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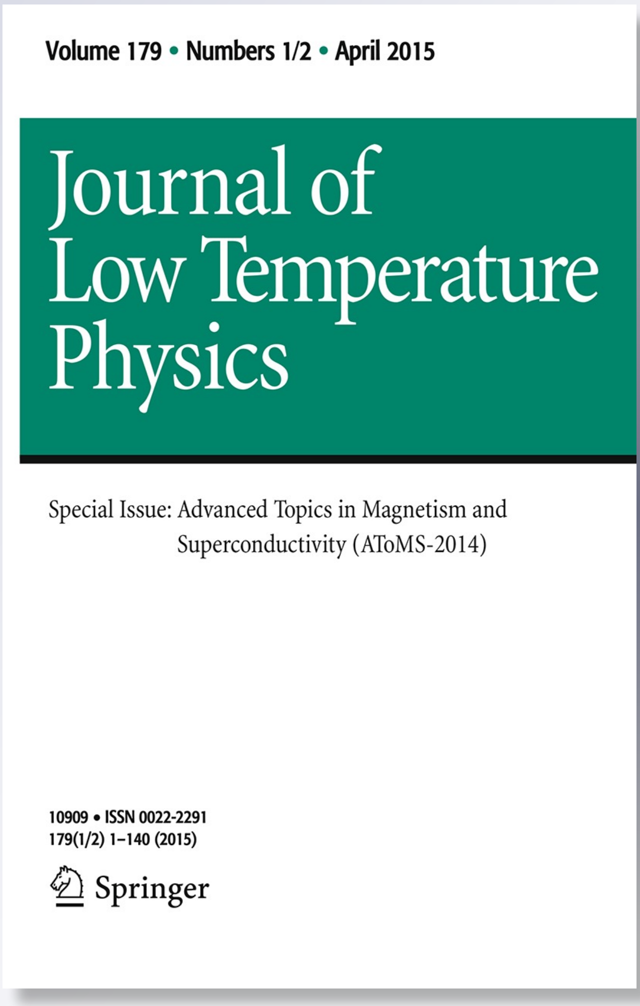

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Multifilamentary MgB_2 Wires Prepared by an In Situ Powder-in-Tube Method

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Abstract MgB_2 has become a commercially attractive material for technological applications for its particular superconducting properties. However, due to its brittleness to obtain wires, a metallic sheath is needed for drawing. In the present work, grade 2 titanium has been used as sheath material, and several multifilamentary wires have been prepared. The powder-in-tube method has been used to prepare the wires with the in situ variant, where the sheath is filled with the unreacted precursor powders (Mg and B). Different thermal treatments have been investigated including several intermediate treatments during the drawing process in addition to the final one. This last treatment is necessary to accomplish the synthesis and heal the cracks generated during the cold work. The superconducting properties were determined by magnetization measurements on a SQUID magnetometer, and the microstructure evolution was followed by TEM and SEM microscopy. Mechanical behavior is also evaluated.

Keywords MgB_2 · In situ · Ti

C. E. Sobrero · M. T. Malachevsky · A. C. Serquis (✉)
Centro Atomico Bariloche, CNEA-CONICET, 8400 S.C. de Bariloche, Argentina
e-mail: aserquis@cab.cnea.gov.ar

