Study of the MgB$_2$ grain size role in *ex situ* multifilamentary wires with thin filaments

A Malagoli, V Braccini, C Bernini, G Romano, M Vignolo, M Putti and C Ferdeghini

CNR-INFM LAMIA, C.so Perrone 24, I-16152 Genova, Italy

E-mail: andrea.malagoli@lamia.infm.it

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Abstract

The MgB$_2$ superconductor has already demonstrated its potential, in particular for DC applications such as magnetic resonance imaging (MRI) magnets, thanks to the low cost of the raw materials and to its simple production process. However, further efforts have still to be made in order to broaden its employment in AC applications such as superconducting fault current limiters (SFCLs), motors, transformers etc. The main issues are related to the reduction of AC losses. Some of these can be faced by obtaining multifilamentary conductors with a large number of very fine filaments and, in this context, the powder’s granulometry can play a crucial role.

We have prepared MgB$_2$ starting powders with different granulometries and by the *ex situ* powder-in-tube (PIT) method we have realized multifilamentary wires with a number of filaments up to 361 and an average size of each filament lowered down to 30 $\mu$m. In particular we have studied the relationship between grain and filament size in terms of transport properties and have shown that the optimization of this ratio is possible in order to obtain suitable conductors for AC industrial applications.

1. Introduction

Nowadays MgB$_2$-based conductors fabricated by the powder-in-tube (PIT) technique can be considered not only as promising superconductors but also as an actual industrial product. In parallel to broad research addressed to improve the critical current density ($J_C$) behaviour, a number of groups have focused their efforts on developing multifilamentary conductors—being more interesting than a monocore from an applications point of view—following the *ex situ* as well as the *in situ* route [1]. On the one hand, the research has been focused on the pinning issue and several doping procedures have been developed in order to improve the behaviour in magnetic field, most of them regarding *in situ* techniques [2–5] although some work has used the *ex situ* method [6]. On the other hand, the clear prospect of various applications has prompted the development of techniques to produce multifilamentary wires [7–10] or cables [11, 12].

Now, a few years since the discovery of superconductivity in MgB$_2$, long multifilamentary strands—of the order of km—have been fabricated by hyper-tech research using the *in situ* method [13] and Columbus superconductors using the *ex situ* technique [9]. The stabilized multifilamentary tape produced by Columbus superconductors has even been successfully employed to realize a low field magnet [14] operating at 20 K for use in a superconducting MRI machine that is on the market at present.

However, in order to make MgB$_2$ useful not only for DC but also for AC applications, further conductor development and optimization are still needed, in particular to reduce the AC losses caused by magnetic hysteresis in the MgB$_2$ core, filament coupling and eddy currents flowing through the metallic matrix. In this context the research works should be focused on multifilamentary strands with a large number of very fine filaments, twisted filaments and non-magnetic and high resistivity sheath.

In particular, the issue regarding the achievement of a large number of very fine filaments (10–30 $\mu$m) seems not to have a simple solution. The *in situ* way has been already employed to realize multifilamentary wires with a number of filaments up to 61 [15] and a filament size down to 40 $\mu$m [7, 16]. However, a $J_C$ degradation has been observed with increasing the number of filaments and in particular the granulometry of the starting precursors seems to be the bottleneck in achieving homogeneous fine filaments.

Even though the *ex situ* conductors did not achieve field performances as good as the *in situ* ones after doping, they did show several industrial advantages such as lower porosity [1],
Figure 1. SEM images of the not-milled (NM, (a)) and milled (M, (b)) powders. In (c) the Gaussian fit of particle size distribution is reported after measuring about 500 grains for each sample. The average diameters are 1.5 \( \mu m \) and 450 nm, respectively, for the NM and M powders.

Figure 2. Cross sections of the unsintered wires described in table 1.

The possibility of being used to realize React \& Wind coils [17], homogeneity over long lengths, better mechanical properties, MgB\(_2\) phase and granulometry control [9].

In previous works we showed the positive effect of a finer MgB\(_2\) granulometry on the superconducting properties of \textit{ex situ} monocore tapes [18] and we investigated the feasibility of \textit{ex situ} wires with very thin filaments down to 30 \( \mu m \) [10]. In this paper, by exploiting the possibility of modifying and controlling the grain size of the starting MgB\(_2\) powders, we study the relationship between the starting granulometry and the final single filament size in terms of transport properties.

