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Superconducting and Microstructural Properties of (Mg+2B)+MgB_2/Cu Wires Obtained by High Gas Pressure Technology

A. Kario[a,b,*], A. Morawski[a], B.A. Głowacki[c], T. Łada[a], M. Smaga[a,d], R. Diduszko[e], D. Kolesnikov[a], A.J. Zaleski[f], A. Kondrat[f] and D. Gajda[g]

[a]Institute of High Pressure Physics, Polish Academy of Sciences
Sokołowska 29/37, 01-142 Warszawa, Poland
[b]Faculty of Physics, Warsaw University of Technology, Warszawa, Poland
[c]Department of Materials Science and Metallurgy, University of Cambridge
Pembroke Street, Cambridge CB2 3QZ, England
[d]Faculty of Mechatronics, Military University of Technology, Warszawa, Poland
[e]Industrial Institute of Electronics (PIE), Warszawa, Poland
[f]Institute of Low Temperature and Structure Research, PAS, Wrocław, Poland
[g]Int. Lab. of High Magnetic Fields and Low Temperatures, Wrocław, Poland

In order to improve the overall critical current characteristics of Cu sheathed *in situ* MgB_2 wires a special architecture of the wire, and processing parameters were used. The study presents the influence of the *ex situ* MgB_2 chemical barrier between *ex situ* core and Cu, suppressing the reaction of Cu with Mg. Wires, doped with 10 at.% SiC of 18 nm average grain size, were fabricated from MgH_2 and B or from Mg and B powders, using the powder-in-tube method. The methods of rotary swaging or drawing were used as the alternating wire-forming processes. The samples were annealed under high Ar gas pressure (hot isostatic pressing) at 750°C and 1.0 GPa for 15 and 30 min. A significant difference in Cu distribution across the wires for a long and short time of sintering was observed. The formation of microstructure in the powder-in-tube process and the relationship between the microstructure and critical current density J_c values, are discussed in this paper.

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*corresponding author; e-mail: kario@unipress.waw.pl

1. Introduction

Superconductivity in MgB_2, T_c = 39.5 K, was discovered in 2001 [1] and the first Cu/MgB_2 wires were reported only a few months later [2]. Manufacture of MgB_2 wires seems to be very promising for application at liquid hydrogen temperature of about 20 K [3]. As it was shown in Table, the critical current densities for MgB_2 are similar to NbTi and Nb_3Sn at 4.2 K, but its T_c is much higher. The production cost of MgB_2 already is much lower than the other superconducting materials, therefore this material may be very competitive to NbTi and Nb_3Sn wires, in such applications as high field magnets, magnetic resonance imaging (MRI), fusion reactors, and current leads [4].

TABLE

Properties of the practical superconductors compared with MgB_2, data taken from [5].

Material	T_c [K]	Critical current density at 4.2 K [A/cm^2]	H_{C2} at 4.2 K [T]
NbTi	9	$\approx 10^6$	11–12
Nb_3Sn	18	$\approx 10^6$	25–29
MgB_2	**39**	**$\approx 10^6$**	**15–20**

Cu was used as the sheath material, because of its high thermal and electrical conductivity, high ductility, diamagnetic nature, and low cost [6]. In MgB_2 wires the Cu sheath and Mg components react and form a lot of undesired Cu–Mg and Cu–Mg–O compounds, for example Mg_2Cu, $MgCu_2$, Cu_4MgO_5 which results with a significant overall J_c reduction.

In order to reduce unfavorable reaction of Mg and Cu, the *ex situ* MgB_2 coating of the central *in situ* MgB_2 core was applied. Magnesium diboride reacts with Cu in temperatures higher than 750°C, and likely decomposes to Mg–Cu compounds and higher borides [7].

Doping with 10 at.% of nanometer-size SiC helps to improve the flux pinning and J_c in high magnetic field of the MgB_2 samples, as reported by Dou et al. [8]. We have used the Mg+2B with 10 at.% SiC for *in situ* central core and concentric *ex situ* tube outside acting as a diffusion barrier.

