Preparation of SiC Doped In-Situ MgB$_2$ Mono- and 7-Filamentary Wires by Continuous Tube Forming and Filling Technique

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Abstract. Long lengths of in-situ SiC doped MgB$_2$/Fe mono-filamentary wires with high critical current densities and 7-filamentary MgB$_2$/Nb/Cu/Fe wires with better thermal stability have been fabricated by either continuous tube forming & filling (CTFF) technique or combining both powder in tube (PIT) and CTFF process, respectively. Particular efforts were made in view of the optimization of the manufacturing and annealing processes of the wires. The as obtained wires were sintered under a vacuum furnace at different sintering temperatures and the optimized sintering of the MgB$_2$ wires were investigated by the analysis of optical microscope, XRD, SEM, and the transport $J_c$ measurements. The $J_c$ value in a 8 at.% SiC doped MgB$_2$/Fe mono-filamentary wire is more than $10^4$ A/cm$^2$ at 4.2 K and a field of 11 T. While in doped 7-filamentary wire, the similar $J_c$ value ($10^4$ A/cm$^2$) is obtained at 4.2 K and a field of 7.5 T. Moreover, the $n$ factors are determined to be 33 and 10 at 11 T in the mono- and 7-filamentary MgB$_2$ wires with SiC doping, respectively, indicating the possibility to use the as fabricated MgB$_2$ wires in the persistent mode for fields from 0.5 T to 10 T at 4.2 K.

1. Introduction
MgB$_2$, a superconducting material with $T_c = 39$ K [1], has attracted much more attention worldwide since its discovery in 2001 due to its advantages such as weak link free grain boundaries [2], large coherence length and low material cost. It thus becomes a very promising material for potential application such as MRI at 20-25 K. Over past 6 years, many groups have obtained high properties in the MgB$_2$ wires and tapes through the powder in tube (PIT) method with either in-situ or ex-situ routes [3-8], and the $J_c$ values of those wires are at the level of $10^6$ A/cm$^2$ (4.2 K, 0 T). Recently, multi-filamentary MgB$_2$ wires such as 18- or 36- Nb/Cu/monel filamentary wires could be fabricated by another technique called continuous tube forming & filling (CTFF) process, as reported by OSU and Hyper Tech [7, 9]. As an alternative, the CTFF process is considered as a competitive means to the PIT method in the near future [7, 10-12]. One of the advantages of this process is to fabricate the multi-composite layers [12], which leads to a low cost and a large scale-up of the wire production. Despite of many advantages of CTFF method, there are only a few scientific report concerning the manufacturing and properties of the wires by this technique. In this work, long length of SiC doped...
mono- and 7- filamentary MgB$_2$ wires have been produced by CTFF technique using Mg and B powders. The effects of the processing and sintering parameters on the properties of the MgB$_2$ wires were investigated by the analysis of optical microscope, XRD, SEM, and transport $J_c$ measurements. The details of the technical process for developing multi- filamentary MgB$_2$ composite wire by combining both PIT and CTFF methods was discussed.

2. Processing details

The nano-sized SiC doped MgB$_2$/Nb/Cu/Fe 7- filamentary composite wires have been produced by combining both CTFF and PIT process using Mg (99.8%, -325 mesh) and amorphous B (99.9%, -325 mesh) powders. The mixed powders with the atom ratio of Mg:B = 1.1:2 and 8 at.% SiC (particle size ~30 nm) were well mixed and filled into the foils of Nb by CTFF technique. The Nb foil was overlap-closed in the milling line and then filled again into a contact-closed Cu foil (see figure 1). After being drawn, this mono- filamentary wire was cut to some pieces that were inserted parallelly into a Fe sheath, followed by drawing to fabricate MgB$_2$/Nb/Cu/Fe multi- filamentary wires with a final size of 1 mm external diameter.

![Figure 1. Schematic sketch for fabricating the MgB$_2$/Nb/Cu/Fe multi- filamentary wire.](image1)

![Figure 2. Optical image of the cross section of the as fabricated multi-filamentary MgB$_2$ wire.](image2)

Figure 2 shows optical micrography of the as produced 7- filamentary MgB$_2$/Nb/Cu/Fe wires. It was found that the 7- filamentary wire has uniform cross section. Compared to the MgB$_2$ filament diameter of 500 μm in the mono- filamentary wire reported in our previous work [12], the diameter of a single MgB$_2$ filament in the 7- filamentary wire was about 100 μm. In another word, the cross-section area of a single MgB$_2$ filament in a 7- filamentary wire was decreased by 90% compared to that of the MgB$_2$/Fe mono- filamentary wire. At the same time, it was obviously found that the MgB$_2$ filaments are surrounded uniformly by the Nb foils, and the arrangements of Nb and Cu foils as well as Fe sheath are very clear without cracks.

