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Properties and stability of Cu–YBaCuO composites elaborated by extrusion of an elemental powder mixture

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To produce mechanical reinforcement of a Cu matrix without any loss of conductivity for low temperature applications, it is proposed to replace classical alumina particles by superconducting particles. This paper describes a first attempt to synthesize copper composites containing 5 wt% YBaCuO and 20 wt% YBaCuO by using a powder processing route. The resulting mechanical and electrical properties are related comparatively to usual ODS Cu alloys. It is shown that a crucial difficulty remaining to be cleared up is the decomposition of the orthorhombic $YBa_2Cu_3O_{7-x}$ superconducting phase occurring during the elaboration process. Addition of an *in situ* oxygen donor, such as Cu_2O oxides in the initial powder mixture, appears insufficient to stabilize the oxygen stoichiometry of the superconducting particles. Conclusions are drawn as a guideline for further process designing.

1. Introduction

The discovery of superconducting materials such as $YBa_2Cu_3O_{7-x}$ with high T_cs, above nitrogen boiling temperature, promises widespread applications. However, fabrication of these materials poses many problems related to some of their inherent properties such as brittleness, generally associated with a ceramic compound, and the instability of the superconducting phase. While considerable improvements have been made in the preparation of superconducting films, attempts are still being made to realize practical applications such as wires. A number of metal–YBaCuO [1, 2] and polymer YBaCuO [3] composites were proposed to enhance the strength and the ductility, but they have been unsuccessful because of too low a critical current density J_c (the lower limit of a useful J_c is ca. 10^4 A cm^{-2}, but really useful values lie between 10^5 and 10^6 A cm^{-2}).

In another field of application, intensive investigations for the past 20 years have led to the development of dispersion-strengthened Cu [4–6]; this is a generic term used to describe strengthening of a Cu matrix arising from a fine and uniform dispersion of refractory oxides, such as alumina. This technique is a unique way to improve the mechanical properties of the matrix while preserving high electrical conductivity.

The primary objective of this study was to verify if, for low temperature applications, the substitution of alumina particles by superconducting particles offers a convenient way to obtain mechanical reinforcement of the matrix without any loss of conductivity. So, this work is an attempt to synthesize Cu–YBaCuO composites by a powder processing route.

2. Experimental procedure

The initial Cu and YBaCuO powders used in this study were provided by Eckard-Poudmet Co. and High Tech. Co. (HTC), respectively. The atomized Cu powder ranged from 20 to 50 μm, while the YBaCuO powder particle size was not larger than 3 μm. The X-ray diffraction (XRD) pattern (Fig. 1) shows that the major phase constituent in this latter powder is orthorhombic $YBa_2Cu_3O_{7-x}$. These two powders were dry-mixed for 3 h in a planetary ball-mill and the mixture was compacted in a cold isostatic press under an applied pressure of 330 MPa. The complete densification of the resulting compact was obtained by hot extrusion at 700 °C with an extrusion ratio $\eta = 25$ (η = initial section/final section). Mechanical characteristics of the as-extruded products were derived from tensile tests at 77 and 300 K, and from compression tests at room temperature, both performed on a 1122 model Instron machine with a crosshead speed of 0.5 mm min^{-1}. The samples, dimensions are illustrated in Fig. 2.

An alternative elaboration route was also tested. It consists of replacing pure Cu powders by oxidized Cu powders obtained by two different methods. The first method samples resulted from a simple room-temperature exposition in air of Cu powders for one year.

The second method samples were prepared by heating pure Cu powders for 15 min at 300 °C in flowing O_2. The Cu oxide content ranged approximately between 10 to 50 wt %. The elemental powders (10 wt % YBaCuO + 90 wt % oxidized Cu) were mixed for 1 h in a planetary ball-mill and then compacted into pellets under a pressure of 440 MPa using an MTS hydraulic machine. Sintering was then performed at different temperatures ranging from 400 to 600 °C in an Ar atmosphere.

Composition, crystalline phase and microstructural details of elaborated samples were examined by XRD (θ–2θ), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and energy dispersion analyses.

Electrical resistivity was measured at 77 K and at room temperature using a conventional four-point method with a stabilized current intensity of 0.1–2 A.

3. Results and discussion

3.1. Mechanical properties

Tensile and compression behaviours at 300 and 77 K are shown in Fig. 3a and b, respectively. In compression, the yield stress is significantly increased when the YBaCuO content increases from 5 to 20 wt % (Fig. 3b). In tension, an opposite behaviour is observed (Fig. 3a) as the 20 wt % YBaCuO composite curve displays a brittle rupture for a strain $< 1\%$.

