Formation of Mg$_2$Si inclusions in *in situ* SiC doped MgB$_2$ wires made from variable concentration of large micrometer-size Mg powder by continuous method

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Abstract. In the continuously manufactured SiC doped *in situ* MgB$_2$ wire made from 100-150 μm size Mg powder and nanosized Boron, there is formation of the Mg$_2$Si micro-inclusions in the body of the wire in addition to elongated Mg$_2$Si inclusions three orders of magnitude larger by volume, localized in position of original elongated Mg ribbons. Provision of excess of Mg powder up to 15% was conducted in aim to satisfy full use of the B particles and reduction of large Mg$_2$Si inclusions. Microstructural reflectivity and EDAX SEM analysis of phase formation in the wire prove that complex solid-liquid reactions in Mg-Si-C-B systems take place during the first few minutes of reactive diffusion processes. Result of the $J_c(B, T)$ characteristic is provided to discuss the influence of SiC doping on conductor characteristics in magnetic field. Analysis of the influence of Mg$_2$Si inclusions on artificial pinning mechanisms is discussed in conjunction with possible improvements in product, process and performance.

1. Introduction

MgB$_2$ conductors are paving their way towards being conductor of choice at elevated cryogenic temperatures for MRI and cable applications [1, 2]. To improve performance of the *in situ* Powder-in-Tube MgB$_2$ conductors at higher magnetic fields, SiC was commonly added to the core of the conductor to complement formation of the carbon doping and Mg$_2$Si formation of the pinning centres [3]. A recently proposed novel continuous manufacturing technique, where metallic Mg was deformed to the elongated ribbons [4] shows characteristic feature of formation of large spectrum of Mg$_2$Si inclusions in the volume of the superconductor during heat treatment [5]. Because formation of the larger inclusions does not benefit pinning of the final MgB$_2$ conductor, one may want to minimise such effect by introduction of smaller Mg particles or by providing excess of Mg to satisfy full use of the B particles during in situ diffusion process. As it was reported in literature, excess Mg addition significantly improves the critical current of in situ MgB$_2$ wires [6]. In this paper we will be analysing the effect of extra Mg addition to the core of the stoichiometric Mg$^+2$B mixture on the transport critical current values at external magnetic flux densities in range of 1-6 T at different temperatures (but keeping the constant 10%SiC addition to the resulting Mg$^+2$B mixture).

2. Experimental

*In situ* MgB$_2$ wires were prepared using amorphous boron from Pavezyum, Turkey that has a purity of 95-97% and main particle size of 200 nm. Magnesium was used with a particle size of 100 - 150 μm. The nano-SiC dopant used, has a particle size of 40 - 60 nm.
During the mixing process: oxygen, hydrogen and moisture levels were monitored. For all the wires with SiC, doping level was kept constant at the level of 10%SiC addition to the resulting Mg+2B mixture. The detailed description of the chemical composition of the superconductive cores is presented in Table 1. The mixed powders are introduced into a “U” profile of metal/titanium sheath with liquid carrier. To define the effect of extra Mg addition to the core of the stoichiometric MgB$_2$, 7.5% and 15% extra magnesium was added to the original stoichiometric wire, see Figure 1.

| Wire ref. | Composition       | ACTUAL ratio (Mg% / B%) relative to STOICHIOMETRIC ratio (Mg% / B%) |
|-----------|-------------------|------------------------------------------------------------------|
| S-15      | 15% extra Mg      | 115%                                                             |
| S-7.5     | 7.5% extra Mg     | 107.5%                                                           |
| S-0       | 0% extra Mg       | 100%                                                             |

Figure 1. SEM image of the polished cross section of the S-15 conductor, overall diameter equal 0.75 mm; (for description of the wire core composition see Table 1). The black areas represent boron powder and white areas represent magnesium powder.

3. Results

SEM longitudinal cross-section of sample S-0 presented in Figure 3, reveals the location of large Mg$_2$Si inclusions formed in the area where elongated magnesium filaments were before sintering. One can assume that during preparation of the Mg-B-SiC mixture, the SiC nanoparticles most likely could stick to Mg large particles and this could be a reason for accelerated localized formation of Mg$_2$Si inclusions in the original Mg location. Such large Mg$_2$Si inclusions do not contribute to flux pinning and improvement of the critical current.

