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Spark plasma sintering of MgB_2 in the two-temperature route

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ABSTRACT

Superconducting bulks of MgB_2 were obtained by an *ex-situ* two-temperature route applied to spark plasma sintering (SPS). Processing of samples was performed at lower temperatures than previously reported. Samples produced by the two-temperature route show a higher morphological uniformity, a higher density (above 98%), a higher Vickers hardness, and undesirable stronger microscale flux jumps, as indicated by magnetic relaxation measurements when compared to a sample obtained by the one-temperature route (95.3% relative density). At the same time, all sintered samples show approximately constant crystallite size, critical current density, irreversibility field, critical temperature, weight fraction of impurity phases (MgB_4 and MgO), and the amount of carbon accidentally introduced during SPS processing.

1. Introduction

MgB_2 is a promising material for the next generation of superconductivity applications. However, owing to the high volatility of Mg, a severe problem is that the porosity in the bulks is usually high, especially when prepared by the *in situ* reaction between Mg and B. Low density has dramatic consequences on supercurrent-carrying area leading to a low critical current density, J_c [1,2]. It is essential to prepare MgB_2 materials with high densities and improved grain connectivity. In reality, in order to successfully compete with practical Nb-based superconductors, the challenge is to simultaneously achieve a high level densification and to control grain boundaries, disorder/morphology and defects for the enhancement of current-carrying ability of MgB_2 in the absence of additions or substitutions.

Sintering is a complicated process of microstructure evolution, with the main outcome being porosity elimination. However, in polycrystals, accelerated grain growth always accompanies the final-stage sintering. On the other hand, a nanostructured MgB_2 ceramic is of high interest because it is well established that grain boundaries have a strong vortex pinning effect [1]. Therefore, a higher density of boundaries in the volume unit as for a nanostructured ceramic is a powerful strategy to enhance J_c. MgB_2 bulks with high density have been produced mostly by pressure-assisted methods such as hot isostatic pressing (HIP) [3,4], hot pressing (HP) [5,6], and spark plasma sintering (SPS) [7–16]. In general, to obtain a nanostructured ceramic SPS is suitable because it uses high heating and cooling rates impossible to achieve with the other methods. It should be also noted that SPS has some particular features related to pulsed current application that is leading to benefic non thermal effects. Although still not well understood and controversial, literature indicates on formation of hot spots, enhanced surface electro diffusion producing a grain boundaries "cleaning" effect, spark or spark plasma phenomena [17]. Consequences are accelerated sintering, sintering temperature may be lower, and defects possibly useful for vortex pinning in the particular case of superconductors may occur. All these features of SPS allow production of MgB_2 bulks of top quality (Table 1). We note that it is still unclear if thermal conditions are optimum and one can observe that especially maximum temperature in the SPS processing is within a large range. On the one hand, this is due to the processing route, namely *in situ* reactive SPS applied on mixtures of Mg-based powders and B or *ex-situ* applied on MgB_2 powders. For similar pulsed current features, the differences can be due to equipment specifics (most experiments were conducted on German or Japanese SPS machines, but very often they are not specified, see Table 1), size of the graphite die/punches unit, use of a thermocouple or a pyrometer to monitor temperature, the amount of powder to be consolidated. Comparative analysis of the results is also difficult because of different raw materials and due to measurements interpretation. In such circumstances it is of interest to carefully conduct systematic experiments and apply the same equipment and procedures. This may suggest fine optimization processes and in this work we follow this idea.

Dancer et al. [13] found that above a density of 90% in the ex-situ SPS processed samples at 1250 °C there is no need for full

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Table 1
MgB_2 samples without additions obtained by SPS: details of raw materials, processing and results as extracted from literature.

