

Microstructure and Transport Properties of Compaction-Modified In Situ Fe/MgB₂ Wires

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Abstract This study has shown the effect of excessive mechanical deformation by pressing and consecutive heat treatment, respectively, on the microstructure and transport properties of mono-core sintered in situ Fe/MgB₂ wires. These wires were pressed into short tapes under 1 GPa uniaxial pressure. Transport properties like critical temperature, transition width and engineering critical current density of the same samples were determined before and after pressing and after annealing. Phase formation and grain size of the samples were studied with XRD. The SEM analysis indicated that the mechanical deformation reduced initial voids to a large extent but caused cracks, increased the number of grain boundaries and introduced weak links. The subsequent heat treatment on the pressed samples improved the microstructure and the grain connectivity. Possibility of a final densification of the reacted in situ wires was discussed in terms of transport properties.

Keywords MgB₂ wire · Amorphous nano boron · Mechanical deformation · Porosity

1 Introduction

The main focus on the superconductor magnesium diboride (MgB₂) is to produce utilizable long-length superconducting wires for large-scale applications. There are several properties making the MgB₂ material so special among other superconducting materials [1]. Its high superconducting critical temperature ($T_c = 40$ K) benefits from recent developments on cryocooling systems instead of liquid helium. MgB₂ is made of widely available cost-effective chemical constituents and forms a unique simple crystal structure with a low anisotropy. The chemical and mechanical compatibility of MgB₂ with various metals and metallic alloys makes the fabrication of MgB₂-based wires, tapes and cables a versatile possibility. The excellent performance of the in situ MgB₂ samples at high magnetic fields can be a big advantage in superconducting magnet applications.

A considerable enhancement in critical current density (J_c), upper critical field (H_{c2}) and irreversibility field (H_{irr}) for the MgB₂ wires was achieved by carbon doping in various forms which serves as active pinning centres [2–8]. On the other hand, avoiding the agglomeration of nano carbon or nano boron is crucial to fabricate homogeneous long-length wires [9, 10]. The MgB₂ wire fabrication by using the powder-in-tube (PIT) method is a straightforward procedure in which the metallic tube is filled with pre-reacted MgB₂, ex situ, or unreacted Mg and B then heat treated, in situ. Recently, MgB₂ wires have been also manufactured with alternative filling techniques [11, 12]. The ex situ-processed MgB₂ wires are generally for low field applications due to the weaker inter-grain connectivity [13]. The in situ wires are more flexible in terms of the incorporation of additives which improve their high field performance. On the other

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hand, the core density of in situ MgB_2 wires after the formation of the superconducting phase is rather low, and its microstructure is extremely porous [14, 15]. Deformation of in situ MgB_2 wires after phase formation is unavoidable due to mass density considerations because densification of the packed MgB_2 powders is incomplete when the wire fabrication process is completed [15, 16]. Even in multifilament wires with smaller filament size, MgB_2 filaments are not fully dense since $\text{Mg} + 2\text{B}$ has a lower theoretical density than MgB_2 . Porosity occurs in the superconducting core after heat treatment; an extra densification is necessary to get rid of this porous structure, and with no doubt, there is a cost in terms of critical current density [16].

The application of various mechanical deformations and subsequent heat treatment is a common approach [15–18], but processing of in situ MgB_2 wires and tapes has not yet been completely resolved [19]. In this study, a series of experiments has been planned in order to increase the superconducting core density of the mono-core in situ Fe/MgB_2 wire samples. The excessive mechanical deformation and consecutive heat treatment have been applied in a two-step experiment on the wire samples. The purity and particle size of the precursor Mg and B powders, heat treatment conditions, type of sheath material, etc. have crucial importance in order to obtain high-performance in situ MgB_2 wires and tapes. In the present study, a special $\text{Mg} + 2\text{B}$ mixture is used so as to reduce the agglomerations of boron nano particles upon drawing which badly affect homogeneity of the core along the wire. The additional processing steps are performed on thin Fe/MgB_2 wires with an outer diameter of 1.0 mm which is appropriate for the superconducting coil fabrication.