As it is well known, the large pores reduce overall transport current significantly [9]. To overcome the problem of pores existence with pure grains and agglomerates connectivity, and low density of the samples, which causes low I_c, we decided to use several high pressure methods — cold isostatic pressing (CIP), hot isostatic pressing (HIP), and hydro extrusion (HE). This results in higher densification, porosity reduction, and increases in the critical current density J_c of the wires.

2. Preparation of the powder precursor and wires

The commercial powders of Mg (99.8% purity) and MgB_2 from Alfa Aesar, MgH_2 from ABCR GmbH Karlsruhe and SiC from Nanostructured & Amorphous Materials Inc. were used. The amorphous boron powder was provided by the University of Geneva. The crystal structure and phase purity of Mg, MgH_2 and B powders used in MgB_2 wires preparation have been examined by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The results are presented in figures below. The SEM microstructure of magnesium strips is about a few hundreds micrometers wide and several hundreds micrometers long (Fig. 1).

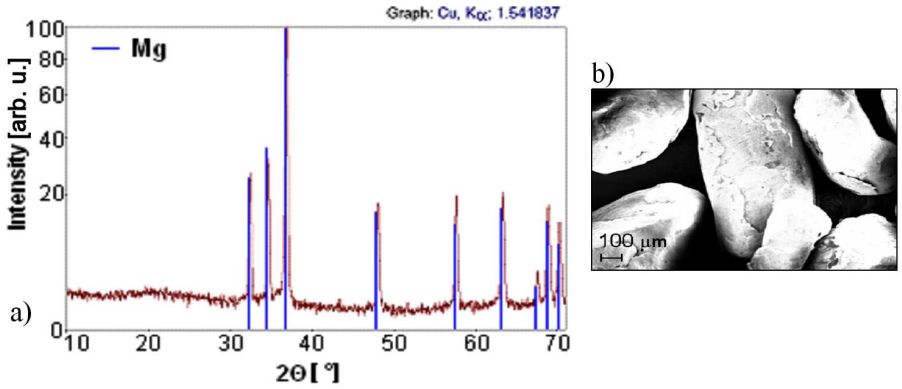

Fig. 1. Magnesium powder: (a) XRD, (b) SEM.

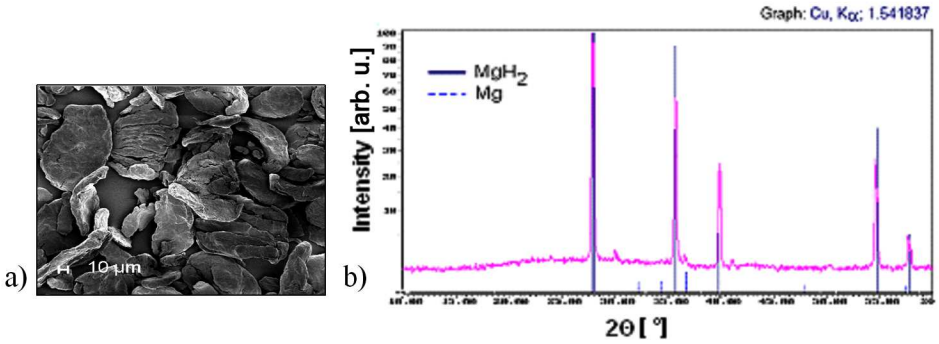

Fig. 2. MgH_2 powder: (a) SEM, (b) XRD.

The 98% pure crystalline MgH_2 powder, consisting of 60 μm size agglomerates with an average round shaped grains of 270 nm has been used, Fig. 2.

The average grain size of boron amorphous powder was about 100 nm, and material has a negligible amount of crystalline B_2O_3 and $B(OH)_3$, as is shown in

the XRD in Fig. 3a. Both crystalline compounds decompose during low temperature annealing below 200°C.

