Synthesis of Dense Bulk MgB2 by Infiltration and Growth

Mr. Ashutosh Bhagurkar¹, Dr. Hari Babu Nadendla²  
BCAST, Brunel University London, Uxbridge, UK, UB8 3PH.

Dr. Akiyasu Yamamoto³  
Department of Applied Physics, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan.

Mr. Anthony Dennis⁴, Dr. John Durrell⁵, Prof. David Cardwell⁶  
Department of Engineering, University of Cambridge, Trumpington Street, Cambridge, UK, CB2 1PZ.

Summary

The study reports processing of bulk superconducting MgB₂ by an Infiltration and Growth (IG) process, a novel and unique method capable of producing dense large shapes with complex geometries which are not easily achievable by conventional sintering method. MgB₂ phase formed via following 3 stages: (1) intermediate boride formation (2) bulk liquid Mg infiltration and (3) MgB₂ layer formation. A maximum trapped field of 3 T has been measured at 5 K at the centre of a stack of two bulk MgB₂ samples fabricated using this technique, highest value obtained IG processed bulks. C-doping in MgB₂ lattice showed significantly high critical current density (Jₐ) at higher external fields.

1 Motivation

Superconductivity in magnesium diboride (MgB₂) was discovered in 2001. The relatively high Tc (39 K), high critical current density, long coherence length (~6 nm), low raw material cost, lower density and relative ease of fabrication make this material an exciting choice for practical applications [1, 2]. Furthermore, lower anisotropy and strongly linked current flow in untextured polycrystalline samples of bulk MgB₂ has enabled the development of different processing routes to fabricate MgB₂ in the form of wires, tapes, thin films and bulks [3, 4]. Conventionally, MgB₂ is synthesized either by an ex situ or in situ sintering technique. However, relatively poor self-sintering nature of MgB₂ grains leaves weaker inter-grain coupling in ex situ sintered samples. As a result, overall connectivity is often poor in these samples. Whereas in situ route often results in formation of highly porous structure due primarily to high vapour pressure of Mg [5]. A Number of studies have shown that high pressure and elevated temperature are effective in promoting MgB₂ phase formation and subsequent sintering [6, 7]. Although this approach results in a high critical current density, the need to use large pressure vessels represents a significant practical limitation for the development of a practical process and of the achievable dimensions in the final MgB₂ sample.
In this work, dense bulk MgB$_2$ is fabricated by the infiltration of liquid Mg into porous B precursor. This relatively simple method not only results in the formation of hard, dense structures but also has the potential to fabricate complex geometries, which is not achieved easily using conventional sintering techniques. Detail experimental procedure can be found in [8, 9]. Resultant samples are characterized using various techniques and underlying mechanism is briefly discussed. Finally, trapped magnetic field on bulks fabricated by this method is reported.

2 Results and Discussion

Phase Analysis and Connectivity

XRD analysis (Figure 1(a)) confirms that the specimen consists of a majority MgB$_2$ phase with residual MgO and Mg. The presence of Mg is associated with the dense packing of the MgB$_2$ unit cell, which creates voids that become occupied by surrounding liquid Mg during processing, Figure 1(b) shows the variation of resistivity with temperature for the MgB2 bulk sample between 300 K and 5 K in an applied external field up to 9 T. The sample exhibits a very low residual resistivity of 2.64 $\mu$Ωcm and a residual resistivity ratio (RRR) of 5.63, which is comparable to values observed for single crystal MgB2 samples (typically 1-2 $\mu$Ωcm measured in-plane). The normal state electrical connectivity (K) (or effective cross sectional area), which is defined by Rowell [10] as the ratio of difference of resistivity between a single crystal to that of a polycrystalline material, is calculated for the MgB$_2$ bulk sample from the following expression:
where $\rho_{sc}$ is the resistivity of an MgB$_2$ single crystal averaged over random orientations and $\rho$ is the resistivity of MgB$_2$ fabricated by infiltration and growth. The connectivity obtained here is significantly higher than that observed in bulk MgB$_2$ samples synthesized by both ex situ ($\sim$10%) and in situ ($\sim$30%) ambient pressure processing routes \cite{5}. It is noted that connectivity value obtained here is slightly altered owing to presence of residual Mg in the sample microstructure.

**Trapped Magnetic Field**

Superconducting “permanent magnets” have the potential to generate magnetic fields that are significantly higher than conventional Nd-Fe-B magnets, which are limited generally to less than 2 T. Therefore bulk superconductors can act as energy storages devices.

