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Effect of C and SiC additions into *in situ* or mechanically alloyed MgB_2 deformed in Ti sheath

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ABSTRACT

Effect of 3.4 wt.% C and 5 wt.% SiC doping into the standard *in situ* (***IN***) process and mechanically alloyed (***MA***) MgB_2 was studied. Powders of ***IN*** and ***MA*** process were carried out in air and in argon filled glove box, respectively. Wire samples were prepared by two-axial rolling deformation of ***IN*** and ***MA*** powders inside the Ti tube. Titanium as sheath material allows to use higher sintering temperatures, we used 700 °C and 800 °C for 30 min in Argon. Critical current densities (J_c) were measured at variable temperatures 4.2 K, 10 K, 15 K and 20 K in the external magnetic fields ranging to 15 T. Critical temperatures, upper critical fields and irreversibility fields of ***IN*** and ***MA*** with SiC and C additions are compared and discussed. The highest transport properties were observed for wires with ***MA*** SiC doped MgB_2 in the whole scale of temperatures 4.2–20 K. Upper critical field was rapidly enhanced in the case of carbon doped ***MA*** samples at 4.2 K. ***MA*** samples have shown decreased J_c values for higher temperatures (15 K, 20 K), in some case even worse than for the not doped reference ***IN*** sample. Carbon substitution and grain connectivity of analyzed samples are compared and discussed. Presented results show that for 20 K applications some new ways (additions) have to be found for increasing the J_c substantially.

1. Introduction

Discovery of superconductor MgB_2 in 2001 with critical temperature 39 K [1] has brought a new hope for substitution of convectional superconductors like Nb_3Sn or NbTi and for future applications without expensive liquid helium cooling. Despite of all promises of this new material, relatively low H_{c2} and soft $J_c(B)$ characteristics of MgB_2 has forced to find the way for increasing of these parameters. The idea to add a small size normal particles to the MgB_2 phase, which would acts as pinning centers (normal zones where the magnetic flux lines can be fixed) has been followed with the aim of increased $J_c(B)$ and H_{c2} [2]. Addition of nano-sized SiC particles has been realized firstly by Dou et al. [3]. Many research teams have used the same addition material and attributing it the effect of improved pinning [4,5]. Later on, it was found that SiC is decomposed during the sintering treatment and carbon atoms are partially substituting boron in the MgB_2 cell, which results in slightly lowered critical temperature, but also to considerably increase upper critical field. Consequently, also $J_c(B)$ dependences of SiC doped samples especially at 4.2 K are improved [6–8]. Up to now, large number of different carbon containing particles have been used for $J_c(\mu_0 H)$ dependences [9–18]. The highest J_c level 10^4 A/cm^2 at 16.4 T and 4.2 K was reported by Häßler et al. recently for nano-carbon doped MgB_2 prepared by mechanical alloying [19]. The aim of this work is to investigate the effect of SiC and C additions into two differently prepared MgB_2 powders on the resulting superconducting characteristics. Carbon substitution and grain connectivity of analyzed samples are compared and discussed.

2. Experimental

2.1. Samples preparation

Standard *in situ* (***IN***) and mechanical alloying (***MA***) routs of initial powder mixtures preparation have been used. Commercial

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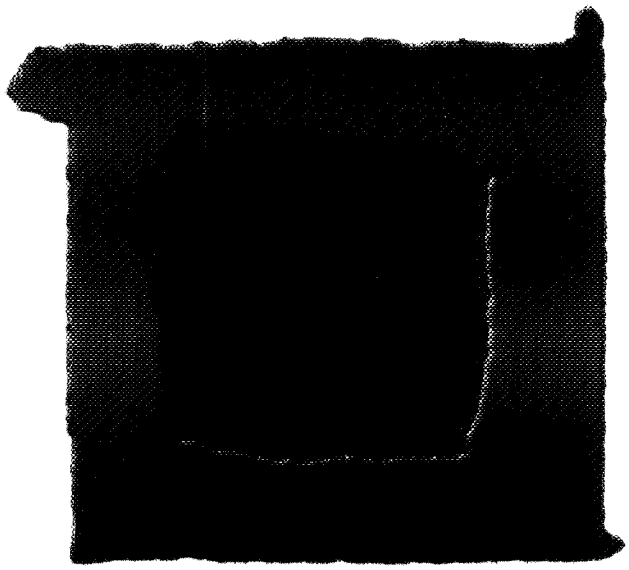

