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Field-Assisted-Sintering of MgB_2 superconductor doped with SiC and B_4C

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Field Assisted Sintering Technique (FAST) is currently used to consolidate ceramic, metal and composite powders. This method combines a pulsed electrical current with simultaneous application of an external pressure. In this article we report fabrication by FAST of high density MgB_2 ceramic with addition of 5% SiC and 5% B_4C. The influence of sintering conditions such as temperature and time on bulk density, morphology and superconducting properties of the samples was investigated. All samples had bulk density of more than 90% of the theoretical one and the same critical temperature T_c = 38.5 K from magnetisation measurements. These preliminary results suggest that FAST is a promising method for processing of MgB_2 superconductor.

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1. Introduction

Discovery of superconductivity in MgB_2 at 39 K has generated great interest [1]. MgB_2 has the highest T_c know for non-oxide compounds and differs from metallic superconductors [2].

This material is usually prepared from a mixture of Mg and B in sealed Ta tubes with excess Mg, but these specimens are usually very porous and mechanically weak [3]. To achieve fully dense MgB_2 bulk specimens, other methods from powder metallurgy as hot isostatic pressing [4], high pressure sintering [5, 6], mechanical alloying of Mg and B powders with subsequent hot compaction [7], self-propagating high-temperature synthesis (SHS) [8] have been used.

Doping with various elements or compounds into MgB_2 has been found to enhance the critical current properties [9-11]. In this respect, best results were obtained by using nano-SiC [12,13], SiC whiskers, nanometre Si/N/C [14] and B_4C [15], that showed a positive influence on irreversibility field (H_{irr}) and critical current density J_c under magnetic fields.

Newly developed sintering techniques employing application of electrical field (Field Assisted Sintering Techniques or FAST) are currently used to consolidate ceramic, metal and composite powders [16-21]. These techniques apply at the same time a pulsed electrical current and an external pressure. The pulsed current is claimed to promote electrical discharges at powder particle surfaces, thus activating them for subsequent bonding. The benefit of this activation is in the elimination of surface contaminants and in short densification time. Second aspect is an important advantage since short processing time at high temperatures is necessary to minimize the associated grain growth. This is particularly important in the case of nano-powders. However, the nature of electrical field interaction with powders system is not clear, and it depends on the powder properties.

Recently, spark plasma sintering (SPS) has been applied to achieve fully dense undoped MgB_2 [22]. The method is similar to ours, but considering the fundamental and practical aspects from the previous paragraphs, it would be of interest to study FAST processing and properties of doped MgB_2 ceramic. Based on these results on pure MgB_2, the present work is aimed at production and characterization of FAST compacted MgB_2 samples doped with nanometre SiC and submicron B_4C.

2. Experimental

MgB_2 powder was supplied by Alpha Aesar (average particle size is 2.3 μm), SiC nanopowder from Merck (about 45 nm), and B_4C powder from HC Starck Grade HS type (0.8 μm).

For each experiment about 3 g of MgB_2 powder without or with doping compound was loaded into a graphite die with 1.9 cm diameter punches. Prior to powder loading, MgB_2 and SiC or B_4C were mixed in a 0.95:0.05 molar ratio using a mortar and pestle in argon atmosphere for 30 min. After loading the powder into the die (also in argon atmosphere), samples were processed using a “Dr Sinter” (Sumitomo Coal Mining Co, Japan) sintering machine. Sintering was performed in vacuum (6-15 Pa). The temperature was measured by a thermocouple (type K) placed at half of the thickness of the die wall. A uniaxial pressure of 63 MPa was applied during sintering for all samples. In the FAST apparatus, we used a default 12:2 (on:off) current pulsed pattern. The waveform is not square and, in fact, is composed of several spikes (pulses) separated by a current-free interval [23]. Regardless of the pattern, each pulse has the same period of about $3\cdot10^{-3}$ s. Thus, the pattern of 12:2 has a sequence of 12 pulses "on" and 2 pulses with no current (off). The total time of one sequence (cycle) is about 0.04 s. The operating voltage and the peak current were below 10 V and 1000 A, respectively. The FAST machine also provides shrinkage and shrinkage rate measurements. The FAST processing parameters are shown in Table 1, MB, MBSC and MBBC representing pure MgB_2, SiC-doped and B_4C – dope samples, respectiveluy.

