Improvement of critical current density on *in situ* PIT processed Fe/MgB₂ wires by oleic acid addition

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Abstract:

High performance Fe-sheathed MgB₂ monocoreshave been fabricated by *in situ* method using cheap oleic acid additions as a reliable C source for B lattice substitution. We have analysed the cases of B or Mg+B powders soaking in oleic acid and the influence of the heat treatments used at different steps of wire manufacturing on their superconducting properties. X-ray diffraction, electronic microscopy and thermogravimetric analysis, together with magnetic and electric transport measurements have been used to characterize the wires. Doping with oleic acid improves considerably the critical current densities, J_c , at medium and high magnetic fields at 5 and 20 K, without deterioration of J_c at low magnetic fields.

1. Introduction

Metal/MgB₂ composite wires and tapes are good candidates for practical large-scale superconducting applications at operation temperatures in the range of 20-30 K. Long length conductors with high critical current densities, J_c , were first fabricated by the powder-in-tube (PIT) technology [1-6] using *in situ* and *ex situ* procedures and various metal cladding to avoid reactivity with MgB₂ constituents. Attempts to reduce the high porosity inherent to PIT *in situ* wires or to improve the grain connectivity on-PIT *ex situ* conductors [7,8], have been followed by different processing routes. One to be remarked is the internal Mg diffusion (IMD) [9], which with in-situ reactions, produces a hollow cylinder of highly dense MgB₂ with high J_c values [10,11].

Improvements of J_c performances at high fields are also needed for many applications [7]. Doping with different elements and compounds was intended to enhance the flux pinning of pure MgB₂ materials without deterioration of other relevant superconducting properties. By grain refinement and by the addition of carbon, or carbon containing compounds, significant enhancement of the superconducting properties has been obtained [8,12]. Ternary Mg(B_{1-x}C_x)₂ compounds are isostructural in a wide range of compositions, with carbon randomly substituting boron in the MgB₂ lattice. This causes a reduction of the unit cell *a*-parameter, while the *c*-axis remains constant, and the H_{c2} anisotropy and critical temperature, T_c , decrease. Moreover, the irreversibility line $H_{irr}(T)$, the magnetic flux pinning, and $H_{c2}(0)$ increase with C substitution [13,14]. Consequently, carbon chemical doping of MgB₂ has been widely searched and it is a very effective way to improve $J_c(H)$ performances at low temperatures.

On composite wires and tapes, using both pre-reacted MgB₂ and un-reacted Mg and B, C doping has been reached with many carbon sources [12]. Among inorganic compounds, the addition of SiC nanoparticles [15], graphite powders [16, 17], nano scale diamond powders [17], carbon nanotubes [18] or carbon nanoparticles [19], induces the partial substitution of B by C, and it is compatible with long length wire fabrication procedures.

Organic liquids like acetone, ethanol and toluene were introduced to help the homogeneity of Mg and B mixtures during wet ball milling [20] being removed before wire manufacturing. This avoids particle agglomerations and produces materials with smaller grain sizes and higher J_c values, but also may induce C doping. Fe sheathed wires made with B and MgH₂ powders mixed with aromatic hydrocarbons (benzene, naphthalene and thiophene) were reported [21] to produce effective C doping and J_c improvements. From the shift of characteristic XRD peaks, the substitution of B lattice sites by C atoms, *x*, is estimated to be < 0.015, at least one order of magnitude lower than the total amount of C added to the precursors. Moreover, it was realized that mixtures of B powders with malic acid dissolved in toluene after vacuum drying, help to form homogeneous C coatings of B grains. Those treated grains mixed with Mg powders yield materials with improved J_c and substitutions x < 0.035, much smaller than the initial C provided in the precursor [22]. By now, hydrocarbons, carboxylic acids, carbohydrates, alcohols, ketones, amines, etc, in the form of powders, liquids or solutions, have been used as C sources for B+Mg or MgB₂ powders [12]. However, there is little knowledge on the substitution mechanisms, the chemical processes involved and the carbonaceous secondary phases created in each case.

