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High-energy ball milling and Synthesis temperature study to improve superconducting properties of MgB_2 *ex-situ* tapes and wires

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Abstract— MgB_2 monofilamentary nickel-sheated tapes and wires were fabricated by means of the *ex-situ* powder-in-tube method using either high-energy ball milled and low temperature synthesized powders. In the first part of the paper it will be shown the effect of milling on tapes realized with powders synthesized at 900°C. The milling time and the milling revolution speed were tuned in order to maximize the critical current density (J_c) in field: the maximum J_c value of 6 x 10^4 A/cm^2 at 5K and 4T was obtained for the tape prepared with powders milled for 144h at 180rpm. In the second part of the paper we study the effect of the powders synthesis temperature in a wire configuration. Various synthesis temperature were investigated (730-900°C) finding a best J_c value for the wire prepared with powders synthesized at 745°C. We speculate that this optimal temperature is due to the *fluidifying* effect of unreacted magnesium content before the sintering process which could better connect the grains.

***Index Terms*— critical current, magnesium diboride, ex-situ, high energy ball-milling, synthesis temperature**

I. INTRODUCTION

A great deal of work on MgB_2 development has been done by many groups since MgB_2 was discovered [1], and significant progress is being made in improving basic properties such as the critical current (J_c), the upper critical field (H_{c2}) and the irreversibility field (H_{irr}). Most of these efforts have been focused on the improvement of the high-field J_c and H_{c2} by chemical doping with carbon (C) containing compounds, such SiC, C, B_4C and carbon nanotube (CNTs) [2]-[7].

However, the doping effects have been limited by the agglomeration of nanosized dopants and poor reactivity between boron and C.

Moreover, the self-field and the low-field J_c were depressed due to the decrease in the superconducting volume.

To improve these properties, various methods have been reported. They include, for example, a ball-milling method [8], [9], excess Mg addition [10], low-temperature solid-state reaction [11] and the use of MgH_2 powder instead of Mg [12].

The majority of these works have been made on bulks and on *in-situ* wires and tapes so, no systematic study of the effects of ball-milling parameters and synthesis temperature on *ex-situ* conductors has been performed yet.

The *ex-situ* technique permits the development of long conductors and multifilamentary tapes easier than *in-situ* method [13], allows a better control of the granulometry and purity degree of the starting powders, and the conductors obtained are more homogeneous.

However, the J_c behavior in magnetic field for the samples prepared by the *ex-situ* way is not so good as for the *in-situ* samples. Therefore, a further development of the starting MgB_2 powders is needed to make the *ex-situ* conductors definitely competitive.

In this paper, we present the results obtained by changing the properties of the starting MgB_2 powders on the J_c vs B behavior by two ways: varying high-energy ball milling parameters and varying the synthesis temperatures.

II. EXPERIMENTAL DETAILS

MgB_2 powders were prepared from HC Stark amorphous B (95-97% purity) and Sigma Aldrich Mg (99.99% purity): the powders were mixed and underwent a heat treatment at various synthesis temperature between 730 and 900 °C. In order to reduce the oxygen contamination the whole process was performed in glove box with a directly linked oven and using high purity Ar flow. Furthermore, for the study of milling effect, only powders synthesized at 900°C were high-energy ball milled in a planetary ball mill with WC jar and media for different milling times and/or for different milling revolution speed with a fixed ball to powder ratio of 12.

Monofilamentary tapes and wires were then fabricated by means of the *ex-situ* powder-in-tube technique [14]: previously synthesized MgB_2 powders were packed inside Ni tubes, the tubes were grove rolled and drawn down to a diameter of 1.4 mm. We used the wire configuration to study the synthesis temperature behavior. Instead, for the high energy ball-milling study, we used a tape of about 0.35 mm in thickness and 4 mm in width.

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The superconducting transverse cross section of the conductor was 0.6 mm^2 for the wire and 0.2 mm^2 for the tape configuration. All tapes and wires, after the deformation process, were sintered at 920°C in Ar flow.

The microstructure of MgB_2 powders was investigated using a Scanning Electron Microscope (SEM) with which the grain size distribution was carried out, and X-ray diffraction (XRD) to identify the purity phase and to estimate the crystallite size.

