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Processing of dense bulk MgB_2 superconductor via pressure-assisted thermal explosion mode of SHS

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Abstract

Bulk MgB_2 superconductor was synthesized from elemental Mg–B blends employing Reactive Forging (RF)—thermal explosion mode of Self-propagating High-temperature Synthesis (SHS)—under a moderate pressure of 200 MPa. RF of the stoichiometric Mg–2B blend conducted at 800 °C yielded near-single-phase albeit porous (92% TD) MgB_2, whereas RF at 1000 °C produced a fully dense material containing significant amounts of MgO and MgB_4. The addition of 20–30 wt.% Mg to the starting blend improved material's consolidation behavior at 800 °C, as well as hindered the formation of MgB_4 at 1000 °C. For all the compositions and RF conditions, the combustion temperature, T_{comb} of approximately 1200 °C was measured. Plastic deformation at T_{comb} of the ductile MgO phase and/or residual Mg resulted in full density consolidation of the synthesized material. In all the specimens, a superconducting transition was observed at 39 K regardless of their porosity and the amount of second phases. Above 39 K, the electrical resistivity of dense MgB_2 specimens with residual metallic magnesium was 30 times lower than that of the 92% dense near-single-phase MgB_2.

Keywords: Self-propagating High-temperature Synthesis; Pressing; Borides; Superconductivity; Microstructure-final; MgB_2

1. Introduction

Since the discovery of 39 K superconductivity in magnesium diboride (MgB_2) was first announced by Akimitsu and coworkers[1] this simple binary compound has been the focus of scientific attention. A great number of papers investigating the superconductive properties of MgB_2 have been published, however no convenient route of processing dense bulk MgB_2 has been proposed. Bulk MgB_2 is typically produced by consolidation of MgB_2 powder. To achieve high density, the material is hot pressed at high pressure and temperature for several hours, e.g. 1 GPa at 800 °C for 1–5.5 h,[2] 3 GPa at 950 °C for 2 h,[3] 3.5 GPa at 1000 °C for 2 h,[4] and even 6 GPa at 950 °C for 0.5 h.[5] Although reasonably dense laboratory specimens were obtained under above conditions, the realization of the MgB_2 potential as a material for various practical applications requires the development of more simple and cost-effective processing techniques.

Reaction synthesis of dense MgB_2 directly from the elemental powders via the $Mg + 2B \rightarrow MgB_2$ reaction seems an attractive alternative to the existing methods 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. In the latter case, the process is called Self-propagating High-temperature Synthesis (SHS), or combustion synthesis.[6,7] The term SHS is used to describe processes where initial reactants, when ignited, 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. To the best of our

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knowledge, only one attempt to synthesize MgB_2 by SHS was reported,[8] however again, the standard approach of processing a porous "cake", crushing it into powder and consolidation by conventional hot pressing was used. In the present paper, a single-step SHS synthesis of dense bulk MgB_2 employing thermal explosion under a uniaxial pressure—Reactive Forging (RF), is reported. Earlier, such approach was successfully used for the fabrication of a number of dense ceramics and composites.[9,10]

2. Experimental

In the present work, fine Mg (<44 μm) and B (∼5 μm) powders from CERAC were used. The powders were mixed in the 1-to-2 atomic ratio to yield MgB_2. In addition, two Mg-rich blends (Mg–2B + 20 or 30 wt.% Mg) were prepared. All the blends were attrition milled in a dry argon atmosphere for 1 h, with 5:1 balls-to-powder weight ratio. The blends were compacted into ∼90% dense 15 mm thick tablets of 18 mm diameter at 600 to 1000 MPa.

The synthesis of MgB_2 was accomplished employing thermal explosion under a uniaxial pressure RF. Compacts were placed between preheated to 800 or 1000 °C rams of an Instron testing machine (Fig. 1). A low pressure of 0.5 MPa was applied to provide a good contact between the compact and the rams. Rapid heating of the compact from the hot rams resulted in the ignition of the self-sustained $Mg + 2B \rightarrow MgB_2$ reaction in thermal explosion mode. Temperature during Reactive Forging was measured by a W–3Re/W–25Re thermocouple (d = 0.2 mm) placed into a drill hole in the middle of the specimen (Fig. 1). A computer card (National, Ltd.) provided accurate temperature monitoring (±2.5 °C) with time resolution of 0.001 s. For densification the MgB_2 product, a moderate pressure of 200 MPa was applied immediately after thermal explosion and released after ∼1 min. More details about Reactive Forging can be found elsewhere.[9,10] The process was performed in open air.

