The Effect of Ball Milling and Fatty Acid Addition on the Properties of MgB_2 Wires

Carlos Laliena, Elena Martínez, Luis Alberto Angurel and Rafael Navarro

***Abstract*—Improved inductive critical current density, J_c, at medium and high magnetic fields, B, has been obtained in MgB_2 wires made from ball milled and carbon doped precursors. The analyzed Fe-sheathed mono-filamentary wires have been manufactured by the powder-in-tube (PIT) and *in-situ* methods. C doping has been achieved by the addition of fatty acids, in particular oleic acid ($C_{18}H_{34}O_2$). In order to enhance the $J_c(B)$ performance and the homogeneity of the wires, we have analyzed the combined effects of ball milling and oleic acid addition. The changes in the microstructure, phase composition and superconducting properties for different milling parameters and fixed amount of acid addition have been analyzed.**

***Index Terms*— ball milling, critical currents, doping, MgB_2, superconducting wires.**

I. Introduction

GRAIN REFINEMENT [1]-[3] and carbon doping [4]-[7] are two processes widely used to improve the $J_c(B)$ performance of metal composite MgB_2 wires and tapes. Ball milling of MgB_2 precursor powders may produce very fine and well mixed precursors with higher reactivity, yielding *ex-situ* tapes with small grains and improved density of grain boundaries, without introducing additional magnetic flux pinning mechanisms [1],[2]. Moreover, Häßler *et al.* [3] have observed an improvement of $J_c(B)$ values at high fields for *in-situ* reacted MgB_2 bulks and wires made from ball milled precursor. Also, this enhancement has been correlated with the milling energy, E_t, which depends on the rotation speed, ω_p, and milling time, t.

On the other hand, the enhancement of $J_c(B)$ values of MgB_2 bulks and wires by carbon doping has been widely sought in literature by using different carbon sources [4]-[6]. C atoms partially substitute B in the MgB_2 lattice, which results in an increase in the upper critical magnetic field, H_{c2}. Moreover, the dopant introduces secondary phases that may act as pinning centres [6]. The addition of a liquid organic compound, which decomposes at temperatures below the reaction temperature of MgB_2 and gives a fresh C-source [4], has some advantages compared to the conventional C doping by dry solid-state process. Recently we have reported J_c enhancement by the addition of oleic acid to the Mg+B powders [7]. Nevertheless when the acid is added to the B powders, we have observed a lack of homogeneity across and along the wires. Ball milling would be an effective method to improve the homogeneity of the wires and to reduce the grain size of the precursor powder.

In this contribution we report on the combined effects of ball milling and oleic acid doping for Fe-sheathed mono-filamentary MgB_2 wires manufactured by the powder-in-tube (PIT) technique and *in-situ* reaction. With this aim, a characterization of the microstructure, phase composition and superconducting properties of the wires made from precursors with different milling parameters, with and without oleic acid addition has been done.

The composite wires were manufactured by the PIT technique and *in-situ* reactions using Fe tube (99.5%, Goodfellow), with an outer diameter of 5 mm and a thickness of 0.25 mm. The tubes were hand filled with mixtures of Mg+B or Mg+(oleic acid coated B) powders, mechanically sealed at both ends and drawn through round dies down to a final outer diameter of 1.1 mm. In all cases an intermediate anneal was performed during drawing to reduce the Fe sheath's work hardening.

Starting materials were commercial Mg powders (99.8%, Goodfellow, maximum particle size of 250 μm), amorphous B powders (99%, New Metal & Chemicals Ltd, mean particle size lower than 1 μm), and liquid oleic acid (99%, Alfa Aesar). The initial powder mixing was performed in a Retsch MM 200, during 3 steps of 5 minutes each. The used planetary ball mill (Retsch PM 100) has a sun disk of radius $r_p = 7$ cm and a
WC jar with inner radius $r_v = 5.25$ cm. The ratio of the WC balls mass to the powder mass was $\beta = 36$.

Six Fe-sheathed MgB_2 wires with the characteristics collected in Table I have been manufactured. The reference wire W0 was made by direct mixing Mg and B powders with 1:2 stoichiometry and a softening treatment at 550ºC × 0.5 h. Three un-doped wires W0-MA, W0-MB and W0-MC were made with Mg+B powders with (1.05:2) proportion. In two of them, W0-MA and W0-MB, the precursors were milled with 1 minute pauses and rotation sense changes every 3 minutes, to avoid local heating that may lead to MgB_2 formation. The effective milling times, t, are collected in Table I. An intermediate softening heat treatment at 400ºC × 1 h was done in both cases.

