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Synthesis Temperature Effects on Ex-Situ Manufactured MgB2 Wires Useful For Power Applications

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ABSTRACT:Ex-situ powder in tube manufacturing process is based on the filling of a metal sheath with pre-synthesized MgB2 powders. It is necessary for MgB2 used in wire manufacturing to have the required properties of grain size and connectivity. Synthesis temperature for MgB2 is an important parameter to improve the quality of powders and subsequently enhance performances of wire for large-scale applications. In this work we investigated the effect of synthesis temperature on morphology, and how this is reflected on superconducting properties. A detailed study on the influence of MgB2 synthesis temperature on grain size has been given, evaluated through SEM images and magnetic measurement, by applying a model for average grain size distribution based on the penetration of magnetic field in the superconductor, that was found to be in agreement with several other methodologies. Engineering current density has been evaluated from direct measurement using a four-probe configuration.

KEYWORDS:SPION, Stirring rate, Coating materials, Magnetic characteristics, Biomedical applications.

I. INTRODUCTION

The importance of MgB2 as a possible candidate for practical applications came up since its discovery in 2001 [1], and recently its increasing its interest as a consequence of the performance reached in practical applications. Nowadays a new challenge must be engaged for MgB2 developers: very fine particles have to be synthesized in order to reach very fine filaments in multi-filamentary wires, i.e. 10 μm or less. Winning that challenge will be possible to reduce the AC losses and then open a wider scenario for MgB2 applications [2]. It must keep into account the role played by the precursors, in fact MgB2 synthesis take place in rapid way [3] at 650 °C (Mg melting point) in which B is solid. Very fine precursors, especially B, are fundamentals to obtain very fine MgB2 powders. Powder in tube (PIT) technique has been immediately employed to manufacture long length wire [4] and tapes [5]. PIT process can be divided in two different procedures, ex-situ [6] and in-situ [7], according to the place (or step) at which MgB2 is synthesized. In-situ PIT expects the synthesis inside the metal sheath, after wire winding, while for ex-situ PIT MgB2 is synthesized before tube filling. In-situ manufactured wire permits to reach higher Jc [8], but low density can be reached, due to the presence of voids, led by the volume reduction of reaction between Mg and B. Recently new branches of PIT technique have been developed in order to overcome drawbacks of typical in-situ and ex-situ PIT. An example is the mixed technique, developed by Nardelli [9] is based on the use of ex situ synthesized MgB4 (instead of B) as precursor, which is successively reacted in situ to MgB2 during final heat treatment, by restoring stoichiometry mixing MgB4 powder with Mg. This permits to reduce the volume reduction [9] typical of the in situ synthesis of MgB2, which is reflected in a high voids-density for in situ wires. In this way, both the positive benefits of each process (in situ and ex situ) are simultaneously verified. A totally different approach has been used for the so-called “2nd generation MgB2 wire”, based on the Reactive Liquid Infiltration (Rli) technique developed by Giunchi [10]. Mg powders are substituted with a Mg rod centred along the metal sheath, then filled with B powder, weighted in order to maintain the correct stoichiometry. In this way it is possible to obtain hollow wires with very high critical currents, thanks to a dense layer of MgB2 in contact with metal sheath.

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Since the discovery of superconductivity in MgB2 our group chosen to work with the ex-situ PIT technique [11], that despite lower Jc, permit to manufacture homogeneous long length wire more easily [12]. The main advantage of ex-situ process is the possibility of powder manipulation, e.g. by ball milling. Ball milling process can be used to introduce doping in MgB2 [13], but also for reducing grain size [14]. Filling metal sheath with finer MgB2 powder permits to reach higher Jc due to higher MgB2 density and enhanced grain boundaries pinning force [14].

