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Production by solid/liquid reaction and characterization of high purity MgB_2 powders and thick films for superconducting application

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Abstract

The preparation of highly pure MgB_2 powder is here presented. The two steps preparation method, together with an ad hoc projected reactor, permits us to obtain the desired stoichiometric phase without MgO impurities and other degradation compounds, which depress the superconductive properties. The formation of a liquid phase during the first step of the preparation leads to small grain size particles. New techniques of film preparation (Electrophoretic deposition) have also been approached. By this method thick films suitable for practical applications have been obtained in a very simple and reproducible way at room temperature. Electrophoretic deposition has been carried out with success on low cost substrates. The deposited thick films looks to be very homogeneous, with the same crystal structure of the starting materials and without impurities and can be easily syntherised.

Keywords: Borides; Electrophoretic deposition; Films; Powders-gas phase reaction; Superconductivity

1. Introduction

Very recently magnesium diboride has been found to have superconducting properties with $T_c = 39$ K close to the value predicted by BCS theory.[1–3]

MgB_2 has the hexagonal AlB_2 type crystal structure, where the boron atoms form graphite-like sheets separated by hexagonal close-packed layers of Mg atoms. These metallic B layers seem to play a crucial role in the superconductivity of MgB_2.[4]

The great interest of this material is mainly the low cost potential, a low anisotropy, large coherence lengths and transparency of grain boundaries to current flow, in comparison to curprates.[5]

The synthesis of magnesium diboride is very simple; nevertheless, the quality of commercially available MgB_2 powders is not very high: it is usual to find in the powders a certain amount of MgO or other degradation compounds, e.g. MgB_6 or MgB_{12}. From this point of view, it is fundamental to use, during preparation, an Mg-vapour rich atmosphere, free of oxygen traces.

MgB_2 has been synthesized in many forms: bulk, thin films, wires, tapes and single crystal.[6–8] As far as powder preparation is concerned, reaction on B powder by an Mg rich phase is the most commonly used method.

Here, is presented the preparation of highly pure MgB_2 powder. In view of practical applications, powders are deposited on an inert substrate (Ti/Al_2O_3) by the electrophoretic technique to obtain a thick film and investigate its superconducting properties. As proved by studies on YBCO electrophoretic deposition carried out by our group, it is possible to obtain a superconducting thick film adhering well on Ag foils with complex geometric surfaces as, for example, tubes, rings, etc.

2. Experimental

2.1. Preparation

Mg pellets and B powders were mixed together in a weight ratio higher than 1:2 and pressed to about 10 tons in a pellet of 1 cm^3. The pellet was made to react in

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an ad hoc quartz device, described in the following, filled with 200 mbar ultra pure Ar atmosphere. Temperature was increased to 650 °C and maintained for 30 minutes and then to 850 °C for 150 min. After the preparation, MgB_2 is again pressed into a new pellet after a new addition of Mg. The pellet has been syntherised for 150 min at 850 °C in the ad hoc device.

2.2. Characterization techniques

SEM micrographs have been observed on all synthesized and deposited powders by means of JEOL apparatus (Philips 515 model equipped with PV9900 EDS). XRPD data have been collected by means of Phillips 'Xpert diffractometer (PW1710 model) equipped with graphite monochromator and Cu-K_α radiation. Diffractometric data have been used to refine cell parameters with XRD123 programs (http://www.polito.it).

2.3. Electrophoretic deposition

Commercial and laboratory prepared MgB_2 powders were deposited by means of ElectroPhoretic Deposition (EPD) technique. The deposition substrate was obtained by depositing by e-gun Ti thin film on Al_2O_3 substrate. Before the electrophoretic deposition, MgB_2 was previously dispersed in acetone to obtain a well dispersed suspension in a non-oxidizing medium. The powder was deposited under about 30 V electric field by means of AMEL potentiostat model 552. EPD has been performed under stirring for 10 min.

After deposition the thick film has been syntherised in the ad hoc device for 90 min at 850 °C in Ar atmosphere.