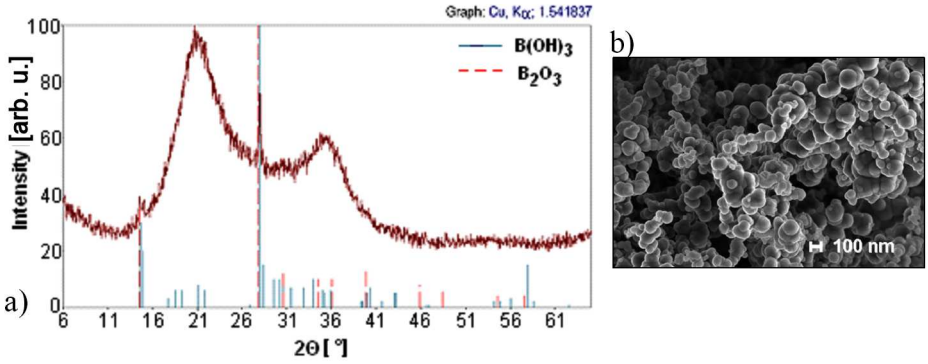

Fig. 3. Boron powder: (a) XRD, (b) SEM.

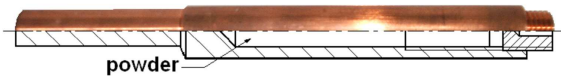

Fig. 4. Cu billet.

Fig. 5. HIP experiments set.

To obtain MgB_2 wires in copper we use the powder-in-tube (PIT) method, which was applied for many other superconductors [5]. Starting powders were mixed in a nominal composition ratio (Mg:B = 1:2) and densificated in sequence by CIP at pressure 0.3 GPa. This process assures a better density of the samples after sintering and enables us to design a suitable architecture of the core of the wire.

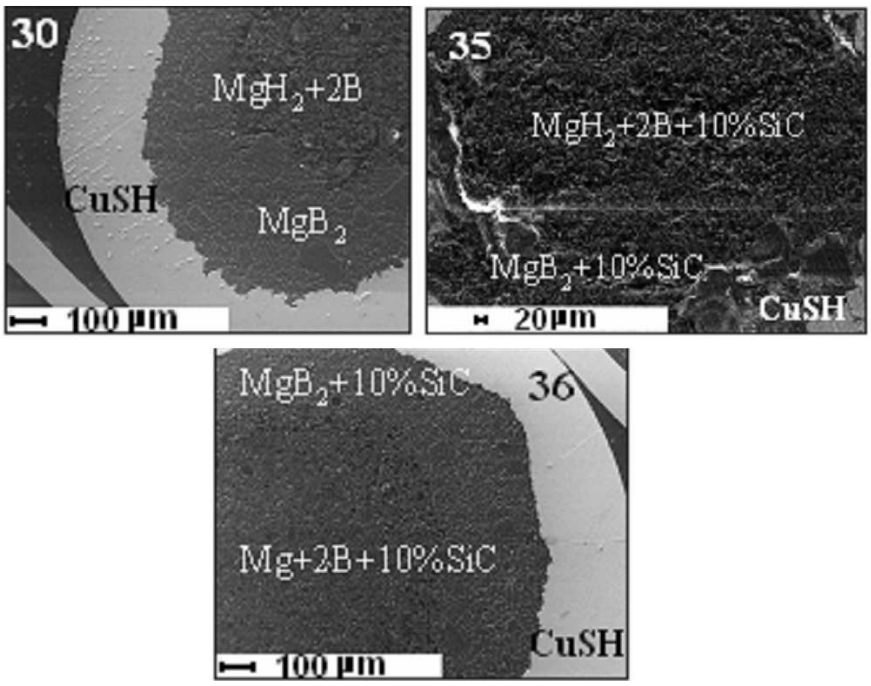

Fig. 6. SEM pictures of wires cross-sections; the two cores system in Cu.