Short pieces of about 6 mm in length cut from the Ni-sheated tapes and wires were employed to perform magnetization measurements vs. magnetic field in a commercial 5.5 T MPMS Quantum Design Squid magnetometer. The magnetic field was applied perpendicular to the tape surface and critical current density values were extracted from the *M-H* loops applying the appropriate critical state model. Demagnetization corrections are negligible at field above 0.7 T, being the Nickel saturation field [15].

III. Results and Discussions

It is well known that the critical current density of MgB_2 *ex-situ* conductors is directly influenced by the micro structural properties of the initial superconducting powders.

The aim of this work is to study how optimize these properties to improve the critical current density behaviour of the superconducting tapes and wires following two ways: by varying the milling time and/or energy in a high energy ball-milling process or by varying the powders synthesis temperature.

Critical current improvement through high energy ball-milling

The ball-milling effect is well known: it is used to reduce the powders average grain size to improve the performances of the samples in magnetic field.

In our previous work [16]-[18] we have shown how J_c increases when the milling time and/or the milling revolution speed increases. In both cases we obtained an improvement until a maximum value is reached and then a decrease for higher milling times and/or speeds.

Here we perform a more detailed study and show how this feature is correlated to the empirical parameter which we will call *"Milling Parameter"* (MP); i.e. the product between the square of the milling revolution speed (rpm^2), proportional to the milling energy, and the milling time (h). MP represents, apart a constant factor, the power transferred from the milling process to the powders (for a detailed study on ball-milling parameterization see the work by Mio et al. [19]).

Our data are summarized in Fig.1a where the critical current density as a function of the magnetic field is shown at 5 K as extracted from the *M-H* loops with the field perpendicular to the tape surface. For simplicity the symbols used in Fig.1a are the same for all the subsequent plots.

