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ORIGINAL PAPER

Superconducting Properties and Microstructure Changes after Heat Treatment of In Situ MgB_2 Wires with Ex Situ MgB_2 Barriers

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Abstract

In our article, we show the results for wires with in situ MgB_2 core doped with 8 at % of nano-SiC and ex situ MgB_2 barrier doped with 8 at % of nano-diamond. All wires were annealed under high isostatic pressure of 1 GPa for 15 min in a temperature range from 700 to 800 ℃. Measurements were made using the vibrating magnetometer. The critical current density was determined with the Bean model. The study of the structure and composition of the MgB_2 material were performed by using a scanning electron microscope (SEM). Our results show that annealing at 700 ℃ under isostatic pressure of 1 GPa allows to significant reduction of Mg and nano-SiC migration from the in situ MgB_2 core to the ex situ MgB_2 barrier. Further studies indicate that annealing at 750 ℃, under the same pressure of 1 GPa, also inhibits the migration of Mg and nano-SiC from the in situ MgB_2 core to the ex situ MgB_2 barrier. However, annealing at 800 ℃, and under the pressure of 1 GPa, leads to the total penetration of the barrier by Mg and nano-SiC.

Keywords Ex situ MgB_2 barrier · MgB_2 wires · Mg diffusion · Cu shield · Critical current density

1 Introduction

In the Mg + 2B compound, the synthesis reaction depends mainly on Mg, due to its low melting point of 650 ℃ under normal pressure [1, 2], compared to boron, which has a very high melting point of 2075 ℃, and its influence of atomic diffusion is very little. Moreover, the research shows that the isostatic pressure increases the melting point of Mg, e.g. 1 GPa, from 650 to 725 ℃ [1, 2]. The results presented by Gajda et al. [3, 4] show that heat treatment for temperatures at which Mg is in the solid state allows to obtain small grains and a large number of connection between grains. This leads to a high magnetic and transport critical current density (J_{mc} and J_{tc}). Additionally, it was noticed that heat treatment temperature above the Mg melting point leads to the formation of large grains and reduces the number of connections between grains [3, 4]. This decreases the J_{mc} and J_{tc} in the MgB_2 material. Recent studies pointed out that the density of the unreacted Mg + 2B compound has a great influence on the synthesis reactions at Mg solid state [4] e.g. annealing temperature of 630 ℃ for precursor powders of Mg and B with high density of unreacted compound Mg + 2B (1.5 g/cm^3) allows for a more complete synthesis reaction compared to the lower density of the unreacted compound M + 2B (1.38 g/cm^3) [4]. Moreover, the density of the unreacted compound Mg + 2B has a greater influence on the synthesis reaction with Mg in the solid state than the grain size of B [3].

The diffusion barriers in MgB_2 wires have are very important. They inhibit Mg reactions with the wire sheath, e.g. copper (Cu) sheath. This allows to obtain a large amount of superconducting phase. Moreover, the metal diffusion barriers are essential in multi-filament MgB_2 wires, in which have small amount of superconducting material. The lack of metal barrier causes Mg to react with the wire sheath e.g. Cu, and significantly reduces the amount of superconducting material. Currently, the diffusion barriers in MgB_2 wires are made with Nb, Ta, Ti, and Fe [5–7]. The measurements show that MgB_2 wires without diffusion barriers have significantly lower critical current density, especially in high

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magnetic fields, than MgB_2 wires with metal diffusion barriers [8, 9]. Unfortunately, these barriers are expensive and their hardness increases after cold drawing. The higher hardness might lead to damage of the metal barrier, e.g. during the reduction of the wires diameter. The hardness of metal barriers is reduced by thermal treatment after cold drawing, which improves the ductility of the diffusion metal barriers. The costs of these technological processes (e.g. cold drawing and recrystallization) and the high price of the metal used for the barriers significantly increase the final cost of MgB_2 wires. A search for a different solution led to the idea of using a cheap, easy-to-produce reacted MgB_2 material [10, 11]. It turns out that the cold drawing process does not increase hardness of ex situ MgB_2 diffusion barrier because it is made of ex situ MgB_2 powder [10, 11]. This means that the ex situ MgB_2 barrier does not require annealing process after cold treatment. Additionally, ex situ MgB_2 barrier has significantly cheaper components than metal diffusion barriers. All this reasons decrease the final price of MgB_2 wires with the ex situ MgB_2 barrier compared to MgB_2 wires with metal diffusion barriers.

