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Disordered nanocrystalline superconducting magnesium diboride: A significant improvement in in-field critical current density

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Nanocrystalline superconducting MgB_2 bulks were prepared by high pressure sintering of ball milled MgB_2 powders. A significant improvement in the in-field critical current density J_c has been obtained in the bulk sintered at 700 °C. The value of J_c reaches as high as 10^5 A cm^{-2} at 5 K, 8 T and 10^4 A cm^{-2} at 15 K, 6 T. Intragranular defects and a large number of grain boundaries acting as pinning centers are both responsible for the higher J_c.

Keywords: Metallic superconductors; Borides; Nanocrystalline materials; Ball mill; High pressure technique

There is growing concern over the enhancement of superconducting properties of MgB_2, with a transition temperature T_c of 40 K [1], as it shows promising potential for practical applications in the temperature range 15–25 K, readily accessible with cryocoolers. However, the critical current density J_c, which is crucial for practical applications, drops rapidly with increasing magnetic field, mainly due to a lack of natural flux pinning centers. MgB_2 has a relatively larger coherence length ξ of ~65 Å, suggesting that nanoparticles with a size close to 2ξ in MgB_2 can act as effective pinning centers. Numerous efforts have been made to improve J_c via doping, with nano-SiC particles proving to be the most effective and repeatable dopant [2–5]. However, agglomeration of the nanodopant can result in inhomogeneous MgB_2. Therefore, it is of great importance to improve the J_c performance of undoped MgB_2 without using an expensive nanoparticle dopant. Grain boundaries have been shown to be one of the most important pinning centers in MgB_2 and not to be obstacles to current flow [6]. This provides a clue to obtain a high J_c in MgB_2 with smaller grain size by inducing a large number of grain boundaries to act as flux pinning centers. Accordingly, the synthesis and investigation of MgB_2 with nanostructural particles, wires, thin films and bulks have been reported by several groups [7–11]. As we know, high temperature sintering benefits the consolidation of grains but also causes rapid grain growth. Low temperature sintering of elemental Mg and B, below the melting point of Mg, has been shown to result in grain refinement at the expense of a very long time to ensure complete reaction [12]. Therefore, there is still a great challenge to achieve highly dense MgB_2 bulks with nanoscale grains.

In this work disordered nanocrystalline MgB_2 bulks were prepared by high energy ball milling and high pressure sintering. According to the literatures MgB_2 powders with smaller grain sizes could be achieved by ball milling Mg + B powders [11,13–16]. However, fine Mg + B powders are highly reactive, making MgO and B_2O_3 formation easy [14,15]. Here, instead of Mg + B powders commercial MgB_2 powders (Alfa-Aesar) were used as the raw material. The ball milling process was performed in a high energy ball mill with a tungsten carbide (WC) vial using 8 mm diameter WC balls under a purified argon gas atmosphere. The ball to powder mass ratio was 10:1, and the milling speed was 400 rpm. High pressure sintering is beneficial for preparing highly dense bulk materials without excessive grain growth. The milled powders were then pressed into pellets and wrapped in Ta foil. The pellets were about 6 mm in

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diameter and 3 mm in height. Finally, the samples were sintered in a six anvil apparatus at temperatures of 500–900 °C for 30 min under a high pressure of 5 GPa.

Phase analyses of the samples were performed using X-ray diffraction (XRD). The structural parameters and phase content were determined by X-ray Rietveld analysis. The grain size and lattice strain were deduced from the XRD data using the Williamson–Hall method [17]. The morphology and microstructure of the samples were investigated by field emission scanning electron microscopy (FE-SEM) and transmission electron micros copy (TEM). Superconducting properties were obtained using a Quantum Design Physical Properties Measurement System (PPMS-9). J_c values were calculated from the width of the magnetization hysteresis loops (ΔM) based on the Bean's critical state model [18]. Flux pinning force F_p was calculated using the equation $F_p = \mu_0 H J_c$.