Finally, the as obtained wires were all wrapped in tantalum foil and annealed at different temperatures for 15 min by a conventional vacuum furnace under a pressure of $10^{-3}$ Pa. The XRD and SEM were used to characterize the phase formation and microstructure of the sintered MgB$_2$ wires. The transport critical currents were measured on 45 mm long wire samples (cut from the long length wire) in a He bath at 4.2 K. The voltage contacts were 10 mm apart, and the voltage criterion used was 1 μV/cm. The magnetic field was parallel to the surface of the wire.

3. Results and discussion

3.1. Optimization of the sintering temperatures in the MgB$_2$ wires

Figure 3 presents the XRD patterns for the 8 at.% SiC doped MgB$_2$ mono- filamentary samples made by CTFF method and sintered at different temperatures from 500 to 900 °C for 15 min. As observed in the patterns, Mg phase still exists when annealing at both 500 °C and 550 °C. With the increase of the
temperatures from 600 to 900 °C, MgB$_2$ phase is completely formed and becomes the main phase in the samples. Besides, the MgO, Fe$_2$O$_3$, and Mg$_2$Si as impurity phases are also detected. At these temperatures, no diffraction peak from SiC are identified, which suggests that the nano-sized SiC is decomposed during the heat treatment and the existence of Mg$_2$Si phase is due to the rapid reaction of Mg and SiC. It is found that the Mg$_2$Si peak becomes weak, but the MgO and Fe$_2$O$_3$ peaks tend to be stronger with the increase of the sintering temperatures. Finally, it was optimized that high purity of MgB$_2$ could be formed in the MgB$_2$ wires annealed at 800 °C for only 15 minutes. Therefore, the mono- and 7- filamentary wires were annealed by this optimization.

Figure 3. X-ray diffraction patterns of MgB$_2$ core in MgB$_2$/Fe mono-filamentary wires made by CTFF method and sintered at different temperatures.

Figure 4. SEM images for MgB$_2$ core cross section. (a) 7- filamentary wire, (b) mono- filamentary wire.

Figure 4 displays SEM microstructures of the cross section of polished MgB$_2$ multi- and mono-wires annealed at 800 °C for 15 minutes, respectively. It can be seen that the sintered MgB$_2$ filaments in both 7- and mono- filamentary wires have a good homogeneity and there is no reaction layer such as Fe$_2$B found between the interface of the core and sheath materials in 7- filamentary wire. According to the present experimentation, as observed by the cross section of the annealed wire, the density of the MgB$_2$ core is still lower than that of the wire made by PIT method [13], which is due to that, unlike the PIT method, in the case of CTFF process, the mixed powder was filled into U type slot of the sheath material in the production line without any pressure on packing the powder. Therefore, it is still an important subject to increase the filling factor during the fabrication of the wires by CTFF method.

3.2. Transport $J_c$ properties in the fabricated MgB$_2$ wires

Figure 5 shows the $J_c$ values at 4.2 K for the SiC doped mono- and 7- filamentary wires. The wire samples used for the measurement are 1 mm diameter, 45 mm of length cut from the whole wires. For comparison, the transport $J_c$ value of un-doped mono- filamentary wire [12] is also added in figure 5. The filling factor of the MgB$_2$ filament in this 7- filamentary wire was approximating 3 times less than that of the mono- filamentary wires. The error bars in all curves are around ±1 %. Compared with undoped MgB$_2$ wire, the high $J_c$ values are observed in both doped wires. The $J_c$ value of the doped mono- filamentary wire, being $10^4$ A/cm$^2$ at 4.2 K and 11 T, was higher than that of doped multi-filamentary one, in which the similar $J_c$ value ($10^4$ A/cm$^2$) was obtained at 4.2 K and in a field of 7.5 T. It is also found that the two mono- filamentary samples are all quenched above a given current density, presumably due to the larger core thickness and bad thermal stability. Fortunately, at low-field, the current in the 7- filamentary sample was still kept stabilized, and could be obtained at a field of 0.5 T.
It is evident that the multi-filamentary wire has a better thermal stability compared to that of the mono-filamentary wires. It is well known that the amount of the heat generated in a filament dissipation process is proportional to the filament volume, whereas the cooling efficiency is proportional to the filamentary surface. It is indicated that the cross-section area of a single MgB$_2$ filament in a 7-filamentary wire is decreased by 90% compared to that of the mono-filamentary wire. Meanwhile the introduction of the Cu layer in the composite wire leads to the existence of current through the multi-filamentary wire at low-field, which thus in somehow, improves the thermal stabilization. At present, compared with the mono-filamentary MgB$_2$ wire, the $J_c$ value in 7-filamentary MgB$_2$ conductors prepared by CTFF + PIT technique is little low, which might be due to the lower filling density and the poor connectivity of grains. To further increase the thermal stability of this material, it will be essential to use thinner cores or to produce multi-filamentary wires with large number of MgB$_2$ filaments.