The studies conducted so far showed that SiC and C doping of MgB_2 materials lead to the significant increases in B_{irr}, B_{c2}, and J_{c} [12–14]. Furthermore, thermal treatment under high pressure allows the increase of the phase density and homogeneity of the MgB_2 material, promotes the formation of small grains, and increases the number of connections between the grains in MgB_2 wires with Nb diffusion barrier [15].

Our research shows that the synthesis reactions in MgB_2 wires with the ex situ MgB_2 barrier should be carried out at the temperature which Mg is in the solid state or not higher than approx. 25 ℃ above the Mg melting point. This allows the formation of a large amount of superconducting phase in the in situ MgB_2 material and limits the diffusion of the doping from the in situ MgB_2 material to the ex situ MgB_2 barrier. This allows to obtain high critical parameters (T_{c}, B_{irr}, and J_{c}) in MgB_2 wires with ex situ MgB_2 barrier.

2 Materials and Methods

The ex situ MgB_2 material was made with commercially available, high-purity powders from Alfa Aesar. Moreover, the barrier was doped with 8 at% of nano-diamond (nD). In situ MgB_2 material was produced from Mg with 99.8% of purity and amorphous nanoboron precursors powders, as a wire core. Additionally, in situ MgB_2 was doped with 8 at.% nano-SiC (Nanostructured & Amorphous Materials Inc.). Both materials were treated under cold isostatic pressing (CIP) of 0.3 GPa. The total fill factor of superconductors was about 40% (whole MgB_2 material: in situ MgB_2 core and ex situ MgB_2 barrier). The in situ MgB_2 wires with ex situ MgB_2 barrier were made in a GlidCop sheath of 1.2 mm diameter. The thermal treatments were carried out in the isostatic process at a 5 N purity argon atmosphere, with a pressure of 1 GPa, at various temperatures ranging from 700 to 800 ℃ for 15 min of annealing time (Table 1) [16]. The magnetic measurements were performed using vibrating magnetometer (VSM) at a temperature of 4.2 K. These measurements allow us to determine the critical temperature (T_c), irreversible magnetic field (B_{irr}), and the magnetic critical current density (J_{mc}). J_{mc} was calculated using the Bean model ($J_{\mathrm{mc}} = 15\ \pi\ \Delta\mathrm{m}/4\mathrm{r}$, where r, MgB_2 grain radius and Δm, the thickness of the magnetic hysteresis loop) [17]. The structure and composition were examined with a Zeiss Ultra Plus scanning electron microscope and FEI Nova Nano SEM 230 SEM.

The samples for FEI Nova NanoSEM 230 SEM were performed for cut MgB_2 wires. This greatly reduces contamination that is generated during sample preparation by polishing for SEM analysis. On the other hand, the samples for the Zeiss Ultra Plus scanning electron microscope studies were cut with a wire saw. Care was taken to limit the formation of impurities.

3 Results and Discussion

SEM studies in Fig. 1a–c show that the final structure of nano-SiC doping in situ MgB_2 core with ex situ MgB_2 barrier, during the synthesis reaction, does not depend on the Mg state of matter. This means that, based on the results of Fig. 1a–c, we are not able to accurately determine the effect of the Mg state (solid or liquid) on the admixture distribution, grain size, and critical parameters. Moreover, in Fig. 1a–c, the process of Mg penetration from the in situ MgB_2 core to the ex situ MgB_2 barrier is not visible. This significantly influences the critical parameters of MgB_2 wires.

