, resulting in a clear post-peak behaviour. SEM pictures of whisker debonding, crack bridging and whisker pullout, all demonstrating a suitable filler-matrix interface, are included. The role of the filler morphology and the sequence of the processing steps on the toughening efficiency will be discussed.

Keywords: Bi-high temperature superconductor, Ag, alignation, composite, mechanical properties.

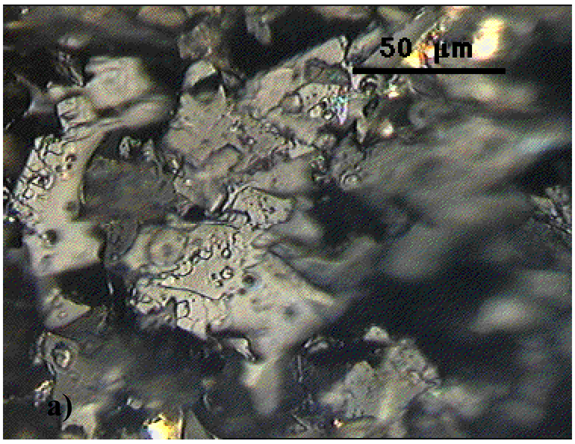
Introduction

High temperature superconductors (HTSC) are brittle by their ceramic nature. In an attempt to improve the mechanical properties of the bulk material many composite-types and fillers were investigated. The fabrication of OPIT tubes has shown to be a promising technique, leading to commercial applications. In this report we comment on our findings in bulk superconductor-Ag composites exclusively. The idea of adding Ag particles was already in 1989 used by Singh et. al. [1] in an $YBa_2Cu_3O_y$ composite, where an increase in strength, probably due to an increase in density was observed. Vipulanandan et. al. [2] used stainless steel fibres to increase toughness of $YBa_2Cu_3O_y$. Unfortunately Ag-coating could not prevent chemical contamination of the superconducting phase. A moderate toughening of the bulk high Tc-fase Bi-HTSC was shown by Yuan et. al. [3], by adding Ag-particles. The objective of this study was to describe the structural interaction between Ag and the high Tc-fase and to increase the toughness and strain to failure of the superconducting composite, while avoiding extensive loss of superconducting properties.

Synthesis.

Composites with variable compositions (0-100 vol. %) of BSCCO precursor powder or ground superconducting 2223 powder were made with three types of Ag-fillers. The mixtures were pressed in bar shapes of 2*2*13 mm with a pressure of 750 MPa. Ag/precursor and Ag/ 2223 mixtures were sintered for respectively 10000 min. and 3600 min. at 860°C in air. Additional composites in a 30 vol.% Ag, 70 vol. %2223 phase were synthesized with 3 different Ag-morphologies: Ag-powder, Ag-whiskers and

Ag-wire. The whiskers were synthesised by spontaneous electrochemical reduction of an aqueous $AgNO_3$ solution at pH 2 on the surface of a Cu wire. The used Ag-powder (< 50 µm) and Ag-wires (Ø: 0,05 mm) were both commercially available (Goodfellow).



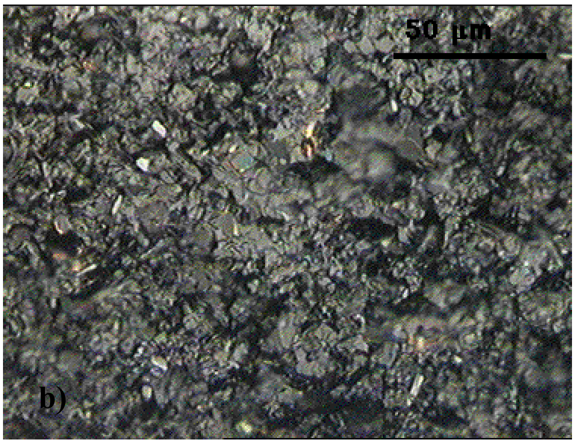


Fig 1: Micrograph of surface of composite with 30 vol. % Ag a) based on precursor powder, b) based on superconducting 2223 powder.

Microstructure.