Figure 1a and b present the FE-SEM images of MgB_2 powders before and after 200 h ball milling, respectively. The initial MgB_2 particles had a platelet-like morphology with sizes in the range 0.5–2 μm (Fig. 1a). After ball milling for 25 h the particles became round and agglomerated together (not shown here). After further milling for 200 h the granular particles became cold welded to each other and could not be well dispersed, as shown in Figure 1b. A typical TEM image together with the selected area electron diffraction (SAED) pattern for the 200 h milled powders are shown in Figure 1c. It can be seen that a large cluster consists of many overlapping nanosized particles with a typical size of less than 20 nm. The presence of closed rings in SAED pattern also indicates a very small grain size of the powders. Figure 1d gives the Rietveld refinement XRD patterns of the as-milled MgB_2 powders (200 h) and bulks, respectively. For the as-milled powders the hexagonal structure of MgB_2 was maintained and the higher background observed under the main peaks provides evidence for partial amorphization. The calculated average grain size and the lattice strain for 200 h milled powders were 7 nm and 1.2%, respectively. Due to the aggregation of grains the calculated grain size is slightly less than that observed in the TEM image. As we know, one of the major disadvantages associated with ball milling is contamination by the milling tools. However, in this work the intensity of WC diffraction peaks is very low and the content of WC is only about 0.3 wt.%, which is far lower than in a previous report [11]. For bulk samples a systematic decrease in the width of the MgB_2 peaks was observed with increasing sintering temperature (XRD pattern for the 500 °C bulk not shown here), indicating improved crystallinity and grain growth. The calculated average grain sizes (lattice strain) are 10 (1.0%), 20 (0.7%) and 90 nm (0.5%) for the bulk sintered at 500 °C, 700 °C and 900 °C, respectively. There is no measurable change in the lattice parameters with sintering temperature, indicating an absence of substitution of carbon for boron during the sintering process. For example, the lattice parameters of the 900 °C bulk are $a = 3.0844$ Å and $c = 3.5220$ Å, which are in good agreement with the previous reported values for Alfa-Aesar MgB_2 [19]. The content of MgO estimated from the Rietveld refinement increased slightly from 2 wt.% for the 500 °C bulk to 3 wt.% for the 900 °C bulk.

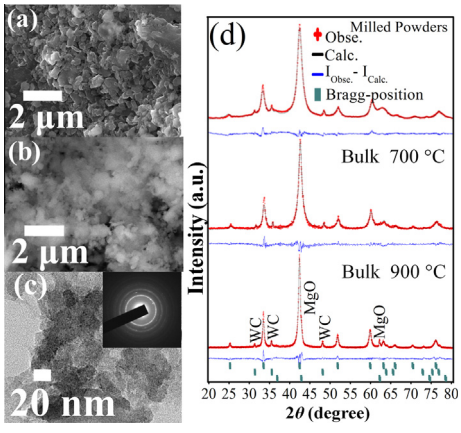

Figure 1. FE-SEM images of (a) initial powders (b) 200 h milled powders. (c) TEM image and corresponding SAED pattern (inset) for the 200 h milled powders. (d) XRD spectra together with the Rietveld refinement patterns for the milled powders and bulks. The bars show the positions of Bragg reflections for the three phases of MgB_2, WC, and MgO from top to bottom, respectively. The weighted residual error $R_{wp} = 6.64\%$, 13.63%, and 14.10%, respectively.

Figure 2a shows the magnetic $J_c(H)$ curves at 5, 15 and 20 K for the MgB_2 bulk samples sintered at different temperatures. The values of self-field J_c are above 10^5 A cm^{-2} for all samples. Clearly, the field dependence of J_c shows many differences for samples sintered at different temperatures. The highest J_c value at 1 T and 5 K exceeded 10^6 A cm^{-2} for the bulk sintered at 900 °C. In particular, the bulk sintered at 700 °C exhibited a significant improvement in J_c under higher fields ($H > 4$ T) at 5 and 15 K. For example, J_c (8 T and 5 K) for the bulk sintered at 700 °C is one order of magnitude higher than that of the bulk sintered at 900 °C. Quantitatively, the J_c for the 700 °C bulk reached 3.1×10^5 A cm^{-2} at 8 T and 5 K, which is competitive with a MgB_2 thin film with a grain size of 10 nm [10], and one order of magnitude higher than that of SiC-doped MgB_2 bulk [2–5]. Further, the J_c value was still of the order of 10^4 A cm^{-2} up to 6 T at 15 K for the 700 °C bulk, which is an order of magnitude higher than that of the 900 °C bulk and is comparable with nanocrystalline MgB_2 thin films [10] and SiC-doped MgB_2 bulks at 6 T and 10 K [3]. At

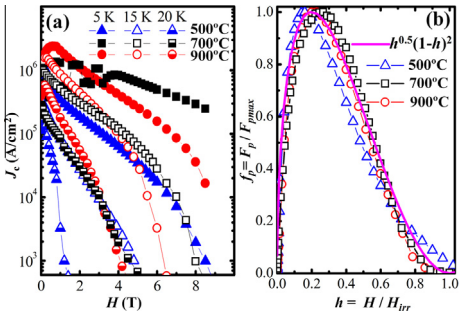

Figure 2. (a) Magnetic $J_c(H)$ curves at 5, 15 and 20 K. (b) Normalized volume pinning force $f_p = F_p/F_{pmax}$ versus the reduced field $h = H/H_{irr}$ at 15 K for the bulk materials.