The microstructure and phase composition of the reactant blend and synthesized material were characterized employing X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive analysis (EDS) and high resolution SEM (HRSEM). The density of RF specimens was measured by the method based on Archimedes principle. Electrical resistivity of the obtained materials was measured by the standard four-point probe technique in a liquid nitrogen and then in a liquid helium.

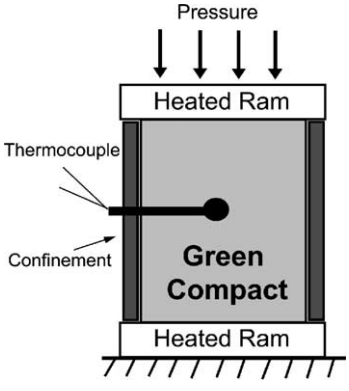

Fig. 1. A schematic of Reactive Forging.

3. Results and discussion

3.1. Stoichiometric Mg + 2B blend

3.1.1. Reactive Forging at 800 °C

A representative heating curve of a Mg + 2B compact during Reactive Forging at 800 °C is shown in Fig. 2 (curve a). It can be seen that thermal explosion (TE) in the specimen was ignited at 650 °C (the melting temperature of Mg), and the maximum combustion temperature reached, T_{comb} was ∼1200 °C. A wide plateau corresponding to the melting of magnesium has been recorded suggesting that a large fraction of Mg was in the liquid state by the time TE was ignited.

According to the results of XRD analysis, Fig. 3(a), full conversion of the Mg and boron reactant powders occurred during thermal explosion, the final product being an almost pure MgB_2. In addition to MgB_2, the XRD pattern in Fig. 3(a) contains small peaks of magnesium oxide, MgO, most probably the product of reaction between Mg and B_2O_3 that is always present on B powder particles. In the corresponding SEM micrograph, Fig. 5(a), the MgO phase can be seen as thin white stripes. Taking into account that Reactive Forging is conducted in open air, the amount of MgO is surprisingly low. It is assumed that the melting of Mg prior to thermal explosion effectively "seals" the Mg–B specimen preventing the penetration of atmospheric oxygen and its reaction with Mg. In the matrix of the specimen reactively forged at 800 °C (Fig. 5(a)), which is largely MgB_2, a few regions of a darker contrast are revealed. Compared to MgB_2, these regions con-

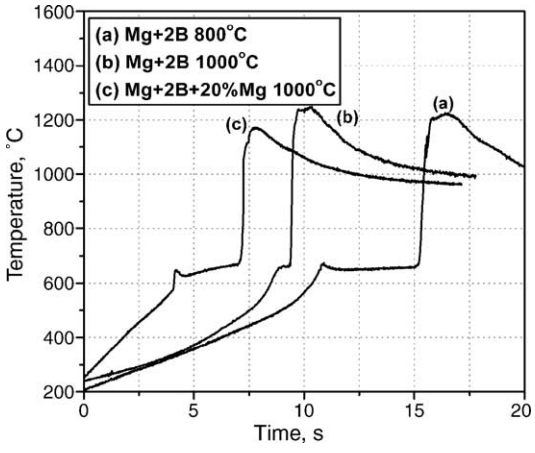

Fig. 2. Temperature evolution curves recorded during Reactive Forging at T_{ram} = 800 and 1000 °C.

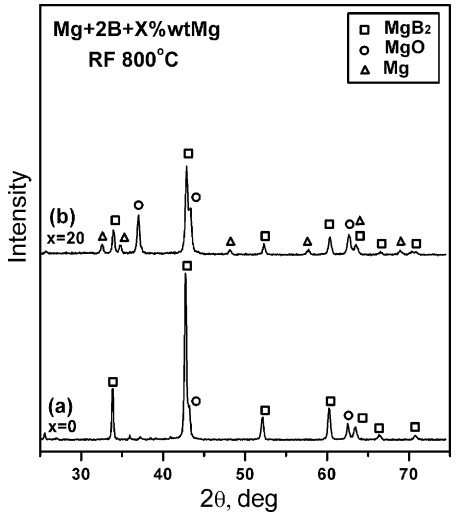

Fig. 3. XRD patterns of (Mg + B) + X wt.% Mg blends after Reactive Forging at 800 °C.

tain more boron (EDS) and are, most probably, MgB_4. This MgB_4 phase could be formed at the combustion temperature of 1200 °C through decomposition of MgB_2 into Mg gas and MgB_4—a reaction that takes place even below 1000 °C at low partial pressures of Mg.[11] Alternatively, the formation of the less Mg-rich MgB_4 boride could be the result of partial evaporation of Mg prior to its reaction with boron. In any case, the fraction of MgB_4 in the product is too low to be detected by XRD.