![Figure 2(a). MgB$_2$ bulk cylinder 32 mm diameter, 6 mm thick and (b) Microwave cavity structure fabricated by Modified Precursor Infiltration and Growth (MPIG) process \cite{11}.](image)

The measured trapped field on a bulks, similar to shown in figure 2(a), as a function of temperature for a single bulk and a stacked pair is shown in figures 3(a) and (b), respectively. A complex cavity structure is also shown in figure 2(b) demonstrating merits of the process. A difference of less than 0.5% in the magnitude of trapped field recorded at the top and bottom surface of the single bulk confirms its homogeneity, given that any cracks, porosity or non-superconducting regions would impede the flow of supercurrent throughout the volume of the bulk. Maximum trapped fields of 2.12 T and 3 T were recorded for a single bulk and stacked pair of bulk samples, respectively.
At 20 K, temperature that can easily achieved with cryogen free cost effective cryo-coolers, 1.35 T and 2 T trapped field was recorded in a single bulk and centre of stack, respectively.

**Process Mechanism**

Three distinct stages: (1) intermediate boride formation (2) bulk liquid Mg infiltration and (3) MgB2 layer formation, were identified in IG process after detailed examination of series of samples prepared with varied heating conditions. This features are sumerisd in the process Schematic shown in Figure 4. The intermediate phase Mg2B25, isomorphous to β-Boron, was detected prior to MgB2 phase formation in stage (1). Owing to an associated volume expansion cracks formed in stage (1) in the β-Boron particles and propagated radially inwards during stage (3).
The growing MgB2 particles sintered simultaneously with formation of grain boundaries during the process, as evidenced by the measured hardness and critical current density in these samples.

C-doping

Carbon is known to substitute B in MgB2 which enhances Hc2, while the defects, small grain size, and nano-inclusions induced by C incorporation improve the (Jc) [12].

![Diagram](Image)

Figure 5(a) showing Jc-B plot of undoped and C-doped MgB2 bulks while (b) describing generation of strain in MgB2 lattice with addition of carbon.

Here, n-B4C was used as source of carbon, As C is already uniformly distributed in B4C on atomic level, and was mixed thoroughly with Boron prior to processing. The sample doped with 10% B4C showed much enhanced flux pinning (Figure 5(a). Critical current density exceeded 10^5 A/cm^2 up to external fields of 4 T at 5 K. Expectedly, Jc dropped quickly at higher temperature (20 K). This is due to the trade-off between enhanced pinning and reduced condensation energy with C-doping. Effect of C-doping is also reflected as broadening of (101) peak in XRD pattern (Figure 1(b)).
3 Summary and Outlook

Dense MgB$_2$ bulks were fabricated by an Infiltration and Growth process, which required no high pressure apparatus and is easily scalable to larger and complex shapes. XRD pattern confirmed predominant MgB$_2$ phase with small amount of Mg. Rowell’s analysis suggested that MgB$_2$ grains are well connected, leading to high J$_c$. An almost identical value of trapped field obtained on each bulk suggests that bulks are extremely homogeneous. A pair of bulk trapped 3 T at the center, which remains the highest obtained value till date for IG processed MgB$_2$ samples. MgB$_2$ phase formation occurred through formation of intermediate phase, associated with generation of cracks in B particle. Finally C doping in MgB$_2$ showed prominent improvement in J$_c$. Therefore future work is aimed investigating origins of high flux pinning and fabricating high performance C-doped MgB$_2$ bulks. This work has potential to enable fabrication of high quality MgB$_2$ bulk components with complex geometry in a variety of engineering applications such as permanent magnets, fault current limiters, efficient energy-storage fly wheel devices, bearings and microwave cavities.

4 References

[1] Nagamatsu J, Nakagawa N, Muranaka T, Zenitani Y and Akimitsu J
Superconductivity at 39 K
Nature
Aoyama-Gakuin University, Japan, 2001.

Anisotropy of superconductivity from MgB$_2$ single crystals
Applied Physics Letters

High intergranular critical currents in metallic MgB$_2$ superconductor
Superconductor Science and Technology

[4] Labalestier D C et al
Strongly linked current flow in polycrystalline forms of the superconductor MgB$_2$
Nature
Towards the Realization of Higher Connectivity in MgB$_2$ Conductors: *In-situ* or
Sintered *Ex-situ*?
University of Tokyo, Japan, 2012.

Superconducting properties of MgB$_2$ bulk materials prepared by high-pressure
sintering.
Applied Physics Letters

Effect of sintering temperature under high pressure on the superconductivity of
MgB$_2$.
Applied Physics Letters
Pohang University of Science and Technology, South Korea, 2001.

Cardwell D A
Synthesis of dense bulk MgB$_2$ by an infiltration and growth process
Superconductor Science and Technology

Characterization of bulk MgB$_2$ synthesized by Infiltration and Growth.
IEEE Transactions of Applied Superconductivity

[10] Rowell J M
The widely variable resistivity of MgB$_2$ samples
Superconductor Science and Technology
Arizona State University, USA, 2003.

Dennis A R, Durrell J H and Cardwell D A
A trapped magnetic field of 3T in homogeneous, bulk MgB$_2$ superconductors
fabricated by a Modified Precursor Infiltration and Growth (MPIG) process
Superconductor Science and Technology

[12] Dou S X *et al*
Enhancement of the critical current density and flux pinning of MgB2
superconductor by nanoparticle SiC doping
Applied Physics Letters
University of Wollongong, 2002.