After CIP, dense samples were inserted into 15 cm long Cu tubes with 13.8 mm outside diameter (Fig. 4). All assembling process was done in Ar atmosphere, because of the high reactivity of Mg with O_2. Closed Cu tubes were drawn and swaged to a wire of 1.4 mm in diameter. Some of them have been hydrostatically extruded to the wire of the diameter of 1.1 mm. After drawing and HE, the wires were cut into short pieces (9 cm) and then annealed in the high pressure chamber (Fig. 5), under high Ar gas pressure of 1.0 GPa, at a temperature of 750°C, for three different times: 10, 15, and 30 min. Some of the samples were also sintered in the vacuum at 700°C for 1 h.

Three samples with different architecture, and special barrier across CIP *in situ* unreacted core and Cu sheath have been prepared. The sample no. 30 has MgH_2 and B in the central core without doping. The sample no. 35 also was obtained from MgH_2 and B but doped with 10 at.% SiC in the central core and in the *ex situ* outside barrier. The central core of the sample no. 36 was made from Mg and B and doped with nano-SiC for both parts of this sample (Fig. 6).

3. Results and discussion

The surface morphologies and microstructure of the samples were characterized by LEO 1520 SEM with a Gemini column equipped with a Link energy dispersive X-ray (EDX) detector, model ISIS, with a Si–Li window.

Figures 7 to 9 show the EDX mapping of secondary electrons (SE), B, Mg, Ar, Si, C, Cu, and oxygen elements of transverse cross-sections of the wire samples sintered for different times and the same pressure–temperature conditions. Comparison between EDX Cu mapping of these samples showed that Cu sheath does not react with *ex situ* MgB_2 diffusion barrier for short sintering times at high argon pressure, as is clearly seen in the Cu map in Fig. 7 and Fig. 8. Chen et al. reported that Cu can react with *in situ* MgB_2 already at temperature of 600°C, creating several Mg phases. The *ex situ* MgB_2 reacts with Cu typically from a temperature of 800°C [7]. In our experiments the $MgCu_2$ or Mg_2Cu phases have been observed only after at least 1 hour of sintering in vacuum (Fig. 9). It was noticed that some Mg from the central core diffused to the *ex situ* MgB_2 outside layer, because of its low melting point (650°C). For HIP-treated samples no trace of Mg–Cu phases were found. We note that the high pressure lowers the Mg diffusion. This geometry enabled us to separate the Cu and Mg elements and resulted in high J_c in Cu sheathed wires.

Phases formed in the cores of the wires were identified using an X-ray Siemens D5000 diffractometer with Cu K_α radiation at 40 kV and 25 mA.

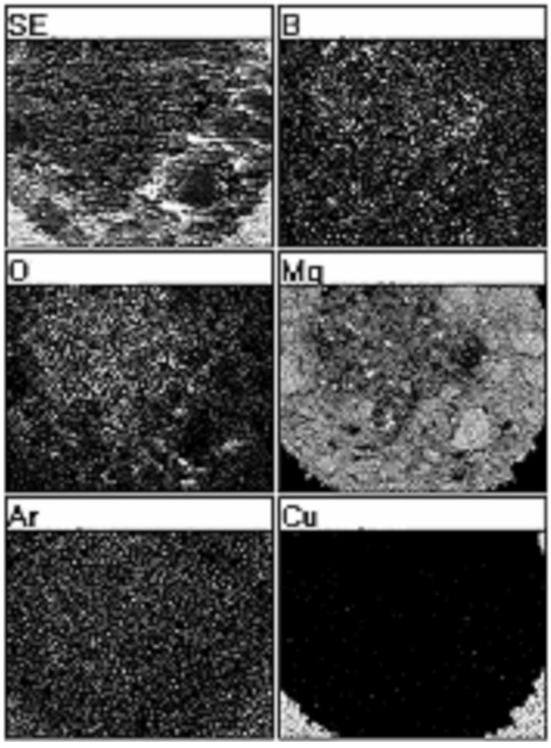

Fig. 7. EDX of the sample no. 35 after HE and HIP at 1.0 GPa, 750°C for 15 min.