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II. Experimental

TABLE I
PROPERTIES OF THE STUDIED SAMPLES

Sample	C doping	Ball Milling		T_c (K)	ΔT_w (K)	*O*-cont. (at %)
		t (h)	ω_p (rpm)			
W0	No	0	0	37.5	0.7	3.5 (0.6)
W0-MA	No	16.5	400	33.0	1.0	6.4 (0.7)
W0-MB	No	3	400	35.0	0.5	8.2 (1.5)
W0-MC	No	4	200	34.5	0.9	9.2 (0.9)
W10B	Yes	0	0	36.0	1.5	5.0 (1.0)
W10B-MB	Yes	3	400	32.5	1.1	13.7 (0.5)

Effective ball milling time (t) and rotation speed (ω_p), critical temperatures (T_c) and transition widths (ΔT_w) derived from $\chi_{ac}(T)$. The oxygen content (O-cont) values and standard deviations have been deduced from FESEM images and EDX analysis.

To reduce the milling energy values, E_t, the precursor powder used for the W0-MC wire was milled at 200 rpm × 4 h without pauses, but changing the rotation sense every 3 minutes. An intermediate anneal at slightly higher temperature 550ºC × 0.5 h was done to increase effective wire softening.

To make both C-doped wires, W10B and W10B-MB, the starting boron powders were first mixed with 10 wt% oleic acid and preheated at 400ºC × 1 h in Ar atmosphere to eliminate oleic excess. Subsequently, the oleic acid coated boron powders were mixed with Mg. Wire W10B was filled directly with these precursor powders whereas for W10B-MB the same ball milling (time and rpm) as for W0-MB was used.

For all wires, a common final reacting treatment at 670ºC × 5 h in vacuum (0.1 mbar) has been done in order to form the superconducting MgB_2 phase.

The magnetic characterization has been done for cylindrical samples with a length of 5 mm and radius R = 0.4-0.45 mm obtained after removing the iron sheath by mechanical polishing. AC magnetic susceptibility as a function of the temperature, $\chi_{ac}(T)$, was measured with a superconducting quantum interference device (SQUID, Quantum Design MPMS-5T) to estimate the critical temperature T_c, defined as the diamagnetism onset, and the transition width ΔT_w, defined as the change from 10% to 90% of the χ_{ac} in-phase component at 5 K. Moreover, at 5 K the isothermal magnetic hysteresis loop $M(H)$ up to 9 T was measured in a vibrating sample magnetometer (VSM, Quantum Design PPMS-9T).

In all measurements the magnetic field was applied perpendicular to the cylinder axis to have the induced superconducting currents mostly flowing along the wire axis. From the width of the magnetic hysteresis loops, $\Delta M(H)$, the inductive critical current densities were derived using Bean's critical state model:

$$J_c(H) = \frac{3\pi}{8}\frac{\Delta M(H)}{R}, \qquad (1)$$

where $\Delta M(H)$ is in A/m, R in m and J_c in A/m^2.

The microstructure and phase composition have been analyzed on polished sections of the reacted wires by a field-emission scanning electron microscope (FESEM, Carl Zeiss MERLIN), using secondary electrons (SE), angle-selective backscattered electrons (AsB), and energy-dispersive X-ray spectroscopy (EDX). In order to reduce the limitations of EDX to quantify light elements as boron and oxygen, identical experimental conditions were used in all cases. X-ray diffraction (XRD) of the precursor powder was also performed with a RIGAKU D/max 2500 Cu Kα.

III. Results and Discussion

A. Homogeneity and Microstructure of Wires

The FESEM (SE) micrographs of Fig. 1 show the longitudinal cross-sections of un-doped wires made with different ball milled precursors.

