

# Formation of High-Field Pinning Centers in Superconducting MgB<sub>2</sub> Wires by Using High Hot Isostatic Pressure Process

D. Gajda<sup>1,2,5</sup> · A. Morawski<sup>3</sup> · A. J. Zaleski<sup>2,5</sup> · M. Akdoğan<sup>4</sup> · H. Yetiş<sup>4</sup> · F. Karaboğa<sup>4</sup> · T. Cetner<sup>3</sup> · İ. Belenli<sup>4</sup>

Received: 2 May 2017 / Accepted: 7 May 2017 / Published online: 24 May 2017  
© The Author(s) 2017. This article is an open access publication

**Abstract** This paper demonstrates the effects of hot isostatic pressure (HIP) on the structure and transport critical parameters of in situ MgB<sub>2</sub> wires without a barrier. Our results show that only HIP and nano-boron allow the formation of more high-field pinning centers, which lead to the increase in critical current density ( $J_c$ ) at high applied magnetic fields. Nano-boron and annealing at a low pressure increase the  $J_c$  in the low magnetic field. This indicates that nano-particles create more high-field pinning centers. In addition, the results show that nano-boron improves the connection between the grains. Scanning electron microscope results show that HIP increases the reaction rate between Mg and B, density, and homogeneity of the MgB<sub>2</sub> material. Additionally, HIP allows to create a structure with small grains and voids and eliminates the significance of the number of voids. High isostatic pressure allows to obtain high  $J_c$  of 10 A/mm<sup>2</sup> (at 4.2 K) in 10 T and increases irreversible magnetic field ( $B_{irr}$ ) and upper critical field ( $B_{c2}$ ).

Measurements show that these wires have high critical temperature of 37 K.

**Keywords** MgB<sub>2</sub> wires · High fields pinning centers · Critical current density

## 1 Introduction

The MgB<sub>2</sub> material has many advantages, such as having a simple and easy structure, high critical temperature, low resistivity in the normal state, high critical current density at low magnetic fields, low anisotropy, and low-cost components and being suitable for the powder-in-tube (PIT) method [1–5]. All of these features make the MgB<sub>2</sub> conductor very interesting for practical applications. However, the formation of the MgB<sub>2</sub> material structure is not easy for two reasons. One is the strong reactivity of pure Mg with, e.g., oxygen and copper [6], and the second is the large difference between the melting points of Mg (650 °C) and B (2075 °C) [7, 8]. Therefore, it is very difficult to perform MgB<sub>2</sub> wires without barriers with good critical parameters even though these wires are cheaper and have a simpler structure.

Moreover, MgB<sub>2</sub> wires are made from Mg particles, which are much larger than B particles [9]. This indicates that the structure of the MgB<sub>2</sub> material depends mainly on the Mg particle size. Pure Mg has several advantages such as high ductility and malleability. These factors allow to form the structure of an unreacted MgB<sub>2</sub> wire by cold working, e.g., cold drawing [10], cold rolling [10], mechanical alloying [11], and cold isostatic pressure [12]. All these methods increase the density of the unreacted MgB<sub>2</sub> material and lead to an increase in critical current density.

The MgB<sub>2</sub> material structure is also influenced by chemical doping [2, 13], the purity level of the components [14],

✉ D. Gajda  
dangajda@op.pl

<sup>1</sup> International Laboratory of High Magnetic Fields and Low Temperatures, Gajowicka 95, 53-421 Wrocław, Poland

<sup>2</sup> Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna 2, 50-422 Wrocław, Poland

<sup>3</sup> Institute of High Pressure Physics, Polish Academy of Sciences, Sokolowska 29/37, 01-142 Warsaw, Poland

<sup>4</sup> Department of Physics, Abant İzzet Baysal University, 14280 Bolu, Turkey

<sup>5</sup> Centre for Advanced Materials and Smart Structures, Polish Academy of Sciences, Okólna 2, 50-950 Wrocław, Poland

and the particle size of the precursor powders [15]. Doping in the  $\text{MgB}_2$  material is used to produce additional flux pinning centers in the  $\text{MgB}_2$  structure. This in turn results in a significant enhancement of the critical current density ( $J_c$ ) [16]. Formation of high-field pinning centers in  $\text{MgB}_2$  wires is very important for applications. The incorporation of carbon into the  $\text{MgB}_2$  material enhances the flux pinning properties of the sample at high applied magnetic fields [13]. Our previous work has shown that it is also possible to create high-field pinning centers by means of the hot isostatic pressure (HIP) process [11].