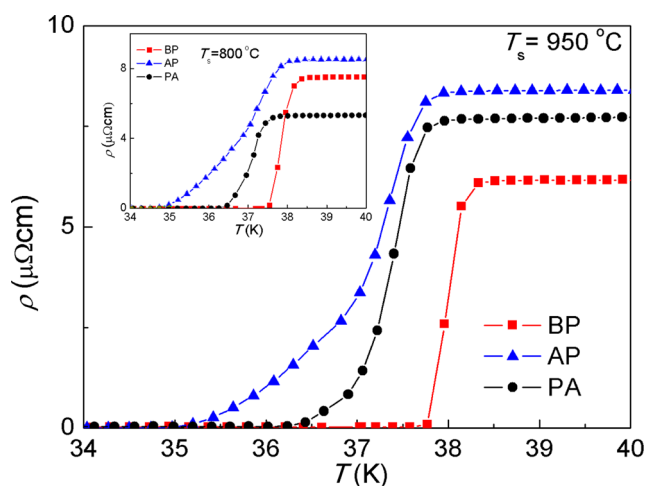


Fig. 1 Resistivity vs. temperature (ρ – T) curves obtained for the Fe/MgB_2 wire sample sintered at $T_s = 950^\circ\text{C}$ for each experimental step. The inset shows the ρ – T curves obtained for the Fe/MgB_2 wire sample sintered at $T_s = 800^\circ\text{C}$. The choice of different colours is a guide for the eyes to follow the experimental steps

2 Experimental Setup

The mono-core Fe/MgB_2 superconducting wires were prepared from magnesium powder (purity 99 %, particle sizes 100–200 mesh ≈ 149 – $74\ \mu\text{m}$), amorphous boron powder (95–97 %) and amorphous nano boron powder ($> 98.5\%$

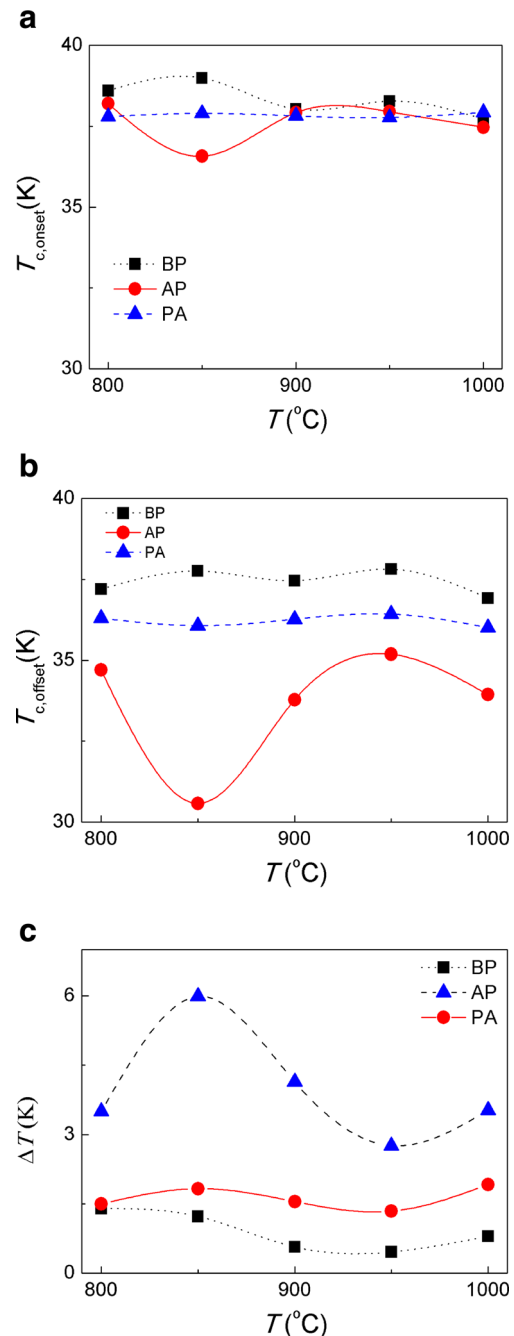


Fig. 2 **a** Variation of the onset critical temperatures ($T_{c,\text{onset}}$) of the five sintered Fe/MgB_2 samples in the BP, AP and PA steps. **b** Variation of the offset critical temperatures ($T_{c,\text{offset}}$) for the same Fe/MgB_2 samples in each step. **c** The superconducting transition width obtained from **a** and **b**

