Characterization of bulk MgB_2 synthesized by Infiltration and Growth

A G Bhagurkar, N Hari Babu, A R Dennis, J H Durrell, D A Cardwell

***Abstract*— Superconducting MgB_2 has been synthesized successfully by a modified Infiltration and growth (IG) technique. The ambient pressure technique is relatively simple and scalable to complex shaped bulks. The extent of MgB_2 phase formation has been found to be influenced strongly by the IG process time and/or temperature and this is reflected in the X-Ray diffraction patterns, magnetization measurements and microhardness. SEM images show a bimodal particle size distribution with 20-50 nm sized fine precipitates in the inter particle region. A critical current density of 400 kA/cm^2 was measured in these samples at 5 K.**

***Index Terms*—Infiltration and Growth, bulk MgB_2, Characterization, Hardness.**

I. Introduction

Superconducting MgB_2 is believed to be strong candidate for commercial applications due primarily to its high T_c, together with strongly connected grain boundaries. This offers great flexibility with the processing, in contrast to HTS materials, where grain alignment is critical and presence of grain boundaries leads to dissipation and the decay of super current [1]. Grain boundaries are, in fact, effective pinning centers in MgB_2 and result in higher critical current density [2]. Conventionally, MgB_2 is synthesized by *in situ* sintering where elemental Mg and B powders are reacted to produce MgB_2. Although the superconducting phase can be obtained with relative ease, the resulting sample is generally only around 50% dense [3]. This is due primarily to the formation of large, porous media inside sintered bulks arising from the volatility of magnesium and large volume contraction in MgB_2 phase formation. Numerous researchers have addressed this problem by reducing the sintering temperature to as low as 500 ºC [4] or via the use of high pressure that confines Mg vapor and promotes subsequent sintering [5]. One approach includes diffusion or infiltration wherein liquid Mg is impregnated into B. Notably, Giunchi *et al* have fabricated high quality bulk MgB_2 using a Reactive Liquid Infiltration (RLI) process [6, 7]. Recently we have developed an "Infiltration and Growth" (IG) process. The technique involves the infiltration of liquid magnesium into predefined boron precursors. This is an ambient pressure technique that results in high density MgB_2 and potentially scalable to complex shaped bulks [8]. Also, the pores resulting from volume contraction are occupied by surrounding Mg, which manifests as very high normal state electrical connectivity and critical current density in the bulk. This paper reports a study of the MgB_2 phase formation in the Infiltration and Growth process for B precursors subject to varying heating cycles. The effect of the IG process on the physical, mechanical properties and phase formation properties of the resultant samples are studied.

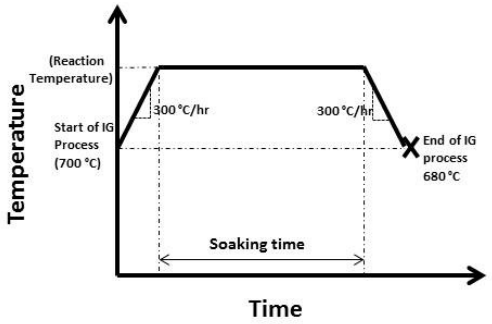

Fig.1. Heating treatment cycle used in the IG process

II. Experimental

Disc shaped precursors (32 mm diameter×4 mm thickness) were prepared from 98% (38 micron) purity crystalline boron powder (HC Starck) under a uniaxial load of 10 MPa. The boron powder exhibited a mixture of fine (2-5 µm) and coarse (up to 30 µm) sized particles on SEM examination. Here, the IG process was slightly modified by melting the Mg ingot in a graphite crucible and submerging a boron pellet in the liquid Mg bath at 700 ºC using a steel mesh (rather than heating a Mg-B-Mg sandwich geometry to the reaction temperature). The assembly was then subjected to the thermal profile shown in Fig 1. A cover gas mixture of N_2 + SF_6 (95:5) was used to reduce the oxidation of Mg. The reacted product was removed from the Mg(l) at 680 ºC. This modified IG method ensures that B precursor doesn't float to the top of Mg(l) pool, thus exposing the entire surface area of the pellet to Mg(l) to enable uniform infiltration and reducing the need for post process machining. Four sets of samples were prepared using this method. Samples 1, 2 and 3 were reacted at 700 ºC, 750 ºC and 850 ºC for 2 hours respectively, whereas sample 4 was reacted at 850 ºC for 4 hours. MgB_2 discs of diameter 32 mm were produced, finally, after slightly grinding. The cross section of each disc was polished and analyzed using various techniques. The microstructure of the infiltrated sample was

This work was supported by KACST-Cambridge Research Centre, Cambridge, UK.