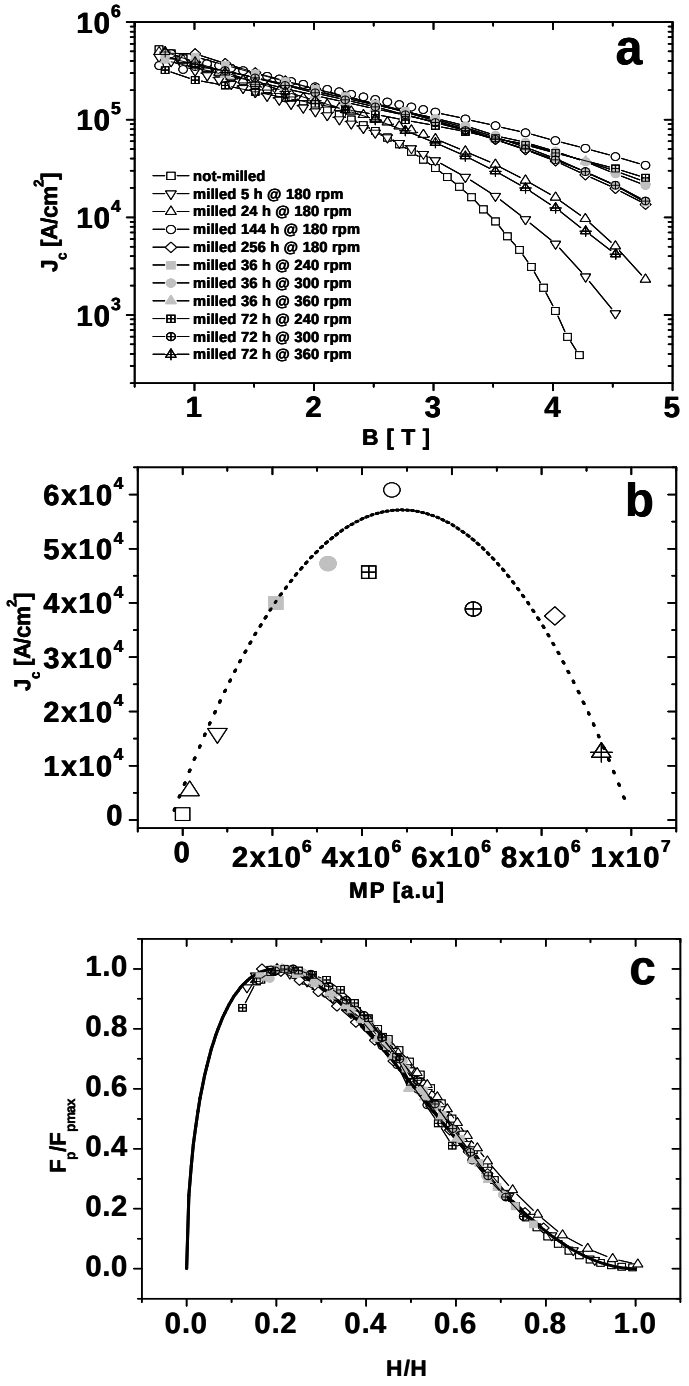

Fig. 1 (a) Magnetic Jc vs B; (b) Magnetic Jc vs MP at 4T,5K; (c) Normalized pinning force vs normalized field.

To better visualize this behaviour we plot in Fig.1b the J_c value obtained at 4T and 5K as a function of MP (the line is only a guide for the eye). We obtained the maximum J_c value of 6 x 10^4 A/cm^2 corresponding to the optimal milled tape for 144h at 180rpm.

Quite similar results can be obtained for the tape whose powders are milled for 36h at 300rpm, thus strongly reducing the milling time.

In our previous work [17] we have shown, by means of magnetization measurements in magnetic field, parallel and perpendicular to the tape surface, that the critical current anisotropy already disappear for this degree of milling.

In Fig.1c the normalized pinning force at 5K is reported as a function of the normalized irreversibility field H/H_{irr}. The irreversibility field was determined with a Kramer linear extrapolation and is indicated in the plot as the Kramer field $H_{irr}=H_k$. For comparison also the theoretical curve of grain boundary pinning model, with its maximum at 0.2, is reported.

As we can clearly see, the pinning force behavior is well described by the grain boundary based pinning model and is the same for all the samples, suggesting that the J_c changes cannot be explained in terms of modifications of the pinning mechanism.

In Fig.2a the average particle size obtained from SEM analysis is plotted as a function of MP. The effect of ball milling is evident already for low MP values, where the particle size abruptly decreases from 1.4 to 0.4 μm. Further increasing MP has only a weak effect on the particle size, which remain almost constant between 0.3 and 0.4 μm.

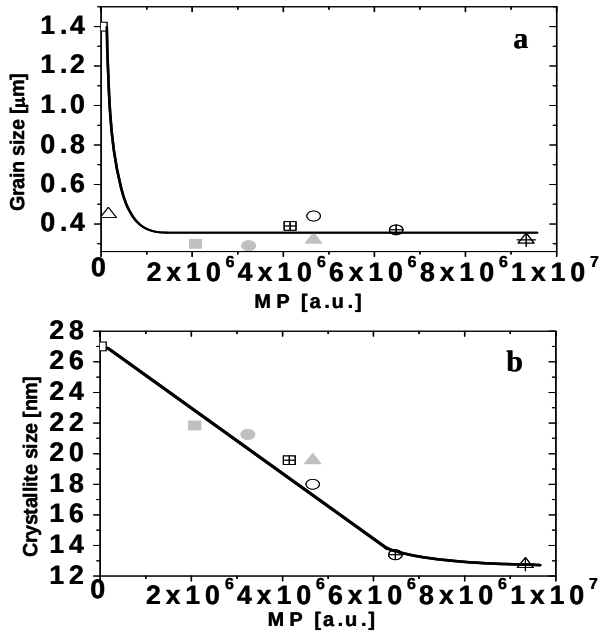

Fig. 2. (a) Average particle size obtained from SEM analysis; (b) Average crystallite size obtained from XRD analysis. The lines are only a guide for the eye.

An interesting result was obtained going to investigate the average crystallite size. In Fig.2b is shown the lower limit of the average crystallite size obtained from XRD analysis. The software is based on Debye-Scherrer formula and give a negligible strain values (of the order of 0.005) for all the milled powders. Also the contamination due to the WC balls and jar is negligible (<0.5 %).