To avoid powder manipulation, that have to last for long time for good results [13, 14], a new procedure to synthesize nano doped B powder [16] has been developed. B synthesized following this technique has nano-metrical grain size and if added proper C-sources [17] (or other elements) during the preliminary steps of that process MgB2 manipulation after synthesis can be avoid, i.e. milling. Once synthesized, B is used to perform MgB2 synthesis that will be used for the ex- situ PIT manufacturing technique. Temperature and time at which MgB2 synthesis is performed can affect on powder or grain boundaries morphology and, as a consequence, on superconducting properties [18]. Our intent in this paper is to evaluate the influence of synthesis temperature of MgB2 on morphological properties, such as average grain size or grain size distribution, and on superconducting properties of powder and wire sample. An explanation of how morphological properties influence performances of final MgB2-conductors will be given.

II. PSYNTHESIS PROCEDURE AND SAMPLE PREPARATION

Four different MgB2 samples have been synthesized and investigated in this paper. B precursor was, synthesized in our laboratory by following the procedure described in ref [16], and heat treated at 1100 °C for 24 hour to remove residual B2O3, thereby used to synthesize the MgB2 powders. Heat treated B is divided in four batches and mixed with MgH2 in an agate mortar. Synthesis was performed in pure Ar-flow, in a furnace directly connected to a glove-box, filled with mixture of Ar and 5% H2 (99.995 % purity), where powders are stocked and manipulated. This permits to avoid contact between powders and air, and further contamination with oxygen [19]. Powder extracted from the furnace, which have the typical dark-grey/black colour of MgB2, are grinded to homogenize and break the agglomerates. X-rays diffraction have been performed to investigate phase formation and presence of secondary phases. In Table 1 is reported a brief description of the samples.

Table 1 – Brief description of samples reported

Sample	SynthesisTemperature	SynthesisTime
MgB-750	750°C	1h
MgB-850	850°C	1h
MgB-950	950°C	1h
MgB-1050	1050°C	1h

Pellets of the different MgB2 powders were prepared by compression for SEM imaging, in order to investigate grain-size distribution and morphology. Grain size distribution have also been investigated from m(T) measurements on dispersed powders [20]. This is a new method for grain-size evaluation, more accurate respect SEM analysis because it takes in account whole sample and not a statistical count of a small portion of pelletized sample.

Ex-situ PIT wires were manufactured from synthesized powders, using an external sheath of nickel with an internal barrier of iron, useful to prevent formation of secondary products. Metal sheaths are filled inside the glove-box used for powder manipulation and sealed with tin caps. Groove-rolling procedure is used to reduce cross section of wires from a round section of 13 mm up to a square section of 1.1 mm × 1.1 mm. 10 cm long wire pieces have been heat treated at 920 °C for 0.3 hour and engineering current density (Je) has been measured by direct transport measurements, using four probe configuration. Engineering current density is the critical current (evaluated as the current that flows when on the wire is measured a voltage of 1μm/cm) per total cross-section of the wire. The magnetic field has been applied perpendicular to current flow, as Je on wire samples do not suffer of orientation influence [21]. Tc is evaluated by measuring the drop of resistivity with a four probe system while cooling down the sample in a helium dewar.

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III. EXPERIMENTAL RESULTS AND DISCUSSION

A. X-Rays analysis

It can be seen from XRD, reported in figure 1, that samples synthesized at lower temperature (750 °C and 850 °C) shows high Mg peaks, due to an excess of unreacted Mg. For high temperature synthesis (950 °C and 1050 °C) Mg content in final MgB2 is reduced [22]. The presence of Mg peak is due to the use of MgH2 to synthesize MgB2: MgH2 is obtained from hydruration of Mg powder, but this process take place only on the surface of Mg grains, leaving the core of the grains as pure Mg. Making stoichiometric calculation for the reaction MgH2 + B led an excess of Mg that can be useful as lubricant for powder during cold working procedure. At 2θ = 40° the peak of Mg2Si has been detected, due to the presence of Si traces in B precursor, that react with Mg during MgB2 synthesis. MgO peak is present in all four samples, as it is impossible to completely prevent its formation. Only secondary peak at 2θ = 62.3° (relative intensity = 52 %) is visible, because most intense peak of MgO, at 2θ = 42.9° is covered by MgB2 peak (2θ = 42.4°). The amount of MgO is very low, thanks to proper stocking and synthesis procedure.