The density of the specimen reactively forged at 800 °C under the pressure of 200 MPa was 2.42 g/cm^3, which is ~92% of the theoretical density of MgB_2 (2.625 g/cm^3). Residual porosity is clearly seen in the SEM micrograph (Fig. 5(a)). The relatively high porosity of MgB_2 reactively forged at T_{ram} = 800 °C under the pressure of 200 MPa must be due to the absence of a liquid or another plastically flowing phase at the relatively low combustion temperature of 1200 °C. It was, therefore, decided to perform Reactive Forging at a higher ram temperature. Our expectation was that a higher T_{comb} would be achieved and, though no liquid would be formed (at high temperatures, MgB_2 decomposes into Mg gas and solid MgB_4[11]), MgB_2 could become sufficiently ductile to promote densification to full density under the applied pressure.

3.1.2. Reactive Forging at 1000 °C

A representative time–temperature curve measured during Reactive Forging of Mg + 2B compact at T_{ram} = 1000 °C is shown in Fig. 2 (curve b). Similar to the experiment at T_{ram} = 800 °C (curve a), a thermal explosion was ignited at 650 °C, but practically no Mg melting plateau was recorded. Instead, TE was ignited immediately after the onset of Mg melting which gives us grounds to believe that the self-sustained reaction between boron and Mg at T_{ram} = 1000 °C proceeded largely in the solid state. The combustion temperature achieved was ~1200 °C which is not higher than T_{comb} at T_{ram} = 800 °C (curve a). This suggests that the increase of T_{comb} of the reaction studied (Mg + 2B → MgB_2) beyond 1200 °C is limited by some energy-consuming process, e.g. decomposition of MgB_2 or evaporation of Mg. This assumption is corroborated by the shape of the heating curves with no well-defined maximum at T_{comb}.

XRD analysis of Mg + 2B specimens reactively forged at 1000 °C, Fig. 4(a) revealed, in addition to MgB_2, a larger amount of MgO (compared to T_{ram} = 800 °C), as well as peaks of MgB_4. These phases can also be detected in the SEM micrograph in Fig. 6(a): white layers of MgO and regions of MgB_2 (bright) and MgB_4 (dark) in the matrix. In addition, numerous small particles of unreacted boron (black) are present in the final microstructure. Apparently, there was not enough Mg to fully convert boron into MgB_2 suggesting that a significant amount of Mg escaped from the reaction zone during combustion. Since similar combustion temperatures were achieved during Reactive Forging at T_{ram} = 800 and 1000 °C (see Fig. 2), the only significant difference between the two processes was the state of Mg during thermal explosion—liquid at T_{ram} = 800 °C and solid at T_{ram} = 1000 °C. In the latter case, the solid-solid Mg–boron compact remains porous during combustion and Mg vapor can easily escape from the reaction zone. Likewise, atmospheric oxygen can easily penetrate into the porous compact and react with Mg forming MgO, hence the large fraction of MgO in the specimen reactively forged at T_{ram} = 1000 °C (Fig. 4(a)).

The density of the specimen reactively forged at T_{ram} = 1000 °C was 2.61 g/cm^3 which is significantly higher than that of the specimen reactively forged at T_{ram} = 800 °C. The absence of pores in the SEM micrograph (Fig. 6(a)), implies that near full density has been achieved. Given the similar combustion temperatures at T_{ram} = 800 and 1000 °C (see Fig. 2), the better consolidation behavior of the specimen reactively forged at T_{ram} = 1000 °C can probably be ex-

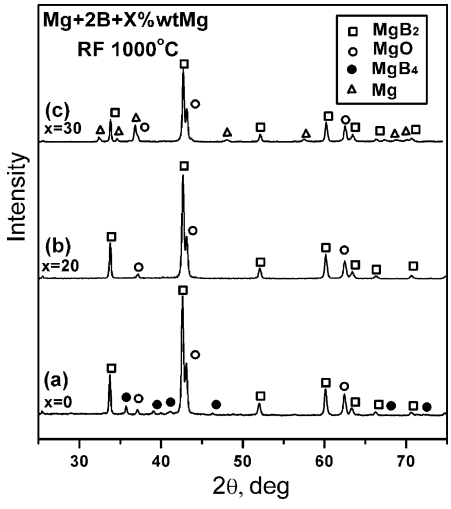

Fig. 4. XRD patterns of (Mg + 2B) + X wt.% Mg blends after Reactive Forging at 1000 °C.