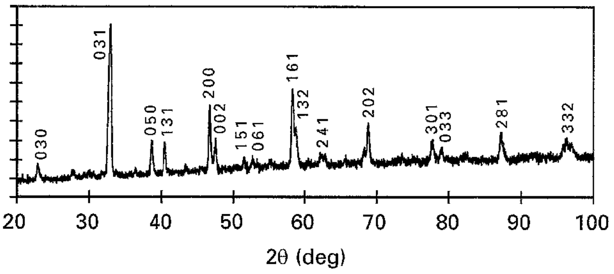

Figure 1 XRD pattern of YBaCuO powder.

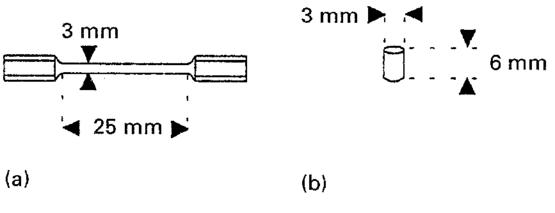

Figure 2 Sample geometry for tensile (a) and compression (b) tests.

The tension yield stress at 77 and 300 K are very similar (ca. 150 MPa), but a higher strain hardening rate is observed at 77 K. In this latter case, the tensile strength reaches ca. 300 MPa for the Cu–5 wt % YBaCuO composite with a strain of ca. 8%. This is a quite satisfactory ductility since it is considerably higher than the strain: fracture ratio mentioned by Salama *et al.* [7] for 85 wt % YBaCuO–Cu composites. However, the tensile strength of our samples are significantly lower than the values generally established for more classical oxide-dispersion strengthened Cu alloys [4–6].

3.2. Electrical properties

The electrical conductivity values of the two composites are gathered in Table I. As was expected, at room temperature the resistivity increases with an increasing YBaCuO content. At 77 K, no electrical conductivity improvement is observed, and therefore we conclude that no superconducting transition has occurred in the dispersed YBaCuO phase.

In composites with YBaCuO contents > 60 wt %, studied by Salama *et al.* [7], continuous paths are formed in the superconducting phase, as the percolation threshold, P_c, in random metal/insulator composites have been located in a range from a few to 30 vol% of metal depending on the shape of the metal particles. For their composites, Salama *et al.* observed critical temperatures > 90 K, but the 40 wt % Cu composite, while exhibiting a high T_c, possessed some residual resistance which disappeared at 47 K. It was therefore concluded that the O_2 content in the superconducting phase is not affected by the presence of Cu.

TABLE I Electrical measurements: 100% IACS: electrical conductivity of a standard Cu; 300 K, 0.58 $\mu\Omega^{-1}$ cm^{-1}; 77 K, 3.98 $\mu\Omega^{-1}$ cm^{-1}

Sample	Resistivity (μΩ cm)	% IACS
300 K		
Cu–5 wt % YBaCuO	1.970	87.5
Cu–20 wt % YBaCuO	2.257	50.9
77 K		
Cu-5 wt % YBaCuO	0.295	85.3
Cu-20 wt % YBaCuO	0.330	49.1

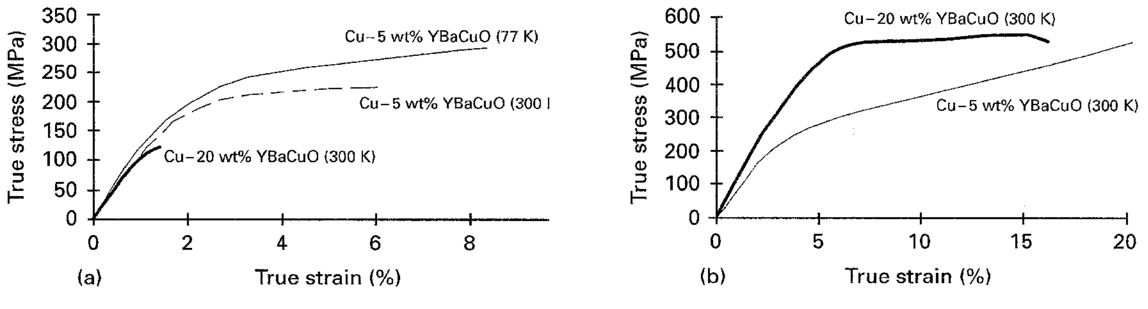

Figure 3 Stress–strain curves for the Cu–20 wt % YBaCuO and Cu–5 wt % YBaCuO alloys at different temperatures. (a) Tensile test; (b) compression, test.