The results in Fig. 1d–f show distribution of Mg in nano-SiC-doped MgB_2 wire with ex situ MgB_2 barrier. Based on these results, we can notice that in samples A and B, the distribution of Mg in the in situ MgB_2 core is slightly different than in the ex situ MgB_2 barrier. A

Table 1 Annealing of the MgB_2 wires with the in situ MgB_2 core, and the ex situ MgB_2 barrier

Ordinal letter	Annealing process parameters Critical parameters		
	P [Pa]	T [℃]	t [min]
A	1 G	700	15
B	1 G	750	15
C	1 G	800	15

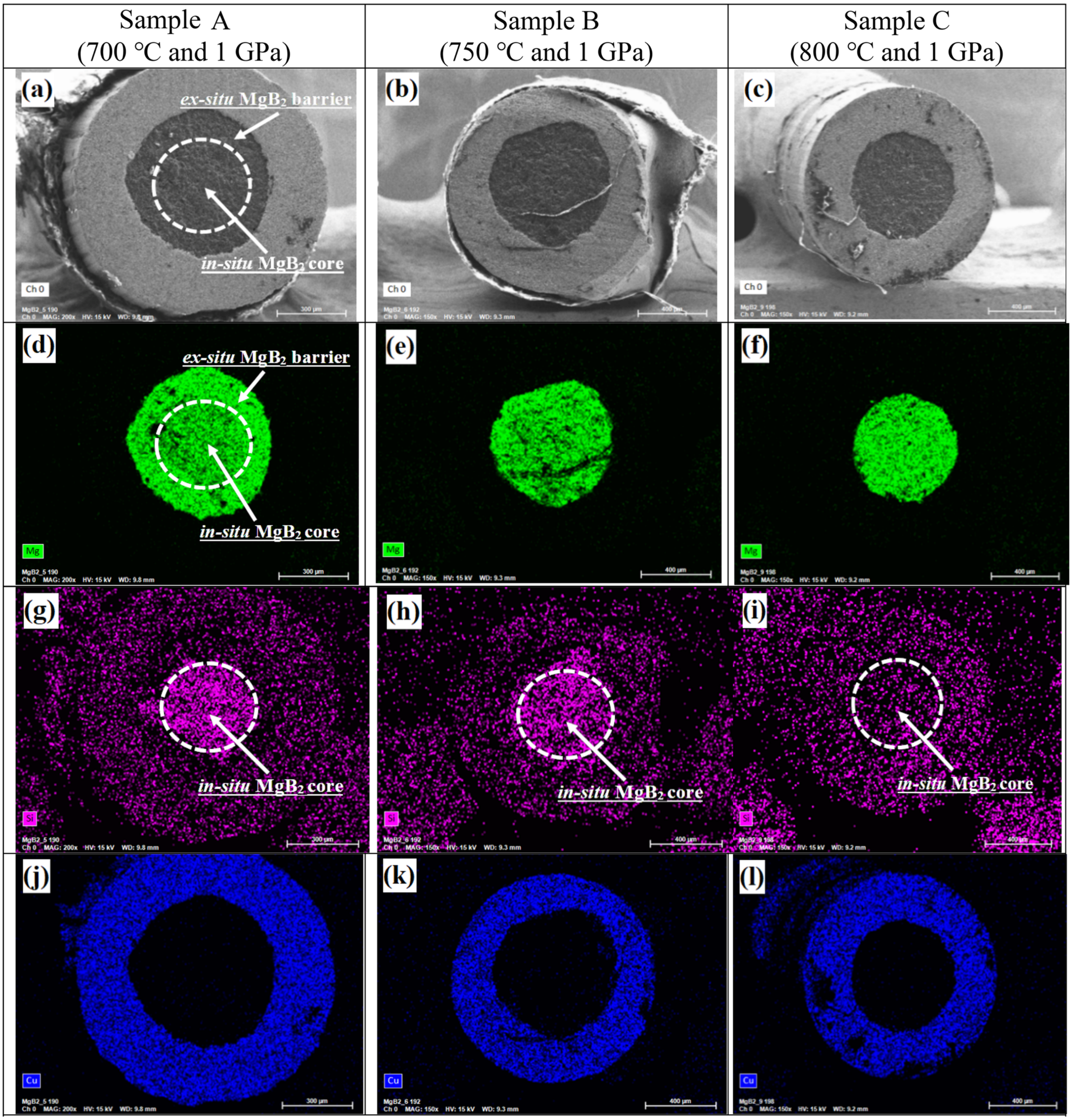


Fig. 1 **a**, **b**, and **c** The low magnification of the cross-section of SiC doping MgB_2 wires with an ex situ MgB_2 barrier; **d**, **e**, and **f** distribution of magnesium (Mg) in the SiC doping MgB_2 wire with the ex situ MgB_2 barrier; **g**, **h**, and **i** distribution of silicon (Si) in the SiC doping MgB_2 wire with the ex situ MgB_2 barrier; and **j**, **k**, and **l** distribution of cooper (Cu) in the SiC doping MgB_2 wire with the ex situ MgB_2 barrier

slightly difference in the distribution of Mg in the structure of MgB_2 wires with the ex situ MgB_2 barrier does not allow to fully confirm the diffusion of Mg from the in situ MgB_2 core to the ex situ MgB_2 barrier during the synthesis reaction in the solid state of Mg, and at the point of the