A common feature of successful doping with C rich organic sources is the production of highly reactive C sources at atomic scale at temperatures below the formation temperature of MgB_2 ($> 580^\circ\text{C}$). Therefore, it is possible to decrease the annealing temperatures needed for effective C doping and obtain higher carbon substitution [12]. This will result in larger lattice disorder and finer grains that would increase magnetic flux pinning, H_{c2} and irreversibility line.

Considering carboxylic acids as C source of MgB_2 composite wires or tapes, there are also chemical interactions with secondary phases present in Mg, B or MgB_2 components, as MgO or B_2O_3 . These effects are more important for acetic [23] or malic [22, 23] acids, which have short aliphatic C- chains with C vs O ratios $r \leq 1$, and stronger acidity than stearic acid [24] with longer chains, $r = 9$.

The effect of oleic acid ($\text{C}_{18}\text{H}_{34}\text{O}_2$, $r = 9$) addition on MgB_2 wires has not been reported so far, but previous results of Devener *et al* [25] have shown that oleic acid binds efficiently to fresh unoxidized boron surfaces via B-O-C bond formation and provides an effective barrier to air oxidation. It is also known that oleic acid surfactant coatings provide chemical stability to magnetic nanoparticles such as Co, Ni, Fe and FePt [26], which easily oxidize. It is very likely that similar effects would operate for Mg fine powders. Consequently, doping with oleic acid would fulfil advantages of best organics liquids in the C substitution of B on PIT composite MgB_2 wires and may prevent further oxidation during fabrication.

In this contribution we report on the addition of oleic acid as C source for B substitution on monocoil MgB_2 wires fabricated by the PIT method with Fe sheaths and *in situ* reaction of the components. Doping with oleic acid is worth to research since it is a liquid at room temperature (melting point 13°C), it may prevent oxidation and it has good lubricant properties, low price and relatively high C/O ratio. In particular, the effects of oleic acid on B, Mg and B+Mg powders during thermal annealing have been studied. The microstructure, phase composition and superconducting properties of these doped wires have been analysed and compared with undoped wires.

2. Experimental procedures

2.1 Preparation of wires

Monofilament conductors have been fabricated by the PIT method using *in situ* reactions of the components and mechanical conformation by drawing through round dies. Fe tubes (99.5%, Goodfellow, with outer diameter 5 mm and 0.25 mm wall thickness) were filled by hand with different precursor powder mixtures (details are given below). During drawing, an intermediate annealing was necessary to reduce Fe sheath's work hardening. The final wires have 1.1 mm outer diameter.

The starting materials were commercial Mg powders (99.8%, maximum particle size $250\text{ }\mu\text{m}$, Goodfellow), amorphous B powders (99% and mean particle size lower than $1\text{ }\mu\text{m}$, New Metal & Chemicals Ltd.) with stoichiometric proportions and liquid oleic acid (99%, Alfa Aesar). All the precursors were mixed during 30 minutes using a Retsch MM 2000 mixer mill. Results on four different wires are reported:

- W0 (*Undoped reference wire*): Made from a dry mixture of Mg and B powders filled into Fe tubes. An intermediate heat treatment at $550\text{ }^{\circ}\text{C} \times 0.5\text{ h}$ in Ar atmosphere was done during drawing.
- W5-n (*Mg+B powders mixed with oleic acid, non-preheated*): Oleic acid (5 wt% of total MgB_2) was mixed with Mg and B powders, and the obtained mixture directly filled into the Fe tubes without pre-heat treatments, thus keeping inside the full oleic amount. The intermediate annealing during drawing was done at $320\text{ }^{\circ}\text{C} \times 24\text{ h}$ (bellow the boiling point of oleic acid, $360\text{ }^{\circ}\text{C}$) in Ar atmosphere.
- W10 (*Mg+B powders mixed with oleic acid and preheated*): Oleic acid (10 wt% of total MgB_2) was mixed with Mg and B powders and before filling the Fe-tube the mixture was pre-heated at $400\text{ }^{\circ}\text{C} \times 1\text{ h}$ in Ar to evaporate less bounded and un-reacted molecules, *i.e.* to eliminate oleic acid excess. Two wires with different intermediate softening annealing during drawing were prepared: $550\text{ }^{\circ}\text{C} \times 0.5\text{ h}$ and $400\text{ }^{\circ}\text{C} \times 0.5\text{ h}$, in Ar atmosphere.
- W10-B (*B powders treated with oleic acid and preheated before Mg mixtures*): First, the B powders were mixed with oleic acid (10 wt% of total MgB_2) and heat treated at $500\text{ }^{\circ}\text{C} \times 1\text{ h}$ in vacuum (0.1 mbar) or Ar, to evaporate oleic acid excess. The resulting powders were mixed with Mg and used to fill the Fe-tubes. An intermediate annealing for Fe softening at $550\text{ }^{\circ}\text{C} \times 0.5\text{ h}$ in Ar atmosphere was done during drawing.