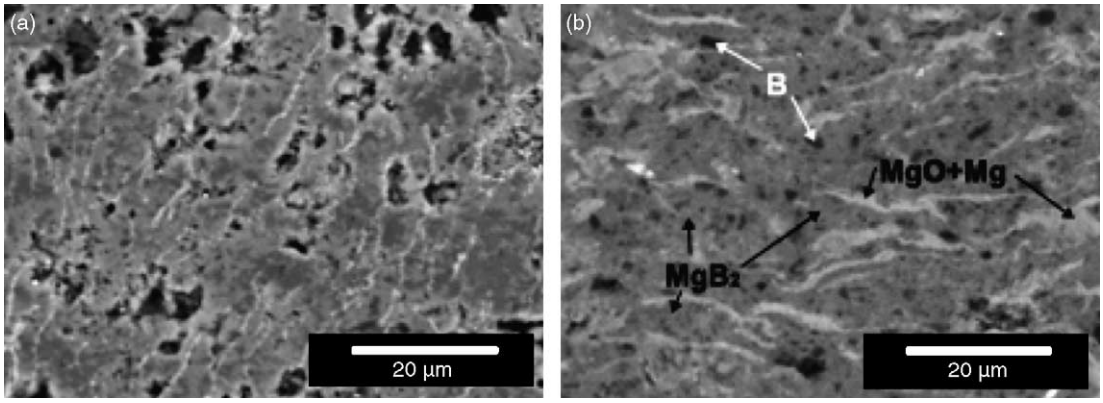

Fig. 5. A representative SEM (BSE) microstructure of MgB_2 reactively forged at 800 °C, 200 MPa from: (a) Mg + 2B powder blend and (b) (Mg + 2B) + 20 wt.% Mg powder blend.

plained by the large fraction of the relatively soft MgO phase which can plastically flow under the pressure of 200 MPa at T_{comb} = 1200 °C. According to the literature data, the yield stress of MgO at 1200 °C can be as low as 70 MPa (100 MPa at 1000 °C).[12] The well-marked orientation of MgO layers normal to the pressure application axis (Fig. 6(a)) is indicative of its plastic deformation.

The results of Reactive Forging of the stoichiometric Mg + 2B powder blend under the pressure of 200 MPa indicate that at T_{ram} = 800 °C a relatively porous MgB_2 is obtained, whereas at T_{ram} = 1000 °C the combustion product is near fully dense however contains significant amounts of MgO and MgB_4 and some unreacted boron. To improve the consolidation behavior of MgB_2 and/or to make up for Mg lost as vapor during combustion, different amounts (20 and 30 wt.%) of Mg were added to the stoichiometric Mg + 2B blend. If some unreacted metallic magnesium were to remain in superconducting MgB_2 specimens after processing, it should have a beneficial effect on material's electrical conductivity at temperatures above T_c.

3.2. Mg + 2B blend with the addition of Mg

3.2.1. Reactive Forging at 800 °C

The addition of 20 wt.% Mg to the Mg + 2B initial blend increased the density of the product reactively forged at