All Ag composites show increased 2223 grain growth, compared to monolithic material (fig. 1) but when used in moderate amounts Ag acts as a useful sintering aid, reducing the overall sample porosity, by means of volume shrinkage, fig. 2 and fig. 3. The grain growth in samples based on superconducting powder is not so high as in composites based on precursor powder, consequently the density is lower in the last type of composites. During sintering the ceramic phase tends to migrate to the surface of the samples and align with the c-axis perpendicular to the surface plane, resulting in a high texturation at the surface of the sample. This is clearly shown in fig. 4 where a cut through a composite with a volume fraction of 20 % Ag shows that almost all the (black) ceramic phase has migrated to the surface. EDX and XRD at the sample surface confirmed this thesis. Samples synthesised from 2223 powder are textured by a deformation-induced texturation: by pressing the 2223 crystals they tend to align with their c-axis parallel with the pressing direction [4].

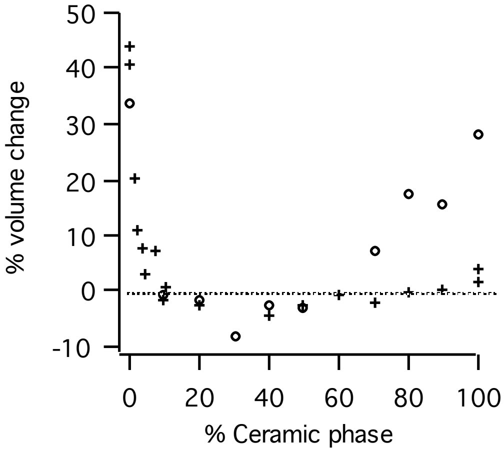


Fig. 2: % Volume change during sintering process for composites based on precursor powder (o) and based on superconducting 22223 powder (+).

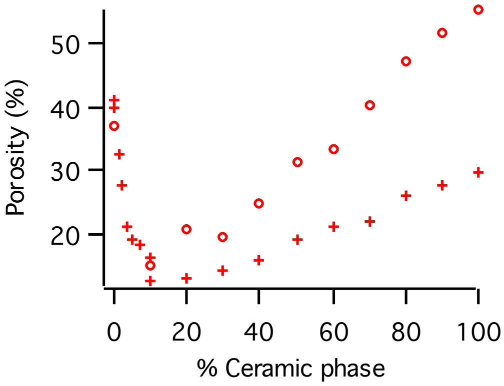


Fig. 3: Porosity of composites based on precursor powder (o), and on superconducting 2223 powder (+).

In composites based on precursor powder a composition of at least 70 vol. % ceramic phase is required in order to supply a rigid matrix and prevent Ag segregation to the bottom of the sample. Such samples show alignation of the high Tc-phase at the Ag-surface, fig. 5. The 2223 crystals grow with their c-axis perpendicular to the Ag-surface [5]. At the interface, between the Ag and the 2223-crystals, a 20 nm thick amourphous nanocrystalline phase is observed (AM-NC). The size of the observed nanocrystals in the AM-NC phase is approximately 10 nm. An intermediate 20 nm thick amorphous-nanocrystalline phase is observed. We assume that first, as a result of the differences in interfacial energies, the ceramic phase grows along the Ag-surface [6]. Followed by an incongruent melting of the aligned Bi-2223 phase close to the interface as a result of the Ag-diffusion.

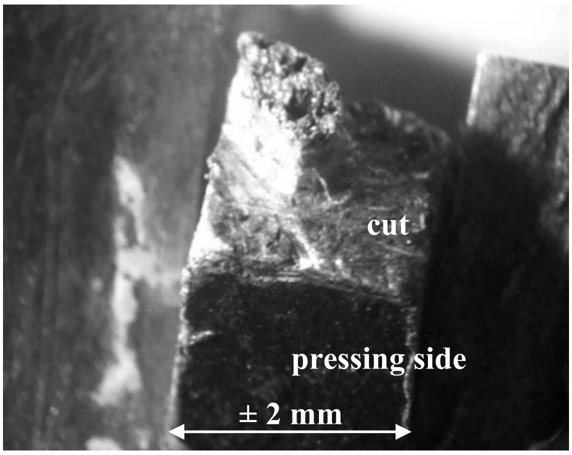


Fig.4: Cut through a composite with high volume fraction Ag.

