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MgB_2 wire diameter reduction by hot isostatic pressing—a route for enhanced critical current density

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Abstract

The effect of wire diameter reduction on the critical current density of pristine MgB_2 wire was studied. Wires were treated by a hot isostatic pressing method at 570 °C and at pressures of up to 1.1 GPa. It was found that the wire diameter reduction induces an increase of up to 70% in the mass density of the superconducting cores. This feature leads to increases in critical current, critical current density, and pinning force density. The magnitude and field dependence of the critical current density are related to both grain connectivity and structural defects, which act as effective pinning centers. High field transport properties were obtained without doping of the MgB_2 phase. A critical current density j_c of 3500 A mm^{-2} was reached at 4 K, 6 T for the best sample, which was a five-fold increase compared to MgB_2 samples synthesized at ambient pressure.

Keywords: superconductivity, MgB, wires, hot isostatic pressing, electrical connectivity

(Some figures may appear in colour only in the online journal)

1. Introduction

Magnesium diboride is a promising superconductor [1] for applications in the form of wires. Intensive research efforts have been made to improve the critical current density, j_c, of such wires [2]. Generally the j_c performance in high magnetic fields and temperatures above 20 K is unsatisfactory for application, due to the poor grain connectivity and pinning properties of this material.

The key parameters requiring improvement in MgB_2 wires are the density of the superconducting core and the grain connectivity [3, 4]. During the wire drawing process, the cores are deformed and their mass density is lower than that of wires obtained by a cold densification [5, 6]. Moreover, when wires filled with a mixture of magnesium powder and boron powder are synthesized *in situ*, significant porosity of approximately 25% appears, due to volume shrinkage during the reaction [2]. A natural solution of these problems is densification of the core material at high pressure [7–9]. This should lead to an increase in grain connectivity.

The aim of this report is to describe a method of manufacturing pristine MgB_2 wires with high critical currents, I_c, by an optimized hot isostatic pressing (HIP) process based on

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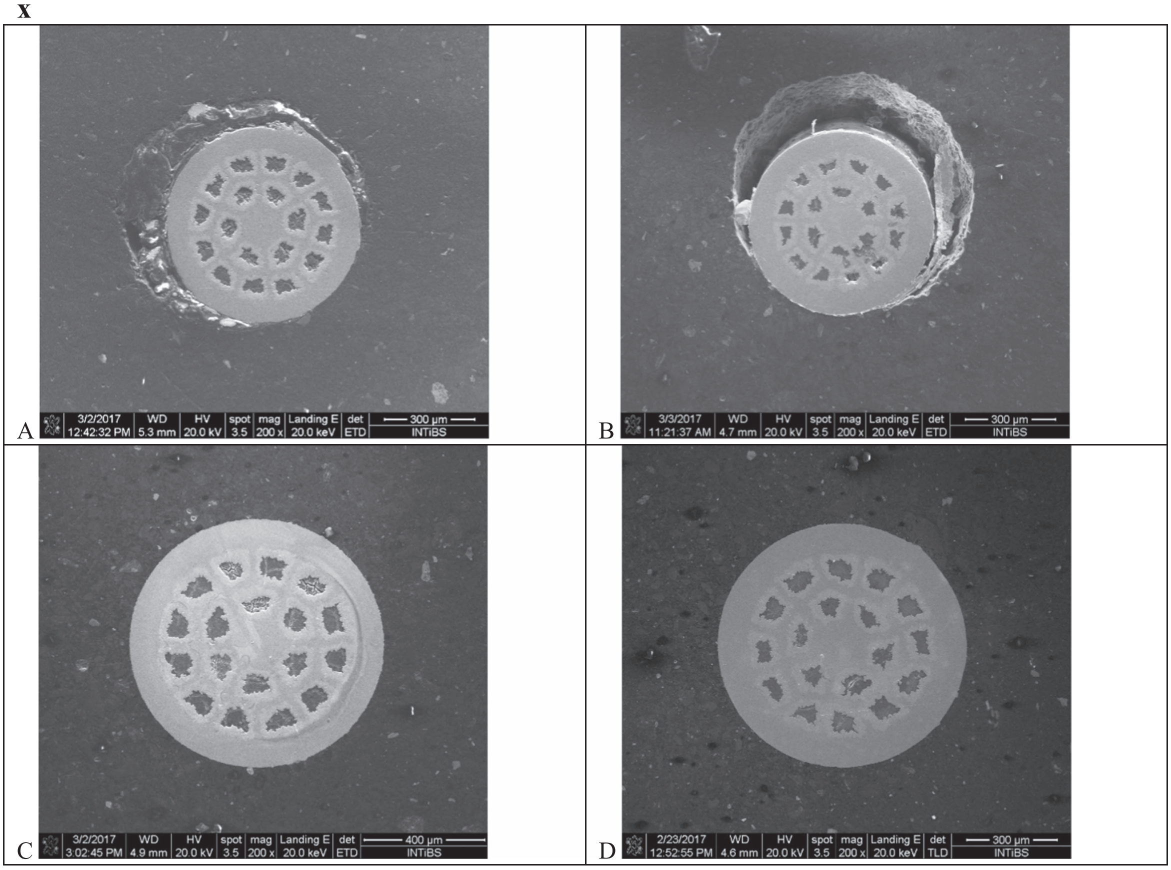