— < 250 nm) by using the in situ solid-state reaction and PIT methods (magnesium and boron powders supplied by Pavezyum Chemical Industry, Turkey). The total weight of the boron powder is composed of 50 % amorphous boron and 50 % amorphous nano boron. First, the stoichiometric precursor Mg + 2B powder was mixed in a ball milling for 3 h. This homogenous powder weighing 15.1 g was filled into a 350-mm-long pre-cleaned iron (Fe) tube with inner/outer diameters of 9 mm/12 mm. A cold drawing method with several intermediate heat treatments under argon pressure and/or argon flow was applied to fabricate the wire samples. The wires of 1.0 mm diameter were cut to 120-mm pieces and sintered in series in a three-zone programmable tube furnace at temperatures of 800, 850, 900, 950 and 1000 °C for 1 h under 5–10 bar argon pressure. The mechanical deformation and subsequent heat treatment processes were applied to these in situ-fabricated wire samples. At first, the wire samples heat treated at different temperatures were tested in the cryostat to measure their transport properties. The same samples were then cleaned to remove soldering and were brought into the tape form by applying a pressure of around 1 GPa (calculated for the area of the pressed tape (2 mm × 20 mm)) between two hardened steel plates. After the samples were pressed, transport properties were measured again in the cryostat to investigate the effect of pressing. These tapes were re-cleaned after measurements and a final heat treatment at a temperature of 850 °C for 1 h was carried out in 5–10 bar argon atmosphere. Each data is analysed on the basis of processing steps: BP, fabrication of initial in situ Fe/MgB₂ mono-core wires, AP, mechanical deformation of the initial wire samples and PA, heat treatment on excessively deformed samples.

X-ray diffraction (XRD) analysis of the wires was studied by a Rigaku Multiflex + XRD diffractometer with a

monochromatic beam (wavelength of 1.54 Å) derived from a CuK α target. A scanning electron microscope (SEM, JEOL 6390-LV) with the accelerating voltage of 20 kV was used to investigate the surface morphology of the mono-core Fe/MgB₂ samples. The dc resistivity measurements (ρ - T) and current voltage (I - V) measurements of the samples were measured in a closed-cycle cryostat with the

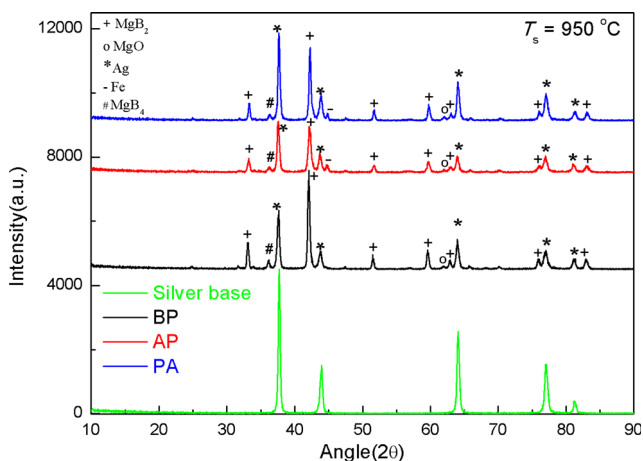


Fig. 3 XRD patterns of the Fe/MgB₂ samples initially sintered at $T_s = 950$ °C before pressing (BP-950), after pressing (AP-950) and after final annealing at 850 °C for 1 h (PA-950). The XRD pattern of Ag base is given since it is used to hold powders during XRD analysis

