Comparative Study of the Continuous and Batch Thermal Processing of MgB_2 Wires

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***Abstract*—The last stage of the manufacturing process requires complex reactive diffusion formation process of MgB_2 in the presence of SiC nanoparticles. Continuous thermal processing was adopted to produce long length MgB_2 *in situ* wires with a homogeneous mixture of micron-sized Mg, nanosized B, as well as SiC dopant powders. This process has enabled the formation of MgB_2 superconducting compound in a relatively short time. Traditional superconductor batch processing requires the wire batch to be heat treated in dedicated large furnaces. Additionally, such a batch process requires controllable slow heating-up, dwelling, and cooling down procedures to ensure uniformity of the superconducting properties along the wire length. Such a prolonged reactive diffusion process does require lower dwelling temperature and can potentially prevent full utilization of the doping materials, resulting in less effective pinning centers formation. On the other hand, continuous wire thermal processing enables rapid formation of the doped MgB_2 with full utilization of the dopant. Also, in the continuous process, the moving thermal front brings complex dynamics to Mg–B, C–B, Mg–Si interaction during MgB_2 formation processes. The manuscript presents a comparative study of the reactive diffusion kinetics, the microstructural formation of the doped MgB_2 compound, and their J_c(B, T) characteristics.**

***Index Terms*—MgB_2 wires, superconducting cable, twisting, critical current, MRI, direct current (dc), gaseous helium cooling, continuous process, heat treatment.**

I. Introduction

THERE is an urgent need for cost effective manufacture and large quantities of MgB_2 superconductors for a variety of applications working at the temperatures range of 15–20 K [1], [2]. Such a need puts a real pressure on the manufacturing capabilities of the traditional powder-in-tube (PIT) batch technology of multifilamentary MgB_2 wires [3]. Our manufacturing technology stages of a single core conductor as well as 6 + 1 architecture were presented in details in earlier publications respectively [4], [5]. This fabrication process has some similarities with other continuous-like processes reported in literature [6], [7].

Heat treatment of the long lengths of the wires can be conducted adopting two principally different reactive diffusion processes: continuous (on-line) and batch process. Both of these processes will enable formation of the MgB_2 cores inside the in-situ conductors, but the question remains which one will be more economic and also which will provide the best critical current values for desired application. It has been proven that heat treatment of our wires with SiC does result in formation of the larger $MgSi_2$ inclusions at moderately low temperatures $\sim$ 550 °C [8] and released carbon substitute MgB_2, facilitating better performance of the conductor at elevated magnetic field. In case of batch process controllable slow heating-up, dwelling and cooling down procedures is required to ensure uniformity of the superconducting properties along the wire length. Such a prolonged reactive diffusion process does require lower dwelling temperature and can prevent full utilization of the doping materials, resulting in less effective pinning centres formation due to grain growth. Additionally, if the mass of the batch is substantial, the heating rate required will need to be correspondingly lower to ensure uniform reaction formation of MgB_2. Therefore, target sintering temperature can be a misleading concept where formation of the MgB_2 and other assisting reactions will place during ramping procedure in an incremental manner rather than sintering at the given temperature.

On the other hand, continuous wire thermal processing enables rapid heating up of the conductor resulting in fast formation of the doped MgB_2 with full utilization of the dopant. High heating rates of undoped MgB_2 were reported to lead to grain refinement [9]. Our previous investigations of the influence of heating rates and annealing temperatures on the J_c of nano-SiC-doped *in situ* monofilamentary MgB_2/Fe wires revealed that higher J_c was obtained with slower heating rates, but the J_c is not very sensitive to annealing temperatures [10].

Our recent results conducted on SiC doped wires prove that critical current measurements of the SiC doped MgB_2 wire after 10 min and 30 min sintering by rapid introduction of the wire to preheated furnace at temperature 700 °C show very similar values [5].