However, our results seem to indicate that a higher increase in Cu led to a degradation of the YBaCuO component phase.

3.3. Identification of crystalline phases

Fig. 4 shows the XRD patterns of a Cu–20 wt % YBaCuO composite before (b) and after (a) sintering. Four peaks on Fig. 4b can be identified as the $YBa_2Cu_3O_{7-x}$ orthorhombic structure. The loss of these peaks on Fig. 4a indicates a microstructural evolution resulting from decomposition of $YBa_2Cu_3O_{7-x}$ during the sintering process.

All consolidated samples have nearly the same composition, namely: (1) Cu; (2) Y-rich phases: MET electron diffraction patterns (Fig. 5) confirm the presence of the $YCuO_2$ compound; (3) phases rich in Ba ($BaCu_2O_2$); (4) phases rich in Cu, Y and Ba ($YBa_2Cu_3O_{9-x}$). As the recorded intensities were very low, due to the small proportion of YBaCuO in the powder mix, XRD patterns of the Cu-5 wt % YBaCuO samples are not presented. The studies carried out using a scanning electron microscope (Jeol 2000) coupled with an EDX Link chemical analyser confirm this identification, although the O_2 content cannot be analysed directly (see Fig. 6). This instability of the superconducting dispersed phase explains the absence of improvement in the composite electrical properties at 77 K.

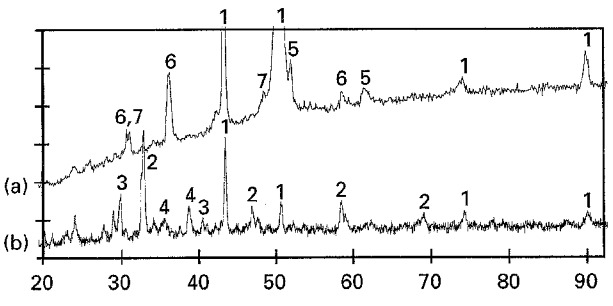

Figure 4 Changes in the XRD spectra of Cu–20 wt % YBaCuO composite before (b) and after sintering (a). 1, Cu; 2, $YBa_2Cu_3O_{7-x}$; 3, Y_2BaCuO_5; 4, CuO; 5, $YCuO_2$; 6, $BaCu_2O_2$; 7 $YBa_2Cu_3O_{9-x}$.

3.4. Microstructures

Use of hot extrusion of previously cold-compacted powders leads to near fully densified products and few porous sites are observed in our samples. The main aspects of the microstructure in Cu–5 wt % YBaCuO and Cu–20 wt % YBaCuO are shown in Fig. 7a and b, respectively.

In Cu-5 wt % YBaCuO samples, the various oxide phases resulting from the decomposition of YBaCuO are dispersed in the Cu matrix (Fig. 7a), whereas the Cu grains are completely surrounded by these residual oxides in Cu–20% YBaCuO samples (Fig. 7b).

The rather low tensile strength of the Cu–YBaCuO composites is almost certainly due to the fact that oxide particles are too large and too roughly dispersed in the Cu matrix to be efficacious strengthening reinforcements.

Conversely, the high brittleness of the Cu–20 wt % YBaCuO composite is attributed to the smaller volume fraction of the metal phase which can no longer play its role as binder. Moreover, it is well known that serious problems can arise from insufficient grain boundary cohesion in the oxide phases.

3.5. Influence of copper oxide addition

Several previous studies devoted to the preparation of YBaCuO superconductors or YBaCuO–metal composites have revealed a great instability in the superconducting properties, depending on elaboration process details [8–11]. This instability was principally attributed to a loss of oxygen stoichiometry during the fabrication process [1, 2, 7]. The control of oxygen stoichiometry is critical, as the level of oxygen in the YBaCuO compound needs to be in the 6.9 ± 0.1 range to obtain superconducting properties > 77 K. It was shown by Chen *et al.* [2], that stability can be retained in YBaCuO–metal composites, even with highly reactive metals such as Al, when 5 vol % AgO_2 is added in the powder mix. It was suggested that the decomposition of AgO_2 at ca. 200 °C during the final sintering provides oxygen, allowing stoichiometry stabilization of the $YBa_2Cu_3O_{7-x}$ compound in the composite. It is the reason why, following this concept, we also attempted to prepare Cu–YBaCuO composites with oxidized Cu powders as starting components.