3. Results and discussion

The preparation method in two steps at different temperatures permits us to obtain very small particles. This is due to the fact that the first step leads to the liquid phase of Mg, which wets the boron particles before starting to react. The reaction therefore proceeds simultaneously on many sites of the pellet leading to a small granulometry of the powder, as demonstrated by SEM micrographs, not reported for the sake of brevity. The Mg rich atmosphere used during the annealing allows us to obtain final compounds with a stoichiometric ratio very close to the theoretical 1:2. The Mg rich atmosphere is guaranteed by using a high Mg/B ratio during the preparation of the pellet. No degradation compound, as MgB_6 or MgB_{12}, is found in the final products, as shown by X-ray diffraction pattern reported hereafter.

The SEM micrograph of MgB_2 powder after preparation and syntherisation is reported in Fig. 1. The hexagonal microstructure is well evident. Particles are very small (less than 1 μm) and seem to be quite well syntherised.

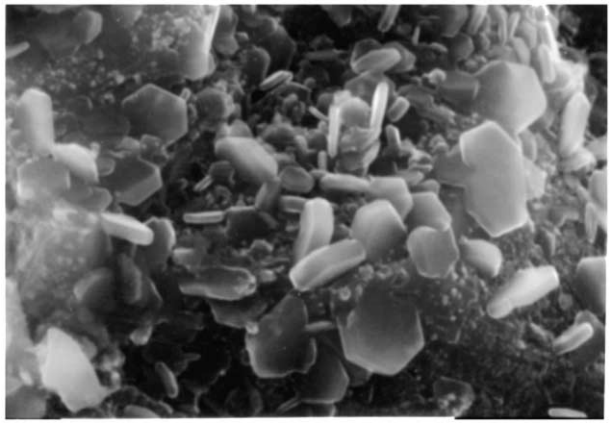

Fig. 1. SEM micrograph of MgB_2 powders after preparation and syntherisation (7400×).

X-ray diffraction pattern of MgB_2 powder after preparation and syntherisation is reported in Fig. 2. The compound is highly pure and all peaks of MgB_2 hexagonal phase (S.G. P622 n.177) are present.

Cell parameters have been refined: $a_0 = 3.090$ Å, $c_0 = 3.520$Å.

Some traces of metallic Mg are detectable since this element is present in excess during the synthesis. The absence of peaks of MgO is noticeable, which is, in general, easily produced, in the presence of oxygen traces. The absence of MgO has been obtained by using an ad hoc projected device. It consists of a quartz tube, which can be directly connected to a high vacuum pump through a glass tube in which it is possible to control the internal pressure and to insert gases. The high vacuum makes it possible to fill the device only with the desired gas (Ar in this case) without any presence of O_2 traces during the entire annealing process.

Electrical characterization has been carried out. AC susceptibility (Fig. 3) shows a net transition at about 39 K with $\Delta Tc = 2$ K.

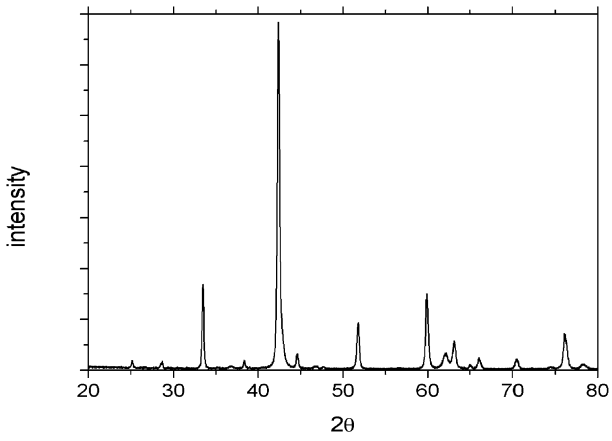

Fig. 2. XRPD of MgB_2 powders after preparation and syntherisation.

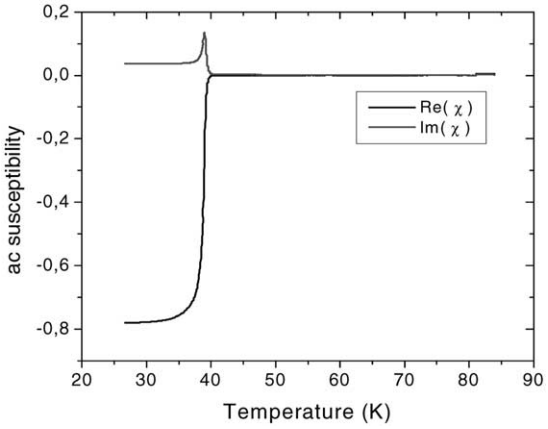

Fig. 3. Susceptibility measurement of MgB_2 pellet.

