Self-Propagating High Temperature Synthesis of MgB₂ Superconductor in High-Pressure of Argon Condition

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Article info

Abstract

Magnesium diboride can be synthesized under argon ambient, elevated or high pressures. High-pressure syntheses are promising methods for manufacturing of the bulk MgB_2 superconductor material. We have been used high pressure of Ar gas in order to investigate its effect on properties of MgB_2 superconductor such as critical temperature and current density. Bulk MgB_2 superconductor was synthesized from elemental Mg–B powders in thermal explosion mode of self-propagating high-temperature synthesis (SHS) under argon pressure of 25 atm. XRD pattern of the as-synthesized product indicates an almost complete conversion of the reactants to the MgB_2 single phase. Most of the diffractions peaks are related to the MgB_2 polycrystalline bulk material. The impurity fraction is less than 24.3% in total sample and identified as MgO and MgB_4 secondary phases. The positive effect of pressure of Ar gas during synthesis of MgB_2 on critical current density J_C has been confirmed. The critical current density of the sample was achieved in high pressure reactor was 3.8×10^6 A/cm². A superconducting volume fraction of 16% under a magnetic field of 10 Oe was obtained at 5 K, indicating that the superconductivity was bulk in nature. The succeeded level of superconductor parameters of the high-pressure synthesized MgB_2 and the possibility to produce a large bulk products make this technology very promising for practical applications.

1. Introduction

The superconductivity in MgB_2 was first announced by Akimitsu group [1] at a remarkably high critical temperature of 39 K for its simple hexagonal structure. Since 2001 there has been a renewed interest developing MgB_2 superconducting properties due to the two-gap mechanism of superconductivity. The MgB_2 is usually produced by reaction of fine magnesium and boron powders, thoroughly mixed together and heated at a temperature around or above the melting point of pure magnesium (> 600 °C). Following this process, the resulting MgB_2 phase presents a powder nature, with particle size distribution related to the size of the precursor's mixture [2–3], and typically lying in the range of 0.1–10 microns. In type II superconductors, as MgB_2, the intensity that the magnetic flux lines are pinned in the materials defines the maximum critical current density that the material can carry under a certain applied magnetic field (H). The pinning is due to defects in the superconducting material, which comprise: precipitates of normal phases (or with distinct properties when compared to the superconducting phase), grain boundaries, dislocations, or other heterogeneities of the superconducting matrix [4–5].

MgB_2 has a transition temperature T_c of about 40 K, the highest in conventional superconductors and nearly two times the previous record in such superconductors. The crystal structure of MgB_2 which consists of honeycombed boron layers and magnesium layers located in between the boron layers. The hexagonal unit cell has the lattice parameters a = 3.086 Å and c = 3.524 Å [1]. Reaction synthesis of bulk MgB_2 directly from the elemental powders via the $Mg + 2B \rightarrow MgB_2$ reaction seems an attractive alternative to the existing methods

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of processing this material. Since the reaction of MgB$_2$ formation is accompanied by a large negative volume change (~ 25%), the final product is expected to be porous if no external pressure is applied. The synthesis reaction may proceed in the isothermal, diffusion-controlled regime or in a non-isothermal, self-sustained manner. The process is called SHS, or combustion synthesis [6–7]. The term SHS is used to describe processes where initial reactants ignited and thermal front propagates to spontaneously transform into products due to the exothermic heat of reaction. While the advantages of SHS include very high reaction rates and elimination of the need for high temperature furnaces due to self-generation of heat, its major limitation is the high porosity of combustion products. In the present paper, a single-step SHS synthesis of MgB$_2$ employing thermal explosion under high pressure of argon is reported. Earlier, such approach was successfully used for the fabrication of MgB$_2$ with high critical current density in Ar atmosphere [8]. The aim of the present investigations is to find effect of the high-pressure conditions of synthesis MgB$_2$ materials on high critical current density and to study the correlations between the materials structure and properties. We succeeded in the synthesis of MgB$_2$ – based materials with critical current density (J$_C$) higher than those reported by Kijoon H.P. Kim et al. [9] and A. Serquis et al. [10].