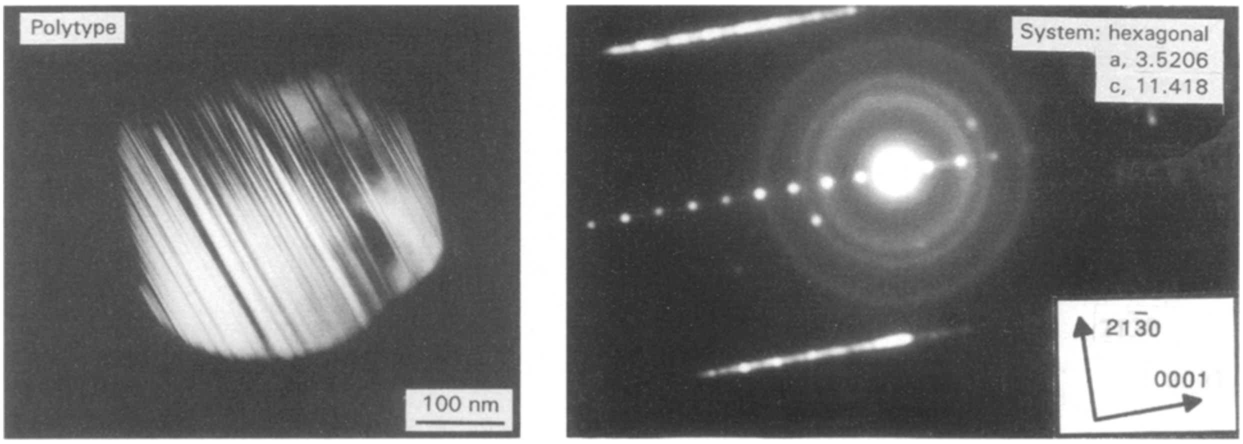

Figure 5 Electron diffraction pattern of the $YCuO_2$ compound (dark field image).

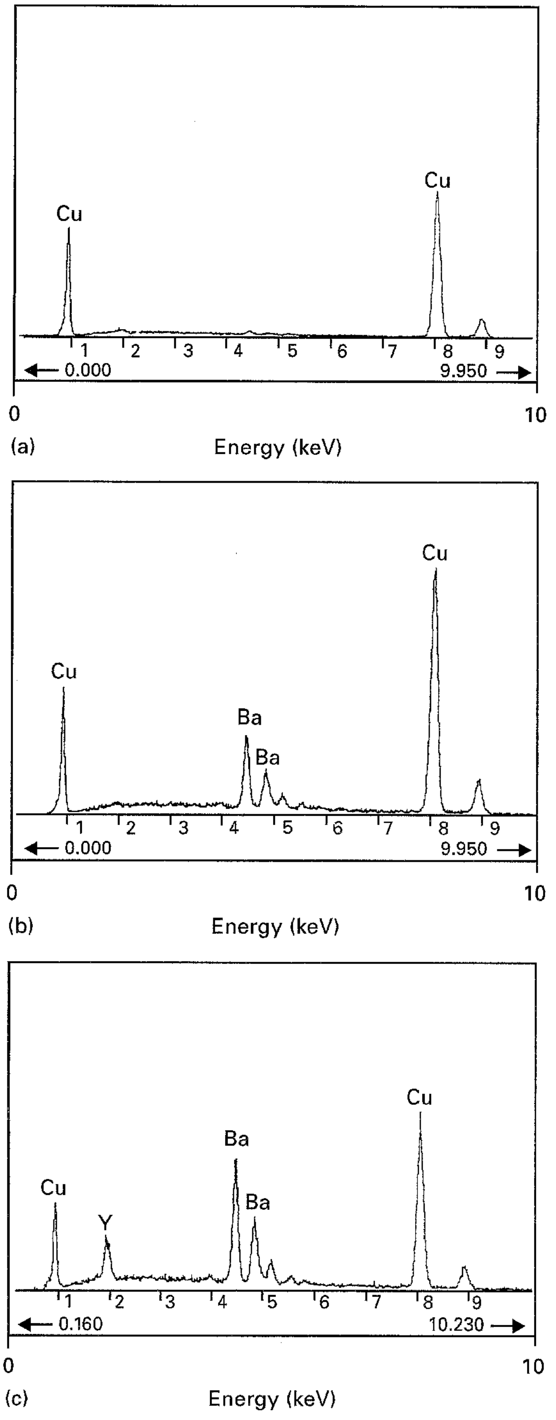

Figure 6 Results of EDS analysis for a Cu-20 wt % YBaCuO sample after hot extrusion: (a) Cu; (b) phase rich in Ba ($BaCu_2O_2$); (c) phase rich in Cu, Y and Ba ($YBa_2Cu_3O_{9-x}$).