Additionally, some chemical additives also accelerate the reaction rate (e.g., Sn [17], because it has a lower melting point). This leads to an increase in the number of superconducting phases, the formation of small  $\text{MgB}_2$  grains, and the improvement in grain boundary pinning. Annealing of Mg in the liquid state gives rise to large voids (large shrinkage—25%), which reduce the density of the  $\text{MgB}_2$  material and the number of connections between the grains, leading to a reduction in the  $J_c$  of  $\text{MgB}_2$  wires [2, 5, 18]. On the other hand, annealing of Mg in the solid state requires long annealing times to obtain a superconducting phase. However, a long annealing time leads to the formation of larger grains, which effectively reduce the number of grain boundaries. The poor connection between the grains and large number of voids significantly reduce the critical and mechanical parameters of the  $\text{MgB}_2$  wires. These adverse effects limit the feasibility of these wires in applications. In the present study, we show that annealing the  $\text{MgB}_2$  wires by using the HIP process eliminates these problems and allows the formation of a greater number of high-field pinning centers in the  $\text{MgB}_2$  wires with the contribution of the use of nano-sized boron.

## 2 Experimental Details

The starting materials in this work are commercially available powders of magnesium (Pavezyum company atomized magnesium, 99%, particle sizes 74–149  $\mu\text{m}$ ), amorphous boron (Pavezyum company boron 95, 95–97%, particle sizes  $<1 \mu\text{m}$ —50%), and amorphous nano-boron (Pavezyum company nano-boron,  $>98.5\%$ , particle sizes  $<250 \text{ nm}$ —50%) from Pavezyum Advanced Chemicals (Turkey). The Mg + 2B stoichiometric ratio is homogeneously mixed by means of rotary ball milling for 3 h at ambient conditions. The unreacted monofilament wires are produced by PIT in an iron shield of 9:12-mm inner/outer diameters with a filling factor of about 50% at the Abant İzzet Baysal University in Turkey [19, 20].  $\text{MgB}_2$  wires are HIP processed at the Institute of High Pressure Physics in Warsaw. The wire samples are annealed at 740 °C for 40 min at a pressure of 0.1 MPa (sample A) and 1.1 GPa (sample B).