2. Experimental

The available high-pressure apparatuses (Fig. 1) with 45 cm^3 working volume can allow us to obtain the bulk MgB$_2$. The main element of the setup is a thick walled metallic spherical reactor vessel without welded seams, with a wall thickness of 60 mm and a capacity of 45 l. Corps is mounted on a metal frame, made of corner 60×60 mm, and provided with an upper and a lower cap which fasten with nuts on eight studs 35 mm in diameter. For the thermocouple wires and the power supply are installed in the bottom cover current fittings. Filing and release of argon is carried out through a flexible high-pressure hoses fitted with quick connections (manufacturer "HANSA FLEX HIDRAVLIK ALMATY"), which are mounted on the top cover. A tubular heating furnace is placed inside high pressure reactor that allows preheating the sample to 1000 °C. The heater furnace is made of an alundum tube with diameter of 70 mm and a height of 250 mm and wound on its of a nichrome

wire with a diameter of 2 mm. The furnace power was 1.2 kW. For the control of measurements of temperature change of SHS processes are used computer desk setting of temperature. The method of direct measurements of signals from thermocouples installed inside the reactor, passed through an electrically conductive stoker of a bottom cover on the shielded wire to the system LTR-U-1 module and sub-module LTR27 H-27T (L-CARD).

Magnesium diboride was synthesized from the following powder reactants: metallic magnesium (>98.0% purity), amorphous boron (94% purity). Powders blended in stoichiometric proportions (55.3% Mg and 44.7% B) were dry homogenized. The homogeneous powder mixture was compacted under a pressure of 40 t to obtain tablets 30 mm in diameter and 15 mm in thickness. High-pressure of argon up to 25 atm has been created inside the reactor. The tablet samples were ignited by heating tubular furnace (Fig. 1) which is located in high pressure reactor. Self-sustaining synthesis was initiated at about 650 °C. The maximum combustion temperature increased up to 1100 °C and the reaction was completed after 3 s.

The composition and crystal structure of the product at room temperature were evaluated by X-ray diffraction (XRD) with CuK$_\alpha$ radiation (λ = 1.54056 Å). The particles morphological features and microprobe analysis were determined by thermal field emission Scanning Electron Microscopy (SEM, Jeol-7100F). The sample magnetization over a broad range of temperatures (1.9–300 K) and magnetic field up to 9 Tesla are carried out with a Quantum Design PPMS EverCool-II system having Vibrating Sample Magnetometer (VSM) attachment.
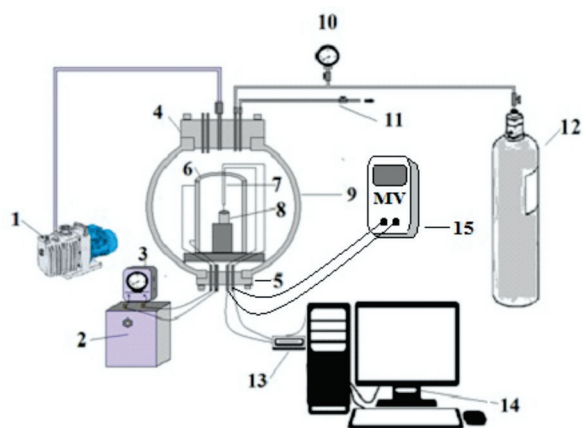

Fig. 1. High pressure reactor: 1 – compressor; 2 – transformer; 3 – ampermeter; 4 – top cover; 5 – bottom cover; 6 – tubular furnace; 7 – thermocouples; 8 – sample; 9 – main body; 10 – manometer; 11 – valves; 12 – gas; 13 – data registering machine LTR-U-1; 14 – computer.

3. Results and Discussion

The thermodynamic estimation of the equilibrium composition of multicomponent multiphase systems requires minimization of the thermodynamic free energy (G) subject to mass and energy balances [11]. The thermodynamic calculations were made using "Thermo" software [12], which includes database with thermochemical properties of approximately 3000 compounds. We used additionally the thermo-chemical computer code HSC Chemistry-7 for prediction of the adiabatic temperature and equilibrium compositions [13]. The Fig. 2 shows adiabatic temperature and end product composition dependence on boron content (moles) in the Mg-nB system. While increasing the boron concentration up to the stoichiometry point (n = 2), the solid amount of MgB_2 (S) and adiabatic temperature gradually increase up to a maximum ~1600 K. At this point, the only product observed was the magnesium diboride. The small plateau of temperature curve at n = 1.4–1.8 was observed due to liquid Mg converting to Mg vapor. When n was increased from 2 to 4, MgB_2 (S) phase starts to decrease by converting in to MgB_4 (S), which completes at n = 4. Further increase of boron concentration results in transformation of MgB_4 (S) to MgB_{12} (S).