Also, our earlier research conducted on short duration annealing of *in situ* copper-cladded MgB_2 wires (in range of 600 °C–750 °C, with heating ramp rate of 150 °C/min) show

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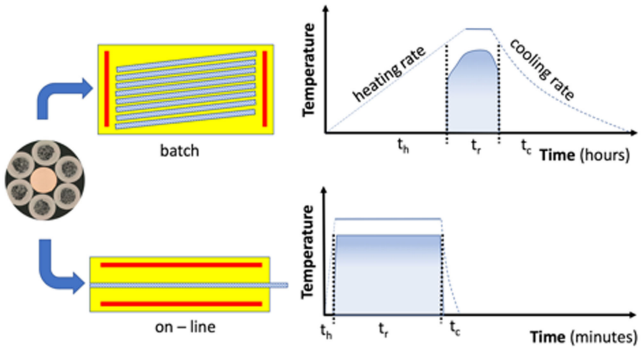

Fig. 1. Schematic illustration of the two different heat treatment procedures (*batch* and *on-line*) of MgB_2 formation in twisted multifilamentary MgB_2 conductor (under protective gas atmosphere). Schematic plots of heat treatment stages for *batch* and *on-line* procedures are described in Table I. t_h time of heating, t_r reaction time and t_c is a cooling time. Graded areas under $T(t)$ profiles represent schematically the variable kinetic of formation of MgB_2. It is evident that the definition of the actual reaction time and therefore effective reactive diffusion process of MgB_2 phase formation in *batch* process is much more complex in comparison to *on-line* process.

that the microstructure and properties of the wires are strongly dependent on the heat treatment temperature and ratebut are quite insensitive to the reaction time: a short heat treatment for 5 min at 700 °C was sufficient for obtaining the highest critical current achieved [9]. The possibility of using lower reaction temperatures and durations may also offer an opportunity for reducing the extent of grain coarsening, resulting in finer grains and enhanced flux pinning.

Results of Fe *in-situ* sheathed wires doped with nano-SiC particles sintered at temperatures ranging from 580 °C to 1000 °C for 5–30 min with heating rate of 10 °C/min shown that samples sintered at a lower temperature have a very fine and well consolidated grain structure while samples sintered at a high temperature contain large grains with easily distinguishable grain boundaries [11]. Low temperature sintering resulted in a higher concentration of impurity precipitates, larger resistivity, higher J_c up to 15 T and lower T_c values.

The influence of different heating rates, on the microstructure and superconducting properties of the undoped MgB_2 bulk was reported in literature and no obvious variation in the grain size was found except for the changes in morphologies [12]. This brings necessity to further investigate the differences between continuous (on-line) and batch process it in the wire forms.

However, there is a significant difference between rapid heating and rapid cooling of the short pieces of the wire which are introduced directly into the preheated furnace and continuous *on-line* annealing of long lengths of the wires.

In *on-line* processing there is a risk of creating a thermal front that can potentially bring complex dynamics to reactive diffusion processes between Mg-Si, Mg-B, C-B interaction during MgB_2 formation processes, resulting in more complex percolative MgB_2 formation [13]. Therefore, presented research will address the above issues.

In this manuscript we will be investigating the possible differences in the conductor properties under two principally different reactive diffusion processes: continuous (*on-line*) and batch process.

TABLE I
SINTERING PROCEDURES OF WIRES AT REACTION TEMPERATURE 700 °C

Total heat treatment time	t_h (min)	$t_{r\ at\ 700oC}$ (min)	t_c (min)	comment
S1-12	2	8	2	direct insertion
S1-32	2	28	2	direct insertion
S2-10	1.5	7	1.5	*on-line*
S2-20	3	14	3	*on-line*
S2-30	5	20	5	*on-line*
S3-1200	420	0	780	*batch*

II. HEAT TREATMENT

A. Heat Treatment Procedures

Consideration is given to both continuous (*on-line*) and batch process as presented schematically in Fig. 1.