Figure 1. Cross-section of polished wires. Left: 1 bar sintering (120 min, 570 °C). Right: 1 GPa sintering (180 min/210 min, 570 °C). Top: nominal wire diameter 0.63 mm. Bottom: nominal wire diameter 0.83 mm.

the reduction of the wire diameter. It is necessary to add that a hot isostatic pressure was used in the present work, in contrast to the cold pressing [10, 11] and hot pressing [12–14] used by other research groups. The fabrication and characterization of short samples can lead to the implementation of a production process for long length wires.

Several methods were undertaken to improve current carrying properties by an enhancement of the flux pinning. This approach is especially effective at high magnetic fields, due to an increase in the irreversibility field (H_{irr}). Proton irradiation [15] and chemical doping were widely used to introduce additional pining centers into a superconductor to enhance critical current density. For example, doping by C, SiC [16] is a promising route to improve j_c of MgB_2 compound. Another method is doping by rare earth oxides [17] or by double doping [18], i.e. by C and rare earth oxides.

The high pressure synthesis presented in this work introduces changes in the material microstructure, which improves the flux pinning. In high pressure Mg the melting temperature considerably increases [19]; however, a solid state synthesis is possible. In such cases the grain growth is limited [20–22]. It enhances the concentration of grain boundaries, which can act as effective pinning centers. Using a high pressure method, we have fabricated undoped MgB_2 wires with good transport properties at high magnetic fields—a region typically devoted to doped material.

2. Experimental details

Hyper Tech green *in situ* MgB_2 wires [23] were used for the investigation. Cores containing a mixture of boron and magnesium powders were surrounded by a niobium and copper sheath. A batch of 18 such cores was surrounded by a common Monel sheath. Wires of two diameters were fabricated, i.e. with nominal outer diameters of 0.63 mm and 0.83 mm.

The high pressure synthesis of the superconducting wires was performed in an argon high pressure vessel under isostatic conditions (HIP) [24]. Prior to sintering, wire samples with lengths of 10–15 cm were closed at the ends by crimping and enveloped in Teflon tape to prevent gas penetration into their cores. Most of the samples were synthesized at 1.1 GPa pressure. Additionally, traditional sintering in argon flow (called '1 bar') was carried out as a reference. A relatively low sintering temperature of 570 °C was applied. This temperature was chosen in order to obtain, during the formation, small-sized grains. The synthesis was performed in the solid state both for the '1 bar' and HIP samples; the melting temperature of Mg is 650 °C under normal pressure and about 750 °C under 1 GPa pressure. The sintering time was varied in the range of 120–210 min, which is reasonable for the applied synthesis temperature range.

Table 1. Parameters of wires and sintering, with dimensions of the sample cross-section, changes in superconductor area at wire cross-section, and values of critical current density at selected conditions.