Two different final annealing conditions to form the superconducting phase have been studied: $700\text{ }^{\circ}\text{C} \times 2\text{ h}$ and $670\text{ }^{\circ}\text{C} \times 5\text{ h}$, in vacuum (0.1 mbar).

2.2 Physical characterization

The phase composition and microstructure of the wires was analysed by X-ray diffraction (XRD, RIGAKU D/max 2500 Cu $K\alpha$) and field emission scanning electron microscope (FESEM) using angle selective backscattered electrons (AsB), which gives information of phase composition and crystal orientation, and energy dispersive X-ray spectroscopy (EDX).

Thermogravimetric analysis (TGA) was performed using a TA Instruments SDT Q600 system to register the weight loss along programmed temperature scans of oleic acid and mixtures of oleic acid with Mg, B and Mg+B powder samples. Pt crucibles and a heating ramp of $20\text{ }^{\circ}\text{C min}^{-1}$ from room temperature up to $550\text{ }^{\circ}\text{C}$ in Ar flow were used.

The magnetic measurements were carried out on 5 mm long cylindrical samples using a superconducting quantum interference device (SQUID, Quantum Design MPMS-5T) and a Physical Properties Measurement System (Quantum Design PPMS-9T and PPMS-14T) with the field perpendicular to the sample axis and zero-field cooling. AC magnetic susceptibility χ_{ac} (in-phase, χ' , and out-of-phase, χ'' components) was measured as a function of temperature at a frequency of 120 Hz and magnetic field amplitude of 0.1 mT. Magnetization measurements were done at 5 K and 20 K. To avoid the contribution of the Fe-sheath in the magnetic measurements, it was removed by careful mechanical polishing.

Electric transport measurements were performed inside the bore of a 8 T coil magnet immersed in liquid helium using wire sample lengths of 3.7 cm, maximum currents about 220 A and magnetic fields perpendicular to the wire. In order to avoid the heating of

the sample, current pulses of 2 s were applied to measure the voltage versus current curves, $V(I)$. Four points technique was used and the critical current was estimated by the usual $1 \mu\text{V}/\text{cm}$ criterion.

3. Results and discussion

3.1 Structure, C doping and microstructure of wires

The XRD patterns obtained on wire cores, after removing the Fe sheath, show in all wires the characteristic peaks of the MgB_2 main phase together with small amounts of MgO and without signatures of other crystalline compounds. In Figure 1 the characteristic Bragg reflexion peaks (002) and (110) of the MgB_2 structure are displayed. It is observed that the position of (001) peaks remains invariant for all wires while the (110) peak moves toward higher 2θ angles on doped wires. This indicates that the doping has not affected the c -axis cell parameter while the a -axis decreases (see Table 1), which confirms the random substitution of B by C in the MgB_2 lattice [13]. The averaged doping amount, x , of the $\text{Mg}(\text{B}_{1-x}\text{C}_x)_2$ grains in the wire core have been obtained from the estimated a -unit cell parameters and using the nearly lineal dependency $a(x)$ observed by Kazakov *et al* [27] for doped single crystals. The error in the estimation of carbon doping is about 15-20%, therefore, x of wire W10 would be higher but close to the W10-B one. In the figure it is also observed that the height of MgO peak is similar for all samples, although slightly higher for W5-n and lower for W0.