Fig. 1. Cross-section of MgB2/Ti wire deformed by TAR and annealed at 800 °C. Outer dimensions are 1 × 1 mm.

precursor powders Mg (99% purity, ~20 μm particle size) and amorphous B (99%, ~1 μm) powders without addition (***IN0***), mixed with 5 wt.% of SiC (***IN5SiC***) nano-particles (20 nm) and with 3.4 wt.% of spectral carbon C (***IN3C***) were homogenized by ball milling for 40 min, which are named ***IN*** mixture. The handling of starting ***IN*** materials was carried out in air. ***MA*** powder mixture was prepared from Mg and B (in the of 1:2) milled together with 5 wt.% of SiC (***MA5SiC***) and 3.4 wt.% of C (***MA3C***) for 50 h in a planetary ball mill at protecting Ar atmosphere [20]. Due to very small size particles and the large corresponding surface area, the handling of ***MA*** materials as the storing of the milled powders was carried out in argon filled glove boxes. Described above powder mixtures were used for a single-core Ti sheathed wires made by powder-in-tube (PIT) process and named as: ***IN0*** – reference sample, ***IN3C***, ***IN5SiC***, ***MA3C*** and ***MA5SiC***. Ti sheath was used because of its inert behavior and not observed chemical reaction with boron and magnesium temperature [21,22], for used sintering conditions. Heat treatment conditions (800 °C and 700 °C) were chosen due to the highest J_c for SiC doped and not doped samples [23]. Wires having the starting fill factor of 45% were deformed initially by rotary swaging (from 6 to 10 mm diameter) by 50% of area reduction and than by groove and two-axial rolling (TAR) combination into the square wire of 1 × 1 mm^2 size (see Fig. 1).

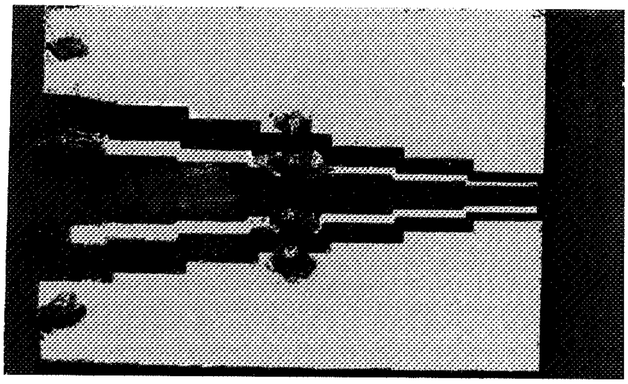

Fig. 2. The sample holder for four probe measurement of MgB2 cores. MgB2 core (in the middle) reached length 3–6 mm.

All as deformed samples were finally subjected to sintering treatments at two different temperatures 700 °C and 800 °C in the high purity argon atmosphere for 30 min.

2.2. Samples characterization

Critical currents of wires were measured by a standard four probe method at 4.2 K, 10 K, 15 K and 20 K in the external fields up to 15 T, using the criterion 1 μV/cm.

Samples for resistive measurements of MgB_2 cores were prepared by careful mechanical ridding of Ti sheath. Approximately 3–6 mm longer MgB_2 core pieces connected to the current and potential contacts by colloid silver see Fig. 2. Resistances of extracted cores were then measured in He vapors at variable temperatures and magnetic fields by four probe method using DC current of 1 mA. Upper critical fields and irreversibility fields were determined as the fields, where temperature-dependent resistance at constant magnetic field $R(H_{c2}, T)$ were 90% and 10%, respectively of normal state resistance at 39 K.

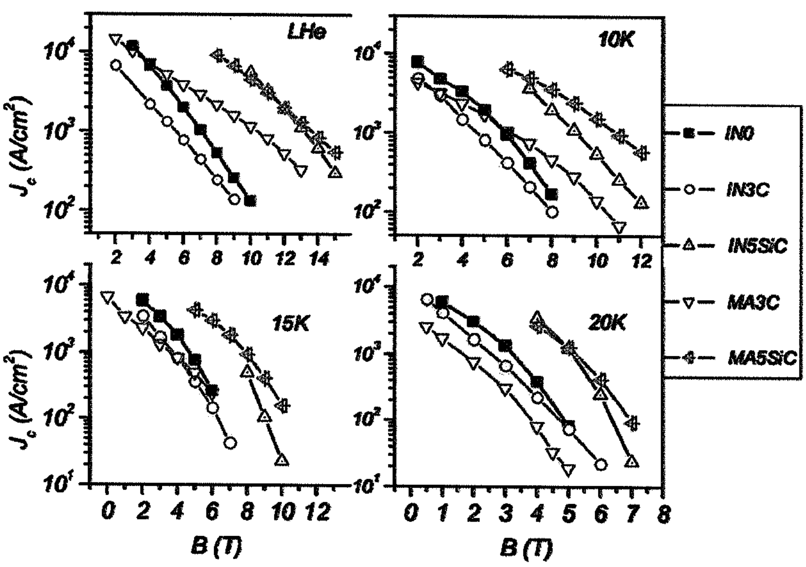

Fig. 3. Critical current densities measured at different temperatures: 4.2 K, 10 K, 15 K and 20 K.