2. Experimental details

MgB\(_2\) multifilamentary wires were realized by the \textit{ex situ} PIT method [9]. MgB\(_2\) powders were prepared from commercial amorphous B (95–97% purity) and Mg (99% purity): the powders were mixed and underwent a heat treatment at 910 °C in Ar. As described in our previous work [18], the granulometry of the so-obtained MgB\(_2\) powders was analysed by a scanning electron microscope (SEM) and an average grain size of about 1.5 \( \mu m \) was estimated (see figures 1(a)–(c)). A part of these powders was ball milled and MgB\(_2\) with an estimated average grain size of 450 nm was obtained (see figures 1(b) and (c)). Both not-milled (NM) and milled (M) powders were used to fill two nickel tubes with an outer diameter of 21.34 mm and a thickness of 2.11 mm. After drawing to the proper size, such monofilaments were then stacked into 19- and 91-subelement arrays inside an external monel tube with an outer diameter of 21.34 mm and a thickness of 2.11 mm. After drawing and groove rolling, 19-filament and 91-filament square wires (1.7 \( \times \) 1.7 mm\(^2\)) for each powder (NM and M) were obtained. Moreover, for each powder, 19-filament wire was prepared using Ni external tube. Nineteen elements of these Ni-sheathed 19-filament wires were restacked into a monel tube and, after the cold deformation described above, two 361-filament square wires (1.7 \( \times \) 1.7 mm\(^2\)) were obtained. Finally by a further special deformation step the 91- and 361-filament square wires were formed into wires with a circular cross section with a diameter of 1.7 mm.

In table 1 a summary of the prepared samples and their geometrical characteristics is reported while in figure 2 the cross sections of the wires are shown. All these multifilamentary samples were heat treated at 980 °C for 3 min using a continuous heat treatment system.

Transport critical current (\( I_c \)) measurements were performed over \( \sim \)10 cm long samples at the Grenoble High

![Table 1. Summary of the prepared samples and their geometrical characteristics.](image)

| Sample No | No of filaments | Powder Filling factor | Average filament size (\( \mu m \)) | External shape |
|-----------|----------------|-----------------------|-----------------------------------|----------------|
| 19NM      | 19             | Not milled 33          | 270                               | Square         |
| 19M       | 19             | Milled 33              | 270                               | Square         |
| 91NM      | 91             | Not milled 30          | 110                               | Square         |
| 361NM     | 361            | Not milled 15          | 30                                | Square         |
| 361M      | 361            | Milled 15              | 105                               | Round          |
| 91Mr      | 91             | Milled 14              | 30                                | Round          |

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![Figure 1. SEM images of the not-milled (NM, (a)) and milled (M, (b)) powders. In (c) the Gaussian fit of particle size distribution is reported after measuring about 500 grains for each sample. The average diameters are 1.5 \( \mu m \) and 450 nm, respectively, for the NM and M powders.](image)

![Figure 2. Cross sections of the unsintered wires described in table 1.](image)
Figure 3. Details of the filaments inside the 91 and 361 multifilamentary wires with NM and M powders after the heat treatment performed at 980 °C for 3 min: the undesired layer does not exceed 8 µm. (This figure is in colour only in the electronic version)

Magnetic Field Laboratory (GHMFL) at 4.2 K in magnetic field up to 13 T, the current was applied perpendicular to the magnetic field. The criterion for the \( I_c \) definition was 1 µV cm\(^{-1}\).

3. Results and discussion

In figure 3 details of the filaments inside the 91 and 361 multifilamentary square wires after the heat treatment are shown. By SEM analysis the interface between MgB\(_2\) and Ni sheath has been investigated, giving special attention to the comparison between the M and NM samples. As reported in [19], a MgB\(_2\)Ni\(_{2.5}\) reaction layer appears during the final heat treatment depending on temperature and time. As was expected, the milled powders are slightly more reactive, nevertheless the undesired layer does not exceed 8 µm: the MgB\(_2\) homogeneity is preserved even in the samples with the thinner filaments.

The measured critical current densities for all the square samples are reported in figure 4, while in figure 5 the \( J_C \) values at 5.5 T are shown.

\( J_C \) improves with milling for all samples as already described in our previous work [18]. Focusing on the behaviour of the NM samples, passing from 19 to 91 filaments a remarkable \( J_C \) degradation is evident, that is partially recovered on going to 361 filaments. On the contrary, for the milled samples 19M and 91M have almost identical \( J_C \)—a slightly better behaviour in field being observed in 91M. When the number of filaments increases up to 361, \( J_C \) decreases staying, though, above the 361NM.

However, such \( J_C \) behaviours in field cannot be explained and well understood simply with the milling effects. Actually in these complex conductors several factors have to be taken into account which have an effect on the transport properties: the starting granulometry of the MgB\(_2\) powders, the cold deformation force and the final filament size. As already observed [18] in the ex situ PIT technique, the strong cold deformation—besides compacting the powders inside the sheath and thus improving the connectivity—has a crushing effect and further reduces their average grain size. But on the other hand, when it is particularly hard the cold deformation could cause micro-cracks or filament sausaging which act as obstacles to the percolative current paths. In this context it is clear that the flow of the MgB\(_2\) grains or agglomerates inside the sheath during the drawing or rolling depends also on the starting granulometry and final single filament size. Therefore, in the final analysis, the capability of these conductors to transport high critical currents crucially depends on a proper balance of these parameters.