Considering the full width at half-maximum (FWHM) values of the reflexion peaks, it is observed that FWHM of (001) peaks remain constant for all wires, while (110) peaks become broader for doped wires, with higher width for W5-n (see Table 1). The similarities in FWHM of the (002) peak and the differences in the (110) one in the wire with larger C doping, is a strong indication of an increase of crystallographic disorder or a reduction of crystallinity, but it also may be due to segregations of phases with different C content or to lack of homogeneity in the doped grains.

Figure 1. Detail of X-ray diffraction patterns of the wire's superconducting cores at angles around (002), (110) and (102) MgB_2 peaks. The (220) peak of MgO is also shown.

Table 1 Lattice parameters obtained from Rietveld refinements and FWHM of the (110) peak deduced from XRD measurements of core wires. Critical temperatures T_c and transition widths ΔT_w obtained from χ_{ac} . Average substitution of B by C in $\text{Mg}(\text{B}_{1-x}\text{C}_x)_2$ grains estimated from the $a(x)$ variation according to [27], which gives relative uncertainties within 15-20%.

Wire	FWHM (110) in deg	a (Å)	c (Å)	T_c (K)	ΔT_w (K)	x
W0	0.45	3.0858	3.5250	37.5	0.7	0
W10-B	0.49	3.0817	3.5265	36.0	1 or 2	0.010
W10	0.53	3.0798	3.5243	35.2	0.7	0.016
W5-n	0.80	3.0684	3.5248	34.5	13.6	0.051

$\chi_{ac}(T)$ measurements have been used to determine the critical temperatures, T_c , and to analyze the sharpness of the superconductor to normal state transitions in all wires. The measured $\chi_{ac}(T)$ curves are shown in Figure 2. The T_c values of the wires, determined by the onset of diamagnetism by $\chi'(T)$, have been collected in Table 1. They decrease from 37.5 K for the undoped wire (W0) down to 34.5 K for W5-n one and are in good agreement with the expected variations from the estimated C substitution [27].

Figure 2. In-phase and out-of-phase components of the magnetic ac susceptibility $\chi_{ac}(T)$ of the wire superconducting cores.

The transition widths, ΔT_w , defined as the temperature interval from 90% to 10% of $\chi'(5K)$ (*i.e.* of complete diamagnetism), are also collected in Table 1. Both W0 and W10 wires have the same value $\Delta T_w = 0.7$ K for all annealing conditions, while for the W10-B wire, $\Delta T_w = 2$ K for final annealing at $700^\circ\text{C} \times 2$ h and decreases to $\Delta T_w = 1$ K for $670^\circ\text{C} \times 5$ h. The wire W5-n shows very wide transition, $\Delta T_w = 13.6$ K, which likely indicates the presence of important amounts of non-superconducting phases in this wire.

The FESEM micrographs on transverse cross-sections of these wires with different magnifications are displayed in Figure 3. The overall transverse cross-section of W10 wire, displayed in Figure 3(a) shows the porous microstructure of the core typical of the *in situ* PIT wires. The surrounding Fe sheath shows reactivity with B in a layer of 5-8 μm , which is similar for all fabricated wires and cannot be seen in this low magnification micrograph. There are voids of several microns, which were left by Mg when it diffuses into the B particles, and MgB_2 regions quite uniformly distributed. W10 wires present very homogeneous MgB_2 phase compositions for all annealing conditions, as may be seen in the enlarged micrograph of Figure 3(b), which is similar to the microstructure observed on undoped wire W0.

Figure 3. FESEM (AsB) images obtained on polished cross-sections of wire W10 annealed at 670 $^{\circ}\text{C}$, 5h for two magnifications: (a) and (b); and wire W10-B for different final annealing: (c) 700 $^{\circ}\text{C}$ $\times$ 2h and (d) 670 $^{\circ}\text{C}$ $\times$ 5h.