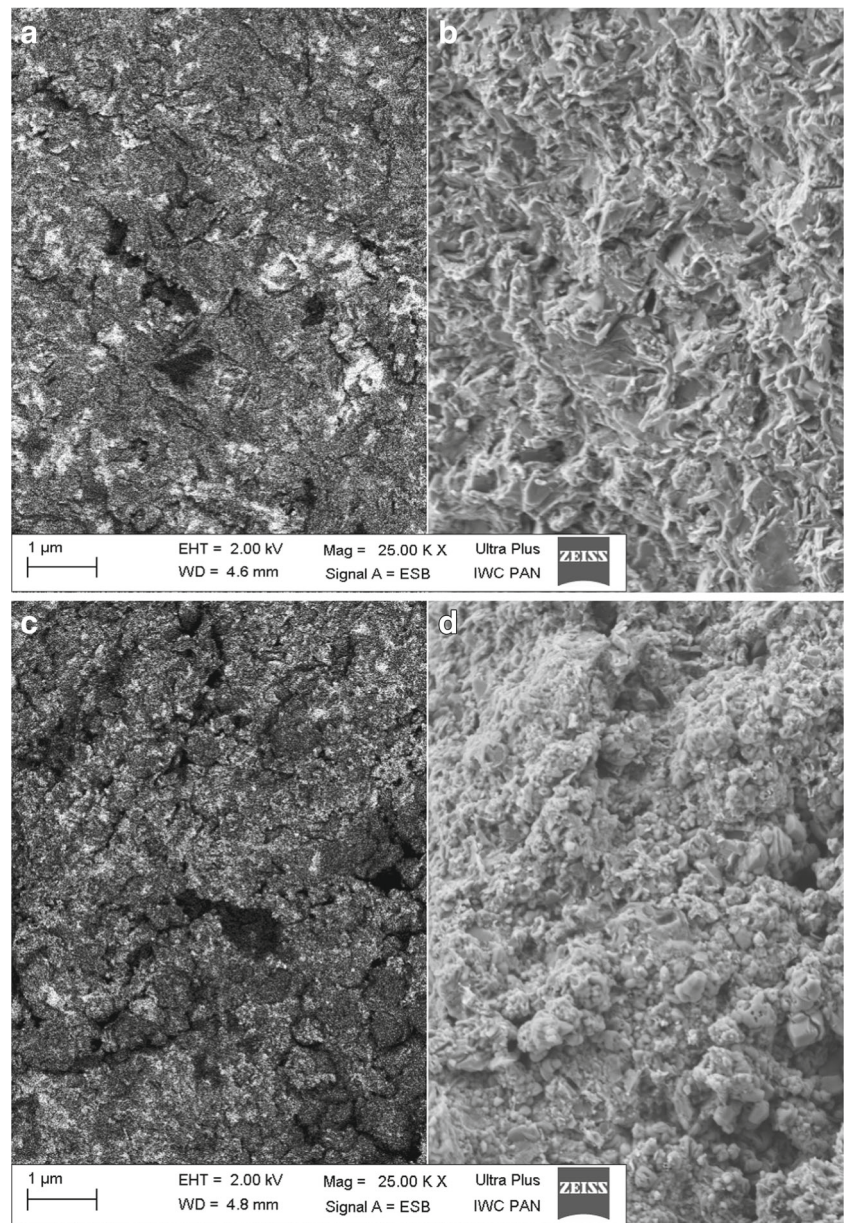
**Fig. 1** Pressure chamber. Maximum isostatic pressure of 1.6 GPa and maximum annealing temperature 2000 °C

HIP is made in 5-N argon atmosphere in a high-gas-pressure chamber [21]. Figure 1 shows the pressure chamber. In the first step, we increase the pressure. In the next step, we increase the annealing temperature. After completion of the process, in the first step, we reduce the annealing temperature. In the next step, we reduce the pressure. Critical current ( $I_c$ ) measurements of the  $\text{MgB}_2$  wires are made by using a four-probe resistive method at a temperature of 4.2 K for constant current in the range of 0 and 150 A in the presence of an external magnetic field applied perpendicularly to the sample surface at the International Laboratory of High Magnetic Fields and Low Temperatures (ILHMFLT) [22]. The  $I_c$  is determined on the basis of 1  $\mu\text{V}/\text{cm}$  criterion. Transport current (15 Hz and AC current,  $I_{AC} = 100 \text{ mA}$ ) is applied by using a physical properties measurement system (PPMS Model 7100, Quantum Design) at ILHMFLT. The values of irreversible magnetic field ( $B_{irr}$ ), critical temperature ( $T_c$ ), and upper critical field ( $B_{c2}$ ) are determined with the criterion of 10, 50, and 90% of normal-state resistivity before transition, respectively. Analysis of the microstructure is performed by a Zeiss scanning electron microscope (high-resolution low-energy type) at the Institute of High Pressure Physics, PAS, in Warsaw.

## 3 Results and Discussion

Figure 2a, b shows that annealing the wire samples at a low pressure leads to the formation of large amounts and large areas of pure Mg (light areas—Fig. 1a), whereas annealing at a high pressure significantly reduces the size and the number of areas of pure Mg (Figs. 1d and 2c). This indicates that HIP accelerates the rate of reaction in the  $\text{MgB}_2$  material and leads to the formation of more superconducting phases. In addition, annealing at a high pressure (Fig. 2d) affects the granular structure of the  $\text{MgB}_2$  material and yields the production of smaller grains than that of sample A (Fig. 2b).