These crystallite size values, lower than those obtained for the particle size from SEM analysis, ranging from 13 to 27 nm, suggests that the grains are polycrystalline agglomerate of smaller crystallite and that ball milling continues to be effective increasing MP.

A complete characterization of the optimal milled tape has been done in our recent work [18] where H_{c2}, magneto-resistivity and magneto-optical measurements have been performed. For this tape, the perpendicular critical field at 25K increases from 6T (for the not milled sample) to 9.5T. Our analysis correlate the J_c in-field improvement to the enhanced H_{c2} value due to extra electrons scattering coming from the reduced crystallite size, comparable to the mean free path of MgB_2.

Nevertheless, at higher MP, the disorder increases, as in C-doped or in neutron irradiated sample [20] and this may be the reason why J_c decreases for higher MP values. In order to confirm this hypothesis we are planning to perform H_{c2}, magneto-resistivity and critical temperature measurements on the whole set of tapes.

Critical current improvement through synthesis temperature

As we said in the introduction, most of the studies on the synthesis of MgB_2 are done for bulks or for *in-situ* tapes or wires.

Here we report on the behaviour of the critical current density of MgB_2 *ex-situ* wires as a function of synthesis temperature. We explored various temperatures ranging from 730 to 900°C synthesizing and managing the powders in a glove box, to avoid any oxygen contamination effects, until the powders were sealed into the tube. The oxygen content is in fact a crucial parameter for what concern the J_c in-field behavior of the samples and can affect the pinning mechanism [21].

The main and substantial difference respect to bulk and *in-situ* conductors fabrication process is that in the *ex-situ* process the powders undergoes two heat treatments.

The first heat treatment is analogous to the bulk synthesis process while the second happen at the end of the mechanical deformation process in order to sinter the grains between them and relax the powders and the sheath strain [14], [22].

So, we have powders synthesized at various temperature while the final wires are all sintered at the same temperature of 920°C.

In Fig.3 is shown the magnetic J_c at 5K as a function of the perpendicular applied magnetic field for the wires synthesized at various temperatures. For simplicity the symbols used in Fig.3 are the same for all the subsequent plots.

We remind here that these samples are square wires and they therefore show a better in-field J_c respect to the flat tapes of Fig.1a.

For some wires the data at lower field are not reported because of the presence of flux-jumps in the hysteresis loop due to magnetic and/or thermal instabilities. Even without these data points it is clear that the wire synthesized at high temperature (900°C) has a lower J_c than of those synthesized at low temperatures (around 745°C).

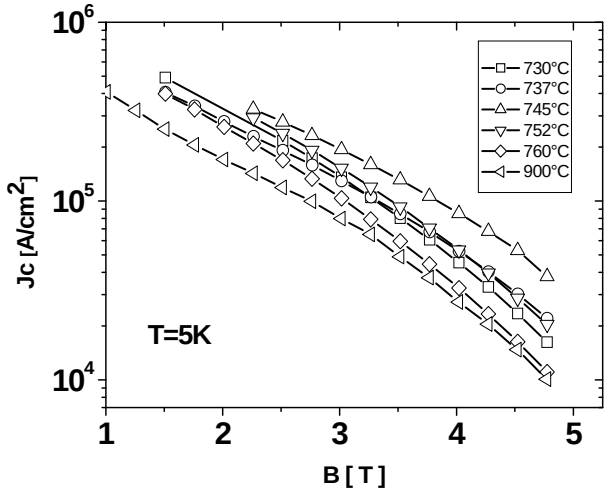

Fig. 3. Magnetic Jc vs B for the wires synthesized at various temperature

The wire with the highest J_c is obtained for the synthesis temperature value of 745°C.

To better visualize the effect of synthesis temperature we plot in Fig.4 the J_c value obtained at 4T and 5K as a function of synthesis temperature.