Table 1. The FAST conditions and density data.

Sample	T_{max} (°C)	Heating rate (K/s)	$t_{dwelling}$ (s)	T_d (°C)	Density (g/cm^3)
MB	960	190	280	920	2.39
MBSC	1000	200	120	955	2.37
MBBC	1000	200	160	960	2.08

The density was calculated from measured mass and specimen size using a 0.1 mg Mettler Toledo balance ((AB204-S type) and a 0.001 mm digital Mitutoyo micrometer. X-ray diffraction (XRD) patterns on the FAST-pellets were obtained with a Scintag diffractometer using CuKα radiation. Critical temperature of the samples was estimated from the zero-field-cooling magnetisation curves as the onset point of the superconducting transition. Data were measured between 5 and 46 K under a magnetic field of 20 Oe and by a SQUID-5T magnetometer (Quantum Design).

3. Results and discussion

The density data for the three samples are shown in Table 1. The FAST pellets have bulk densities above 90 % of the theoretical values (Table 1).

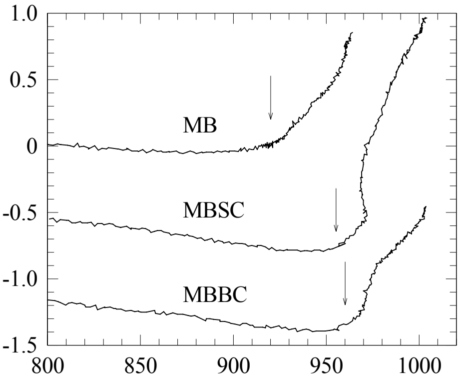

Fig. 1. Displacement (shrinkage) vs. temperature for all samples; MB = MgB_2, MBSC = 0.95 MgB_2:0.05 SiC; MBBC = 0.95 MgB_2:0.05 B_4C.The arrows show the onset temperature (T_d) of the densification process.

For 0.95 MgB_2 + 0.05 B_4C a smaller density is observed because of lack of total chemical reaction between two components, and probably due to a lower sintering temperature. In Fig. 1 the displacement vs. temperature plots for all three types of FAST processed sample are shown.

The onset temperature (T_d) of the densification process is lower for pure MgB_2 sample, and higher for the doped superconductor samples (see Table 1). This T_d value seems to be influenced by the rheological properties of the doping material in the guest matrix (MgB_2) at high temperatures.

The X-ray patterns recorded from undoped, and SiC and B_4C doped MgB_2 after FAST processing are shown in Fig. 2. The XRD pattern for the undoped samples reveals that the main phase is MgB_2 as minor impurities MgB_4 and MgO. Same impurity phases were found also in the doped samples, apparently with the lowest amount in the MBBC sample. The addition of SiC (MBSC sample) leads to formation of an extra impurity phase $MgSi_2$. In the XRD pattern we cannot detect the presence of any (free) SiC, suggesting that there was a reaction between Mg and SiC at chosen temperatures. In addition, the full width at half maximum (FWHM) of the (110) peak (at 2θ = 60.02°) for the SiC-doped sample was larger than that of undoped and B_4C-doped samples. Also, for the SiC-doped sample, as can be observed in Fig. 2, the (110) peak shifts towards higher angles, while no change was observed in the position of the (002) peak (2θ = 51.86°). This reflects the degradation of crystal quality caused by various types of lattice defects or intragranular precipitates which usually act as effective pinning centres [24]. Therefore, a larger J_c value in high magnetic fields is expected for SiC-doped as compared with for the others samples.

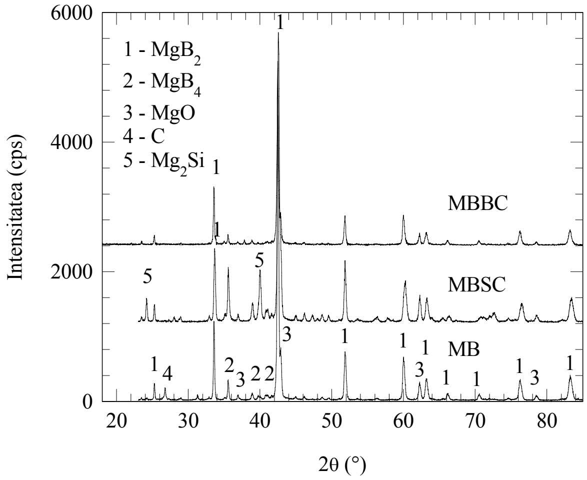

Fig. 2. X-ray patterns for all samples after FAST processing.