Nominal diameter mm	Sintering pressure	Sintering time min	Wire diameter μm	Wire surface area mm^2	MgB_2 cores surface area s_{SC} mm^2	Fill factor %	s_{SC} reduction %	j_c @ 6 T, 4 K A mm^{-2}	j_c @ 4 T, 20 K A mm^{-2}
0.63	1 bar	120	650	0.33	0.045	14	—	670	83
		180	630	0.31	0.039	12	13	513	—
	0.66 GPa	120	620	0.30	0.037	12	17	810	—
	1.1 GPa	120	630	0.31	0.037	12	18	1144	114
		150	610	0.30	0.030	10	33	1861	150
		180	620	0.30	0.026	9	42	3439	260
0.83	1 bar	120	840	0.54	0.080	15	—	750	56
		180	840	0.55	0.076	14	5	325	—
	1.1 GPa	120	830	0.55	0.067	12	17	1285	84
		150	820	0.52	0.058	11	27	1897	129
		210	790	0.49	0.053	11	34	3111	283

SEM images of the wires' cross-sections for polished samples were used to precisely determine their cross-sectional area. An example of the images is presented in figure 1. It is important to note that the shape of each core was selected by hand, using computer software, which gives a precise measure of the cross-sectional area s_{SC} of the superconductor in wire. These values were later used for calculation of the critical current density and the relative changes of the MgB_2 mass density. The change of mass density depends solely on the variation of the cross-sectional area, because the length of the samples did not change during the sintering process. In such a case, $\rho/\rho_0 = s_{SC0}/s_{SC}$.

Critical current measurements were made with the four-probe method with the 1 μV cm^{-1} criterion. For measurements at 4.2 K a helium bath was used, and heated helium vapor was used to measure at 20 K. The sample's length was about 20–25 mm. A magnetic field was applied perpendicularly to the wire axis. The critical current density j_c was calculated using the superconductor area measured independently for each sample, based on SEM images.

3. Results and discussion

It is known that MgB_2 wire shows a higher transition temperature, lower weight, and potentially lower manufacturing cost than conventional Nb-based superconducting wires or tapes. These superior characteristics offer an opportunity for the development of the next generation of superconducting applications. In this study we have demonstrated a method by which to control the grain connectivity formed inside the filament of pristine MgB_2 wires so as to improve j_c, this being one of the most important parameters for its real application.

In our previous studies we presented selected results [25] on the impact of reduction of wire diameter on the critical current density of MgB_2 wires. In this report we are presenting extended results of the experiment based on the reduction of the MgB_2 wires' diameters, using the HIP method for two diameters and several annealing times.

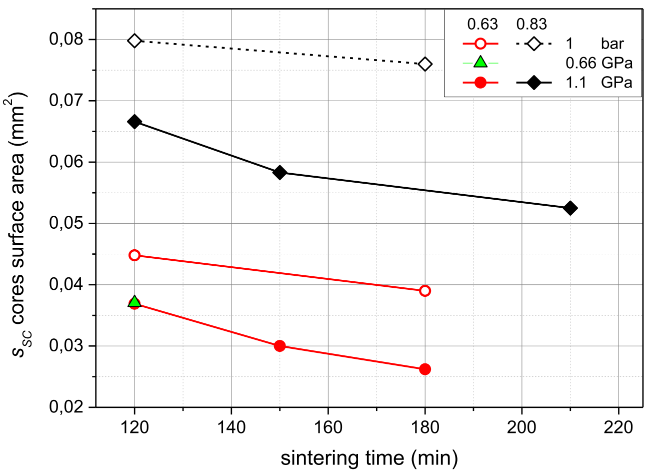

Figure 2. Surface area cross-section as a function of the annealing time at different applied pressures.

The processing parameters and wire parameters after the HIP process are presented in table 1. Optimization of the processing parameters is based on the annealing time and the applied pressure. The changes in wire dimensions are particularly interesting, as high pressure synthesis causes a reduction in the area of superconducting filaments s_{SC}, which also leads to size reduction of the whole wire. These changes are visible to the eye and are presented in figure 1 for both initial wire diameters. The values of superconductor cross-sectional area are shown in figure 2 to highlight that the pressure value is the main factor in the reduction of s_{SC}. At a given pressure, s_{SC} is further reduced by increasing the sintering time. This is probably caused by the sheath strain on the superconducting core. The reference samples were sintered at an ambient pressure of '1 bar' for 120 min and were later used to express changes in dimension or critical currents in relation to these samples.