As presented in Table I we have investigated three different procedures where the maximum sintering temperature in the presented cases was chosen to be 700 °C. S1, wires were rapidly heated by direct insertion to preheated furnace chamber; S2, wires were on-line thermally processed continuously as schematically is presented in Fig. 1. S3 wire was inserted into the furnace chamber at room temperature (RT) and heated to 700 °C, at rate of 100 °C h^{-1} and subsequently cooled to RT. I_c results of all three treatment procedures should provide the answer if the *on-line* processing will be the acceptable or even preferential technique.

All investigated *in situ* MgB_2 wires (OD = 0.75 mm and superconductive powder cross-sectional filling factor = 30%) were prepared using mixture of B-Mg-SiC [5]. Amorphous boron from Pavezyum, Turkey, magnesium from Magnesium

Metal Co., Turkey and SiC dopant from Iolitec, Germany. Amorphous boron has a purity of 95–97% with a narrow particle size distribution with majority at 0.2 μm also minority at 2 μm and some at 7 μm as presented in [5]. Magnesium has a purity of above 99.9% with a particle size of 100–150 μm and nano-SiC has a particle size of 40–60 nm. SiC doping level was kept constant at the level of 10%SiC. During the mixing process oxygen, hydrogen and moisture levels were monitored [5]. 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_2Si micro-inclusions in the body of the wire in addition to elongated larger Mg_2Si inclusions, localized in position of original elongated Mg ribbons.

III. CRITICAL CURRENT MEASUREMENTS

A. Helium Force Vapor Cooled Critical Current Testing of Wires

The transport critical current of the sheathed wires was measured in an efficient helium gas force vapor cooled bespoke system [14] in a uniform magnetic flux density of 1 T. Measurements were conducted using an electric field criterion of $E = 1\ \mu V \cdot cm^{-1}$. Sample voltage contacts were placed 1 cm apart. Wire lengths of 14 cm were used for testing to ensure that

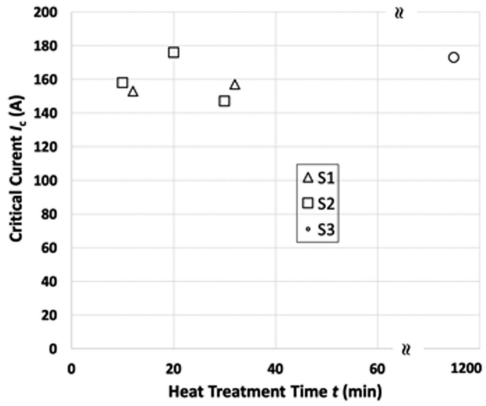

Fig. 2. Comparison of critical current values of metal sheathed MgB_2+10 wt% SiC 0.75 mm wires after sintering according to S1, S2 and S3 procedures described in Table I. Measurements were conducted under magnetic field of 1 Tesla at 20 K [14].

all current is transferred from the sheath to the superconducting core. Current contacts were 4 cm long.

B. Procedure S1

Critical current measurements of the wire sintered according to procedure S1 after 8 min and 28 min sintering at 700 °C Critical current measurements of the wire sintered according to procedure S1 after 8 min and 28 min sintering at 700 °C (sample S1-12 and S1-32 respectively) show almost identical values see Fig. 2 providing evidence that short time sintering presents a credible possibility for the rapid wire sintering. These results can be also supported by our earlier measurements conducted on wires with different metal sheets [5].

C. Procedure S2

The result of a typical wire sintered *on-line* according to procedure S2 (described in Table I) shows a similar critical current value to the samples measured according to S1 procedure, Fig. 2. Also, among three *on-line* S2 wires a maximum I_c value was achieved for S2-20 sample.