Mg transition from solid to liquid [1, 2]. On the other hand, the distribution of Mg in sample C is very homogeneous both in the ex situ MgB_2 barrier and in the in situ MgB_2 core. This means that liquid Mg [1, 2] completely penetrates the ex situ MgB_2 barrier. The transfer of Mg from ex situ MgB_2 to in situ MgB_2 is imperceptible and negligible due to the high melting point (decomposition temperature above 800 ℃) [18] of the ex situ material and the short heating time (15 min.).

The further results in Fig. 1g–i present the Si distribution in the structure of the MgB_2 wires with the ex situ MgB_2 barrier. These results indicate that the nano-SiC particles remain in the in situ MgB_2 core during the synthesis reaction at 700 °C and 750 °C under the isostatic pressure of 1 GPa. On the other hand, thermal treatment at 800 ℃ and the isostatic pressure of 1 GPa lead to the homogeneous distribution of nano-SiC particles in the entire structure of the MgB_2 wire. We performed additional tests for nano-SiC particles in MgB_2 wire with ex situ MgB_2 barrier (linear analysis of composition and EDS analysis). Figure 2a shows that nano-SiC particles remain in the in situ MgB_2 core after annealing at temperature of 750 ℃ and isostatic pressures of 1 GPa. Similar result was obtained for sample A (700 ℃ and