Considering what we have just described, the \( J_C \) of the 91NM is considerably lower than the 19NM one because as the starting powder grains are larger in size with respect to the final filament size, a bad grain flow inside the sheath has brought about micro-cracks. On the other hand, the stronger
cold deformation undergone by the 361NM wire—thanks to the double restacking—brought about a higher powder compaction and therefore a partial recovery of the $J_C$. This still remains limited by the micro-cracks and/or filament sausaging inevitably occurring in obtaining such thin filaments.

Analysing the behaviour of the milled samples it seems that the $J_C$ enhancement in the sample with 91 filaments is due just to the finer grains of the used powder. For the 361M wire we still observe a $J_C$ improvement with respect to the 361NM thanks to the finer grains, even if the effect is again limited by the micro-cracks: the thinner the filaments, the more obstructive are the cracks in the percolative current paths.

The reported $J_C$ were calculated for samples having different superconducting sections: to have an idea of the actual current capabilities of the conductors, in figure 6 the corresponding $I_C$ for the wires prepared with the milled powders are shown.

Moreover, to meet the industrial needs for AC applications employing such MgB$_2$ conductors, the best performing conductors underwent a further special cold deformation step to be given a circular cross section. In figure 7 the $J_C$ of 91Mr and 361Mr (round shaped) samples with 91 and 361 filaments are reported and compared with the corresponding square wires. No significant degradation of the transport properties is observed even after this further cold deformation step.

The measured $I-V$ characteristics, through the analysis of the so-called $n$-value—i.e. the exponential value of the voltage–current characteristic—gave us the possibility to extract information also on the homogeneity of the samples in order to find a better correlation between granulometry, number of filaments and their dimension. In fact, a high $n$-value above 30 is generally interpreted as a sign of a highly homogeneous superconductor with rather strong pinning force. On the contrary, a low $n$-value is due to a wide spread of the critical current distribution inside the superconducting filaments, typically caused by filament sausaging, impurities, voids and micro-cracks. Furthermore, from an applications point of view, a high $n$-value is indicative of the capability of sustaining relevant persistent currents for long periods of time and thus of the possibility of employing a MgB$_2$ conductor to realize windings that can be operated in persistent mode.

The exponential $n$-value was calculated by plotting the voltage–current characteristics in a double-logarithmic scale for the 91M sample at 7 T. A linear behaviour of the voltage data is observed in a decade centred around $1 \mu \text{V cm}^{-1}$.

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A good linearity of the data plotted in double-logarithmic scale over this voltage range was generally observed, as can be seen in figure 8, where the experimental data and the exponential fit are reported for the 91M sample at a magnetic field of 7 T. The $n$-values for both NM and M square wire series are reported in figure 9, and they are quite field dependent. Depending on the sample, below a certain field the $n$-value was hardly quantifiable due to the lack of experimental points caused by very sharp transitions. Both in the 19- and 91-filament samples, the $n$-value increases with milling staying above 30 for magnetic fields up to 8 T and 7.5 T respectively. This
is consistent with the fact that, after milling, the number of grain boundaries, which are pinning centres, is increased and the homogeneity of the powder is improved [18].

Concerning the 361-filament wire the \( n \)-values are lower and about the same in NM and M samples. The corresponding decreased homogeneity is consistent with the occurrence of micro-cracks or filament sausaging which also happens in the milled sample. These last results together with the \( J_C \) behaviour of the 361NM/M samples suggest that to achieve higher \( J_C \) values in such thin filaments it is necessary to further decrease the granulometry of the starting powders.

4. Conclusions

Multifilamentary wires with a number of filaments up to 361 and an average filament size down to 30 \( \mu m \) have been realized by the \textit{ex situ} PIT method using pure MgB\(_2\) powders with different granulometry. By decreasing the filament size a dependence of the transport properties and the homogeneity on the powder grain size has been observed.

In this work we have obtained the best ratio filament size/grain size on a 91-filament wire with an average filament size of about 110 \( \mu m \) and a powder starting average grain diameter of about 450 nm. The obtained \( J_C \) was \( 10^4 \) A cm\(^{-2}\) at 7 T and 4.2 K. The same results have been obtained on round wires which are more suitable for industrial applications.

A finer MgB\(_2\) granulometry seems to be needed to realize very thin filaments (10–30 \( \mu m \)) with high critical current density, although the critical current measured on the 361 sample together with the advantages given by the high number of 30 \( \mu m \) thin filaments could be interesting for low field applications.

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