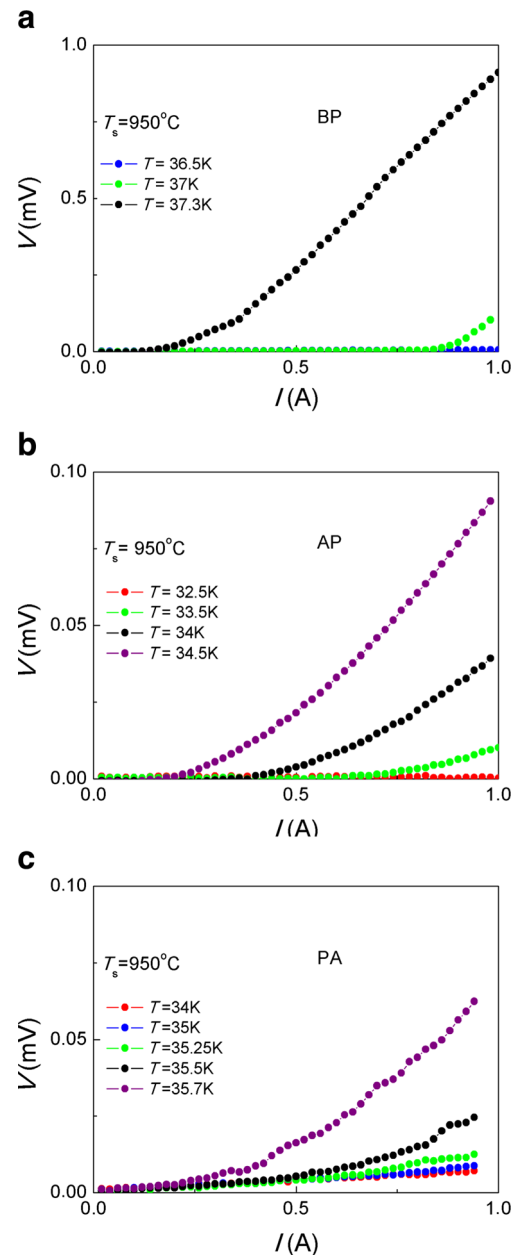


Fig. 4 Current vs. voltage (I - V) curves obtained from the Fe/MgB₂ wire sample which was initially sintered at $T_s = 950$ °C at different steps. The measurements were done at the temperatures of **a** $T = 36.5$ to 37.3 K, step 1-BP; **b** $T = 32.5$ to 34.5 K, step 2-AP; and **c** $T = 34$ to 35.7 K, step 3-PA. In all measurements, a minimum temperature limit is determined by considering the critical current $I_c \geq 1$ A

four-probe method. The $1 \mu\text{V}/\text{cm}$ criterion was used for critical current determination.