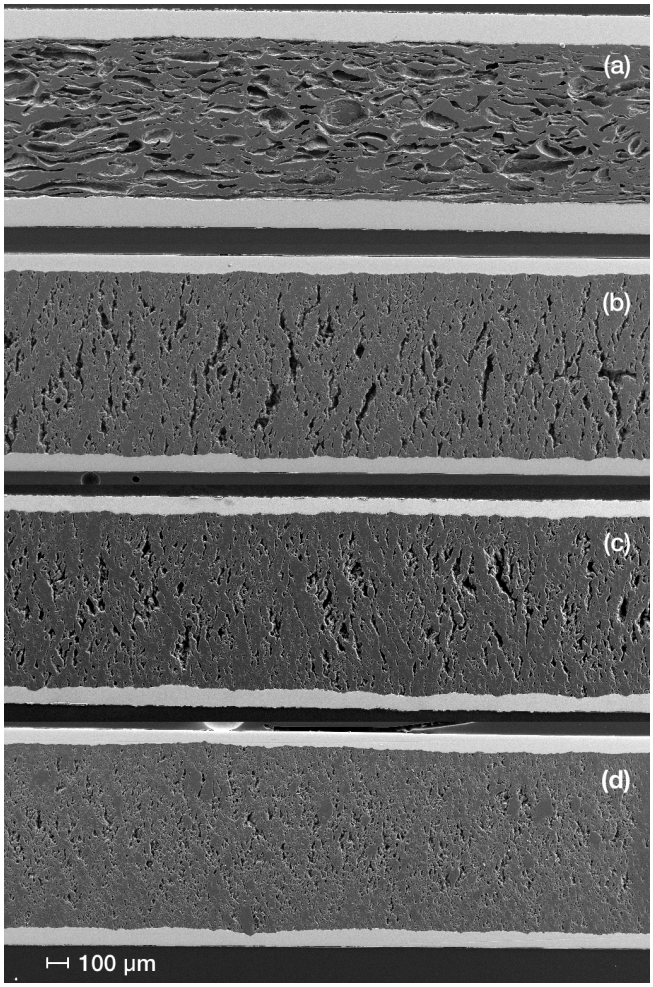

Fig. 1. FESEM (SE) images of polished longitudinal sections of reacted un-doped wires (a) W0, (b) W0-MA, (c) W0-MB, (d) W0-MC, after the final reacting heat treatment. Lighter grey corresponds to wire outsider Fe sheaths; darker grey to MgB_2 and black zones to empty voids and cracks.

The microstructure of the reference wire W0 is shown in Fig. 1(a). The core displays characteristic irregular voids of different shapes and sizes (up to 300–400 μm), left by Mg when it reacts with B to form the superconducting MgB_2 phase. Voids closer to the Fe sheath are more elongated and parallel to wire axis, whereas those at the centre tend to be more isotropic because the decreasing shear stress transmission from the sheath to the core center during drawing. The core represents 75% of the wire cross section.

The effect of ball milling in the microstructure of W0-MA and W0-MB wires is observed in Figs. 1(b) and 1(c). These wires present a denser and more homogeneous core than W0, also smaller voids, in agreement with reported results [3]. The core section is 85% of the wire cross section. Transversal cracks, clearly seen in these wires, would reduce severely the overall transport J_c values. The size of the cracks diminishes upon reducing the ball milling time as can be seen in Figs. 1(b) and 1(c). Both wires were difficult to draw, as they presented some mechanical conformation problems, such as shear bands, narrowing and wire fracture, making it hard to get long wires.

The energy per unit mass transferred by ball milling, E_t/m, has been recognized as a good parameter to analyze the effects of milling. For similar ball mill and precursor powder, E_t/m has been quantified with the following expression:

$$\frac{E_t}{m} = c\beta \frac{(\omega_p r_p)^3}{r_v} t, \qquad (2)$$

where c is a dimensionless constant of the order of 0.1 [3]. That study also concluded that the higher the milling energy, the denser the filaments become. Simultaneously, the deformability of the wire deteriorates.

The precursors used for W0-MA and W0-MB wires have energies $E_t/m \approx 1\times10^8$ J·kg^{-1} and $E_t/m \approx 2\times10^7$ J·kg^{-1}, respectively. The hard workability and the crack distribution observed in their microstructure agree with the results reported in [3].

To visualize the effect of reducing the E_t/m energies, another wire was prepared with precursor powders milled at smaller rotational speed, W0-MC, so that $E_t/m \approx 3\times10^6$ J·kg^{-1}. This wire presents a more homogeneous microstructure, as it is seen in

Fig. 1(d), and the size of cracks has further reduced. Nevertheless, the transversal orientation remains, and the porosity increases toward the center, as for the un-milled wire.

XRD analysis of the precursor powder used for W0-MA wires indicates the presence of small amounts of already reacted MgB_2 phases (mechanical alloying) as well as MgO. MgB_2 phase is hardly seen in W0-MB precursor and disappears in the W0-MC precursor, in agreement with [3].