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observed by scanning electron microscopy (SEM), and phase identification was carried out using X ray diffraction. The magnetization response of sample was measured using a superconducting quantum interference device (SQUID) magnetometer. Critical current density was calculated from the measured magnetic moment using Bean model [9]. Microhardness was used to measure hardness of samples with .1 kg load, 5 second dwell time (Buehler Micromet- 5101) while Semi-micro hardness was measured with 20 Kg load, 10 sec dwell time (Wilson Hardness).

III. Results and Discussion

A. Phase Analysis

X ray diffraction patterns for crystalline boron powder and samples 1-4 (bulk) are shown in Fig 2. The patterns for samples 2-4 are normalized with respect to highest intense MgB_2 (101) peak at ≈42.4º.The crystalline B powder shows the presence of a small amount of impurities, which are observed as extra peaks in XRD pattern. Sample 1, which was reacted at 700 ºC for 2 hours, shows a little signs of infiltration, resulting in a powdery specimen, with the majority of the sample present as a highly B rich, lesser known Mg_2B_{25} phase. Samples 2-4 show majority MgB_2 phase content with residual Mg and a very small amount of Mg_2B_{25}, the fraction of which continues to decrease with increase in reaction temperature and/or soaking time. This suggests that Mg_2B_{25} is probably one of the intermediate phases stable at room temperature that forms during the MgB_2 phase transformation process. Existence of Mg_2B_{25} phase in MgB_2 was first reported by Giunchi *et al* in RLI process [7]. Although it is somewhat suppressed in the current study. This is likely to be due to the nature of the IG process, where a Mg rich environment is maintained during the course of the reaction. As expected, the fraction of this phase present is found to be 3-4 times higher inside larger MgB_2 grains than the average value due to slower reaction kinetics [7].This phase was not observed in the IG samples processed earlier, due possibly to the amorphous B used that is generally more reactive than the crystalline variety of the powder.

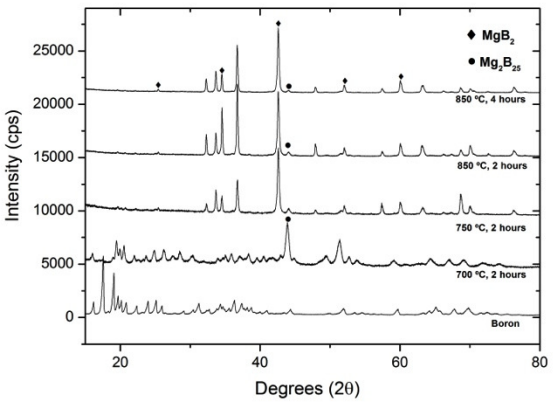

Fig. 2. X Ray diffraction pattern for crystalline boron powder and IG processed samples

Interestingly, the amount of MgO, which could be detrimental to the electrical connectivity of the bulk sample, appears to be very low. This is one of the important advantages of the modified IG process (immersing the B precursor inside the Mg(l) bath minimizes contact with the atmosphere).

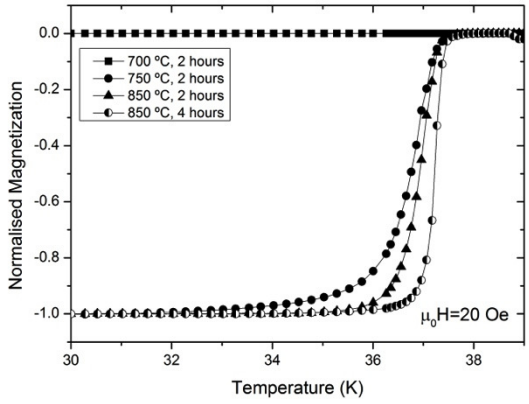

Fig. 3. Normalized magnetization response of samples under an external field of 2 mT

B. Magnetization Measurements

Figure 3 shows the normalized magnetic moment as a function of temperature in the range 30-39 K under zero field cooled conditions at 20 Oe. The absence of a superconducting transition for sample 1 confirms absence of the MgB_2 phase in the sample. Samples 2,3 and 4 however, show a strong superconducting transition at 37.4 K. This slightly lower T_c is attributed to the relatively impure powder (98% purity) used in this study. The width of transition decreases gradually from ~6 K to <1 K in samples 2-4. This reconfirms incomplete MgB_2 phase formation as suggested earlier by larger fraction of Mg_2B_{25} phase in the XRD pattern. Phase formation; however, appears to be near complete in sample 4, suggesting improved reaction kinetics with increased reaction time and/or temperature.