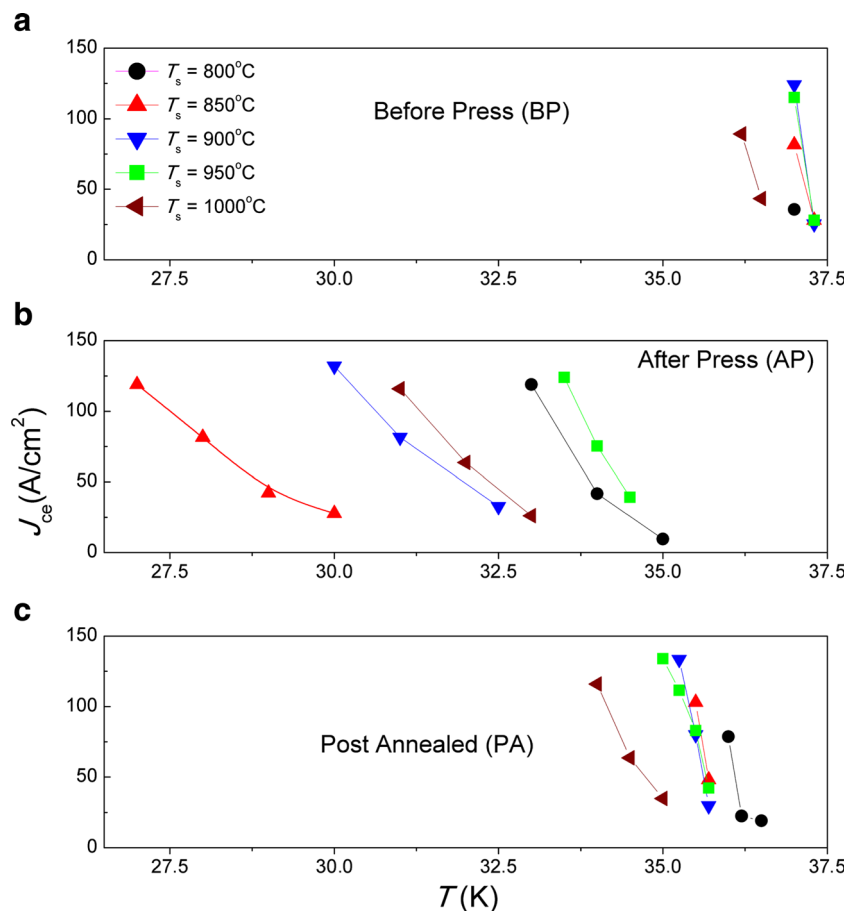
3 Results and Discussion

Figure 1 shows the ρ - T curves obtained from dc electrical resistivity measurements of the sample, initially sintered at 950°C , before and after additional processing steps. The in situ BP-950 wire sample has a sharp superconducting transition with a critical temperature $T_c = 38.3 \text{ K}$. The same sample after mechanical deformation (AP-950) is found to possess a lower T_c with a broadening in the superconducting transition. Besides that, the mechanical deformation also affected the resistivity values at 40 K ($\rho_{40\text{K}}$). It is found that the $\rho_{40\text{K}}$ value measured for the AP-950 sample is greater than that of the BP-950 sample. This behaviour is also consistent with the results obtained from the other samples. As an example, the same results are presented in the inset in Fig. 1 indicating the resistivity measurements of the BP-800, AP-800 and PA-800 samples. At the final step, additional annealing at 850°C recovered the superconducting features although not fully. The broadening of the superconducting transition was improved a lot, but the

T_c was still below the initial values together with a higher resistivity at 40 K . On the contrary, the inset in Fig. 1 clearly shows that the PA-800 sample has a lower 40-K resistivity in comparison to the BP-800 sample, as distinct from the PA-950 sample.

Figure 2 indicates the details of the superconducting transition by means of $T_{c,\text{onset}}$, $T_{c,\text{offset}}$ and ΔT curves for all samples at every step. In Fig. 2a, it is observed that the samples have close $T_{c,\text{onset}}$ values in each step as functions of the initial sintering temperatures. In the results, the only anomaly found was for the sample initially sintered at 850°C . In Fig. 2b, it was represented that the effect of excessive mechanical deformation is quite evident for all the samples. Here, it is also remarkable that the final annealing process improves transition temperatures of the samples considerably. In Fig. 1, the resistivity curves showed a tail behaviour in the $T_{c,\text{offset}}$ region after mechanical deformation. Figure 2c indicates that such a case is not to be presumed to exist in the onset of the superconducting transition. As readily seen in Fig. 2c, the broadening of the superconducting transition occurs in a $T_{c,\text{offset}}$ end. This type of broadening arises due to the formation of a large number of microcracks which contribute to weak-link behaviour because the subsequent heat treatment highly eliminated the tail behaviour as shown

Fig. 5 Temperature dependence of the engineering critical current density $J_{ce}(T)$ after each experimental step **a** BP, **b** AP and **c** PA for the samples initially sintered at different temperatures from $T_s = 800$ to 1000°C



in Fig. 2c. We suggest that the heat treatment re-joined the grains and improved the microstructure of the sample by a considerable amount.

Figure 3a–c exhibits the XRD patterns of the sample initially sintered at 950 °C at different processing steps. These patterns were obtained from separately prepared samples. In this stage, a silver base was used as holder in order to eliminate the amorphous effects which prevent small diffraction peaks, such as Mg and MgB_4 , to be seen. The analysis of XRD patterns revealed the presence of a well-formed MgB_2 phase at all stages of the experiments. The XRD peaks obtained from the samples sintered above 900 °C showed some MgB_4 phase which is difficult to avoid at high sintering temperatures [20]. The Fe peak in XRD patterns appeared for only processed samples because superconducting cores were mechanically removed from the Fe sheath.