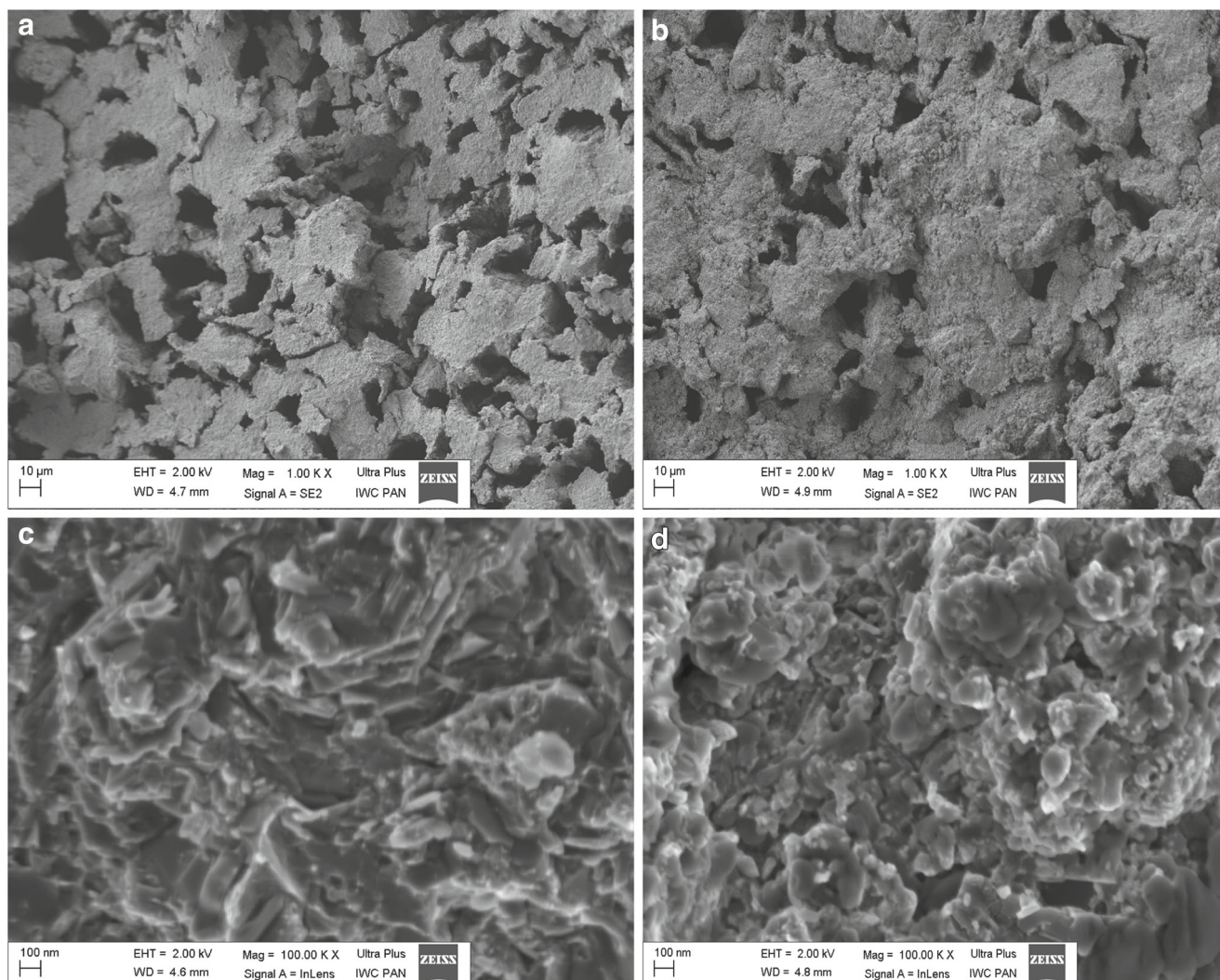
**Fig. 2** The SEM analysis of sample cross sections in **a** the mode of backscattering electron (ESB) for sample A (0.1 MPa), **b** the mode of secondary electron for sample A, **c** the mode of ESB for sample B (1.1 GPa), and **d** the mode of secondary electron for sample B. In **a** and **c**, *light areas* indicate areas with a large number of Mg