Extracted cores were characterized also by magnetic measurements using MPMS measuring system.

Critical temperatures were for both resistive and magnetic measurements determined at temperature matching half of the corresponding superconducting phase transition.

3. Results and discussion

3.1. Transport current characteristics

The transport current characteristics of wires ***IN0–MA3C*** annealed at 800 °C/30 min measured at 4.2 K, 10 K, 15 K and 20 K are shown by Fig. 3a–d. The lowest current density at 4.2 K was obtained for ***IN3C*** wire and the highest ones for SiC doped ***IN5SiC*** and ***MA5SiC*** samples, Fig. 3a. The increase of temperature to 10 K moved together the characteristics of ***IN0, IN3C, MA3C*** and decreased J_cs of ***IN5SiC*** in comparison to the best wire ***MA5SiC***. Not doped ***IN0*** wire has higher J_cs than carbon doped samples ***IN3C*** and ***MA3C*** at 15 K (see Fig. 3c) and the difference is increased at 20 K, Fig 3d. The highest current densities are measured for SiC doped samples ***IN5SiC*** and ***MA5SiC*** at 20 K as well as 4.2 K. Decrease of critical current densities with temperature is most remarkable for sample which contained mechanically alloyed carbon doped powder ***MA3C***. Above 15 K the J_cs of carbon doped wires are worse than for the reference sample ***IN0***.

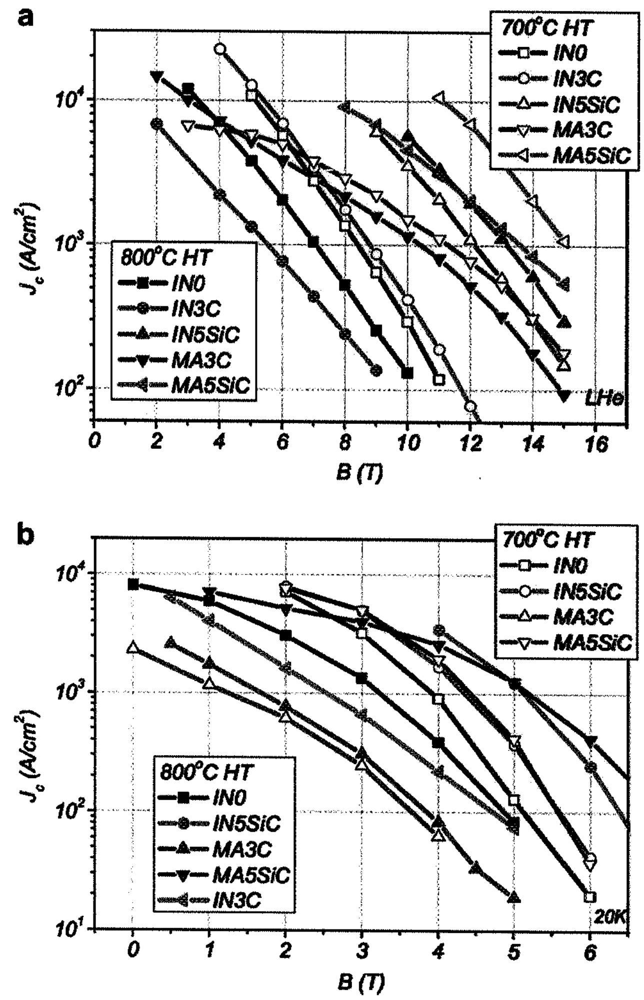

Fig. 4. $J_c(B)$ behavior for samples sintered at 800 °C and 700 °C and measured at *LHe* (a) and 20 K (b).