Figure 4a–c belongs to the results of the transport critical current I_c measurements of the sample initially sintered at 950 °C at different steps. The I_c values were determined using the 1 $\mu\text{V}/\text{cm}$ criterion for transport current of up to a maximum of 1 A in a certain temperature range. The results were found consistent with the results of resistivity measurements. A large degradation was observed in the I_c values after mechanical deformation, and they were increased by an additional heat treatment process. This directly indicates that an excessive mechanical deformation is desirable to fill the voids but leads to the formation of many new grain boundaries inside the sample. The transport engineering critical current density (J_{ce}) of the samples is represented in Fig. 5a–c. The J_{ce} values of the post-annealed samples are almost as large as those of the initial Fe/ MgB_2 wire samples. On average, the total cross-section area of any pressed sample is 15 % less than that of an initial sample. In that case, it is expected that J_{ce} values will be larger due to decrement of the cross-sectional area from 0.00785 to 0.00667 cm^2 , but the results showed almost equal J_{ce} values. By considering the high rate of J_{ce} re-gains in our work, it is suggested that a small degradation of J_{ce} may be compensated and even exceeded by sintering the wires initially at a temperature which is lower than that of the final annealing after mechanical compaction.

The SEM images in Fig. 6a–c are very suggestive of further processing of the wire samples. These images show that a dense MgB_2 core with microscale voids is achieved for the in situ–reacted BP-950 wire sample. Its dense superconducting core has self-field $I_c \geq 1$ A in the vicinity of T_c as shown Fig. 4a. This is a significant result in terms of the accomplishment of fine grain connectivity during the reaction process for the BP-950 sample. Figure 7b, c gives information about the microstructure of the samples AP-950 and PA-950 after mechanical deformation and consecutive heat treatment, respectively. It seems that these voids are

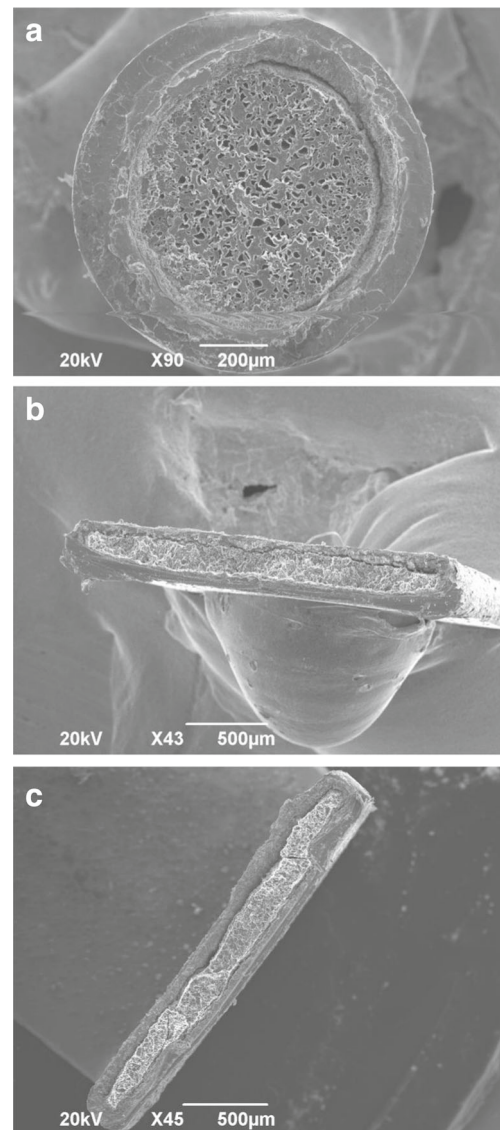


Fig. 6 SEM images of Fe/ MgB_2 samples sintered at $T_s = 950$ °C in **a** BP with magnification of $\times 90$, **b** AP with magnification of $\times 43$ and **c** PA with magnification of $\times 45$

totally removed, and the core density is further increased after pressing the sample. Densification upon mechanical deformation corresponds to about 30 % volume reduction in a superconducting core. Mass density difference between $\text{Mg} + 2\text{B}$ and MgB_2 leads to ~ 23 % void formation. The rest of the volume reduction is expected to be due to incomplete densification during drawing. Nano pores may be present in the MgB_2 core even after pressing, but the mass density of the core in our samples approached full density according to SEM examinations. However, the transport measurements also revealed the existence of several grain boundaries arising from the crushing of superconducting grains into smaller pieces which was supported by grain size values such as 283.9 Å (BP), 184.6 Å (AP) and 284.3