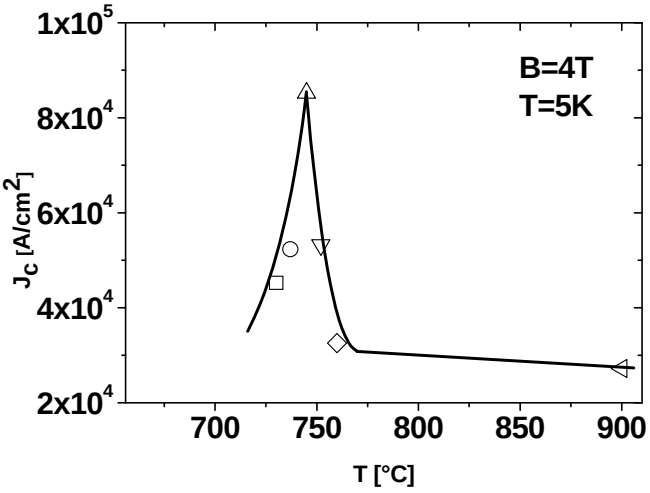

Fig. 4. Magnetic Jc vs synthesis temperature at 4T, 5K. The line is only a guide for the eye

The critical current density first increases slowly, decreasing the temperature from 900 to 752°C and then rapidly increases reaching a maximum at 745°C. Further reducing T gets J_c worse again.

In Fig.5 the magnesium relative content is shown as a function of the synthesis temperature. This can be roughly estimated from the ratio between the XRD intensities of the (101) peak of MgB_2 and the (220) peak of Mg for all the samples.

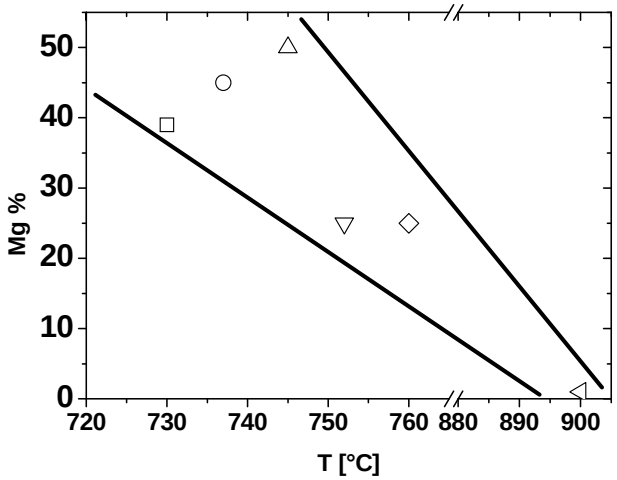

Fig. 5. Relative magnesium content vs synthesis temperature. The lines are only a guide for the eye.

As foreseen, the amount of unreacted Mg increases by lowering the synthesis temperature therefore decreasing the amount of reacted MgB_2.

We speculate that the wire synthesized at high temperature (900°C) has a lower J_c with respect to the others because the absence of Mg and B during the mechanical deformation process is detrimental to a correct grain packaging.

The presence of the latter could act as a *fluidifying* for the MgB_2 grains, resulting therefore more connected. This could happen because during the deformation process, where the grains are subjected to stress and cracks, the presence of Mg and B can fill the voids left from the imperfect packaging of broken grains.

The subsequent sintering at 920°C then, has the double aim to complete the chemical reaction between the unreacted Mg and B and to finally sinter and relax the whole grains.

It is a middle way between the *in-situ*, where the deformation can pre-activate some Mg and B atoms to form MgB_2 before the final sintering, and a full *ex-situ* process, where the MgB_2 phase is completely developed before the deformation take place.

IV. CONCLUSIONS

We studied the properties of ex-situ MgB_2 tapes and wires finding the optimal parameters to improve the J_c for the high-energy ball milled tapes and for the wires realized at various synthesis temperature. We obtained the maximum J_c value of 6×10^4 A/cm^2 corresponding to the optimal tape prepared with powders synthesized at 900°C and milled for 144h at 180rpm.

Similar results can be obtained for the tape milled for 72h at 240rpm then strongly reducing the milling time.

The best synthesis temperature is found to be 745°C, where J_c presents a maximum. We speculate that this maximum is due to a balanced amount between unreacted magnesium content and reacted MgB_2 before the final sintering process.

REFERENCES

[1] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenital and J. Akimitsu, "Superconductivity at 39 K in magnesium diboride", *Nature*, 410 (2001) 63.

[2] S. X. Dou *et al*, "Enhancement of the critical current density and flux pinning of MgB_2 superconductor by nanoparticle SiC doping", *Appl. Phys. Lett*., 81 (2002) 3419.