A similar FESEM analysis has been performed for W10-B. We have observed that in this wire there are large areas of size 250 - 400 μm without voids, unlike W0 and W10 wires, which show a homogeneous distribution of voids. For annealing condition of 700 $^{\circ}\text{C}$ $\times$ 2 h, areas with two-phase compositions are abundant, as seen in Figure 3(c). EDX analysis proves that darker grey areas correspond to boron rich zones, while light grey ones are MgB_2 . In the overall view of the cross-section of this wire, it is seen that these darker grey zones are more abundant in the centre of this dense large areas while the lighter grey ones are closer to voids. When longer annealing times and slightly lower temperatures are used, 670 $^{\circ}\text{C}$ $\times$ 5 h, more areas with homogeneous phase composition are observed (see

Figure 3(d)) in agreement with [11], although zones with boron rich phases still persist. These results indicate that there is a lack of precursor distribution homogeneity in wire W10-B, probably due to the agglomeration of boron powders.

EDX analysis reveals the presence of similar oxygen content for W10 and W10-B, ~ 5 at%, which is slightly higher than for the undoped wire, ~ 3.5 at%. This may be due to the additional oxygen introduced by the carboxylic groups of the oleic acid. Then, the main difference between these wires is the homogeneity, which would be originated in the precursor powders. Oleic acid seems to agglomerate boron particles adding difficulties to the subsequent homogeneous mixing with Mg powders. Nevertheless, this effect does not appear when oleic acid is added to the Mg+B mixture, as in W10.

The FESEM analysis of wire W5-n (not shown) displays phases different to the above reported ones and EDX analysis reveals the presence of regions with very high oxygen content (up to 15-20 at%). Moreover, a considerably amount of carbon should be present as secondary phases, since just ~ 5 at% of carbon coming from oleic acid has substituted B in MgB_2 . Nevertheless, since samples were coated with carbon for FESEM observations, it was not possible to quantify it with EDX. These carbonaceous phases will act as weak links between MgB_2 superconducting regions, which will be the reason of the large transition width observed in the magnetic susceptibility.

3.2. Influence of the B or Mg+B powders oleic acid soaking and initial heat treatments

Thermogravimetric analysis has been used to analyse the effect of oleic acid addition on B, Mg or B+Mg powders. The Weight loss (%) and Derivative Weight – $dW(T)$ – curves as a function of temperature are displayed in Figure 4. A needed reference is the weight losses of liquid oleic acid –see Figure 4(a)– which has a single and smoothed step down, starting at 200 °C, with maximum of the $dW(T)$ curve at 330 °C, due to the dragging off of its vapour by the Ar flow, and finishing around the atmospheric pressure boiling point (360 °C).

For B powders mixed with oleic acid in proportions similar to the one used in W10-B wire precursors –see Figure 4(b)– there is an initial weight loss with maximum of the $dW(T)$ curve at 95 °C. This is due to the elimination of the water produced by the chemical reaction of oleic acid carboxylic groups ($-\text{COOH}$) with boron oxides present in the B powders to form oleyl borates with water evolution. The dragging of loose bounded oleic acid molecules starts around the same temperatures than liquid oleic acid (~ 200 °C) and $dW(T)$ has a large maximum at 260 °C. This maximum takes place at lower temperatures than in Figure 4(a), due to small amount of oleic acid. The results of B+oleic are similar to those seen for oleic acid coatings in Co and Ni nanoparticles [26] analysed with TGA and NEXAFS techniques. They also observed thermal desorption of oleic acid at around 240 °C (i.e. weight loss in TGA and NEXAFS spectra corresponding to oleic acid). While at higher temperatures, between 360 and 430 °C, they observed weight loss, but also changes in the NEXAFS spectra, with disappearance of C to O double bonds, and just the peak of C=C double bonds in graphitic C remained. Consequently, the peak at 380 °C in Figure 4(b) should be associated with the thermal decomposition (pyrolysis) of oleic acid bounded to B grains producing a carbon rich coating.

Figure 4. Weight loss (%) and corresponding Derivative Weight (%/°C) curves for: (a) oleic acid, (b) B + 20 wt% oleic acid, (c) Mg + 20 wt% oleic acid and (d) Mg + B (1:2 atomic proportions) + 10 wt % oleic acid. (The estimated error is ± 1 wt%). The temperatures at which the Derivative Weight curves show a maximum are indicated.