Scanning electron microscopy (SEM) results indicate that sample A has a large number of big voids (Fig. 3a) and big grains (Fig. 3c). The high-pressure annealing process is able to reduce the number of voids (about 100%) significantly (Fig. 3b), creates small grains (Fig. 3d), and increases the density of the superconducting core with a greater number of connections between the grains. Figure 4 also shows the results of energy-dispersive spectroscopy (EDS) analysis which is obtained from the fracture surface of samples A and B to avoid penetration of iron during polishing. The EDS analysis shows that the samples have good purity levels. Sample B (annealed under 1.1 GPa) has a small amount of iron in comparison to that of sample A (annealed under 0.1 MPa) as shown in Fig. 4b, c. Carbon

and oxygen are formed during the preparation of the samples for SEM analysis (Fig. 4). Studies indicate that oxygen can create precipitation of MgO [6, 9, 18]. This precipitation can create surface or point (thickness close to the coherence length) pinning centers. These pinning centers significantly increase the  $J_c$  in low and middle magnetic fields and poorly increase the  $J_c$  in high magnetic fields.

The results in Fig. 5a show that the HIP process does not improve the  $B_{irr}$ ,  $T_c$ , and  $B_{c2}$  at low applied magnetic fields ranging from 0 to 1 T. A gradual increase in the critical parameters of sample B,  $T_c$  is raised about 2 K and  $B_{irr}$  and  $B_{c2}$  are enhanced about 15%, is observed when the magnetic field is increased towards 8 T as shown in Fig. 5a, b. For applied magnetic fields above 8 T, a remarkable

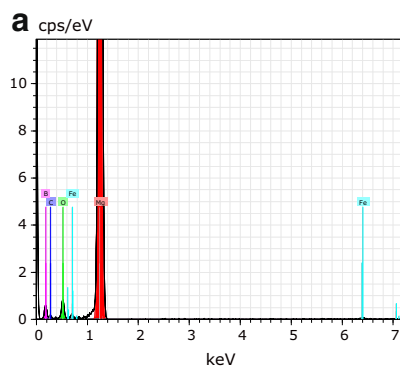


**Fig. 3** The cross section in the mode of secondary electron (SE). **a** The sample annealed at an isostatic pressure of 0.1 MPa. **b** The sample annealed at an isostatic pressure of 1.1 GPa. Images with bigger magnification. **c** Sample A (0.1 MPa). **d** Sample B (1.1 GPa)

improvement in  $T_c$  (more than 3 K) and in  $B_{irr}$  and  $B_{c2}$  (about 20%) is achieved. The results in Fig. 5c show that the high pressure significantly increases the  $J_c$  above 5 T at

4.2 K (e.g., in 7 T, the HIP process enhances twice the  $J_c$ , and in 9 T, the HIP process enhances five times the  $J_c$ ), but does not contribute to the  $J_c$  below 5 T.

**Fig. 4** The EDS analysis of sample cross sections for **a, b** sample A (0.1 MPa) and **c** sample B (1.1 GPa)



**b**

Element	norm. C[wt.%]	Atom. C[at.%]
Carbon (C)	3.59	4.73
Oxygen (O)	3.27	3.23
Magnesium (Mg)	53.28	34.65
Iron (Fe)	0.74	0.21
Boron (B)	39.12	57.18