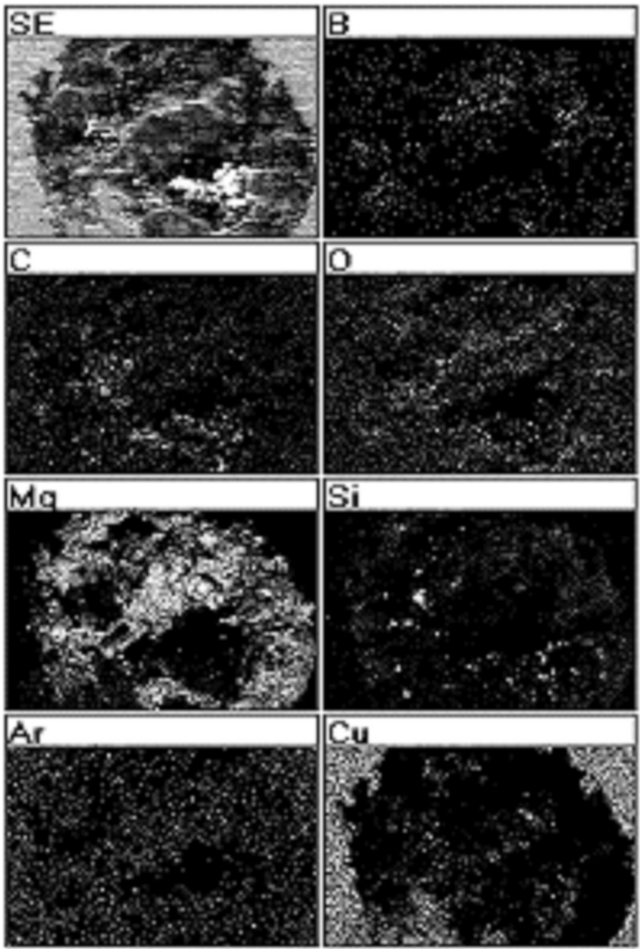

Fig. 8. EDX of the sample no. 30 HIP-ed at 1.0 GPa, 750°C for 30 min.

The XRD patterns presented in Fig. 10 of the specimen no. 30 after HIP obtained after various times (10 to 30 min) prove MgB_2 as the main phase. Very fine grains with the negligible content of MgO phase were found.

The Cu_4MgO_5 phase was hardly detected, it seems that this phase is the low conducting one. Perhaps the compound Cu_4MgO_5 has been grown on the Cu–Mg contact surface of *ex situ* MgB_2 outside core, as an effect of negligible MgB_2 surface decomposition with Cu contact, in the presence of OH anions. These both phases have been found as impurity phases only.

The Cu diffraction peaks presented in Fig. 11 are due to the admixing of the Cu sheath material to the investigated samples during extracting it from the Cu sheath for characterization. An identical problem was observed for the samples no. 35 and no. 36.