Figure 3 shows the transport properties of manufactured MgB_2 wires measured at $T = 4.2$ K and 20 K. The values of

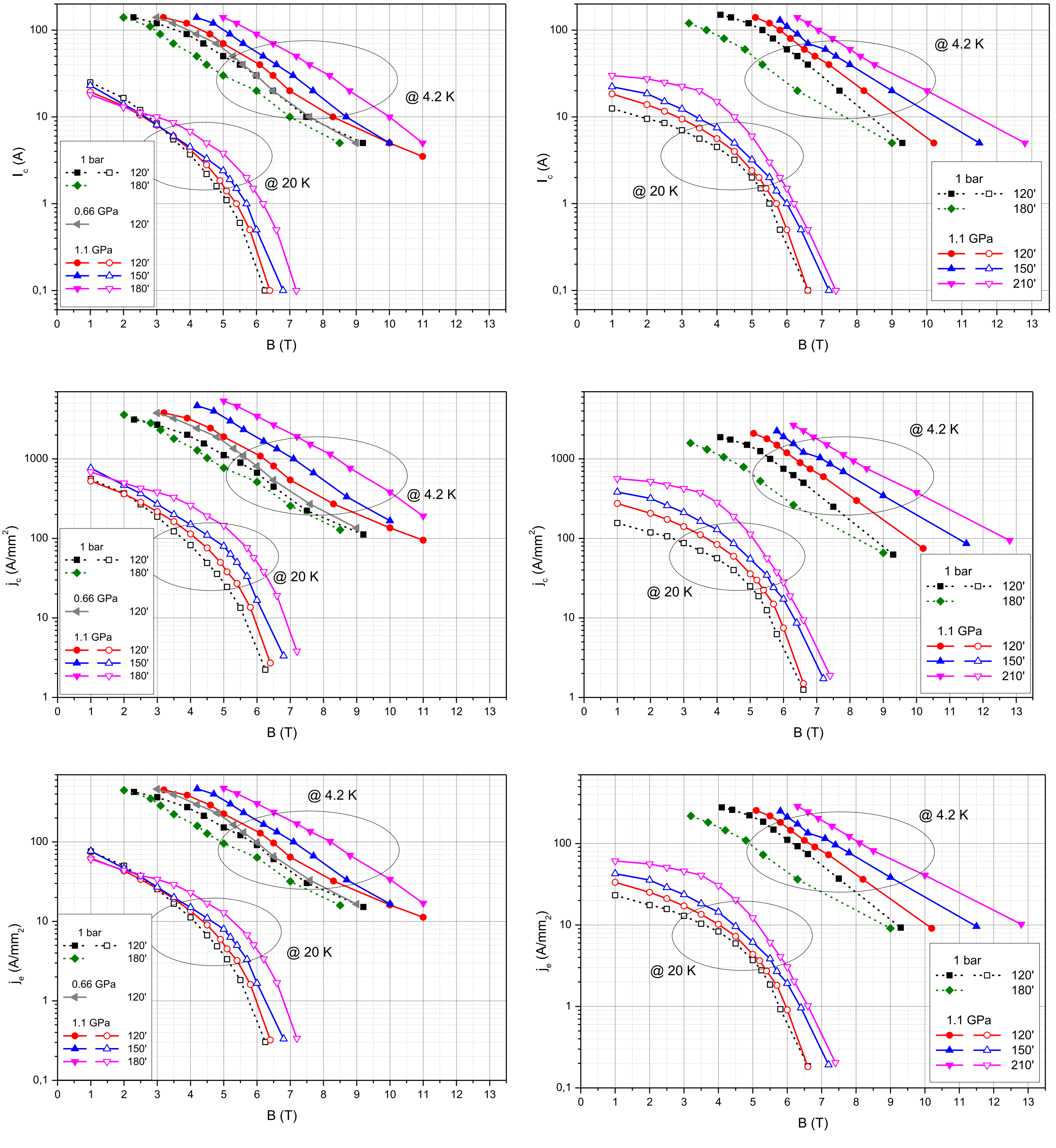

Figure 3. Critical current properties for wires of 0.63 mm nominal diameter (left) and 0.83 mm nominal diameter (right). Plots show critical current I_c (top), critical current density j_c (middle), and engineering current density j_e (bottom).

critical current I_c, critical current density j_c and engineering current density j_e are presented on separate plots. It is important to note that in this investigation both superconductor and wire area vary between the samples, and the j_c and j_e values are calculated independently for each sample. The j_c measured for samples of both diameters slowly and nearly linearly decreases with increasing magnetic field measured at $T = 4.2$ K. The highest j_c was measured for wires annealed for $t = 210$ min at 1.1 GPa pressure. On the other hand, the j_c measured at $T = 20$ K decreases steeply with increasing magnetic field, and similar to the data obtained at $T = 4.2$ K, the highest values were obtained for wires annealed at a pressure of 1.1 GPa for 210 min.