D. Procedure S3

As it was discussed earlier, see Fig. 1, the variable kinetic of formation of MgB_2 is an inherent part of the *batch* procedure (S3). As result, it becomes evident that the definition of the actual reaction time and therefore effective reactive diffusion process of MgB_2 phase formation in *batch* process is much more complex in comparison to *on-line* process. Considering that the first reaction of MgB_2 takes place at $\sim$ 620 °C we have conducted initial preliminary estimation of the t_h, t_r and t_c parameters to be used in S2-20 to result in a similar degree of reactive diffusion and grain growth as in S3-1200, see Table I. Comparative critical current measurements conducted at 20 K and 1 T revealed that the critical current value achieved for sample S3-1200 was identical as achieved for S2-20 wire. In our procedure S3-1200 formation of MgB_2 was conducted at both, *solid-state* and *liquid-state* reactive diffusion processes of MgB_2 formation, therefore further research is required to define thermal division between *solid-state* and *liquid-state* reactive diffusion processes of MgB_2 formation, influencing transport critical current properties of the conductor heat treated as a *batch*.

TABLE II
SERIES OF *On-Line* SINTERED SAMPLES ACCORDING TO PROCEDURE S2

Total heat treatment time	t_h (min)	$t_{r\ at\ 700oC}$ (min)	t_c (min)	comment
S2-5	2	1	2	simulation *on-line*
S2-7	2	3	2	simulation *on-line*
S2-12	2	8	2	simulation *on-line*
S2-32	2	28	2	simulation *on-line*

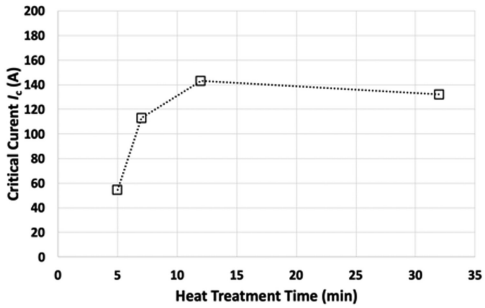

Fig. 3. Comparison of critical current values of metal sheathed MgB_2+10 wt% SiC 0.75 mm wires sintered using simulation *on-line* according to procedure S2 listed in Table II for the total heat treatment time of 5, 7, 12 and 32 min, measured at 4.2 K and magnetic flux density of 3 Tesla, see Table II.

E. Liquid Helium Cooled Critical Current Measurements of On-Line Sintered Wires

To define importance of dynamic *on-line* sintering parameters such as: time of heating, t_h, reaction time, t_r, and cooling time, t_c, series of experiments according to procedure S2 were conducted, listed in Table II. Wires described in Table II were continuously inserted into the tubular furnace to simulate *on-line* process.

The critical current measurements of the S2 wires listed in Table II were conducted in a uniform magnetic flux density of 3 T at liquid helium using an electric field criterion of $E = 1\ \mu V{\cdot}cm^{-1}$. The $I_c(t_r)$ results are presented in Fig. 3. It is evident that 8 minutes reaction time at 700 °C (S2-12) was sufficient to achieve the best performance at 3 T.

IV. CONCLUSION

The critical current values of rapidly heated wires show that production of the long lengths of the superconductive MgB_2 wires with narrow particle distribution of boron and magnesium, enabling formation of MgB_2 superconducting compound in a relatively short time, is a viable solution to achieve low cost MgB_2 wires. Additionally, there is a scope for further improvement of our MgB_2 wires once used Mg particles size will be $\sim$ 30 μm, that way, substantially improving uniform spread of

the Mg_2Si inclusions, enhancing an effective volume pinning force at higher magnetic flux densities.

In *on-line* processing of our Mg-B-SiC wires, where thermal front could potentially bring complex dynamics to reactive diffusion processes between Mg-Si, Mg-B, C-B interaction during MgB_2 formation processes, resulting in more complex percolative MgB_2 formation we have seen similar I_c performance compared to batch sinter processing.

However, future in depth analysis will be conducted to define conditions at which such effect may occur and in order to further optimize on-line heat treatment conditions of our MgB_2 conductor production. Presented results therefore clearly offer the opportunity for *on-line* thermal treatment process that can be adopted in large-scale production rather than the usual batch heat treatment process.

Comparative critical current measurements conducted, indicate that further research is required to define thermal division between solid state and liquid state reactive diffusion processes of MgB_2 formation. Such research will reveal which of the on-line or batch formation microstructures will be more suitable for application in MRI machines operating at 3T.

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