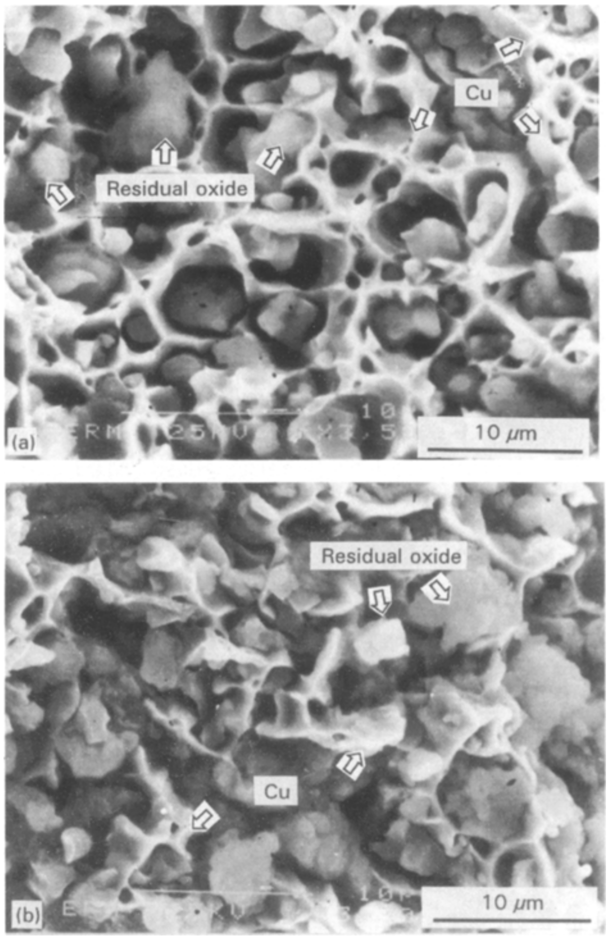

Figure 7 SEM micrographs of the fracture surface after hot extrusion: (a) the Cu–5 wt % YBaCuO alloy, brittle phases (resulting from YBaCuO decomposition) are enveloped in Cu grains; (b) the Cu–20 wt % YBaCuO alloy, Cu grains in this specimen are enveloped in brittle phases.

It was expected that Cu_2O oxide would act as an *in situ* oxygen donor, since its decomposition occurs at ca. 400 °C and sintering was performed between 400 and 600 °C. Therefore, the stability of the oxygen stoichiometry of the superconductive dispersed phase in the Cu matrix was believed to be achieved. Unfortunately, such a result was not observed in our experiments. For all our samples, and consequently for all elaboration conditions, the XRD patterns are nearly the same as the one presented in Fig. 4a. Regardless of the amount of oxygen supplied by the decomposition of Cu_2O, the deterioration of the $YBa_2Cu_3O_{7-x}$ orthorhombic phase could not be avoided. The products generated are the same as those mentioned above. The reason why the stability of the superconductive oxide was not maintained, while it was the case for the Ag_2O–YBaCuO composite, is still unclear. A possible explanation of this difference may result from the low xygen pressure in the case of the Cu_2O dissociation at temperatures ranging from 400 to 600 °C, and therefore insufficient diffusion of oxygen in the bulk of YBaCuO powders.

Further studies are necessary to clarify this. We probably need to find a compromise between YBaCuO, Cu and CuO_2 ratios. It is well known that small variations in the conditions of the elaboration process can drastically change the structures and properties of these kind of composites.

4. Summary and conclusion

This work was a first attempt to design new dispersion-strengthened Cu alloys with YBaCuO fine powder as the reinforcing dispersed phase. An improvement in strength of the Cu matrix, without any loss of conductivity, was expected for applications below T_c.

To date, the main conclusions are as follows:

1. The Cu-5 wt % YBaCuO samples exhibit a good ductility, whereas a content of 20 wt % of oxide leads to highly brittle behaviour.

2. The strength improvement is relatively low compared to that obtained in conventional ODS Cu alloys where the reinforcing phase is much more finely dispersed in the matrix.
3. No improvement in conductivity is observed when the temperature is decreased to 77 K.
4. Microstructural analyses indicate a great instability of the $YBa_2Cu_3O_{7-x}$ supraconductive phase. Attempts to ensure the stability of oxygen stoichiometry by Cu_2O addition in the initial powder mixture failed.
5. For technical applications, modifications of this powder processing route are needed. Efforts have to be made to obtain finer dispersions and to prevent orthorhombic $YBa_2Cu_3O_{7-x}$ decomposition.

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