Figure 4 shows the pinning force density F_p versus the magnetic field for wires of both diameters. The obtained results indicate that the pinning force density measured for the wires annealed at 1.1 GPa pressure is much higher than for wires annealed at ambient pressure at $T = 4.2$ K. The highest

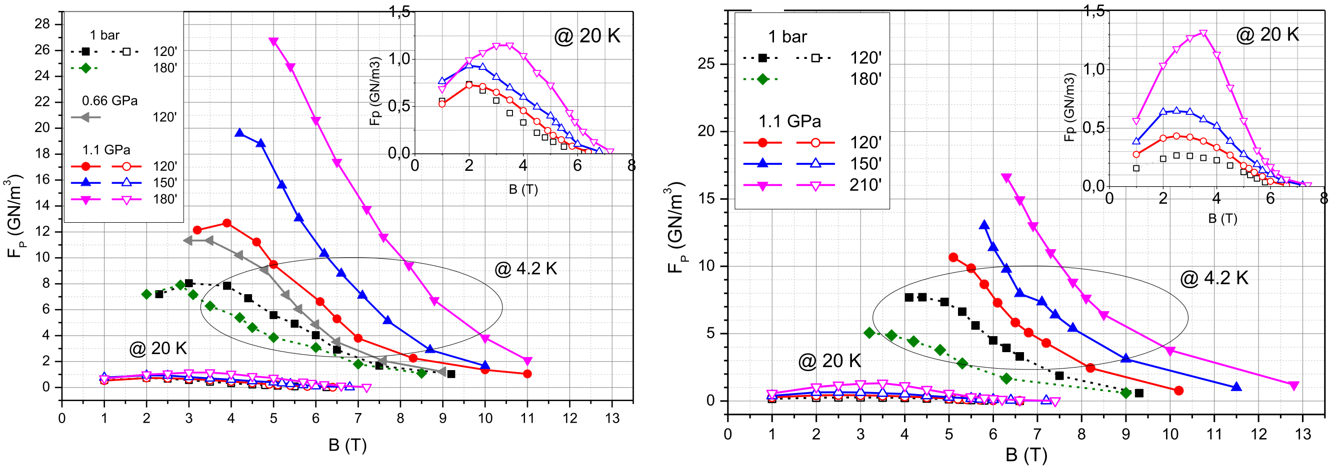

Figure 4. Pinning force density obtained for wires of 0.63 mm nominal diameter (left) and 0.83 mm nominal diameter (right).