Figure 2. a) SEM Longitudinal cross-section of sample S-0 revealing the location of the formed Mg$_2$Si inclusions in places where the original extended Mg ribbons were present in unreacted in situ wire [4] see Figure 1, scale as in Fig b). On Figure b) the square dotted region is magnified and presented in c) one may notice that the larger boron particle was only partially converted to MgB$_2$ despite proximity to
the original Mg source due to rapid kinetics of formation of the Mg$_2$Si at ~550°C that overtook conversion of Mg to MgB$_2$ compound. The critical current of the wires was measured in the range 20 - 30K and magnetic flux density of 1 T using a bespoke helium force vapor cooled critical current testing facility [7], where measurements at 4.2 K were conducted at magnetic flux density of 2 - 6T at the University of Twente, as described in previous publication [5].

Results of image analysis of SEM cross sections of the wires summarised in Table 2 revealed that fewer voids were formed with increased amount of added magnesium and calculated amount of 10%SiC (as presented in Table 1).

**Table 2** Porosities of the MgB$_2$-S-C-Mg wire cores after sintering process

| Wire ref. | Porosity (% vs total core cross section) |
|-----------|----------------------------------------|
| S-15      | 17.4%                                  |
| S-7.5     | 24.4%                                  |
| S-0       | 25.6%                                  |

**Figure 3.** SEM images of the polished cross-section of the central superconductive core of metal/Ti sheathed wires sintered at 700°C for 30 min, overall diameter of the wires 0.75 mm; a) wire S-15, b) wire S-7.5. There is evidence of the unreacted larger boron crystals present in the core. The white square fields marked have been magnified and presented correspondingly in Fig 4.

**Figure 4.** Enlarged white frames of SEM images of the polished cross-section of the central superconductive core of metal/Ti sheathed wires corresponding to images a) and b) Figure 3. Notice that additional to well-defined zones of Mg$_2$Si formation as in sample S-0 (Figure 2) there are different shades of grey across the core of MgB$_2$ conductor especially in sample S-15 indicating ‘infiltration’ - coexistence of MgB$_2$ with Mg-Si phase.
As presented in Figure 4, sample S-15 has shown more explicitly some areas between pure Mg$_2$Si and MgB$_2$ being infiltrated by additional Mg and Si supplemented phase, which resulted in reduction of the effective porosities (Table 2). It is expected that such a microstructural modification of the core of the wire should not provide improvement of the critical current performance of the S-15 wire. There is also a large population of sub-micron Mg$_2$Si inclusions and unreacted B in all the investigated wires, see Figure 4, that contribute as effective pinning centers. Also Mg-C-B interaction during reactive diffusion processes of MgB$_2$ formation should improve carbon doping of the resulting MgB$_2$ wires resulting in higher $J_c$ at elevated magnetic flux densities.

Transport critical current measurements conducted at 4.2 K show a higher critical current density for stoichiometric wire (S-0) up to 6 T external field strength (Figure 5). As presented in Figure 6, critical current density at low external magnetic flux density of 1 T and range of temperatures 20-28 K of the identical diameter wires was higher for stoichiometric wire (S-0). This result can be attributed to better percolative current paths where fine pinning defects are less important.

![Figure 5](image1.png)

**Figure 5.** Transport critical current density of the wire: S-0, S-7.5 and S-15 measured at 4.2 K show very similar performance of the wires overdoped with Mg, whereas sample S-0 with stoichiometric Mg shows systematic higher $J_c$ improvement at lower magnetic flux density below 6 T.

![Figure 6](image2.png)

**Figure 6.** Transport critical current density versus temperature at magnetic flux density of 1 T measurements of samples: S-0, S-7.5 and S-15. The overall diameter of the wire without insulation was
equal to 0.75 mm. It is evident that samples with excess of magnesium show lower $J_c$ values at elevated temperature.

Conclusions

There seems to be no clear benefit of using excess Mg in our continuous technology of \textit{in situ} wire manufacturing to increase $J_c$ at low temperatures in magnetic flux density of 2-4 T where the main application of MgB$_2$ MRI will be. Also at elevated temperatures for superconductive cable manufacture where low magnetic flux densities are present, a stoichiometric composition of our (SiC doped) wires perform better than compositions with excess Mg where process of formation of an additional Mg$_2$Si, cannot be prevented that was also confirmed by another research outcome [8]. Excessive formation of the Mg$_2$Si causes reduction of the effective percolative cross section of the superconductive paths and subsequently reduction of the transport critical current values at lower magnetic flux densities and also at elevated temperatures. It can be assumed that discussed unfavourable effect of excessive Mg$_2$Si formation is related to specific manufacturing process of our continuous wires with large size excessive amount Mg powder in presence of SiC. Therefore, our future wire development will focus on replacement of the SiC doping with carbon coping and also with smaller particle size of Mg powder.

References

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