C. E. Sobrero
e-mail: sobrero@cab.cnea.gov.ar

J. M. Vallejos
Facultad de Ingenieria - UN del Nordeste, 3400 Corrientes, Argentina

V. San Martin
Facultad de Ciencias Exactas y Naturales, UN de la Pampa, 6300 Santa Rosa, La Pampa, Argentina

1 Introduction

The high critical temperature (T_c) of magnesium diboride (within the intermetallic compounds) makes it an interesting material for magnetic applications as wires can be operated in the 20–30 K temperature range, using a cryocooler in place of liquid helium [1]. Besides its T_c, it is noteworthy its low density that allows the fabrication of lighter magnets and the possibility to easily produce circular or rectangular cross sections in the wires that adequate to different processes and winding needs. One of the most common methods to obtain superconducting wires and tapes is the so called powder-in-tube (PIT). A metal sheath is filled with the precursor powders (in situ variant) or with reacted powder (ex situ variant) and is drawn and/or rolled to its final dimensions. This method has been successfully employed by a large number of groups [2,3]. Increased critical current density (J_c) and irreversibility fields (H_{irr}) are strongly related with improved grain connectivity [4]. The in situ variant of the PIT method may improve it. The addition of an extra amount of Mg in the precursor mixture induces the formation of a more homogeneous microstructure with a better density, reducing the amount of defects and mechanical strains [5]. The selection of an appropriate sheath to minimize the interaction between the metal and the superconductor is a key factor in the fabrication of PIT wires. During the last past years, different metal sheaths have been employed, including Fe, Nb, Cu, etc. [6–8]. In the present work, multifilamentary MgB_2 wires were prepared starting from Mg powder and carbon-doped B nanopowder in a Ti sheath, employing the in situ variant of the PIT method. A Cu central rod was employed as a temperature stabilizer. Superconducting and mechanical properties were evaluated to identify the better processing conditions for the wires (synthesis temperature, final dimensions, coil radius, etc.).

2 Experimental Details

Wires were prepared by the in situ PIT method. A stoichiometric mixture between magnesium (−44 μm) and carbon-doped boron (30 nm) was weighed after adding a magnesium excess of 5 wt%. Precursors were ball milled in an agate mill inside a glove box before filling a 1/4" diameter grade 2 titanium tube. The sheath was cold drawn using 10 % reduction steps, with an intermediate heat treatment at 400 °C for 20 min, up to a 0.9-mm final diameter. To assemble the multifilamentary wire, a titanium tube was filled with 10 pieces of this wire and a central copper rod. Then the drawing process was repeated up to two different final diameters: 1.25 and 1 mm. Then 7-cm-length wire samples were heat treated at 650 °C in argon for 1 h to synthesize the MgB_2. The resulting microstructures of the different wires were analyzed using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The existing phases were identified by X-ray diffraction. Small reference samples were prepared to characterize the superconducting properties. The critical current density (J_c) was determined from magnetization measurements performed in a SQUID (Superconducting Quantum Interference Device) after zero field cooling [9]. The Bean model for a cylinder was employed, assuming homogeneous cross section along the wire, as observed by SEM (not shown). The critical temperature (T_c) was obtained from

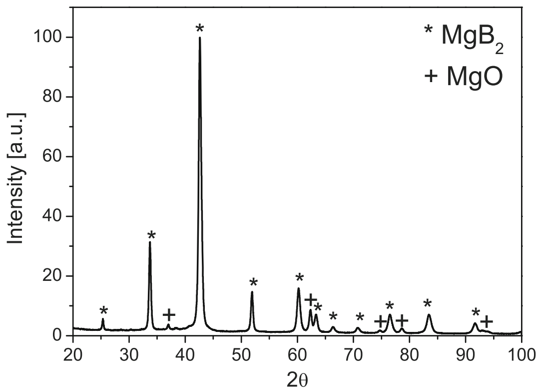

Fig. 1 X-ray diffraction of the synthesized powder

Table 1 Structural parameters refined by Rietveld method

	MgB_2	MgO
Lattice parameter *a*	3.0751 nm	4.2174 nm
Lattice parameter *c*	3.5261 nm	4.2174 nm
ε_g	40×10^{-3}	35×10^{-3}
Crystallite size	43 nm	78 nm

magnetization measurements as a function of temperature. The mechanical strength was evaluated by 4-points bending microstests and conventional uniaxial tension tests.

3 Results

For the X-ray diffraction analysis, a small quantity of the precursor's mixture was synthesized under the same conditions as the wires but in helium atmosphere. The resulting diffractogram with its identified peaks can be observed in Fig. 1. The majority phase is magnesium diboride, with MgO as a secondary phase even if the precursor mixture was prepared in a glove box and the wires were heat treated in argon. This phase is also present in a smaller amount in the starting Mg powder.

The structural parameters as grain size, cell size, and microstrain were obtained from the X-ray diffraction data using the Rietveld refinement program Fullprof [10]. The upper limit of the lattice strains of the grains (ε_g) is obtained using the integral breadths method: $\varepsilon_g = \beta\lambda/4\sin\theta$, with β being the distortion integral breadth, θ the position of the peak maximum, and λ the wave length. The crystallite size is obtained from the inverse of the pure integral breadth. Table 1 shows the obtained values for MgB_2 and MgO. The lattice parameter *a* of the MgB_2 differs from the values reported in the literature as carbon doping produces a decrease in this parameter when C replaces B in the structure [9]. The ε_g values are in the expected range as even if the material was submitted to intense cold work; the final heat treatment relaxes internal strains.