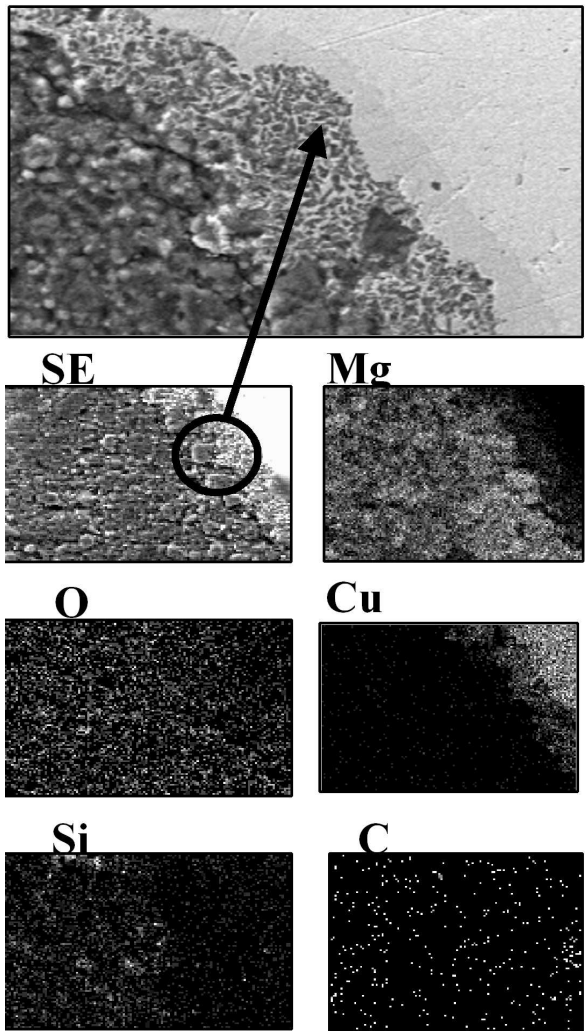

Fig. 9. EDX of the sample no. 36 after sintering in vacuum at 750°C for 1 h.

The magnetization measurements have been performed at 2, 10, 20, and 30 K using a DC Quantum Design MPMS-5 SQUID magnetometer. The critical current density J_c was derived from the width of the magnetization loop M basing on the extended Bean model [10].

The results of magnetic measurements strongly support our microstructural observations. Figures 12 and 13 show the critical current density J_c dependence vs. the magnetic field for mentioned samples at 20 K. We have chosen this temperature for comparison of the J_c because the most promising application of MgB_2 family wires seems to be at liquid H_2 or cryo-cooler refrigeration temperatures about 20 K (one stage refrigeration).

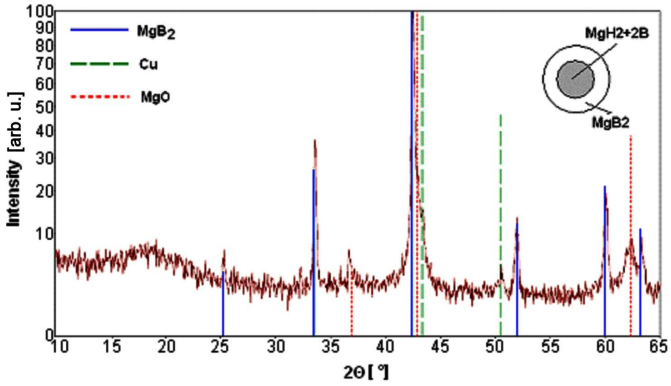

Fig. 10. XRD pattern of wire no. 30 after HIP at 1.0 GPa, 750°C for 10 min.

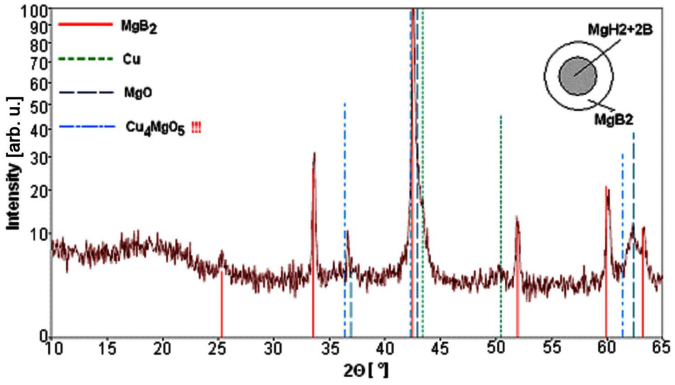

Fig. 11. XRD pattern of wire no. 30 after HIP at 1.0 GPa, 750°C for 30 min.