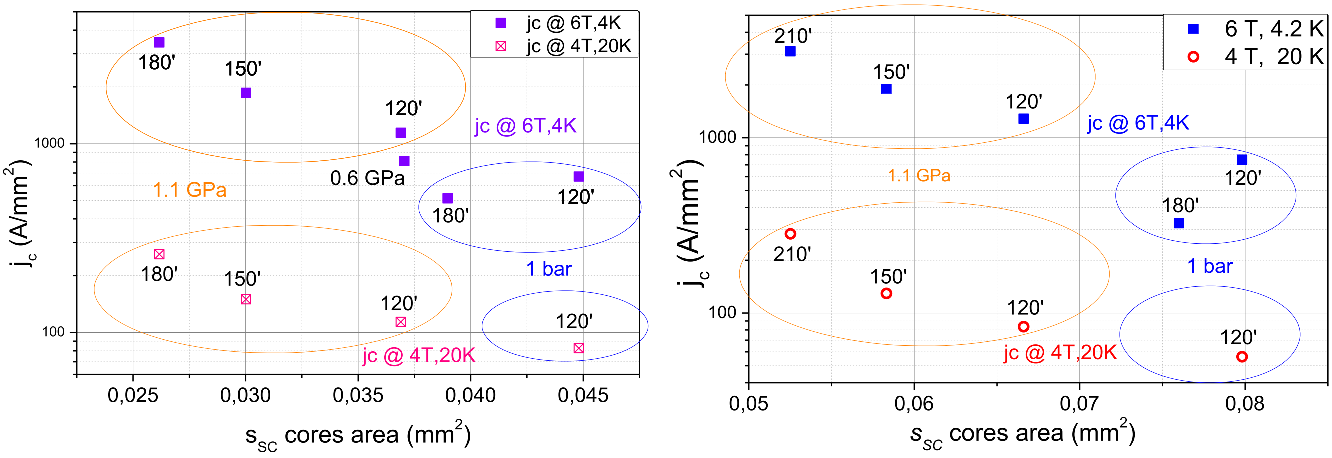

Figure 5. Critical current density j_c at 6 T, 4 K and at 4 T, 20 K as a function of superconductor surface area s_{SC} for wires of 0.63 mm nominal diameter (left) and 0.83 mm nominal diameter (right). Labels next to each point indicate the sintering time of each sample.

measured value was 27 GN m^{-3} in magnetic field B = 7 T for the wire of 0.63 mm diameter; however, the maxima of F_p were not determined for the best samples due to current source limitations. The inset in figure 4 shows similar results obtained at 20 K, with a highest measured value of 1.3 GN m^{-3}.

Usually, a measured increase of pinning force density is explained by an increase in either the number or pinning force of the pinning centers in the superconductor. This approach is based on the assumption that vortex pinning is the main mechanism limiting the critical current. It is not necessarily the case for MgB_2 due to its polycrystallinity, porous structure and percolative current flow.

The main goal was to check if the increase in critical current may be explained by an increase of the number of percolation paths induced by an increase of mass density and grain connectivity of the superconductor. Unfortunately, for multicore wires, extraction of a pure MgB_2 phase from sheath material is impossible and it was not possible to directly measure its density or normal resistivity. Therefore, we show the relation of the j_c values at intermediate magnetic fields (6 T at 4 K and 4 T at 20 K) to the superconductor cross-sectional area s_{SC} per wire, as presented in figure 5. Based on these experimental results, it is clear that there is a strong correlation between the two parameters, where j_c almost monotonically increases with a decrease of s_{SC}.

The wire area cross-section of the superconductor is reduced mainly due to high pressure treatment. During the process the wire length does not change, and therefore it is possible to directly relate the changes of s_{SC} with changes of MgB_2 mass density. Therefore it is reasonable to assume that with increased mass density, the grain connectivity increases [26, 27]. Unfortunately it is not possible to quantitatively relate those two parameters.

Figure 6 shows the relative increase of j_c as a function of relative superconductor mass density, where the reference sample is the one sintered under 1 bar pressure for 120 min. These values are the inversion of the s_{SC} values ratio from table 1, as the mass and length of the superconductor do not change during HIP. The results are presented of measurements at different magnetic fields. A clear, non-linear increase of j_c is seen. The observed increase in some cases depends on the magnitude of the magnetic field. It is important to note that for investigation purposes, a diameter of 0.63 mm is a