Samples of the B nanopowder and of the synthesized MgB_2 extracted from the wires were observed in a TEM, in order to measure the crystallite size. The different

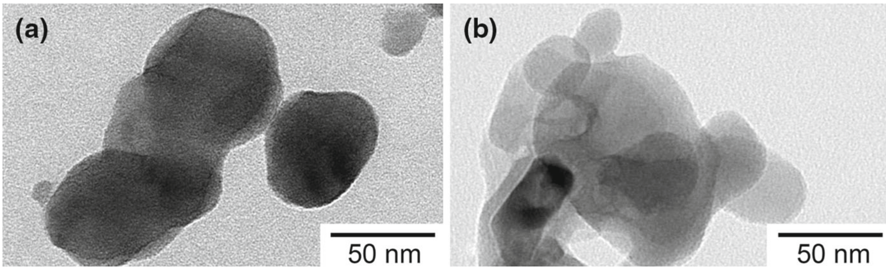

Fig. 2 TEM micrographs **a** C doped B nanopowder; **b** synthesized MgB_2

initial B particle size, due to the melting temperature of both precursors, 2,076 °C for B and 650 °C for Mg, determines the final dimensions of the MgB_2 powder particles [11]. TEM micrographs are shown in Fig. 2 for carbon-doped boron nanopowder and the resulting MgB_2. In Fig. 2b, it can be noticed that the magnesium diboride does not show a high dislocation density, in agreement with the data calculated using Fullprof. The measured size of the magnesium diboride grains is within the range 10–90 nm, with a mean value of 30 nm coincident with the value obtained for the nano B. The value estimated with X-ray diffraction analysis shows a good agreement with the TEM measurements.

The cross section of the different multifilamentary wires after the final heat treatment are shown in Fig. 3. The bundle configuration with 10 Ti-sheathed wires around a copper rod permitted to draw with a low number of intermediate heat treatments and attain a good packing of the powder inside the wire. In Fig. 3d, it can be noticed that the 1-mm-diameter wire has less porosity compared with the 1.25-mm-diameter one (Fig. 3c), due to the further cold work prior to the final heat treatment. After the synthesis treatment, the superconducting core has no appreciable cracks that can be deleterious for the superconducting properties.

To determine the critical temperature, both field-cooled measurement at 30 Gauss and zero-field-cooled measurement were performed between 5 and 45 K. In Fig. 4a, we present the obtained results for the 1.25-mm-diameter wire, similar to what was measured on the 1 mm wire. The measured value was of 33.5 K, with the carbon introduced with the nano boron precursor being responsible for the decreased T_c. To determine the critical current density J_c, the Bean model for a cylinder was employed [9]. Figure 4b shows the curves obtained for the 1- and 1.25-mm wires at 5 K. It can be noticed that the critical current density reaches values around 10^6 A/cm^2 for 1-mm wires at 0 T while for the 1.25-mm wires, this J_c lowers to 4×10^5 A/cm^2. The higher powder packing and less porosity observed in the 1-mm wire lead to a higher magnesium diboride density with a better grain connectivity. Thus, the J_c at 5 T is 3 $\times$ 10^4 A/cm^2 on this wire while it reaches 2×10^3 A/cm^2 for the 1.25-mm wire.

The applicability of these wires is not only related to their superconducting properties but also to their mechanical properties. Particularly, the mechanical strength in bending is an indicative of the winding possibilities. The maximum stress–strain curves were obtained considering pure bending [12]. The outer surface stress-strain curves in 4-point bending configuration are shown in Fig. 5a for the different wires.