For Mg powders mixed with oleic acid samples –see Figure 4(c)– two chemical reactions may take place associated with its carboxylic groups: At low temperatures, it may dissolve the MgO precipitates, usually placed at the Mg metallic surfaces, following the chemical reaction: $2 \cdot \text{C}_{17}\text{H}_{33}\text{-COOH} + \text{MgO} \rightarrow [\text{C}_{17}\text{H}_{33}\text{-COO}]_2\text{Mg} + \text{H}_2\text{O}$, which is enhanced at higher temperatures. This effect is marked by a smooth weight loss due to dragging off of created water molecules peaking at 144 °C. At higher temperatures less bounded oleic acid molecules are dragged off by the Ar flow, but the weight loss rate is much slower than for B powders with oleic. That indicates that oleic acid also reacts with metallic Mg: $2 \cdot \text{C}_{17}\text{H}_{33}\text{-COOH} + \text{Mg} \rightarrow [\text{C}_{17}\text{H}_{33}\text{-COO}]_2\text{Mg} + \text{H}_2$. The Mg oleates produced in the above chemical reaction will start to decompose at slightly higher temperatures (pyrolysis), showing a marked maximum at 380 °C. The pyrolysis is a complex reaction giving oleic acid fragmentation into short-chain hydrocarbons, CO, CO₂ and coke, causing fine MgO or MgCO₃ precipitates.

For B+Mg powders mixed with oleic acid, at temperatures below the MgB₂ formations, the weight losses, displayed on Figure 4(d), almost correspond to the addition of the interactions effects observed on B+oleic and Mg+oleic mixtures. There is an enhancement of water losses by the combined effects of the oleic acid on the Mg and B oxides with a peak at 120 °C. The decomposition of Mg oleate and oleyl borates produces the peak at 390 °C. At intermediate temperatures, less bounded oleic acid molecules are dragged off by the Ar flow.

3.3. Superconducting properties

The inductive critical current densities of the analysed wires have been estimated magnetically from the hysteresis magnetization loop width, $\Delta M(H)$ as:

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

where R is the radius of the cylindrical superconducting core and the magnetic field is applied perpendicular to the wire axis. The local distortions of the core cylindrical shape produced during polishing are estimated to be less than 10%. The measurements were done with this orientation in order to have most current paths along the sample's axis as in transport measurements. Equation (1) is obtained under the assumption of homogeneous induced currents on the length scale of the sample, which will be discussed later. It should be noted that generally it is not valid for fields lower than the penetration field, H_p [28]. However, we have plotted the J_c values at low fields in order to show the presence of flux jumps.

Figure 5(a) shows a logarithmic representation of J_c as a function of the magnetic field at 5 K for all doped samples at two different annealing conditions: 700 °C × 2 h and 670 °C × 5 h. The wire W5-n has the lowest J_c values, while W10 presents the best results, with slightly higher J_c for lower annealing temperatures and longer times. Wire W10-B has higher critical current densities for treatments at 670 °C × 5 h than at 700 °C × 2 h, in agreement with the differences observed on their microstructure.

The comparison between the inductive J_c values of the optimized doped wire W10 and the undoped one W0 at 5 K and 20 K are shown in Figure 5(b) together with the transport J_c measured at 4.2 K. There is a large improvement of J_c at medium and high fields at both temperatures for the doped wire W10. The measured transport values are higher than the magnetic ones, especially for the undoped wire, W0. A remarkable parallelism between magnetic and transport values is found on W10, although the transport experimental facility limits just enable to establish the tendency. It should be noted that the J_c values of wire W10 are similar to those obtained on Fe tapes fabricated with B powders treated with stearic acid [24].

Figure 5. (a) Critical current densities as a function of the applied field at 5 K deduced from magnetization measurements for all doped samples at two different annealing conditions. (b) Magnetic $J_c(H)$ at 5 K and 20 K of wires W0 and W10 annealed at 670°C , 5h. Transport J_c values at 4.2 K are also shown for comparison.