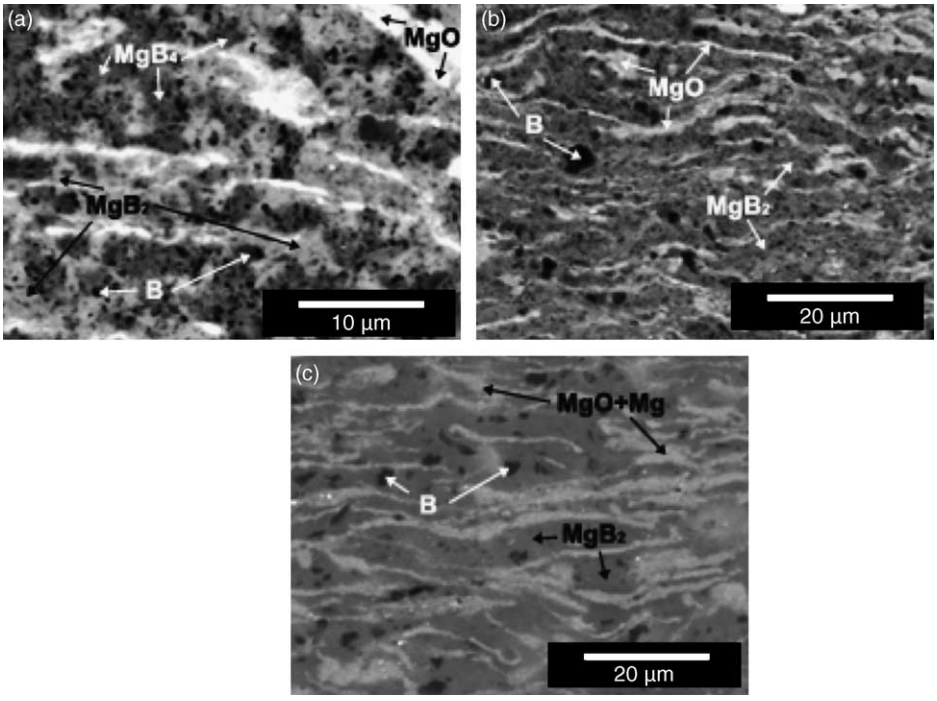

Fig. 6. A representative SEM (BSE) microstructure of MgB_2 reactively forged at 1000 °C, 200 MPa from: (a) Mg + 2B powder blend; (b) (Mg + 2B) + 20 wt.% Mg blend; and (c) (Mg + 2B) + 30 wt.% Mg blend.

800 °C from 2.42 to 2.60 g/cm^3. SEM observation didn't reveal any residual porosity in the material synthesized (Fig. 5(b)), suggesting near full density consolidation. As expected, the RF product of (Mg + 2B) + 20% Mg blend contained MgB_2 as a major phase, as well as some MgO and metallic Mg (Fig. 3(b)). The fraction of MgO is high compared to the corresponding material synthesized from the stoichiometric Mg + 2B blend, possibly due to the oxidation of the excess Mg that remained unbound to boron during combustion. In SEM (Fig. 5(b)), no regions of metallic Mg could be detected. On the other hand, the atomic Mg-to-oxygen ratio (EDS) in the bright MgO layers was ~2-to-1 (versus 1-to-1 for MgO) suggesting a mixture of MgO and metallic Mg. Plastic deformation of both Mg and MgO must be responsible for the successful consolidation of the product during combustion. It should also be noted that some unreacted boron remained in the specimen (see Fig. 5(b)) similarly to the material synthesized from the stoichiometric Mg + 2B blend at 1000 °C (Fig. 6(a)).

3.2.2. Reactive Forging at 1000 °C

A representative time–temperature curve recorded during Reactive Forging of the (Mg + 2B) + 20 wt.% Mg blend at T_{ram} = 1000 °C is shown in Fig. 2 (curve c). In contrast to the stoichiometric blend (curve b) a distinct Mg melting plateau can be seen similar to the one recorded at 800 °C (curve a). The prolonged melting of Mg prior to TE must be due to the diluting action of the surplus Mg decreasing the effective exothermicity of the Mg–boron blend. The maximum T_{comb} was not different from other RF regimes (~1200 °C) supporting our earlier assumption of massive decomposition of MgB_2 and/or evaporation of Mg at 1200 °C. According to the XRD results, Fig. 4(b), the addition of 20 wt.% Mg was sufficient to prevent the formation of Mg-poor MgB_4 the only two phases detected after RF at 1000 °C being MgB_2 and MgO. If any metallic Mg remained in the RF specimen, its amount was below the detection limit of XRD (<5 wt.%). At the same time, measurable peaks of Mg could be detected when a larger amount of Mg (e.g. 30 wt.%) was added to the starting blend (Fig. 4(c)).

SEM images of reactively forged Mg + 2B blends with 20 and 30% Mg, Fig. 6(b) and (c), respectively, show the matrix of MgB_2 with some unreacted boron particles and white stripes of MgO. For 30% Mg, the Mg-to-O ratio in the stripes is >1 (similarly to (Mg + 2B) + 20% Mg blend after RF at 800 °C) implying that they contain some metallic Mg in addition to MgO. On the whole, the microstructure of the (Mg + 2B) + 30% Mg specimen reactively forged at 1000 °C, Fig. 6(c) is very similar to that of the (Mg + 2B) + 20% Mg specimen reactively forged at 800 °C (Fig. 5(b)). No residual porosity was detected by SEM in Mg + 2B blends with added Mg after RF at 1000 °C (Fig. 6(b) and (c)). Again, the plastic deformation of Mg and/or MgO must have promoted the near full density consolidation of MgB_2.