XRD pattern of the as-synthesized product shown in Fig. 3 indicates an almost complete conversion of the initial reactants to the MgB_2 single phase. Most of the diffractions peaks are related to the MgB_2 polycrystalline bulk material. The impurity fraction was less than 24.3% in total sample and identified as MgO and MgB_4 secondary phases. A least-squares fit of the hexagonal structure yields the following lattice parameters a = 3.0834 Å and c = 3.5213 Å with c/a ≈ 1.1420. These values are in a good agreement with published lattice constant a = 3.086 Å and c = 3.524 Å [1].

The typical morphology of as – prepared polycrystalline bulk MgB_2 sample is shown in Fig. 4. The product consist heterogeneously distributed grains having well connected particle conglomerates. In general, the high density MgB_2 samples with less voids exhibits high superconducting homogeneity and strong intergranular current flow [14–16]. The average sizes of MgB_2 particles as determined by the SEM images (Fig. 4) were noted to be about 20 μm. The fact, the preparation of dense MgB_2 bulk superconducting material through the single-step SHS process under Ar gas pressure is beneficiary to enhance the critical current density, J_C. The lower limit for the average crystallite size can be determined from the half width of the
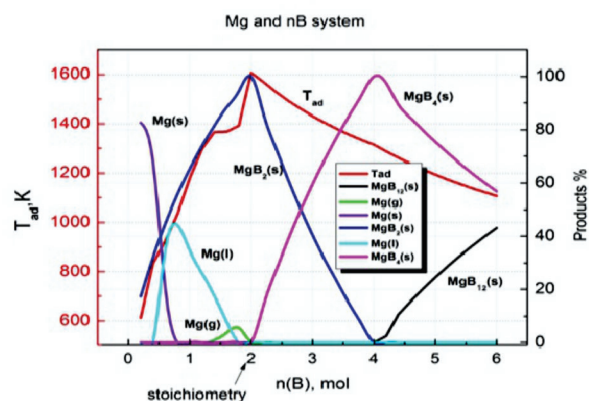

Fig. 2. Dependence of the adiabatic temperature and equilibrium concentration of condensed and gaseous phases during the exothermic reaction on boron concentration in the Mg-nB system (red line is adiabatic combustion temperature).
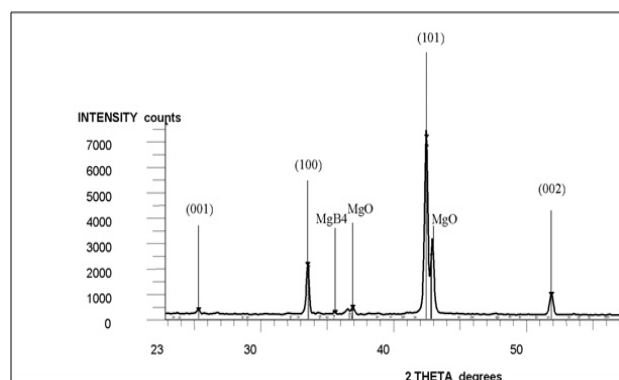

Fig. 3. X-ray diffraction pattern of MgB_2 obtained under 25 atm of argon pressure.
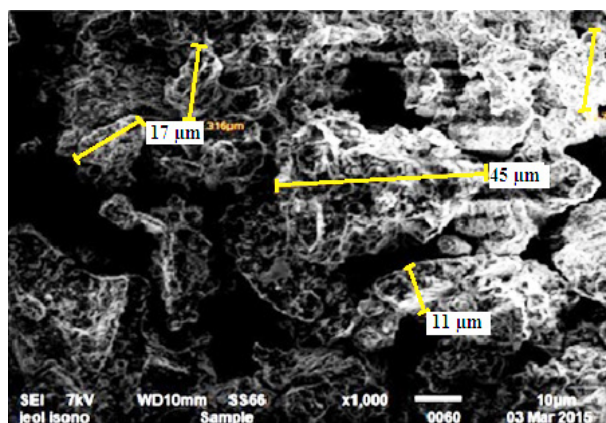

Fig. 4. Typical SEM image of MgB_2 microstructure produce by SHS method under high pressure argon environment.

diffraction peaks using the Debye-Scherer formula [17, 18]. $D = \alpha * \lambda / (\beta * \cos \theta)$, where D is the mean particle size, α is a geometrical factor (= 0.94), λ is the X-Ray wavelength (=1.54056 Å), β is the half width of the diffraction peak, and θ the angular

position of the diffraction peak. By analyzing the (100) peak we obtain D = 10.84 μm. These values are lower than the mean particle sizes estimated by SEM analysis, indicating that the particles are polycrystalline agglomerates of much smaller crystallites. The general behavior of magnetization for as-synthesized MgB$_2$ sample is very similar to that of conventional MgB$_2$ superconductor polycrystalline materials [1]. The negative signals in the zero-field-cooled (ZFC) curve clearly indicate a SC state with an onset transition temperature at T$_C$ = 39 K. Figure 6 shows typical hysteresis loop for MgB$_2$ superconductor material.