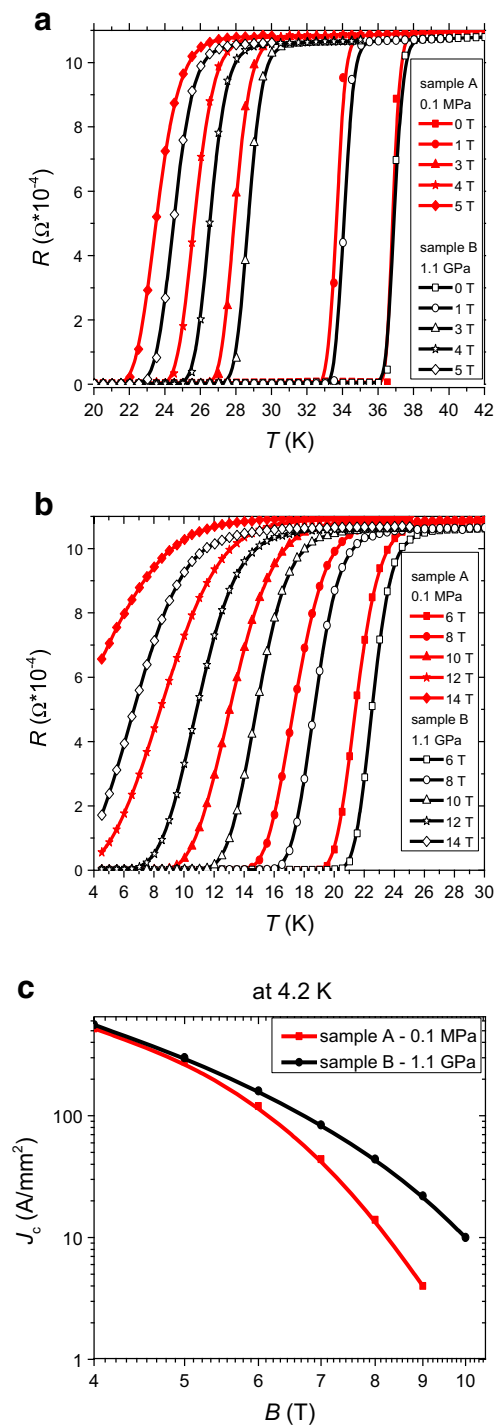
**c**

Element	norm. C[wt.%]	Atom. C[at.%]
Carbon (C)	3.94	5.12
Oxygen (O)	8.60	8.39
Magnesium (Mg)	48.86	31.30
Iron (Fe)	0.48	0.14
Boron (B)	38.12	55.05

Our previous work showed that the choice of HIP and big-particle-sized boron powder significantly increases the  $J_c$  at low and middle magnetic fields, but less increases the  $J_c$  at high magnetic fields (above 6 T) [23]. Such a case substantially limits the use of these wires in high-field applications. The idea behind the present study is to use nano-sized amorphous boron, which accelerates the reaction rate, leading to more superconducting phase formation. According to our knowledge [23], the use of nano-boron increases the  $J_c$  at low and middle magnetic fields, but this is not sufficient to increase the  $J_c$  at high magnetic fields when the samples are annealed under low pressures. Transport measurements reveal that annealing MgB<sub>2</sub> wires at HIP and the use of nano-sized amorphous boron powder allow for a notable increase in  $J_c$  at high magnetic fields (see Fig. 5c). This indicates that HIP results in the formation of high-field pinning centers inside the MgB<sub>2</sub> material if amorphous nano-boron powder is chosen as the starting material. We know that the HIP process increases the number of dislocations [24], which behave as high-field pinning centers inside the material [25]. We observe that the effect of HIP with amorphous nano-boron produces a large number of dislocations in the MgB<sub>2</sub> material. Such an effect is not influential to increase the  $J_c$  at magnetic fields below 5 T. In Fig. 3, we see that HIP significantly reduces the size and number of voids. Voids (larger than the coherence length) create surface pinning centers. Surface pinning centers increase the  $J_c$  in the low and middle magnetic fields [25]. A smaller number of surface pinning centers poorly increase the  $J_c$  below 5 T. In addition, our measurements indicate that high-field pinning centers are not efficient to improve the  $J_c$  at low- and middle-magnetic-field regions. Pham et al. [26] and Akyüz et al. [5] show that in the MgB<sub>2</sub> material, intrinsic pinning centers in MgB<sub>2</sub> single crystals can exist. Their studies indicate that this type of pinning strongly anchored the vortex lattice [5]. Research suggests that the intrinsic pinning centers in the MgB<sub>2</sub> material can create C, which is substituted for B [2, 13]. However, it seems that in the undoped MgB<sub>2</sub> wires, dislocations can create high-field pinning centers.