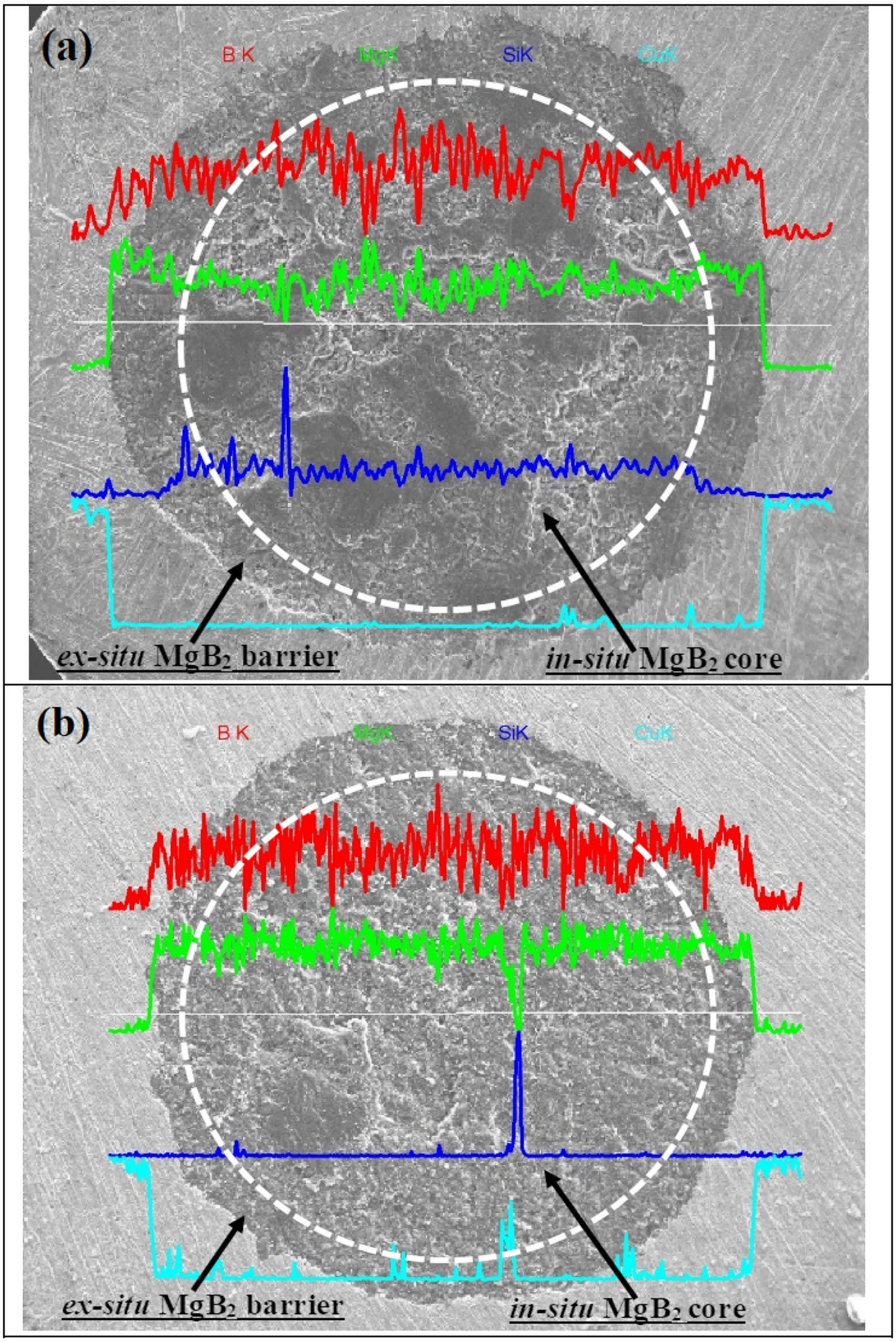
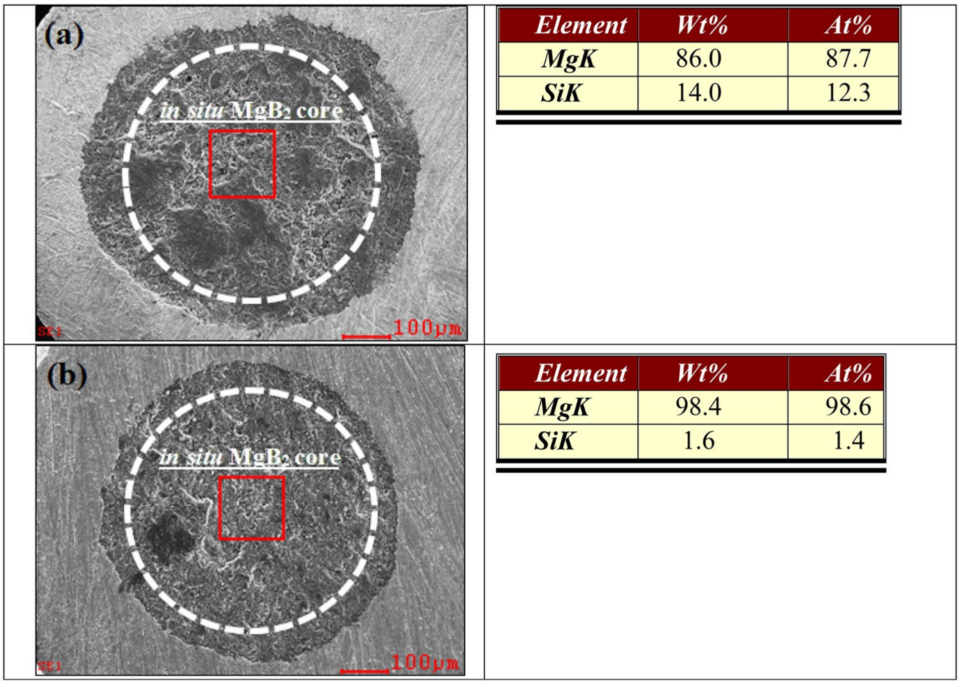