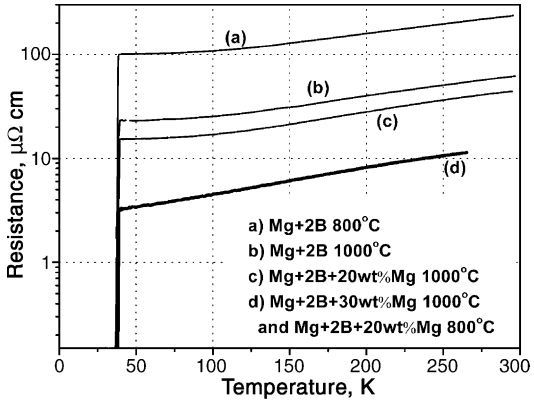

Fig. 7. Electrical resistivity vs. temperature of the MgB_2 specimens synthesized by RF.

3.3. Electrical resistivity

In all the synthesized MgB_2-based specimens, a superconducting transition was recorded at 39 K, regardless of material's density and composition (Fig. 7). The main difference between the tested MgB_2 specimens was their electrical resistivity above T_c. Slightly above the transition temperature, the porous (92% TD) near-single-phase MgB_2 specimen obtained by RF of the stoichiometric Mg + 2B blend at 800 °C had the highest resistivity of approximately 100 μΩ cm. Such high resistivity for the relatively dense product can be explained by presence of submicron/nanoscale flat pores between grains of reaction-synthesized material which can form as a result of a negative volume change during exothermic reactions. Dense MgB_2-based materials had a significantly lower resistivity. The lowest resistivity value of ~3 μΩ cm (30 times lower than that of the porous MgB_2) was obtained for the specimens with residual Mg reactively forged from (Mg + 2B) + 20 wt.% Mg blend at T_{ram} = 800 °C and from (Mg + 2B) + 30 wt.% Mg blend at T_{ram} = 1000 °C. Apparently, the presence of metallic Mg increases the electric conductivity of MgB_2 at temperatures above critical without compromising its low temperature superconducting properties. This suggests that residual Mg can act as a by-pass for electric current after breakdown resulting rapid transition from the superconductive to a normal state.

4. Summary

The main thrust of the present research was the fabrication of dense bulk MgB_2 superconductor from the elemental Mg–B powder blend employing the Reactive Forging technique. The thermal explosion mode of a self-sustained Mg + 2B → MgB_2 reaction (SHS) was ignited in Mg–B compacts by placing them between press rams preheated to 800 or 1000 °C and a moderate uniaxial pressure of 200 MPa was applied immediately following combustion. The pressure applied was considerably lower than those typical of

the current methods of full density consolidation of MgB_2 powder.

At both ram temperatures (T_{ram}) and for all the blend compositions, thermal explosion was ignited by the melting of Mg and the maximum combustion temperature was around 1200 °C. Reactive Forging of the stoichiometric Mg + 2B powder blend at T_{ram} = 800 °C yielded a relatively porous near single phase MgB_2 material. When T_{ram} was raised to 1000 °C, a near fully dense MgB_2-based specimen was obtained. The improved consolidation behavior is believed to be the result of plastic deformation of MgO that was present in the specimen along with MgB_2. In addition, a large fraction of the Mg-poor MgB_4 boride was formed during combustion due to partial evaporation of Mg.

The addition of 20 wt.% Mg to the stoichiometric blend significantly improved the consolidation behavior of MgB_2 at T_{ram} = 800 °C, presumably due to the presence of metallic Mg and to the higher fraction of MgO in the RF product. A similar MgB_2–(MgO–Mg) material was obtained at T_{ram} = 1000 °C when 30 wt.% Mg were added to the Mg + 2B blend. With the addition of only 20 wt.% Mg, no metallic Mg remained in the specimen after RF at T_{ram} = 1000 °C, the final product being MgB_2 with the some MgO. All the MgB_2 specimens reactively forged from Mg–B blends with surplus Mg were near fully dense.

In all the synthesized MgB_2-based specimens, a superconducting transition was recorded at 39 K, regardless of material's density and composition. Above 39 K, the electrical resistivity of dense MgB_2 specimens with residual Mg was 30 times lower than that of the porous (92% TD) near-single-phase MgB_2 suggesting that residual Mg can act as a by-pass for electric current during rapid transition from the superconductive to a normal state.

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