On the other hand, the MgB<sub>2</sub> sample annealed at a low pressure with amorphous nano-boron has surface pinning centers (large voids) as shown in Fig. 3a, and these pinning centers are capable to increase the  $J_c$  at only low and middle magnetic fields. The results of the present work are important for further increasing the  $J_c$  and  $B_{irr}$  in MgB<sub>2</sub> wires. This indicates that nano-particles and HIP create more high-field pinning centers than micro-particles and HIP. Additionally, the transport measurements suggest that nano-boron improves the main connection between the grains.

Our research [27] shows that the HIP process allows to obtain a homogeneous distribution of high-field and high-temperature pinning centers in MgB<sub>2</sub> wires with the Nb



**Fig. 5** Transport  $R$ - $T$  ( $I_{AC} = 100$  mA) curves for samples A and B at **a** low magnetic fields and **b** high magnetic fields. **c** Transport  $J_c$ - $B$  curves for samples A and B

barrier. This is very important because it allows to produce very long MgB<sub>2</sub> wires with a uniform current density. It significantly increases the possibility of using MgB<sub>2</sub> wires.

The use of large boron and lack of barriers significantly lower the cost of MgB<sub>2</sub> wires and increase their reliability.

This greatly increases the possibility of applying this type of MgB<sub>2</sub> wires.

## 4 Conclusions

The results show that amorphous nano-boron and annealing under atmospheric pressure are only capable to increase the  $J_c$  at low and middle magnetic fields. We observe that annealing under HIP allows increasing the density and uniformity of the MgB<sub>2</sub> material, reduces the number of voids, increases the number of connections between the grains, and accelerates the reaction rate. As a conclusion, we find that the use of HIP with amorphous nano-sized boron results in a significant increase in the  $J_c$  and the critical parameters of the MgB<sub>2</sub> wires at high applied magnetic fields. The kind of application of MgB<sub>2</sub> wires will determine the type of heat treatment, size, and purity grains of boron.

**Acknowledgements** This work was supported by the Institute of High Pressure Physics, PAS, and the International Laboratory of High Magnetic Fields and Low Temperatures. It was also partially supported by the Scientific and Technological Research Council of Turkey (TUBITAK) (grant number: 113F080) and partly by the Ministry of Development of the Republic of Turkey under the grant number 2010K120520.