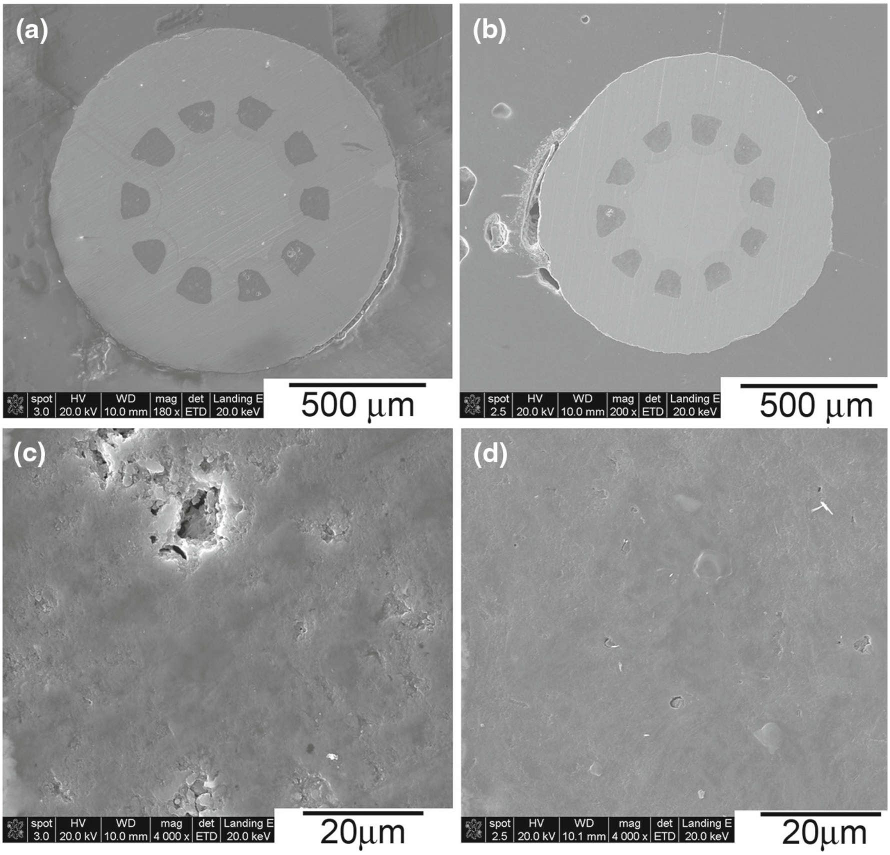

Fig. 3 SEM micrographs for multifilamentary wires with an external diameter of **a**, **c** 1.25 mm; **b**, **d** 1 mm

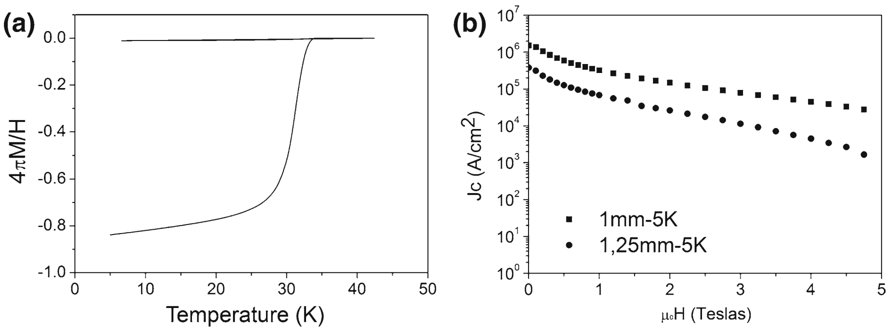

Fig. 4 **a** Magnetic moment as a function of temperature after zero field cooling and at 30 gauss cooling, for the 1.25 mm multifilamentary wire. **b** J_c as a function of field at 5 K, calculated with the Bean model for both multifilamentary wires

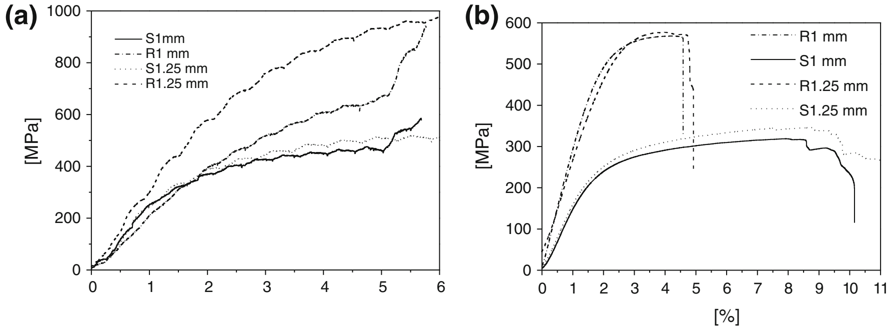

Fig. 5 **a** Maximum normal stress versus strain at the outer surface of the wires measured in 4-point bending. **b** Stress–strain curve obtained from uniaxial stress measurements for the different wires