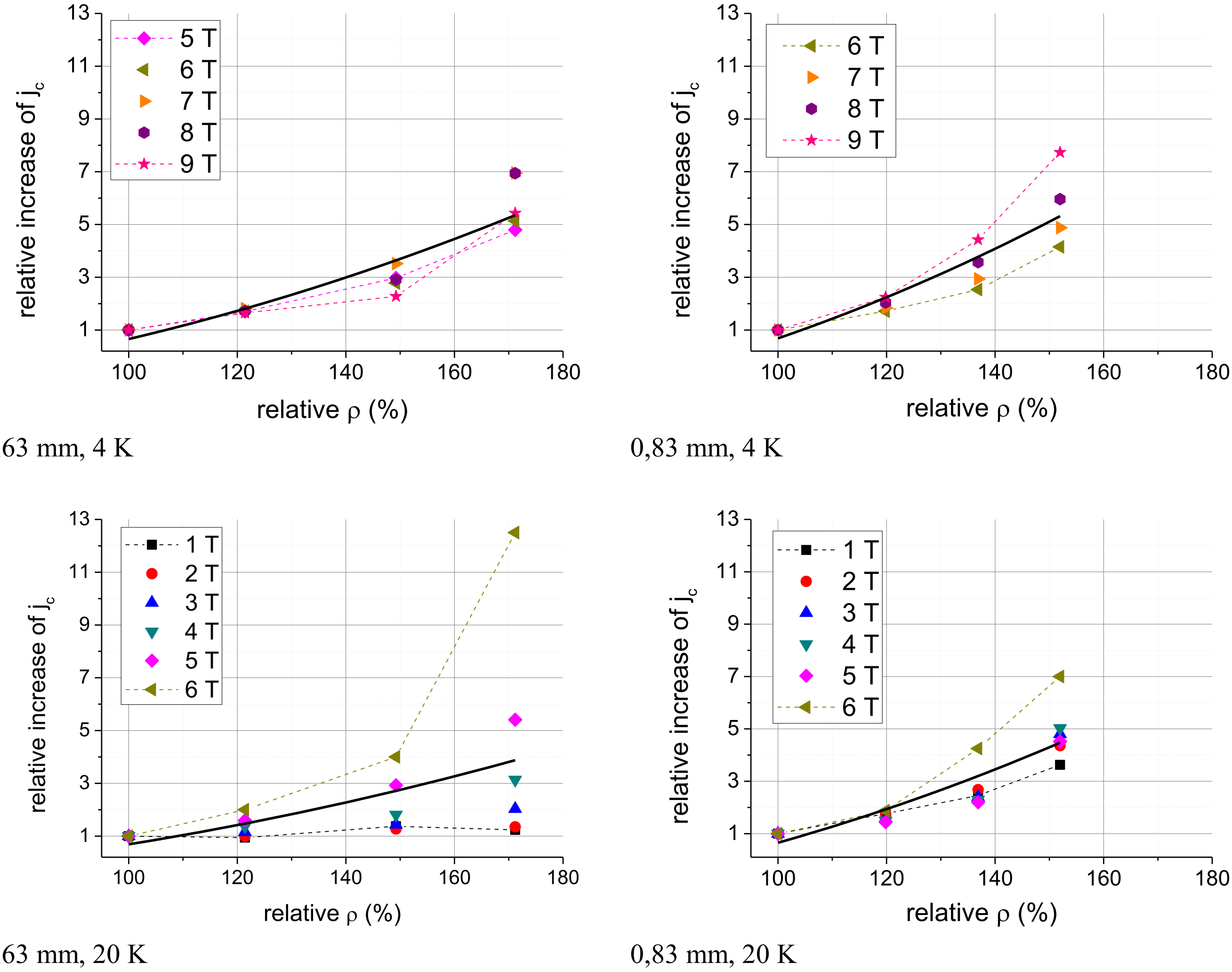

Figure 6. The relative increase of critical current density j_c as a function of the relative increase of the superconductor's mass density. Values are obtained for a sample sintered under normal 1 bar pressure for 120 min. Results are presented for measurements at different magnetic fields. Upper plots show values measured at 4 K, and lower plots at 20 K. Left plots show the results for 0.63 mm nominal wire diameter, and right plots for 0.83 mm. Solid lines show a fitted exponential function.

very low value for a wire. This feature induces random defects in the sheath's structure and causes measurement problems unrelated to the superconductor itself. This is probably the reason for the discrepancy in the data obtained for the 0.63 mm samples at 20 K.

The observed monotonous increase of j_c with increased mass density suggests that improvement of the grain connectivity is the main source of the increased transport parameters. The values of the parameter depend on the magnetic field, i.e. the highest increase of j_c usually was observed for the highest B. Such a relation suggests that there is also a change in the pinning mechanism (pinning density) of superconductors fabricated at high pressure. The grain boundary pinning is the dominant pinning mechanism in pristine MgB_2 material [28], but the increase of j_c at high magnetic fields suggests the presence of additional point pinning centers. This was observed for MgB_2 wires without any dopant. Therefore it is reasonable to assume the point pinning centers are related to very small grains, with size comparable to MgB_2 coherence length $\xi_{ab} = 0.05$–0.10 nm. Such grains are formed under high pressure [29].