Fig. 2 Linear analysis of sample composition for the cross-section of samples: **a** sample B (750 ℃, 1 GPa, 15 min) and **b** sample C (800 ℃, 1 GPa, 15 min)



Element	Wt%	At%
MgK	86.0	87.7
SiK	14.0	12.3

Element	Wt%	At%
MgK	98.4	98.6
SiK	1.6	1.4

Fig. 3 The EDS analysis of samples cross-section for **a** sample B (750 ℃, 1 GPa, 15 min) and **b** sample C (800 ℃, 1 GPa, 15 min)

1 GPa). Figure 2b shows that annealing at the temperature of 800 ℃ and the isostatic pressure of 1 GPa leads to amount reduction of nano-SiC particles in the in situ MgB_2 core and allows to obtain the homogeneous nano-SiC particle distribution throughout the MgB_2 wire with the ex situ MgB_2 barrier. Energy dispersion X-ray spectroscopy (EDS) analysis for samples A and B (Fig. 3a) showed that the nano-SiC particles remain in the in situ MgB_2 core during the synthesis reaction at temperatures of 700 ℃ and 750 ℃ under conditions of 1 GPa isostatic pressure. The situation was different for the temperature of 800 ℃, when a significant reduction of these particles in the core took place. We know that silicon carbide (SiC) has high melting point of about 2730 ℃. Hence, the SiC nanoparticles cannot penetrate to the ex situ MgB_2 barrier from the in situ MgB_2 core, and that in turn means that only liquid Mg from the in situ MgB_2 core can transfer the SiC nanoparticles to the ex situ MgB_2 barrier. On the basis of Figs. 1, 2, 3, it is seen that the SiC nanoparticles from the in situ MgB_2 core do not diffuse into the ex situ MgB_2 barrier during the synthesis reaction in Mg solid state and at temperature which the Mg transition point from the solid to the liquid state. On the other hand, the results in Figs. 1–3 show that the thermal treatment in the liquid state of Mg leads to penetration of ex situ MgB_2 barrier by the SiC nanoparticles.

The results in Fig. 4 show that the solid-state reaction of Mg and the Mg transition point from solid to liquid allow to obtain small in situ MgB2 core grain size, while heat treatment in the liquid state of Mg leads to large MgB_2 grains.

Shi et al. [19] point out that magnetic critical current density (J_{cm}) is dependent on superconducting current paths form different kinds of loops, such as large loops over the whole sample, medium loops among neighboring grains, or small loops within grains. This indicates that J_{cm} is limited by both transverse and longitudinal connectivity [19]. Moreover, it is known that J_{cm} is dependent on grain size, voids, impurities, admixtures, micro-cracks, amount of superconducting phase, and pinning centers [20–23]. The results in Fig. 5 show that the thermal treatment under an isostatic pressure of 1 GPa at the Mg melting point allows to significantly increase the magnetic critical current density (J_{cm}) than solid state annealing of Mg at the

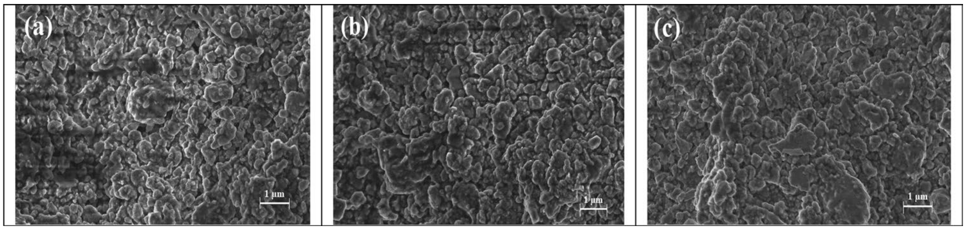


Fig. 4 The SEM images—cross-section of MgB_2 **a** sample A (700 ℃ and 1 GPa); **b** sample B (750 ℃ and 1 GPa); and **c** sample C (800 ℃ and 1 GPa)