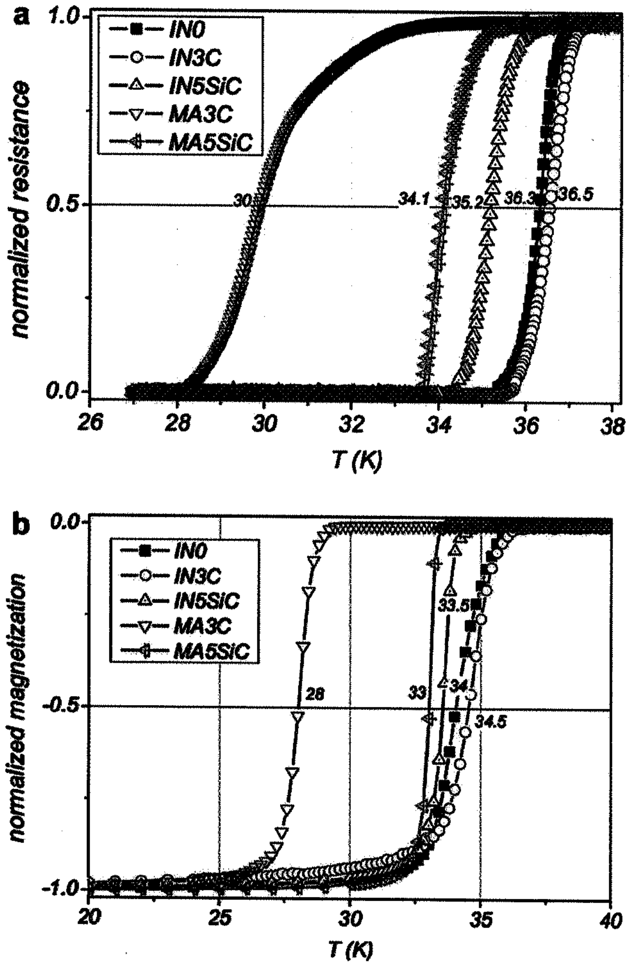

Fig. 5. Normalized transitions measured resistively (a) and magnetically (b).

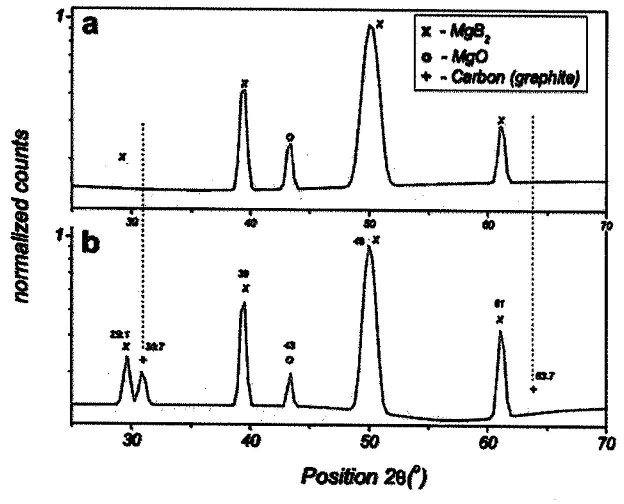

Fig. 6. XRD pattern of ***IN0*** (a) and ***IN3C*** (b). Carbon precipitates for ***IN3C*** sample show not effective substitution of boron by carbon.

Decreased sintering temperature to 700 °C caused significant changes in the transport current properties of compared samples,

Table 1
Critical temperatures and critical magnetic fields.

Sample	Powder	Addition	T_c (resistive) (K)	T_c (magnetic) (K)	$T_c^{res} - T_c^{mag}$ (K)	$\rho^{300} - \rho^{40}$ (μΩ cm)	H_{c2} (20 K) (T)	H_{irr} (20 K) (T)
IN-ref	*in situ*	No	36.3	34	2.3	172.5	9.6	7.1
IN5SiC	*in situ*	5 wt.% SiC	35.2	33.5	1.7	24.4	11.1	8.3
IN3C	*in situ*	3.4 wt.% C	36.5	34.5	2	135	9.5	7.3
MA5SiC	Mech. alloying	5 wt.% SiC	34.1	33	1.1	21	12.3	8.7
MA3C	Mech. alloying	3.4 wt.% C	30	28	2	41.3	10.2	6

see Fig. 4. ***MA5SiC*** wire shows remarkable J_c improvement in liquid He (Fig. 4a) but surprisingly decreased value at 20 K (Fig. 4b). Similar effect can be seen also for ***MA3C***. Standard *in situ* wire ***IN5SiC*** has lower J_c values than ***MA5SiC*** for both temperatures (4.2 and 20 K). ***IN3C*** wire shows slight improvement at 4.2 K and J_cs over the reference sample ***IN0***. This indicates that incorporation of carbon into the lattice is more effective for lower sintering temperature 700 °C than 800 °C, where free carbon is most probably precipitated at grain boundaries (as resistive barrier inside the core) which results in decreased J_c for all working temperatures (see Fig. 3a–d). Carbon incorporated into MgB_2 decreases critical temperature, which influences J_c at 20 K more than at 4.2 K.