Figure 2 shows the FESEM (AsB) micrographs of wires W10B and W10B-MB, in order to analyze the effect of oleic acid addition and ball milling. As previously reported, [7] the direct use of oleic soaked boron powders mixed with Mg, (W10B wire shown in Fig. 2(a)), results in a very inhomogeneous phase distribution within the wire. The large porous microstructure seen in the upper part of the micrograph corresponds to the MgB_2 phase, while the darker zones at the lower part are non-superconducting boron rich phases.

On the contrary, wires made with oleic acid and ball milled precursor present a very good phase homogeneity, as shown in Fig. 2(b) for the W10B-MB wire. Although the microstructure is very similar to the un-doped W0-MB wire with the same milling, Fig. 1(c), cracks are smaller.

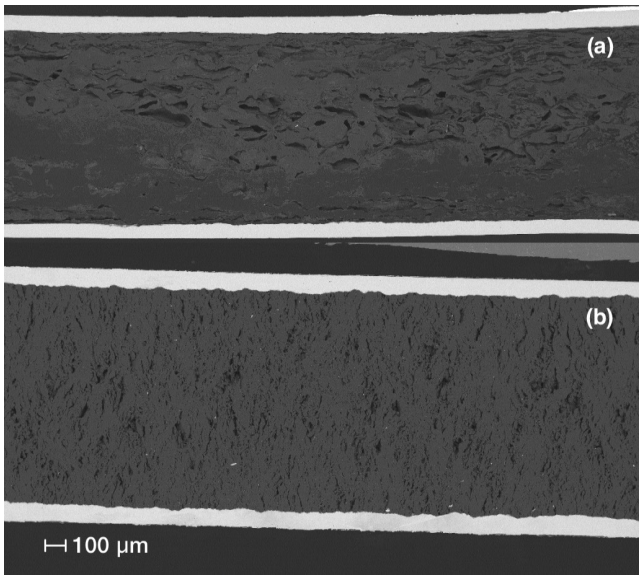

Fig. 2. FESEM (AsB) images of polished longitudinal sections of reacted wires: (a) W10B, made with un-milled and oleic acid doped precursors, (b) W10B-MB, made with milled and doped precursors. Lighter grey corresponds to the Fe sheath; medium grey to MgB_2; darker grey to B rich phase and black zones to empty voids and cracks.

Due to greater oxygen affinity of finer Mg powders to form MgO, and to larger reactivity of smaller grains, any small leak in the mill jar would lead to an increase in the oxygen content. Therefore, it would be expected that the oxygen gathered by the precursor during ball milling would increase with the milling time. Also, because of the oxygen present in oleic acid, the doping process would result in further increase in oxygen content of the superconducting core.

The obtained results agree with some of the above statements (see Table I). The lowest oxygen contents are obtained for un-milled reference wires, W0 (3.5%) and W10B (5.0%). The larger value of the latter would be a consequence of the oleic acid addition. O-content is larger for un-doped and milled wires (W0-MA, W0-MB and W0-MC) but the amount does not correlate with the milling time, probably due to experimental difficulties in jar sealing. Furthermore, the difference of O-content between W0-MB and W10B-MB is more than twice larger than for the corresponding un-milled reference wires.

As seen in Table I, T_c values of wires made from milled precursors are always lower than for the corresponding un-milled wires. The transition width, ΔT_w, is sharp in all wires. These T_c variations could be ascribed to the different oxygen content, present in the form of MgO precipitates. This would lead to a Mg deficiency and therefore deviations from stoichiometry, which would lower T_c in both doped and un-doped wires.

B. Critical current densities

The magnetic field dependence of inductive $J_c(\mu_0 H)$ at 5 K for un-doped wires is shown in Fig. 3. It displays flux jumps at low fields that are larger for the reference wire. The milling process significantly reduces the critical current density at low magnetic fields. This is ascribed to larger oxygen content in ball milled wires. The electrically insulating MgO precipitates would decrease supercurrent paths between neighboring MgB_2 grains reducing J_c, although, would increase the pinning at high fields, and therefore the irreversibility field, H_{irr}(T).