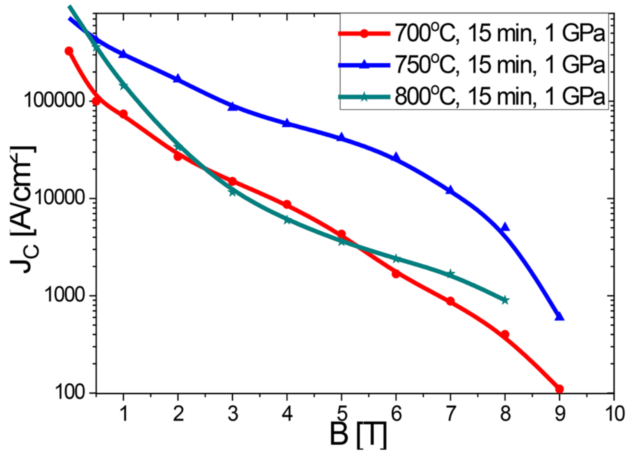


Fig. 5 Magnetic field (**B**) dependence of the critical current density (J_{mc}) at 4.2 K

isostatic pressure of 1 GPa. Such a large increase in J_{cm} in sample B may be the result of several factors e.g. improving and increasing the number of transverse and longitudinal connections between the grains, small grain size, and voids, more superconducting phase in the in situ MgB_2 core, increasing the density of pinning centers. Moreover, the thermal treatment in the liquid state of Mg under isostatic pressure of 1 GPa leads to a significant reduction of J_{cm} in low and medium magnetic fields compared to J_{cm} of sample B (Mg transition from solid to liquid state). This reduction in J_{cm} may be due to the increase in grain size in the in situ MgB_2 core in sample C (Fig. 4c). Larger grain sizes lead to a reduction in the number of inter-grain connections. Another factor which caused the J_{cm} reduction in sample C was the migration of Mg and nano-SiC form the in situ MgB_2 core to the ex situ MgB_2 barrier. This also causes a reduction in the amount of interconnections between the grains in the ex situ MgB_2 barrier, because at the grain boundaries might appear nano-SiC particles, Mg_2Si material and C. Additionally, migration of Mg and nano-SiC into the ex situ MgB_2 barrier reduces the amount of the superconducting phase in the in situ MgB_2 core, which in turn reduces the J_{cm}. Research presented by Wang et al. and Ghorbani et al. also showed that Si cannot be incorporated into the crystal lattice [24, 25]. This indicates that Si is at the grain boundaries and can form low and middle field pinning centers [23]. Li et al. [26] showed that Si can generate thermal stress, which in turn can create high-field pinning centers [21]. This indicates that migration of nano-SiC particle into the ex situ MgB_2 barrier leads to the reduction of the pinning centers density in the in situ MgB_2 core. It also leads to the reduction of J_{cm} in MgB_2 wires with ex situ MgB_2 barrier.

4 Conclusions

Our results show that annealing in the solid state of Mg and at the Mg melting point under the isostatic pressure of 1 GPa significantly reduces SiC diffusion from the in situ MgB_2 core to the ex situ MgB_2 barrier. Furthermore, thermal treatment at the Mg transition point from solid to liquid under isostatic pressure of 1 GPa allows to obtain small grains (in situ MgB_2 core), improves and increases the number of connections between the grains, and also increases the pinning center density and J_{cm}. This is in contrast to the heat treatment of Mg in the liquid state under the pressure of 1 GPa, where the diffusion of SiC from in situ MgB_2 core to the ex situ MgB_2 barrier creates larger grain sizes (in situ MgB_2 core), decreases the number of connections between the grains, and also reduces the pinning center density and J_{cm}.

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