**Figure 5.** Transport critical current densities at 4.2 K in both annealed MgB$_2$ mono- and 7-filamentary wires.

**Figure 6.** Field dependence of the exponential $n$ factors in annealed MgB$_2$ mono- and 7-filamentary wires.

### 3.3. Exponential $n$ factors in the MgB$_2$ wires

As is well known, the exponential $n$ factor of the wires is an important value for realizing the possibility of MgB$_2$ conductor to work in the persistent mode. In this work, the logarithmic curves of $E$ versus $J$ measured at 4.2 K can be reasonably well approximated with the electric field criterion $E_c=10^{-7}$ V/mm: $(E/E_c)\approx(J/J_c)^n$. By fitting this relation to our data in the electric field range of $0.1 \mu$V/cm $< E < 1 \mu$V/cm, we obtained $n$ factors shown in figure 6 for the SiC doped mono- and 7-filamentary wires prepared by CTFF technique. The deviations in all curves are around ±2 %, respectively.

The $n$ factors in the mono-filamentary wire with SiC doping is determined to be 33 at 11 T, while it is 8 in 7-filamentary wire at this field. With the decrease of the measured fields, the $n$ factor in the 7-filamentary wire is 10 at field of 10 T and reaches 380 at 0.5 T. The high $n$ factor at low field in 7-filamentary wire may be related to the corresponding higher local homogeneity. At the same time, the good thermal stability of this wire also contributed to the stabilized current through this wire at low field. In a words, the high $n$ factors in both mono- (at high field) and multi- (at low field) filamentary wires open the possibility to use MgB$_2$ magnets in the persistent mode for fields between 0.5 to 10 T at 4.2 K.

### 4. Conclusion

In conclusion, we have fabricated 20 meters long length of in-situ SiC doped MgB$_2$/Fe mono-filamentary wires with high $J_c$ values by CTFF technique, and 6 meters of MgB$_2$/Nb/Cu/Fe multi-
filamentary wires with better thermal stability by combining both PIT and CTFF process together. The optimized annealing process to form MgB$_2$ phase was 800 °C for 15 minutes. The transport $J_c$ value of $10^4$ A/cm$^2$, measured at 4.2 K and a field of 11 T, was obtained in a mono- filamentary MgB$_2$ wire with 8 at.% SiC doping. Moreover, the $n$ factor in the 7- filamentary MgB$_2$ wire is more than 10 at a field of 10 T and reaches 380 when the field is 0.5 T. It is observed that the multi- filamentary wire has a better thermal stability compared to that of a mono- filamentary wire due to the decrease of its cross-section area by 90% compared to that of the mono- filamentary wire. This result confirms the possibility to use MgB$_2$ multi- filamentary wires for the persistent mode operation. It is found that the CTFF technique as an alternative for fabricating multi- filamentary wire is very competitive compared to PIT method.

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References
[1] Nagamatsu J, Nakagawa N, Muranaka T, Zenitani Y and Akimitsu J 2001 Nature 410 63
[2] Dhallé M, Toulemonde P, Beneduce C, Musolino N, Decroux M and Flükiger R 2001 Physica C 363 155
[3] Flükiger R, Suo H L, Musolino N, Beneduce C, Toulemonde P and Lezza P 2003 Physica C 385 286
[4] Suo H L, Beneduce C, Su X D and Flükiger R 2002 Supercond. Sci. Techno. 15 1058
[5] Serquis A C, Liao X Z, Civale L, Zhu Y T, Coulter J Y, Peterson D E and Mueller F M 2005 IEEE Transactions on Applied Superconductivity 15 3188
[6] Fang H, Xue Y Y, Zhou Y X, Baikalov A and Salama K 2004 Supercond. Sci. Technol. 17 L27
[7] Sumption M D, Bhatia M, Wu X, Rindfleisch M, Tomsic M and Collings E W 2005 Supercond. Sci. Technol. 18 730
[8] Xu H L, Feng Y, Xu Z, Li C S, Yan G, Mossang E and Sulpice A 2005 Physica C 419 94
[9] Sumption M D, Bhatia M, Rindfleisch M, Tomsic M and Collings E W 2005 Appl. Phys. Lett. 86 102501
[10] Collings E W, Lee E, Sumption M D and Tomsic M 2002 Rare Metal Materials and Engineering 31 406
[11] Collings E W, Lee E, Sumption M D, Tomsic M, Wang X L, Soltanian S and Dou S X 2003 Physica C 386 555
[12] Suo H L, Ma L, Jiang J M, Li Y M, Zhang Z L, Liu M, Zhao Y, He D Y and Zhou M L 2007 IEEE Transactions on Applied Superconductivity 17 2822
[13] Balamurugan S, Nakamura T, Osamura K, Muta I and Hoshino T 2004 Physica C 412-414 1186