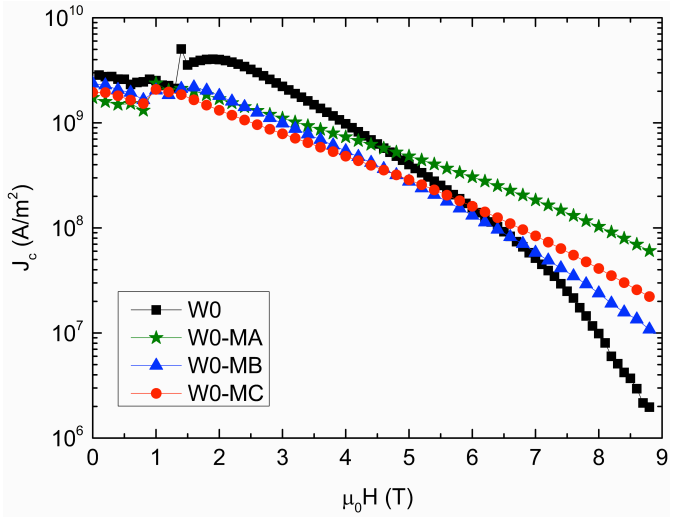

Fig. 3. Magnetic field dependence of the inductive critical current density J_c at 5 K with perpendicular applied magnetic fields, $\mu_0 H$, for un-doped wires with different ball milling precursors.

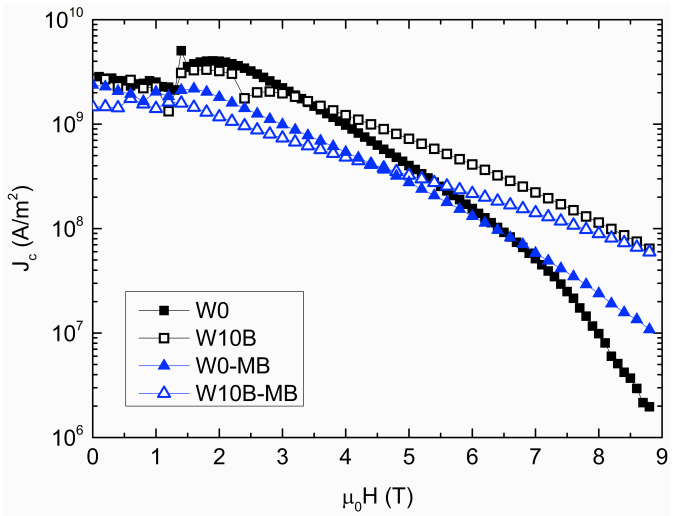

Fig. 4. Dependence of the inductive critical current densities on applied magnetic fields $J_c(\mu_0 H)$, at 5 K, for wires made from ball milled un-doped and ball milled oleic acid doped precursor powders.

Compared with the un-milled wire W0, W0-MA shows a significant $J_c(\mu_0 H)$ increase at $\mu_0 H > 5$ T. It is remarkable that J_c values of W0-MC at high fields are higher than for W0-MB, probably due to a more favorable balance of larger grains but lower crack density.

A comparison of the inductive critical current densities at 5 K of oleic acid doped and ball milled wires is shown in Fig. 4. The wires made from un-milled powders, W0 and W10B, show similar J_c values and large flux jumps at low magnetic fields, whereas for $\mu_0 H > 3$ T, J_c of the doped wire (W10B) is considerably higher.

Considering W0-MB and W10B-MB wires made with precursors with the same ball-milling conditions, J_c values at low fields are lower for the doped wire but there is a crossover at 5 T that supports the positive effect of both oleic acid addition and ball milling to obtain a better $J_c(\mu_0 H)$ dependence. Critical current densities of W10B-MB are lower than the W10B ones, but merge at 9 T, due to a weaker J_c field dependence of the former, made with ball milled precursors. Therefore, a reduction of the O-content during ball milling is necessary to further improve grain connectivity and therefore J_c values of wires with ball milled precursors.

IV. Conclusion

We have studied the properties of *in-situ* reacted PIT mono-filamentary wires to find the optimal ball milling and oleic acid doping to improve J_c at high magnetic fields. Doped and milled precursors lead to wires with good phase homogeneity, but also to a reduction of T_c. The milling process significantly reduces the critical current density of the wires at low magnetic fields, probably due to an increase in oxygen content during ball milling that deteriorates grain connectivity. There is an optimum milling energy transferred to the precursor that combines smaller grains and mechanical workability (disappearance of

transversal cracks), which is similar for doped and un-doped wires. The combination of ball milling and oleic acid doping further improves magnetic flux pinning at high fields and therefore J_c values.

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