3.2. Critical temperatures

Carbon substitution is most effective for MA powder and leads to a new phase composition (e.g. $MgB_{1.87}C_{0.13}$), which is characterized by decreased critical temperature. Normalized transitions measured resistively and magnetically are shown by Fig. 5a and b, respectively. Critical temperatures T_cs were assigned as 50% of corresponding value of normal state at 40 K and are summarized by Table 1.

The middle of the transition below 30 K was measured only for carbon doped ***MA3C*** sample in comparison to $T_c = 34 - 36.3$ K for not doped wire ***IN0***. Wide resistive transition is measured for ***MA3C*** sample, which reflects the highest carbon substitution, lowered phase purity and also weak links between grains can be expected. Sharper transitions are measured for all other samples more differing by critical temperature measured resistively than magnetically. Surprising is the increased critical temperature (by ≈0.3 K) measured for ***IN3C*** sample confirmed by resistive and also by magnetic measurement. This can be partially understood by not effective substitution of carbon into MgB_2 in this wire. The fact of existence free carbon precipitates was confirmed by XRD pattern, where free carbon is well visible at $2\Theta = 30.7°$ as well as 63.7° peak and additional overlaid peaks (Fig. 6).

Difference between T_c values by resistive and magnetic measurements can be explained by the creation of weak links during incorporating of carbon into the MgB_2 lattice. The most remarkable difference was measured for both types of C doped powders.

Generally, the resistive measurements give information for the selected volume of the sample (the best current pass), while the magnetic reflects an averaged volume (whole sample) quality. For sample measured magnetically we obtained lower T_c taken from response of magnetization than $R(T)$ due to different mechanism. In case of magnetization we have measured all superconducting volumes (grains) T_cs. It is remarkable that bad quality parts with low T_c will also affect whole T_c measurement – average T_c through all superconducting volumes. Other mechanism we can find in case of $R(T)$ measurement. We assume selective current paths through sample. Then superconducting current is flowing preferably through the good quality paths – selective T_c of the best superconducting current paths is measured. Note that we use relatively small currents for measurement (1 mA), so penetration to

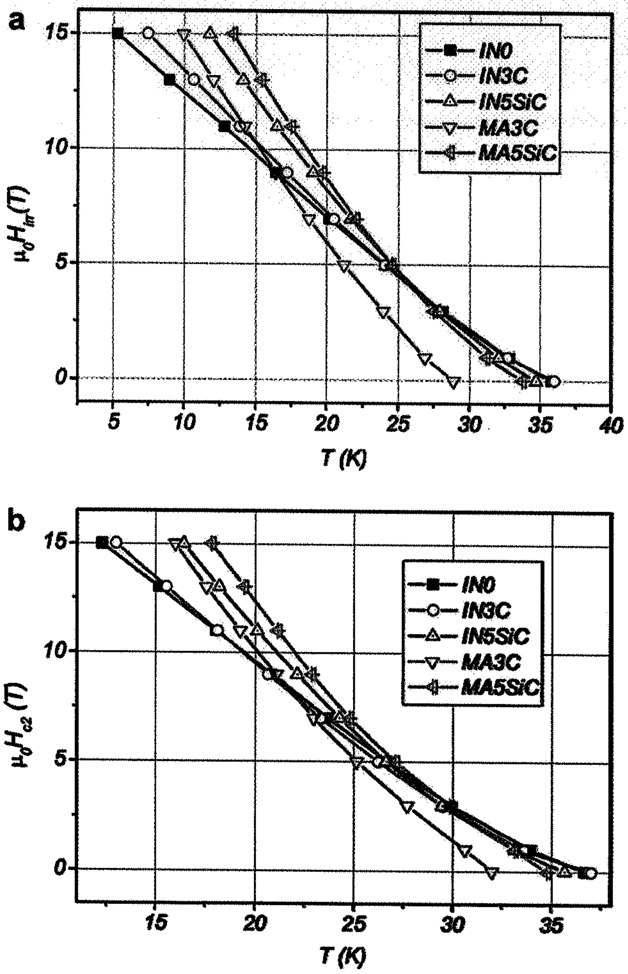

Fig. 7. Irreversibility line (a) and upper critical field (b).