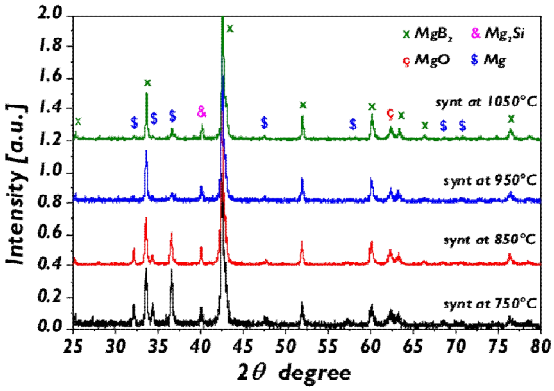

Figure 1. X-rays diffraction of MgB2 powders, synthesized at different temperature, as reported in the graph

B. Grain Size Evaluation

In figure 2 are reported representative SEM images of the four pelletized samples and significant differences cannot beseen in grains shape and dimensions. From images it is possible to evaluate average grain size of four samples andresults are reported in figure 3. It should be mention that by using this technique it is possible to investigate only a smallportion of the sample. In order to overcome this issue, it has been developed a procedure to evaluate grain size frommagnetic susceptibility, reported here:

$$m(T) = A\left(\frac{d - \frac{\lambda_0}{\sqrt{1-t^{1.5}}}}{d}\right)^3$$

Where A = magnetization coefficient, that depend on the sample itself (mass, type, etc.);
d = average diameter ofparticle;
λ_0 = penetration depth length of magnetic field through the sample, for MgB2 it has been chosen as 85 nm;
t =reduced temperature, calculated as a fraction of applied temperature on critical temperature of the sample.
A moredetailed explanation of the model can be found in ref [neo20]. Magnetization curves, m(T), and their fitting resultingfrom our model are shown in figure 3. Average grain size of this analysis are shown and compared with those fromSEM images in figure 4. Compared to average grain size evaluated from SEM images these values are little higher, butin good agreement. Despite images do not shows appreciable differences, it is reported that grain size is influenced bysynthesis temperature as grain growth mechanism that becomes more appreciable by enhancing temperature.

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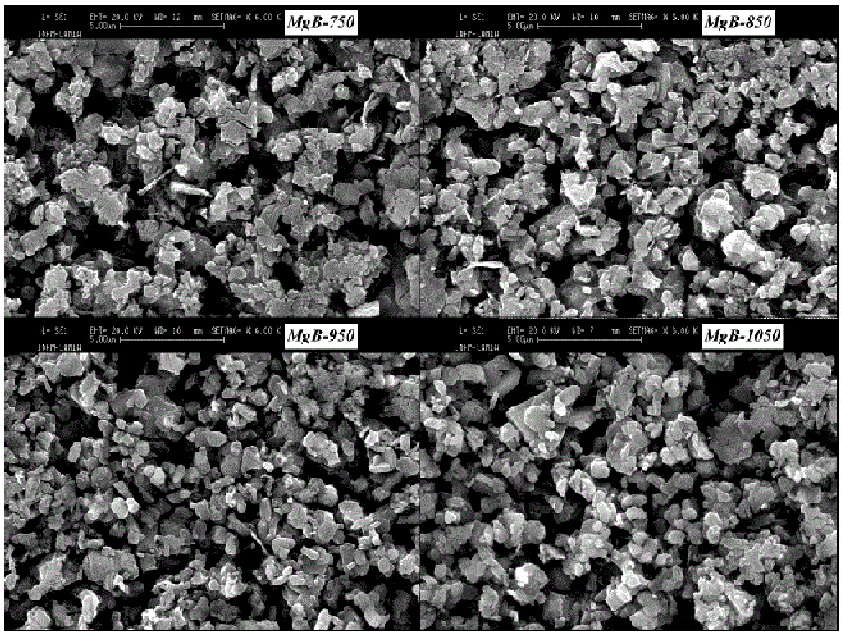

Figure 2. SEM Images of the four different samples. Images have been chosen as representative of the whole sample. In addition it has been reportedthe average grain size.