**Open Access** This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

## References

- Nagamatsu, J., Nakagawa, N., Muranaka, T., Zenitani, Y., Akimitsu, J.: *Nature* **410**, 63–64 (2001)
- Takano, Y., Takeya, H., Furi, H., Kumakura, H., Hatano, T., Toganok, K., Kito, H., Ihara, H.: *Appl. Phys. Lett.* **78**, 2914–2916 (2001)
- Canfield, P.C., Finnemore, D.K., Bud'ko, S.L., Ostenson, J.E., Lapertot, G., Cunningham, C.E., Petrovic, C.: *Phys. Rev. Lett.* **86**, 2423–2426 (2001)
- Sharma, P.A., Hur, N., Horibe, Y., Chen, C.H., Kim, B.G., Guha, S., Cieplak, M.Z., Cheong, W.: *Phys. Rev. Lett.* **89**, 167003 (2002)
- Akyüz, Y., Biçer, A., Gürü, M.: *Mater. Des.* **28**, 2500 (2007)
- Woźniak, M., Hopkins, S.C., Gajda, D., Glowacki, B.A.: *Physics Procedia* **36**, 1594 (2012)
- Kennedy, G.C., Newton, R.C.: *Solids under Pressure*. In: Paul, W., Warschauer, D.M. (eds.), p. 163. McGraw-Hill Book Company, New York (1963)
- Pelissier, J.: *Phys. Scr.* **34**, 838 (1986)
- Tomsic, M., Rindfleisch, M., Yue, J., McFadden, K., Phillips, J., Sumption, M.D., Bhatia, M., Bohnenstiehl, S., Collings, E.W.: *Int. J. Appl. Ceram. Technol.* **4**, 250 (2007)
- Gajda, D., Morawski, A., Zaleski, A.J., Haßler, W., Nenkov, K., Rindfleisch, M.A., Zuchowska, E., Gajda, G., Czujko, T., Cetner, T., Hossain, M.S.A.: *J. Appl. Phys.* **117**, 173908 (2015)
- Strickland, N.M., Buckley, N.R.G., Otto, A.: *Curr. Appl. Phys.* **4**, 688 (2004)
- Hossain, M.S.A., Senatore, C., Flukiger, R., Rindfleisch, M.A., Tomsic, M.J., Kim, J.H., Dou, S.X.: *Supercond. Sci. Technol.* **22**, 095004 (2009)
- Birajdar, B., Eibl, O.: *J. Appl. Phys.* **105**, 033903 (2009)
- Wang, D., Zhang, X., Tang, S., Xu, D., Yao, C., Dong, C., Xu, Z., Ma, Y., Oguro, H., Awaji, S., Watanabe, K.: *Supercond. Sci. Technol.* **28**, 105013 (2015)
- Xu, D., Wang, D., Li, C., Yuan, P., Zhang, X., Yao, C., Dong, C., Huang, H., Ma, Y., Oguro, H., Awaji, S., Watanabe, K.: *Supercond. Sci. Technol.* **29**, 045009 (2016)
- Haßler, W., Herrmann, M., Rodig, C., Schubert, M., Nenkov, K., Holzappel, B.: *Supercond. Sci. Technol.* **21**, 062001 (2008)
- Ma, Z., Jiang, H., Liu, Y.: *Supercond. Sci. Technol.* **23**, 025005 (2010)
- Jung, A., Schlachter, S.I., Runtsch, B., Ringsdorf, B., Fillinger, H., Orschulko, H., Drechsler, A., Goldacker, W.: *Supercond. Sci. Technol.* **23**, 095006 (2010)
- Akdoğan, M., Yetis, H., Gajda, D., Karaboga, F., Ulgen, A.T., Demirturk, E., Belenli, I.: *J. Alloy Compd.* **649**, 1007 (2015)
- Ağl, H., Yetis, H., Akdoğan, M., Altug, C., Akturk, S., Gencer, A.: *Cryogenics* **63**, 138 (2014)
- Cetner, T., Morawski, A., Gajda, D., Haßler, W., Rindfleisch, M., Tomsic, M., Zaleski, A., Czujko, T., Zuchowska, E., Przysupski, P.: *Supercond. Sci. Technol.* **28**, 045009 (2015)
- Gajda, D., Morawski, A., Zaleski, A., Kurnatowska, M., Cetner, T., Gajda, G., Presz, A., Rindfleisch, M., Tomsic, M., Surdacki, P.: *Supercond. Sci. Technol.* **28**, 015002 (2015)
- Gajda, D., Morawski, A., Zaleski, A.J., Akdoğan, M., Yetiş, H., Karaboğa, F., Cetner, T., Belenli, I.: *J. Alloy Compd.* **687**, 616 (2016)
- Serquis, A., Civale, L., Hammon, D.L., Liao, X.Z., Coulter, J.Y., Zhu, Y.T., Jaime, M., Peterson, D.E., Mueller, F.M., Nesterenko, V.F., Gu, Y.: *Appl. Phys. Lett.* **82**, 2847 (2003)
- Livingston, J.D.: GE R&D Center Report (1969–1970) see [www.bnl.gov/magnets/staff/gupta/Summer1968/0377.pdf](http://www.bnl.gov/magnets/staff/gupta/Summer1968/0377.pdf)
- Pham, D., Jung, S.-G., Song, K.J., Ranot, M., Lee, J.H., Lee, N.N., Kang, W.H.: *Curr. Appl. Phys.* **16**, 1046 (2016)
- Gajda, D., Morawski, A., Zaleski, A.J., Haßler, W., Nenkov, K., Maecka, M., Rindfleisch, M.A., Hossain, M.S.A., Tomsic, M.: *J. Appl. Phys.* **120**, 113901 (2016)