Å (PA) obtained from XRD patterns. The poor connections between the grains impeded the J_{ce} ; a subsequent heat treatment is very promising in order to upgrade the microstructure as seen in Fig. 5c. The samples initially sintered at 800 °C showed the highest percentage of recovery in terms of critical current density near T_c , indicating that a final heat treatment at a higher temperature can help to obtain better performance when sintering temperature prior to final mechanical deformation is kept lower. The need for fully dense MgB₂ wire is not only important for critical current density considerations but also crucial for preventing mechanical damage during its use since voids in the core cause mechanical weakening.

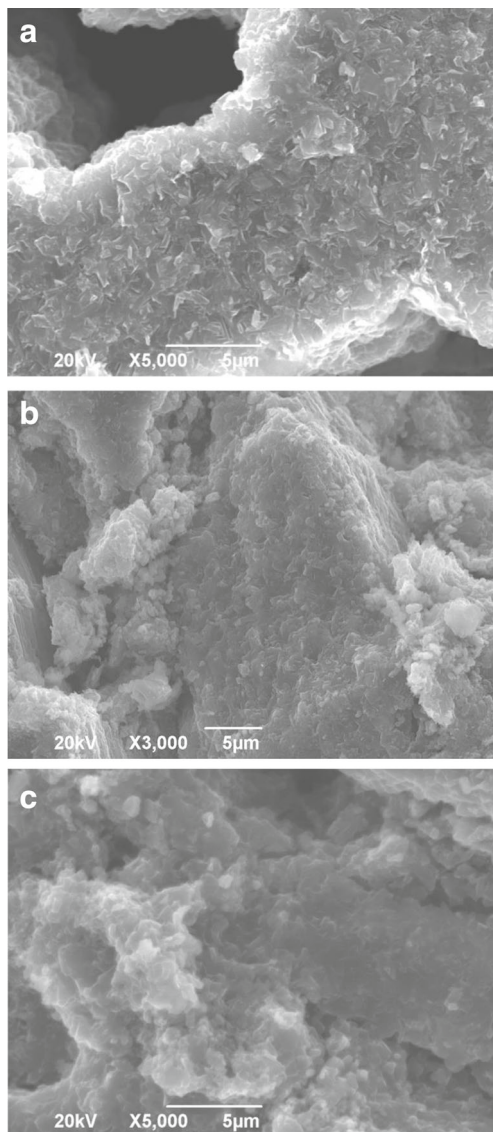


Fig. 7 Microstructures obtained by SEM in **a** BP with magnification of $\times 5000$, **b** AP with magnification of $\times 3000$ and **c** PA with magnification of $\times 5000$ for Fe/MgB₂ samples initially sintered at 950 °C

4 Conclusion

In summary, the application of excessive mechanical deformation on Fe-sheathed MgB₂ wire samples removes the internal voids but causes the formation of smaller grains and additional grain boundaries. This deformation leads to a fast degradation of J_{ce} and T_c values because cracking of MgB₂ material due to the mechanical deformation destroys the percolation paths for current flow, and additional heat treatment re-joined the grain structure and highly improved the grain boundaries. Transport measurements reveal that the transport J_{ce} values were increased to a certain extent, but not totally recovered in comparison to that obtained for the initial Fe/MgB₂ wire. These small differences between the transport properties of the initial wire and the final tape samples suggest that the use of lower sintering temperature and higher annealing temperature after pressing may produce fully dense tapes potentially applicable to superconducting coil fabrication.

We suggest that a small degradation of J_{ce} may be compensated and even exceeded by sintering the wires initially at a temperature being lower than the final annealing after mechanical compaction.

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