[3] J. H. Kim, W. K. Yeoh, M. J. Qin, X. Xu and S. X. Dou, "The doping effect of multiwall carbon nanotube on MgB_2/Fe superconductor wire", *J. Appl Phys*,. 100 (2006) 013908

[4] W. K. Yeoh, J. H. Kim, J. Horvat, X. Xu, M. J. Qin and S. X. Dou, "Control of nano carbon substitution for enhancing the critical current density in MgB_2**",** *Supercond. Sci. Technol.*, 19 (2006) 596

[5] R. A. Ribeiro, S. L. Bud'ko, C. Petrovic and P.C. Canfield, "Carbon doping of superconducting magnesium diboride", *Physica* C, 384 (2003) 227

[6] W. Mickelson, J. Cumings, W. Q. Han and A. Zettl, "Effects of carbon doping on superconductivity in magnesium diboride", *Phys. Rev*. B, 65 (2002) 052505

[7] A. Yamamoto *et a*., "Effects of B_4C doping on critical current properties of MgB_2 superconductor", *Supercond. Sci. Technol*.,. 18 (2005) 1323–8

[8] T. Kondo *et al*, "MgB_2/Fe superconducting tapes made using mechanically milled powders in Ar and H_2 atmospheres", *Physica* C, 426 (2005) 1231.

[9] X. Xu, J. H. Kim, W. K. Yeoh, Y. Zhang and S. X. Dou, "Improved J_c of MgB_2 superconductor by ball milling using different media", *Supercond. Sci. Technol*.,. 19 (2006) L47-L50

[10] R. Zeng *et al*, "Significant improvement in the critical current density of *in situ* MgB_2 by excess Mg addition", *Supercond. Sci. Technol.* 20 (2007) L43-L47.

[11] A. Yamamoto, J. Shimoyama, S. Ueda, Y. Katsura, S. Horii and K. Kishio, "Improved critical current properties observed in MgB_2 bulks synthesized by low-temperature *solid-state* reaction", *Supercond. Sci. Technol.*, 18 (2005) 116-121.

[12] T. Nakane, H. Fujii, A. Matsumoto, H. Kitaguchi and H. Kumakura, "The improvement of in-situ powder in tube MgB_2 tapes by mixing MgB_2 to the starting powder of MgH_2 and B", *Physica* C, 426 **(**2005) 1238

[13] V. Braccini, D. Nardelli, R. Penco, G. Grasso, "Development of ex-situ processed MgB_2 wires and their applications to magnets, *Physica C*, 456 (2007) 209.

[14] G. Grasso et al, "Large transport critical currents in unsintered MgB_2 superconducting tapes", *Appl. Phys. Lett*., 79 (2001) 230

[15] V. Braccini et al,"MgB_2 tapes with non-magnetic sheath: Effect of the sintering temperature on the superconducting_properties", *IEEE Trans. Appl. Supercond*., 15 (2005) 3211

[16] V. Braccini et al , "Improvement of magnetic field behavior of Ex-Situ processed magnesium diboride tapes", *IEEE Trans. Appl. Supercond.* 17 (2007) 2766

[17] M. Vignolo et al, "Development of MgB_2 powders and study of the properties and architecture of ex-situ PIT wires", *IEEE Trans. Appl. Supercond.* 18 (2008) 1175

[18] A. Malagoli *et al*, "Effect of grain refinement on enhancing critical current density and upper critical field in undoped MgB_2 *ex-situ* tapes", *submitted fo publication to the Journal of Appl. Phys.*

[19] H. Mio, J Kano, F Saito, "Scale-up method of planetary ball mill", *Chemical Engineering Science*, 59 (2004) 5909

[20] C. Tarantini *et al*, "Effects of neutron irradiation on polycrystalline $Mg^{11}B_2$", Phys. Rev. B, 73 (2006) 134518.

[21] M. Vignolo *et al*, submitted for publication to ASC 2008.

[22] G. Grasso *et al*," Fabrication and properties of monofilamentary MgB_2 superconducting tapes", *Supercond. Sci. Technol.*, 16 (2003) 271