Measurements were performed at 0.4 mm/min on the wires prior to the heat treatment (R) and after the synthesizing treatment (S). The onset of sheath yielding is not well defined but a linear response is observed up to a strain of about 0.66 %. This value is similar to the onset of critical current degradation reported for transport measurements on bended wires [13]. After the linear response, we observe a wavy curve that can be produced by a combination of sheath yielding and crack formation at the metal-superconductor interface. A third region starts when cracks form in the core, as abrupt stress drops are observed. A degradation of the critical current is then expected exceeding the linear response strains. Conventional uniaxial tension tests were performed in an Instron at a rate of 0.2 mm/min. The obtained curves are shown on Fig. 5b. After the linear response, yielding starts at a strain of around 1.5 %, with a yield stress of about 500 MPa before the heat treatment and 200 MPa after the heat treatment. This last value is in agreement with results reported in the literature for MgB_2 titanium-sheathed wires [14].

4 Conclusions

Multifilamentary titanium-sheathed MgB_2 wires were successfully prepared. The measured superconducting properties are promising for their employment in the fabrication of small coils for laboratory superconducting magnets, even if the T_c is slightly reduced. Based on our results, the bending radius should be such that the surface strain is lower than 0.66 %, both if untreated wires are employed (wind and react method) or if synthesized wires are used (react and wind method), similar to the recommendation for commercial MgB_2 wires. Uniaxial tension tests indicate that during the coil fabrication, it is convenient to maintain tension below the yielding stress to avoid critical current degradation. That is, the wire stress during winding should be kept below 500 MPa for the first method and below 200 MPa for the second one.

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References

1. J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, J. Akimitsu, Nature **410**, 63 (2001)
2. C.S. Li, G. Yan, Q.Y. Wang, G.F. Jiao, A. Sulpice, F. Yang, X.M. Xiong, G.Q. Liu, J.Q. Feng, Y. Feng, P.X. Zhang, Phys. C. **494**, 177 (2013)
3. C.M. Lee, J.H. Park, S.M. Hwang, J.H. Lim, J. Joo, W.-N. Kang, C.-J. Kim, Phys. C **469**, 1527 (2009)
4. A. Serquis, L. Civale, D.L. Hammon, X.Z. Liao, J.Y. Coulter, Y.T. Zhu, D.E. Peterson, F.M. Mueller, J. Appl. Phys. **94**, 4024 (2003)
5. Zongqing Ma, Yongchang Liu, Qi Cai, Phys. C **496**, 49 (2014)
6. D. Shan, G. Yan, l Zhou, J.S. Li, C.S. Li, Q.Y. Wang, X.M. Xiong, G.F. Jiao, Phys. C **483**, 17 (2012)
7. B.-H. Jung, Y.-J. Kim, K.S. Tan, J.H. Kim, X. Xu, S.X. Dou, C.-J. Kim, Phys. C **468**, 1825 (2008)
8. M. Wozniak, S.C. Hopkins, D. Gajda, B.A. Glowacki, Phys. C **477**, 66 (2012)
9. A. Serquis et al., J. Appl. Phys. **92**, 351 (2002)
10. J. Rodríguez-Carvajal, Phys. B **192**, 55 (1993)
11. P.C. Canfield, S.L. Budko, D.K. Finnemore, Phys. C **385**, 1 (2003)
12. M.T. Malachevsky, A.C. Serquis, G. Serrano, J.P. Morales Arias, G. Giunchi, E. Perini, IEEE Trans. Appl. Supercond. **21**, 2676 (2011)
13. Q. Wang, G. Yan, P. Zhang, A. Sulpice, F. Yang, X. Xiong, J. Feng, P. Ji, C. Li, Phys. C **484**, 163 (2013)
14. M. Hanna, H. Fang, Y.X. Zhou, M. Alessandrini, P.T. Putman, K. Salama, J. Mater. Process. Technol. **181**, 44 (2007)