Refs.	Starting material before SPS	SPS machine	Atmosphere/ uniaxial pressure	Heating time or rate/max temp/time other observations	Sample diameter/ thickness or initial powder weight	Final product: density and microstructure	Properties
[7]	Planetary ball milled (SiAlON environment) mixture of MgH_2 (obtained in the lab. from Mg supplied by Chempur, 99.99%) and B amorphous purified in the lab (2.1 wt.% O_2)	Dr. Sinter SPS 515-S, Sumitomo, Japan	Dynamic vacuum/ 40 MPa	6 h/850 °C/ 15 min	15 mm/5–10 mm	By He-gas pycnometer: 2.612 g/cm^3 (99.3%) or 2.59 (98.5%) without considering MgO although it was determined from the chemical analysis; grain size < 5 μm pores < 20 μm	–
[8,9]	MgB_2 supplied by Testbourne Ltd., UK (99.5%, 100 mesh, 3000 ppm C, 1000 ppm Fe)	–	Vacuum of 2.7 Pa/ 30 MPa	–/1250 °C/ 15 min	20 mm/–	>99% in [1] and 97% or 91.2% (2.40 g/cm^3) in [2], (also it is unclear if considering 8% vol. [8] of MgO in the sample) MgO grain size = 480 ± 180 nm [8] MgB_2 grain size = 900 ± 440 nm [8] Pores < 1 μm [8]	T_c = 38.5 K (H = 20 Oe), H_{irr}(0 K)=8.1 T (criterion J_c = 0 A/cm^2)
[10]	MgB_2 supplied by Alfa Aesar (98%)	–	Ar-atmosphere/ 50 Pa	200 °C/min/ 900–1050 °C/ 10–30 min	15 mm/ 10 mm (4.5 g)	By Archimedes: 99% for sample processed at 1000 °C for 30 min or 1050 °C for 10 min	T_c = 38.6 K (H = 100 Oe)
[11]	MgB_2/Fe powder in tube tapes containing a mixture of Mg + B-amorphous	–	Vacuum of10^{-2} Pa/ 40 MPa	–/700–850 °C/ 5–120 min	–	Best results from the density, microstructure and J_c viewpoints are obtained for SPS processing at 800 °C for 15 min	
[12]	Milled for 30 min mixture of Mg (99%, <10 μm) + B-amorphous (96.76%, <3 μm)	–	–/70 MPa (BN coating of the graphite die was used)	100 °C/min/ 600–1200 °C/ 5–20 min	30 mm/–	88% for SPS at 1100 °C for 5 min (densification occurs for SPS above 800 °C). MgB_2 grain size = 300 nm at 700 °C and significant grain growth at higher temperatures.	The highest T_c = 37 K is for SPS sample obtained at 1000 °C for 5 min
[13]	MgB_2 supplied by Alfa Aesar (98%, 325 mesh)	HPD25/1, FCT Systeme GmbH, Germany	Vacuum (5 Pa)/16, 50, 80 MPa	100 °C/min/ 1250 °C/ ~3 min	–	By Archimedes: 97 ± 1% (2.63 g/cm^3) for SPS at 80 and 50 MPa 92% ± 1% (2.52 g/cm^3) for SPS at 16 Pa considering the presence of MgO (7.3–8.6 wt.%).	Vickers hardness: 1050 ± 20 (SPS at 80 MPa) 1100 ± 10 (SPS at 50 Pa) 658 ± 9 (SPS at 16 Pa)
[14]	MgB_2 supplied by Alfa Aesar (98%, 2.3 μm); SEM shows particles of 0.1 μm and aggregates of 2.3 μm	Dr. Sinter SPS 515-S, Sumitomo, Japan	Vacuum (5 Pa)/ 63 MPa	190 °C/min/ 960 °C/280 s. Temp was measured with a thermocouple	1.9 mm/ 3 g	By Archimedes: 91% (2.39 g/cm^3) without considering the occurrence of impurity phases	T_c = 38.2 K (H = 100 Oe)
[15]	MgB_2 as in the Ref. [14]	HPD 5 FCT systeme GmbH, Germany	Vacuum (30 Pa) 95 MPa	160 °C/min/ 1150 °C/ 3 min. Temp was measured with a pyrometer	2 mm/3 g	By Archimedes: 93.2% (2.45 g/cm^3) without considering the occurrence of impurity phases.	T_c = 38.5 K (H = 100 Oe)

elimination of porosity since J_c values from magnetization measurements are not influenced anymore and suggested that microstructural processes begin to be important. To investigate this statement we conducted experiments of two-temperature SPS processing. First, we applied a higher temperature $T1$ for a short time and, then, at a lower temperature $T2$, dwell time was longer. This approach was tested with excellent results on several materials for conventional sintering [18–20]. Wang et al. [18] explained the suppression of the grain growth, while the porosity is eliminated at densities above 90%, because of the higher activation energy of a grain boundary network pinned by triple points and affecting the grain growth than for the grain boundaries that are leading to porosity elimination. Usually the difference ΔT between $T1$ and $T2$ is about 100–150 °C for a non-reactive route. To the authors knowledge only one paper approaches the two-temperature route for MgB_2 synthesis [21]. The paper is however for the *in situ* conventional two-temperature route and ΔT was 440 °C.

In this work, we applied two-temperature route on reacted MgB_2, i.e., the *ex-situ* route. At the same time, we used SPS and the maximum temperature $T1$ was about 100 °C lower than the temperature used by Dancer et al. [13] for a one-temperature SPS route. Apparently, it is possible to compare our results with those from Ref. [13] since SPS machines are of the same type (FCT, Germany) and raw powders are from the same supplier (Alfa Aesar). Lowering the processing temperature is important not only for the suppression of the grain growth, but, perhaps, it is useful to control and virtually to decrease evaporation of Mg during SPS processing. Boiling point of Mg is 1090 °C [21] and, paying attention to the above uncertainties about temperature determination, strong evaporation was noted for SPS processing of MgB_2 above 1050 °C [10] (machine type and temperature measurement device, i.e. thermocouple or pyrometer are not specified). Furthermore, Schmidt et al. [7] reported that peritectic decomposition of MgB_2 into Mg and MgB_4 occurs at 897 °C. Again, a shorter processing time, a lower maximum temperature and a two-temperature sintering might be a useful process to minimize decomposition of MgB_2 and evaporation or oxidation of the free Mg.

2. Experimental

MgB_2 powder (Alfa Aesar, 98% purity), with an average particle size of ~2.3 μm given by the supplier (our SEM images show particles of 0.15–0.3 μm and aggregates of 1–2.5 μm [22], Fig. 1) was