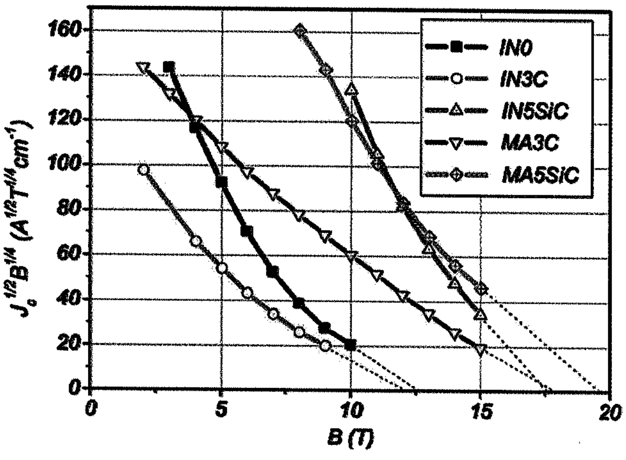

Fig. 8. Kramer plot for MgB_2/Ti wires.

Table 2
Difference of irreversibility fields achieved by several methods: Kramer extrapolation, second order polynomial extrapolation and line extrapolation.

Sample	H_{irr} (polynomial extrapolation) (T)	H_{irr} (line extrapolation) (T)	H_{irr} (Kramer extrapolation) (T)	H_{irr} (H value at 100 A/cm²) (T)
IN0	15.7	15.6	12.6	10.4
IN5SiC	24.2	21.3	17.6	16.6
IN3C	18.3	17.1	12.1	9.5
MA5SiC	26.5	23.8	19.6	18.9
MA3C	21.3	20.4	17.9	15

whole volume can be excluded. As the result we can say that samples with similar T_cs measured magnetically and resistively dispatch good homogeneity of superconducting cores.

3.3. Critical fields

The upper critical fields and irreversibility fields are showed in Fig. 7 were measured by standard $R(T, B)$ method. Measurement was done in 15 T cryostat in flowing He vapor.

The mostly improved dependence of $\mu_0H(T)$ is observed for SiC doped samples both ***MA*** and ***IN***. The values of H_{irr} and H_{c2} for ***MA3C*** sample were the lowest for temperature above 16 K. The slope of irreversibility line for ***IN3C*** sample is only slightly improved, which correlate well with transport measurement, see Fig. 4. The highest H_{c2} values for ***MA5SiC*** can be attributed to a most effective carbon substitution into MgB_2. Moreover, smaller grain size produced by mechanical alloying (intensive milling) can be responsible for improved grain-boundary pinning [13], what is well confirmed by $\Delta\rho$ values [24] (Table 1). Remarkable could be also differences of H_{irr} values at 4.2 K obtained by three types of extrapolation (see Table 2).

One extrapolation refers to commonly used Kramer's plot ($J_c^{1/2}B^{1/4}(B)$, see Fig. 8), two types of extrapolation (line and polynomial of 2nd order) applied for $\mu_0H(T)$ curve (see Fig. 7) and another used was interpolation of H value at 100 A/cm² for $J_c(B)$. One difference is that the Kramer's plot and 100 A/cm² criterion use the data measured for sheathed wires and rest approaches data from naked cores. Lower values of irreversibility field is apparent for those using transport $J_c(B)$ data – Kramer extrapolation and estimation at 100 A/cm². On the other hand, the extrapolations based on the $R(T)$ data show considerably higher (by 5–6 T higher) H_{irr}.

4. Conclusions

Effect of C and SiC particles addition into the MgB_2 superconductor prepared by *in situ* and mechanical alloying technique has been studied.

In both cases critical current densities were enhanced. For low temperatures (below 10 K) higher values of critical current densities and critical fields were obtained by samples prepared by mechanical alloying. On the other hand, standard *in situ* approach balanced critical parameters at higher temperatures (20 K). Main reason is in higher critical temperature of *in situ* approach.

Presented results showed advantages and disadvantages of standard and special approach of preparation techniques of MgB_2/metal wires, compared in one experiment. Mechanical alloying technique need a careful protection of powder against oxidation, while *in situ* process can be done in air conditions, which leads to only slightly lower current densities. Increasing of J_c or H_{c2} leads usually to decrease of T_c. Although complex methods how to increase all important properties is difficult to find, only way how to achieve applicable results is middle course of each.

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