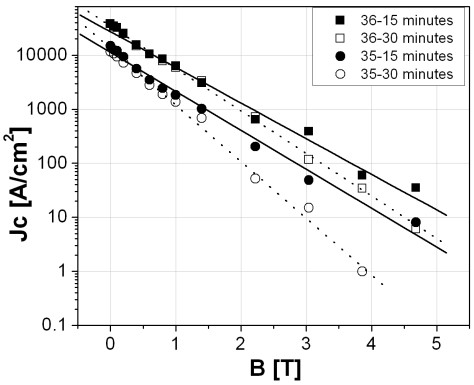

Fig. 12. J_c vs. magnetic field measured at 20 K for wires no. 35 and no. 36 HIP-ed in argon pressure 1.0 GPa, at 750°C for 15 and 30 min.

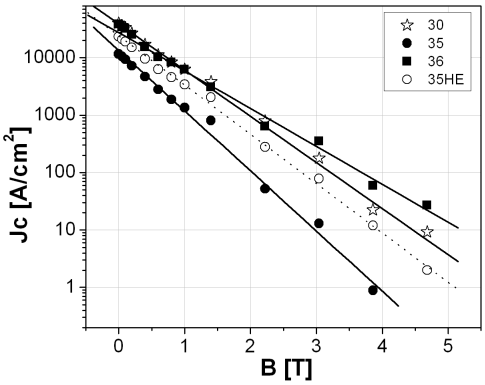

Fig. 13. J_c vs. magnetic field at 20 K for wires no. 30, no. 35 and no. 36 HIP-ed in argon pressure 1.0 GPa, at 750°C for 15 min. 35HE represents conductor no. 36 after HE process.

As it was shown in Fig. 12, the samples HIP-treated for shorter annealing times — i.e. 15 min have a higher J_c than those sintered for a longer time — for example 30 min, especially at higher magnetic fields. It is apparent that the high degradation of J_c is correlated with the existence of the non-superconducting phases for a longer sintering time. The samples no. 36 and no. 30 have a comparable J_c at lower fields, but sample no. 36 has a much higher critical current at higher fields, which is the result of a higher pinning force for samples with SiC nano inclusions.

After HE the wires have a higher J_c especially at higher magnetic fields than the same one after drawing only, see Fig. 13. This is the typical behavior for all measured samples, as for the one chosen for this research, no. 35.

4. Conclusions

The proposed architecture of *in situ/ex situ*/Cu layers of superconductor prevents the formation of Mg–Cu phase at the contact with Cu. This stabilizes the pure MgB_2 phase formation in the inner core of the superconducting wire. Therefore both layers are superconducting and usually admixed with the nano-SiC additives which gives the highest current density calculated to the whole cross-section of the wire. The Cu sheath is known as the best one for the superconducting wires. Our method enabled us to suppress the interaction of Mg in the *in situ* core with the Cu sheath. This is achieved by the use of the MgB_2 *ex situ* layer in between Cu and *in situ* core. The high pressure, temperature reaction, even for the short time treatment, enables one to obtain high densification of the inner core therefore reducing significantly the porosity of the both superconducting layers. Such method enables one to obtain Cu matrix MgB_2 wires characterized by a high overall current density in the single-step procedure. Cu sheath is necessary for thermal stabilization of the high J_c superconducting MgB_2 based wire in practice.

1. The highest current densities of Cu sheathed wires at magnetic fields (here up to 5 T) were obtained for the sample no. 36 made with 18 nm average grains size SiC admixed to both *ex situ* and *in situ* layers. This wire was obtained by HIP process at 1.0 GPa argon pressure at 750°C and with the short time of annealing, i.e. less than 15 min.
2. Considerably lower J_c has been observed for only pure MgB_2 (*ex-in*) wire, obtained at the same technological conditions: pressure, temperature, and time.
3. The critical current density J_c, for the wire sample no. 35 after additional hydro-extrusion process before the last HIP annealing was higher than for the drawn one only, this is due to the higher final density of both superconducting layers.
4. The hot isostatic pressing and multilayer *ex situ/in situ* superconducting composite in Cu sheathed wires with pre-extrusion process are the best, to our knowledge, solution for high J_c MgB_2 based wire and tapes manufacturing.

Acknowledgments

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