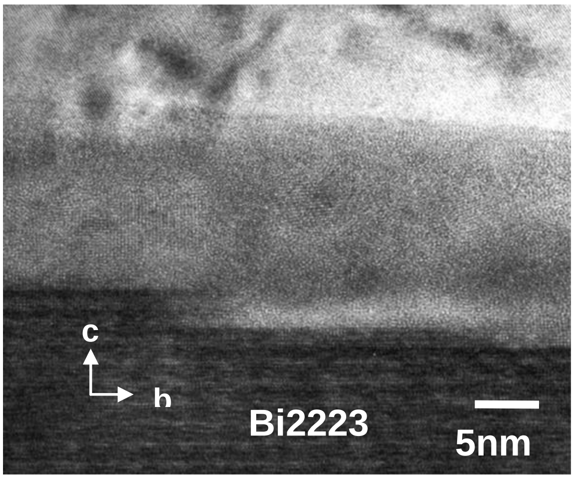


Fig 5: HREM of Ag/2223 interface, showing the Ag-induced c-axis texturing. An intermediate amorphous-nanocrystalline phase is observed.

AC susceptibility measurements show that we can add 30 vol. % filler to the superconductor, without loosing the full diamagnetic exclusion nor reduce the critical current density at 77 K in self field [8]. For this reason all 3-point bending tests were conducted on (30 vol. % Ag/ 70 vol. % BSCCO) composites.

Mechanical measurements.

Unfortunately, and in contrast to composites with superconducting 2223 powder, samples made from precursor are very porous. There is insufficient Ag-ceramic contact to allow toughening mechanism to occur.

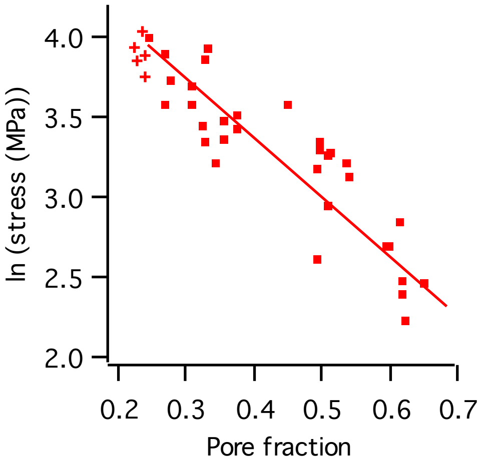


Fig. 6. Maximal applied stress as a function of pore fraction for pure superconductor (ν) and for composites with 30 vol. % Ag-particles (+). The line denotes the relation $\sigma = 130.e^{-3,58p}$.

For this reason, all given mechanical measurements are based on samples synthesised starting from super-conducting 2223 powder. Three point bending tests show that the strength (σ) of the particulate composites is approximately as high as would be expected for monolithic material with the same density, following the relation $\sigma = 130.e^{-3,58p}$, where p is the pore fraction, fig. 6. The modulus of the composite (±3600 MPa) is approximately equeal to the weighted average of the moduli of the monolithic phases: BSCCO ±4800 MPa, (density 73%) and Ag ±700 MPa (sintered Ag bar). This indicates that isostrain conditions are met, which is typical for a composite with a high modulus matrix and a low modulus filler [9]. In comparison to the vickers hardness of the monolithic material the vickers hardness of the composite was decreased (VH BSCCO: 600 MPa; VH composite: 460 MPa). The thermal expansion of the composite ($13,3.10^{-6}$ K^{-1}) is approximately the weighted average of the thermal expansion of the constituent materials (BSCCO: $10,6.10^{-6}$ K^{-1} and Ag: $19,6.10^{-6}$ K^{-1}). From the stress-displacement curve in fig. 7 we deduce that the particulate composite exhibits brittle failure.

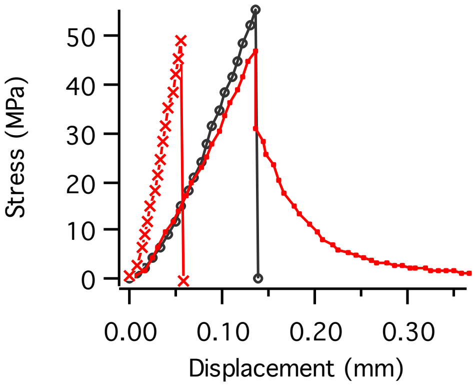


Fig. 7. Stress strain curve of a monolithic (x) a particulate (O) and a whisker composite (λ).