The XRD pattern of the B_4C-doped MgB_2 bulk does not show any significant shift in the peaks positions as compared to undoped sample.

From the temperature dependence of dc magnetisation as a function of temperature (Fig. 3), critical temperature T_c (taken as the onset of the superconducting transition) is the same for all the samples, i.e. 38.5 K. Transition width is however different as follows: magnetisation drop saturates at 36.0 K for the undoped sample, to 34.0 K for the MBBC sample, and at 33.5 K for the MBSC sample. Broader transition of the doped samples is attributed to the dopant incorporation into the MgB_2 structure.

In the case of SiC-doping, the reaction between Mg (from MgB_2) and SiC to form Mg_2Si results in the substitution of B by C in the MgB_2 structure. This mechanism was proposed in ref. [25]. Hence, the resulting MgB_2 will be C-substituted and with a higher amount of impurities, due to formation of Mg_2Si.

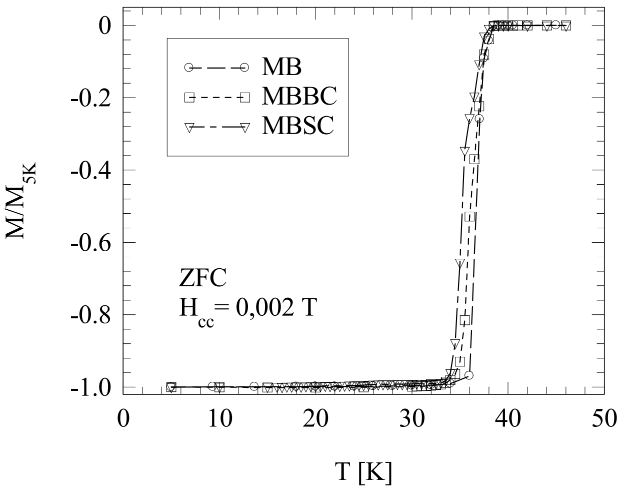

Fig. 3. Reduced magnetisation curves vs. temperature of the samples after FAST processing.

This scenario is in good agreement with our XRD data, namely broadening and shifting of the XRD peaks and a higher amount of impurity phases with occurrence of Mg_2Si phase, as observed in Fig. 2. In these circumstances there is no surprise that the transition width of SiC-doped MgB_2 is the largest among the investigated samples.

The larger width of transition for the MBBC sample than for the un-doped sample is suggesting that addition of B_4C is influencing the quality of MgB_2. However, the influence is lower than in the case of SiC-doping and both magnetisation and XRD data support this observation. Larger transition width for the B_4C-doped sample than for the undoped MgB_2 sample was suggested [26] to be due to the low level substitution of B by C as compared with Si-C doped sample.

4. Conclusions

Samples of MgB_2 undoped and doped with SiC and B_4C were produced by FAST. The effects of FAST consolidation on crystalline structure, impurity phases, superconducting transition and bulk density were investigated. It was found that samples have the same onset T_c = 38.5 K and bulk density above 90% of the theoretical one. Superconducting transition width, impurities and crystal quality were different depending on the doping. Samples are relatively large, 1.9 cm in diameter, uniform and can be easily extracted from the die. Processing times are short for easily attainable and relatively low temperatures. We conclude that these preliminary data are promising for future application.