Calculating critical current density J$_C$ of sample: we were estimated the value of critical current density J$_C$ of obtained sample using the magnetization hysteresis loop and calculated final data by Bean's critical model formulas. A Bean's critical state model formula:

$$J_C = 30 * \Delta M / d \qquad (1)$$

$$\Delta M = (M^+ - M^-) \qquad (2)$$

ΔM is the hysteresis of magnetization per unit volume (emu/cm^3), d is a mean size of particles.

In our case, average size of sample was d = 2*10^{-3} cm and by using formula (1) we have been estimated the value of critical current density of J$_C$ = 6.939×10^6 A/cm^2.

Fig. 5. ZFC (solid symbols) and FC (open symbols) magnetization curves for as prepared MgB$_2$ sample. Inset: Magnetization curves in enlarged temperature scale.

Calculating of superconducting volume fraction (SCF) of sample: The superconducting volume fraction of the sample was obtained using the equation:

$$SCF = -4\pi M \rho/H, \text{ same as: } SCF = [(\Delta M/\Delta H) / (1/4\pi)] \times 100\% \qquad (3)$$

where ΔM = M2-M1, ΔH = (H2-H1), we have been estimated the value of SCF that was equal to be 16%. This value of superconducting volume fraction at a magnetic field of 10 Oe and 5 K indicates that the superconductivity is bulk in nature.
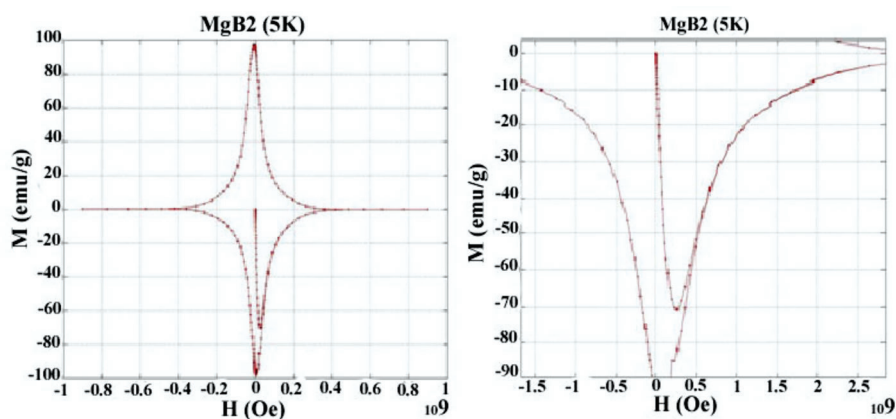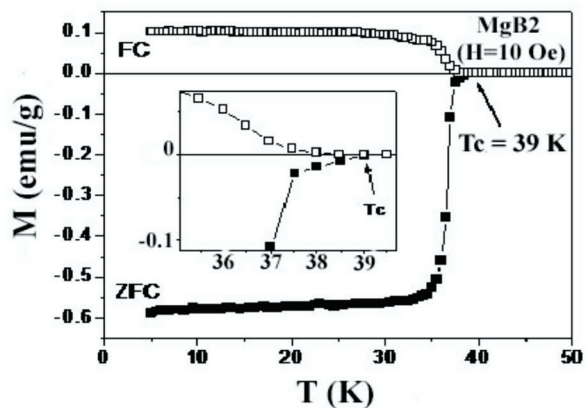

Fig. 6. Hysteresis loop of MgB$_2$ at 5 K.

Conclusions

The positive effect of pressure of argon during synthesis of MgB$_2$ on critical current density J$_C$ has been confirmed. The critical current density up to 3.8×10^6 A/cm^2 was obtained for MgB$_2$ in high pressure reactor. The possibility to produce large bulk MgB$_2$ products during the high pressure SHS process makes this technology very promising for practical applications.

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