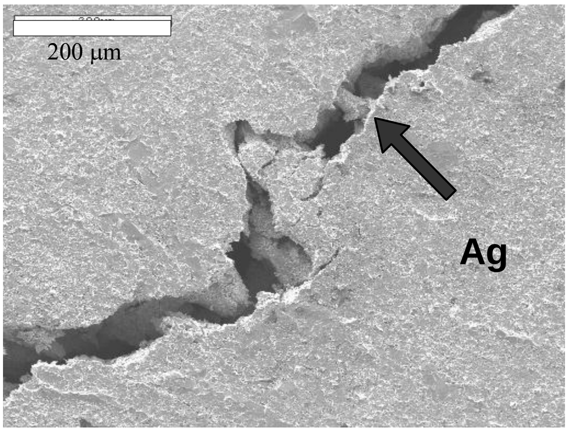


Fig. 8. SEM, bridging by a Ag whisker.

In contrast with this we observe a long tail in the stress-displacement curve of the whisker composites, indicating an increased toughness fig. 7. Due to whisker addition the area under the stress-strain curve is multiplied by 3. This difference in toughness between particle and whisker composites is attributed to the increase in aspect ratio, leading to more efficient toughening mechanisms. Crack bridging and whisker pull-out in a BSCCO-composite is illustrated in the SEM picture in fig. 8.

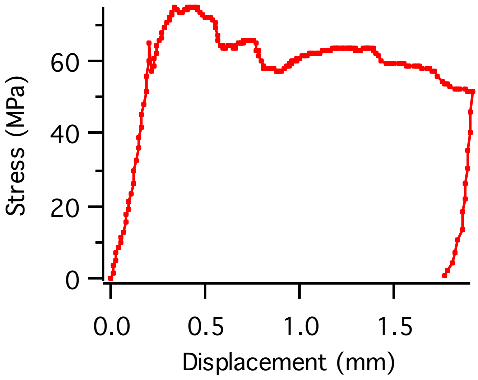


Fig. 9. Stress strain curve of continuous uni-directional composite.

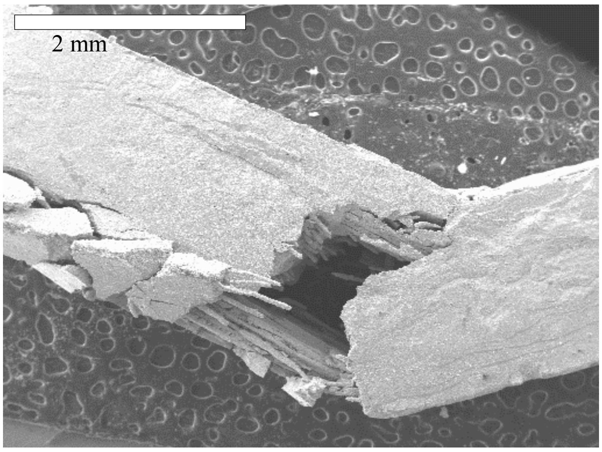


Fig. 10: SEM, bridging and fibre pull out in continuous composite.

The higher aspect ratio of the wires makes the toughening mechanisms in the continuous unidirectional wire composites even more efficient than in the whisker composites. Fig. 9 shows the stress displacement curve of a wire-composite. The increase in absorbed energy and in displacement is now enormous. This is, again, ascribed to toughening mechanisms such as bridging and pull-out which can be observed in the SEM image in fig.10. The synthesis of the composites with continuous unidirectional fibres is more involved than processing with particles or whiskers. However, if the electromagnetic properties are adequate, the increase in toughness clearly makes up for some additional costs.

Moreover, in contrast to Ag-whiskers, wires have the additional advantage to be commercially available.

Conclusion

Effects of silver addition on the volume expansion, porosity and texturation are given and illustrated with measurements of composites based Ag and precursor powder or ground superconducting 2223 powder.

Particle, whisker and continuous unidirectional Ag wire composites were synthesised in order to reveal the importance of the filler morphology. Three point bending tests show that isostrain conditions are met. Due to a small increase in density the strength of the composites is slightly enhanced.

In particulate composites no toughening could be measured. In the higher aspect ratio composites an enormous enlargement of the absorbed energy is observed This is allocated to toughening mechanisms as whisker and wire debonding, crack bridging and pull-out.

We can conclude that toughening of the 2223 phase with high aspect ratio Ag was successful. The complex co-operation of the respective thermal expansion coefficients, the properties of the interface, the morphology and the quantity of the filler leads to tougher, more ductile material. Experiments to assess the electrical properties under strain are underway.

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