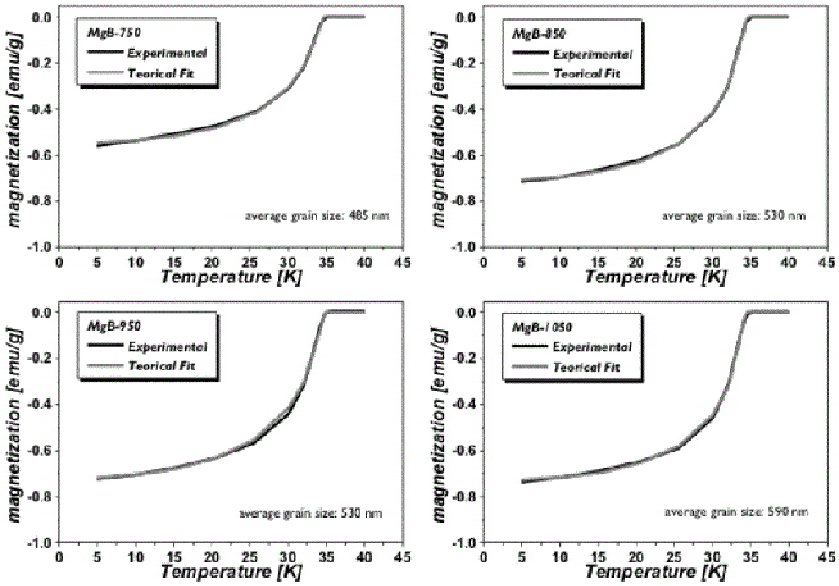

Figure 3. Average grain size evaluation performed on SQUID measurements of magnetization vs. temperature.

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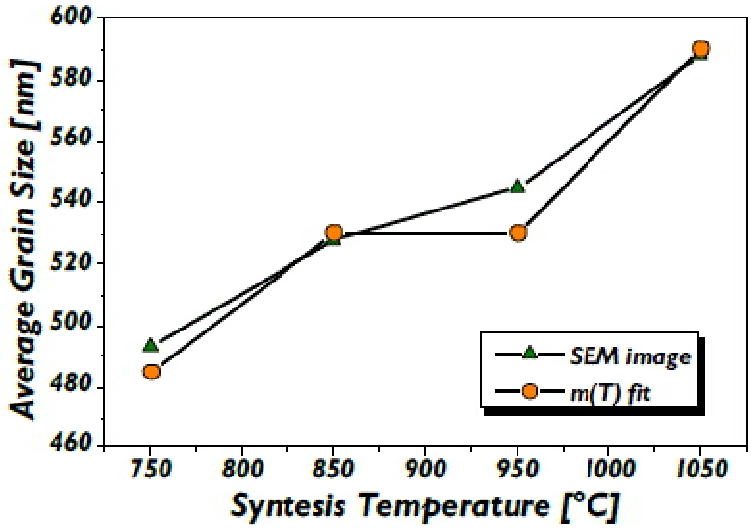

Figure 4. Average grain size measured from SEM images (green triangles) and fitting of magnetization curves (orange circles) in function of synthesistemperature

The fact that the four powders shows similar average grain size distribution is an evidence of the importance of the rawmaterials (or precursors) to synthesize MgB2 with nano-metrical grain size. For MgB2 it is essential to have available Bwith an optimal nano-metrical grain-size distribution.

C. Superconducting properties

Crystalline structure and morphology of different MgB2 sample are not depend to synthesis temperature, but thisparameter can influence grain boundaries structure and so transport properties of polycrystalline samples, e.g. wire,which results in terms of Je are shown in figure 5. Total cross section of the wires is constant for the samples, with avalue of 0.012 cm2. Superconducting cross-section of the sample, in addition to fill factor (FF, ratio betweensuperconducting cross-section and total cross-section of the wire) are reported in table 2.