The analysis of the differences between transport and magnetic J_c values has been studied by several groups (see for example [29-31]). In general, the use of equation (1) is justified by the non-granular behaviour of MgB_2 [32]. However, wire inhomogeneities may lead to the appearance of granularity effects, which at high fields are usually indicated by strong downturns of magnetic $J_c(H)$ curves [29]. When granularity exists, inductive J_c values are lower than transport ones in high fields [29], as in our case. Even so, it must be noted that the high transport critical current values indicate the existence of good connectivity between grains also in these high magnetic fields. In addition to the apparition of granularity, flux creep phenomena would intensify the differences between magnetic and transport values, due to the more restrictive criterion used to define J_c in magnetic measurements compared with transport ones [31].

The measured transport I - V curves ($V \propto I^n$) of W0 and W10 wires are steep. For example, at $\mu_0 H = 8$ T, the estimated n -values are $n \sim 20$ -24 and $n \sim 30$ -33 for wire W0 and W10, respectively. At this field, the transport J_c values of the doped W10 wires are 4 times higher than for W0. The transport critical currents of wire W10-B are much lower, by approximately one order of magnitude, than their corresponding magnetic values (for example transport $J_c = 1.3 \times 10^7$ and $6 \times 10^7 \text{ Am}^{-2}$ at 8 T and 5 T, respectively, were measured at 4.2 K). Moreover, its I - V curve is smooth and shows a resistive tail, in agreement with previous indications of non-homogeneous phase formation on this wire. Similar results are obtained for pre-annealing in vacuum or in Ar.

For the wire with best superconducting properties (W10), a preliminary analysis of the influence on J_c of the annealing conditions at the different steps of the wire manufacturing has also been done. Firstly, it was not observed any relevant difference for wires W10 manufactured with annealing at 400 °C or at 550 °C during drawing, although the former seems to get slightly higher J_c values. Secondly, in order to obtain the optimum pre-annealing conditions of the precursor, we prepared a wire (with precursors: Mg + 2B + 10% weight oleic acid), which was drawn up to 2.5mm diameter without any heat treatment of the precursors or during drawing. Three pieces of 1cm length were cut and heat treated at 400, 450 or 550 °C, respectively, for 1 h and in Ar atmosphere and cooled down to room temperature. These pieces were chosen short enough to allow the vapours generated during the pre-annealing to get out easily. Afterwards, these three pieces were sealed and annealed at 700 °C $\times$ 2h in vacuum. The highest magnetic J_c was obtained for the first one. For this reason the precursors of wire W10 were pre-annealed at 400 °C $\times$ 1 h before wire manufacturing.

Conclusions

A new source of C to fabricate C-doped Fe/MgB₂ composite wires by oleic acid addition has been used. This produces enhanced critical currents at 20 K and 4.2 K in medium and high magnetic fields without deterioration at low fields. Best results correspond to W10 wires, which use mixed Mg+B powders soaked in oleic acid and annealed at 400 °C to eliminate the excess before wire conformation. These wires have 1.6 at% of B substitution by C, a T_c decrease to 35.2 K and improved critical current densities, with good correspondence between transport and magnetic J_c and good homogeneity.

W10–B wires, which use oleic acid soaked B powders annealed at 500 °C before mixing with Mg, have smaller B by C substitution ($x \approx 0.010$) and slightly lower magnetic $J_c(H)$ but show lower homogeneity probably due to caking of oleic acid soaked B powders before mixing.

Doping with oleic acid without heat treatment of the precursors before wire processing to eliminate excess, increases the C substitution to $x = 0.05$ but results in poor superconductivity properties, probably by the large amount of secondary carbonaceous phases and oxides. In this way, wide transition of the $\chi'(T)$ curve and low J_c values, even at low magnetic fields, has been obtained.

Thermogravimetric analysis of the chemical reactions between oleic acid with precursor boron or magnesium powders has proven the formation of oleyl borates and Mg oleate, respectively, during heat treatments at temperatures below oleic acid boiling point (360 °C). The pyrolysis of these salts and of the remnant oleic acid (physically or chemically bonded to the surface of B and Mg grains) produces active carbon sources at temperatures above 380 °C, which facilitate the B by C substitution when the MgB_2 lattice is formed, but also provides the oxygen for final MgO precipitates.

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