The observed increase of critical current density was compared to the mean-field theory for a site percolation problem, as described by Yamamoto *et al* [30]. This model connects the relative density of the superconducting material (packing factor P) to its grain connectivity K:

$$K = \frac{(aP)^2 - P_C^2}{1 - P_C^2} \tag{1}$$

where a is the fraction of grains which are not covered by insulating barriers, under the assumption that this does not change with high pressure sintering. $P_C = 0.3117$ is the critical packing factor for the three-dimensional cubic site system [31]. Unfortunately, it was not possible to extract the superconducting cores from the metallic sheath; therefore neither K nor P was measured directly. Nevertheless, it was possible to fit the relative changes of j_c and mass density according to equation (1), where quantities with a_0 index

Table 2. Parameters of equation (2) (aP_0, y_0) fitted to data on relative increase of j_c to relative mass density increase presented in figure 6. R^2 is the coefficient of determination which describes fit quality. K_0 is the derived grain connectivity for the reference sample and $K_{\max}$ is the derived K for the best high pressure sample. Standard errors describing fit statistical accuracy are also presented.

Wire diameter	Temperature	aP_0	y_0	R^2	K_0	$K_{\max}$
Ø 0.63	4 K	0.41 ± 0.01	-0.34 ± 0.26	0.87	0.08 ± 0.01	0.43 ± 0.05
	20 K	0.50 ± 0.14	-0.31 ± 0.70	0.25	0.17 ± 0.16	0.69 ± 0.65
Ø 0.83	4 K	0.37 ± 0.01	-0.32 ± 0.38	0.81	0.04 ± 0.01	0.24 ± 0.04
	20 K	0.38 ± 0.01	-0.35 ± 0.26	0.79	0.06 ± 0.01	0.27 ± 0.04

represent the 1 bar reference sample. Here, a is constant and x is defined as:

$$x \equiv \frac{\rho}{\rho_0} = \frac{P}{P_0}; \quad a = \text{const.}$$

It was assumed that j_c is mainly related to changes of K according to the equation:

$$y \equiv \frac{j_c}{j_{c0}} = \frac{K}{K_0} + y_0 = \frac{(aP_0)^2}{(aP_0)^2 - P_C^2} \cdot x^2 - \frac{P_C^2}{(aP_0)^2 - P_C^2} + y_0. \quad (2)$$

We neglected the influence of other factors, such as changes in flux pinning, on the slope of the function. However, we had to include a y_0 parameter to compensate for non-connectivity effects. Equation (2) was used to fit the data plotted in figure 6, with aP_0 being a single fit parameter. To provide reasonable statistics, the fitting was performed based on the data measured for all magnetic fields at a given sample/temperature. The values of the calculated parameters are presented in table 2.

Most of the measured samples show a reasonably good fitting of the experimental data, with a coefficient of determination R^2 of about 0.8. It is seen that a power function with a higher exponent demonstrates a better fitting to experimental data. This fact suggests that other factors have an impact on the value of j_c. One of the reasons may be an increase (relation) of the a parameter with HIP sintering. Other factors, related to the vortex pinning, may change the relation between K and j_c. Nevertheless, based on the fitting parameters, it is possible to calculate the values of grain connectivity K, with $K = 0.05$–0.10 after normal pressure sintering and $K = 0.25$–0.40 for the best high pressure synthesized samples. These values can be compared with $K(P)$ curves obtained by other groups [30] for *in situ* and diffusion MgB_2. Such a comparison suggests that we have obtained packing factor values of $P = 0.4$–0.5 for normal pressure and $P = 0.7$–0.8 for high pressure sintered samples. Similar investigations for single core wires, where it is possible to extract and measure directly the properties of superconducting MgB_2 cores, are planned.

4. Conclusions

In summary, we have studied the effect of reduction of diameters of MgB_2 wires by high pressure synthesis on the critical current density and pinning force density. We have shown that such synthesis leads to a significant densification of superconducting wire cores. The increase of mass density induces an increase in critical current density, which is related to the improvement of the grain connectivity described by parameter K. The experimental results were analyzed with the mean-field theory for a site percolation problem, which gives the capability of a rough estimation of the increase in K after high pressure synthesis, from 0.05–0.10 to 0.25–0.40.

Experimental analysis also indicates that a point-type pinning mechanism is partially responsible for the j_c increase, improving mainly the performance at high magnetic fields.

The presented analysis can be used for future density-related investigations of MgB_2 superconductors and can serve as a constructive guide to fabrication of MgB_2 pristine wires under high pressure for application in magnet coils.

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