Table 2 – Superconducting cross-section and fill factor of measured wire samples

Sample	Superconducting cross-section [cm^2]	Fill Factor
MgB-750	0.00286	23.2 %
MgB-850	0.00332	27.5 %
MgB-950	0.00391	32.3 %
MgB-1050	0.00401	33.2 %

It has been reported in literature that low synthesis temperature (700 - 800 °C) are necessary to synthesize MgB2 withhigh Je, or Jc (critical current density), properties [7], but for this particular B precursor higher temperature are requiredto reach high Je. Sample filled with MgB-950 shows higher Je values both at low and high magnetic field, following thetrend of the other Je curves. This is due to proper conditions of grain boundaries and crystallite morphology that can beachieved only under proper synthesis conditions. Samples MgB-750 and MgB-850 shows similar Je, especially athigher field, while for sample MgB-1050 it has been impossible to measure Je, exception made for 0 field. In thiscondition grain boundaries do not permit the proper flow of superconducting current, causing an abrupt decay of Jewhen magnetic field is applied.

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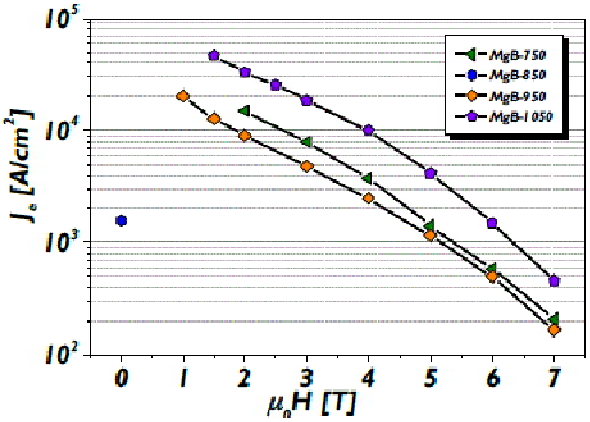

Figure 5. Je of ex-situ manufactured wire samples using the four MgB2 powders.

Tc values of the four samples did not differ from each other. It can be noticed that samples synthesized at lowertemperature (MgB-750 and MgB-850) shows wider transitions, due to the presence of unreacted Mg, identified by Xraysanalysis in figure 1. Samples synthesized at higher temperature shows lower unreacted Mg content and this led tocleaner grain boundaries and sharper transitions.

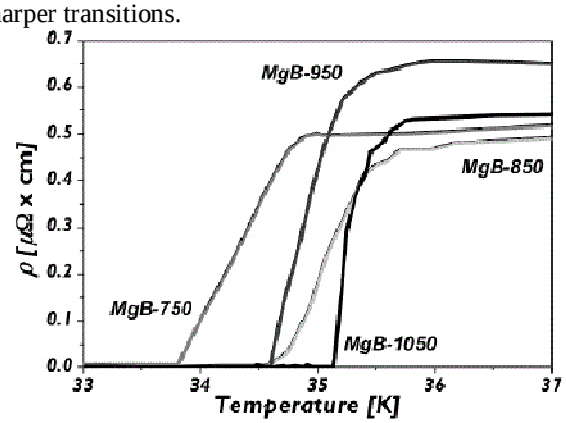

Figure 6.Tc of wire samples, ex-situ manufactured from the four powder samples. Samples synthesized at lower temperatures (MgB-750 and MgB- 850) show broader transitions due to the presence of unreacted Mg. Its content is reduced by synthesis temperature enhancement, and transition aresharper.

IV. CONCLUSION

In With data reported in this paper it has been shown that synthesis temperature can influence grain boundariesmorphology with consequent influence on bulk transport properties. From grain size determination it has been observedthat by enhancing synthesis temperature also grain size is increased. The enhancement is limited, only 100 nm foraverage diameter by enhancing temperature of 300 °C. Best performances in term of current transport have been seenon sample synthesized at 950 °C, that can be taken as the best route to synthesize MgB2 from B produced in ourlaboratory, in order to use MgB2 wires for power application: for the realization of persistent superconducting magnetsJe have to be over 104 A/cm2, value that for sample MgB-950 is achieved under 4 T.

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