A thick film of the as above-synthesized MgB_2 powder has been easily deposited on an inert substrate (Ti on Al_2O_3) by the EPD technique.

The dispersive medium was acetone, which was also chosen for its non-oxidizing characteristics. This solvent has proved to be a good medium to maintain MgB_2 particles in suspension for a long time, higher than those necessary for the EPD.

The electrophoretic deposition has been carried out very simply at room temperature with low voltage fields (30 V) and low current densities (about 1 mA/cm^2). It is noteworthy that the deposition has been carried out on very cheap substrates as, in this case, Ti deposited on Al_2O_3 having lower costs than the Ag foils used in general for the electrophoretic deposition of cuprates.

The deposition does not modify the crystal structure, as demonstrated by the X-ray diffraction pattern reported in Fig. 4. Cell parameters have been refined also after deposition and do not show significant variations from the pure compound, as reported above. No traces of MgO or degradation compounds as MgB_6 or MgB_{12} has been observed.

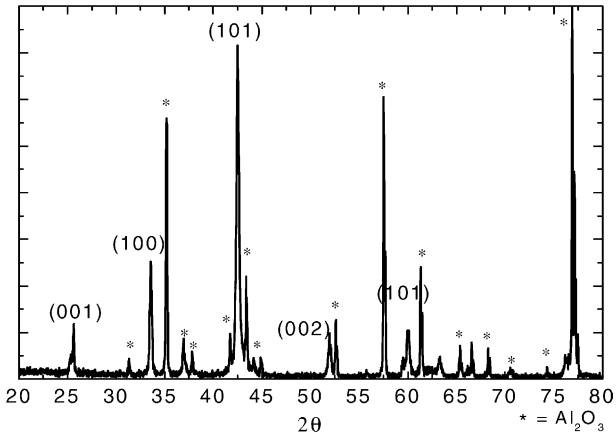

Fig. 4. XRD of MgB_2 deposited on Al_2O_3 by electrophoresis and syntherised.

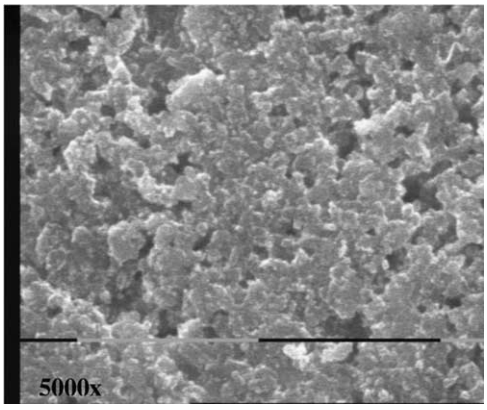

Fig. 5. SEM micrograph of MgB_2 deposited on Ti/Al_2O_3 substrate by electrophoresis and syntherised (5000×).

The electrophoretic deposition leads to a very homogeneous 10 μm thick film (SEM micrograph not reported for sake of brevity). Spherical particles are very well dispersed, but a strict contact among particles has to be obtained to present a high superconductive performance. The film has been syntherised and the result is shown in the SEM micrograph reported in Fig. 5. It can be observed that the particles can be syntherised, obtaining a homogeneous film.

Studies on EPD deposition of MgB_2 at different voltage values, on several substrates and in various dispersive media are actually under investigation.

Susceptibility measurements have not yet been performed, but if the high purity of the deposited powder and the good syntherisation degree is considered, we expect to find critical transition temperature close to that of the bulk (39 K)

4. Conclusions

The two step preparation method presented, together with a suitable reactor, permits us to obtain the desidered stoichiometric phase without MgO impurities, and other degradation compounds, which depress the superconductive properties.

The formation of a liquid phase during the first minutes of the preparation leads to small grain size.

Syntherisation in an oxygen free atmosphere is important in view of obtaining compounds with high superconductive performances.

New techniques of film preparation (EPD) have also been approached. By this method thick films suitable for practical applications have been obtained in a very simple and reproducible way at room temperature.

EPD has been carried out with success on low cost substrates.

The thick films obtained look very homogeneous, with the same crystal structure as the starting materials

and without MgO or other degradation compounds. EPD films can be easily syntherised.

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