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References

[1] J. Nagamatsu, N. Makagawa, T. Muranaka, Y. Zenitani, J. Akimitsu, Nature (London) **410**, 63 (2001).
[2] H. J. Choi, D. Roundy, H. Son, M. L. Cohen, S. G. Louie, Nature **418**, 758 (2002).
[3] S. L. Bud'ko, G. Lapertot, C. Petrovic, C. E. Cunningham, N. Anderson, P. C. Canfield, Phys. Rev. Lett. **86**(9), 1877 (2001).
[4] T. C. Shields, K. Kawano, D. Holdom, J. S. Abell, Supercond. Sci. Technol. **15**, 202 (2002).
[5] Y. Togano, H. Takeya, H. Fujii, H. Kumakura, T. Hatano, K. Togano, H. Kito, H. Ihara, Appl. Phys. Lett. **78**(19), 2914 (2001).
[6] A. Handstein, D. Hinz, G. Fuchs, K. -H. Muller, K. Nenkov, O. Gutfleish, V. N. Narozhnyi, L. Schulz, J. Alloys Comp. **329**, 285 (2001).
[7] A. Gumbel, J. Eckert, G. Fuchs, K. Nenkov, K.-H. Muller, L. Schulz, Appl. Phys. Lett. **80**, 2725 (2002).
[8] W. J. Feng, T. D. Xia, T. Z. Liu, W.J.Zhao, Z. Q. Wei, Physica C **425**, 144 (2005).
[9] S. Ueda, J. I. Shimoyama, A. Yamamoto, S. Horii, K. Kishio, Supercond. Sci. Technol. **17**, 926 (2004).
[10] O. Perner, J. Eckert, W. Hassler, C. Fischer, K. H. Muller, G. Fuchs, B. Holzapfel, L. Schultz, Supercond. Sci. Technol. **17**, 1148 (2004).
[11] B. J. Senkowicz, J. E. Giencke, S. Patnaik, C. B. Eom, E. E. Hellstrom, D. C. Larbalestier, Appl. Phys. Lett. **86**, 202502 (2005).
[12] S. X. Dou, S. Soltanian, J. Horvat, X. L. Wang, S. H. Zhou, M. Ionescu, H. K. Liu, P. Munroe, M. Tomsic, Appl. Phys. Lett. **81**, 3419 (2002); S. X. Dou, V. Braccini, S. Soltanian, R. Klie, S. H. Zhu, S. Li, X. L. Wang, D. C. Larbalestier, J. Appl. Phys. **96**, 7549 (2004); S. Soltanian, X. L. Wang, J. Horvat, S. X. Dou, M. D. Sumption, M. Bhatia, E. W. Collings. P. Munroe, M. Tomsic, Supercond. Sci. Technol. **18**, 658 (2005).
[13] H. Yamada, M. Hirakawa, H. Kumakura, A. Matsumoto, H. Kitaguchi, Appl. Phys. Lett. **84**, 1728 (2004).

[14] X. Jiang, Y. Ma, Z. Gao, Z. Yu, C. Nishijima, K. Watanabe, Supercond. Sci. Technol. **19**, 479 (2006).

[15] A, Yamamoto, J. Shimoyama, S. Ueda, I. Iwayama, S. Horii, K. Kishio, Superc. Sci. Technol. **18**, 1323 (2005).

[16] J. R. Groza, in “Powder Metallurgy”, ASM Handbook, Vol. 7, Materials Park, OH, p. 583. (1998).

[17] M. Omori, Mater. Sci. Eng. A **287**, 183 (2000).

[18] M. Tokita, Mater. Sci Forum, **308-311**, 83 (1999).

[19] D. S. Perera, M. Tokita, S. Morricca, J. Eur. Ceram. Soc. **18**, 401 (1998).

[20] E. M. Carrillo, C. Unvar, J. C. Gibeling, G. H. Paulino, Z. A. Munir, Scr. Mater. **45**, 405 (2001).

[21] C. Gras, F. Bernard, F. Chalot, E. Gaffet, Z. A. Munir, J. Mater. Sci. **17**, 542 (2002).

[22] S. Y. Lee, S. I. Yoo, Y. W. Kim, N. M. Hwang, D. Y. Kim, J. Am. Ceram. Soc. **86**, 1800 (2003).

[23] W. Chen, U. Anselmi-Tamburini, J. E. Garay, J. G. Groza, Z. A. Munir, Mater. Sci. Eng. A **394**, 132 (2005).

[24] A. Yamamoto, J. Shimoyama, S. Ueda, Y. Katsura, I. Iwayama, S. Horii, K. Kishio, Appl. Phys. Lett. **86**, 212502 (2005).

[25] C. H. Jiang, T. Nakane, H. Kumakura, Supercond. Sci. Technol. **17**, 521 (2005).

[26] J. Kortus, O. V. Dolgov, R. K. Kremer, A. A. Golubov, Phys. Rev. Lett. **94**, 027002 (2002).

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