C. Scanning Electron Microscopy

Scanning electron microscope images of polished surfaces for samples 2, 3 and 4 are shown in fig 4. All the images show a relatively dense microstructure and no large pores or voids can be seen. Fig 4(a), (b) and (c) show larger MgB_2 particles, embedded between which are fine, ~1 μm sized grains. Such a bimodal grain size distribution was also observed previously and could be explained by a bimodal distribution of precursor boron powder. Interestingly, the sample microstructure seems largely unaltered by the parameters under which the experiments were conducted. In particular, the population of larger MgB_2 particles in a given area and their individual size is found to be unaffected, which suggests that grain growth has not taken place after 4 hours processing at 850 ºC. However, these larger particles exhibit a number of distinctive features. Figures 4(a) and (c) and, more apparently, Fig. 5(b) show a number of bright Mg veins running across the particle

from its surface to the interior. The reason for such behavior is not yet understood, however its effect is to decrease the distance the Mg atoms need to diffuse in order to achieve complete phase transformation. Also, BSE images (a) and (c) show the presence of a bright layer on individual MgB_2 particles (this is more apparent in the larger MgB_2 particles and less so in the finer particles). These bright regions have been confirmed by EDS point analysis to be Mg-rich and are believed to be the origin of the veins. Fig 4(b) shows a continuous, 10 µm Mg wide channel (dotted red line) originating from the surface of the sample and presumably the primary source of Mg inside the B precursor. Such channels are observed at certain locations in all the samples, although it is yet to be established whether these non-superconducting channels have any effect on critical current density. Finally, Fig. 4(d) shows a higher magnification image of sample 4 (850 ºC, 4 hour), taken in the region between two adjacent MgB_2 particles. The image shows a large density of 20-50 nm thin hexagonal particles. EDS analysis on such an area identifies the constituent elements to be Mg and B. However, the exact composition and phase of these precipitates could not be identified. Such fine precipitates are potentially effective magnetic flux pinning centers inside the MgB_2 bulk superconductor.

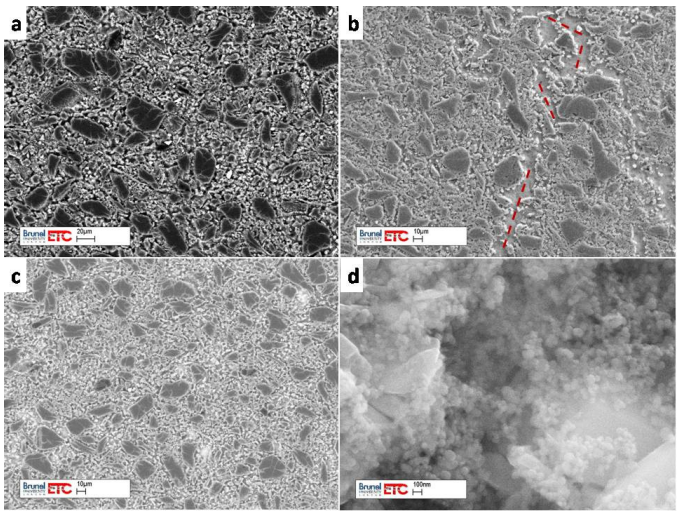

Fig. 4. Scanning electron micrographs of infiltrated and grown MgB_2 (a) sample 2 at 1000x in BSE mode, (b) sample 3 at 1000x in SE mode, (c) sample 4 at 1000x in BSE mode and (d) sample 4 at 100000x in SE mode.

D. Microhardness:

The Semi-micro hardness for MgB_2 bulk samples 2, 3 and 4 is shown in Fig. 5(a). Indentations along cross section were made at 7, equally spaced points between edges of specimen, from top to bottom. Hardness measured at each point is plotted against geometrical location of the indent. Length of diagonal of indent was between 300-500 µm, depending on hardness at each location. It is evident from samples 2 and 4 that the hardness increased with increase in reaction temperature by a constant value along the entire cross section. This demonstrates clearly that an increase in the MgB_2 phase fraction results in increased hardness of the bulk superconductor, and, therefore, hardness can be interpreted generally as the extent of MgB_2 phase formation. Samples 2 and 3 show a rather interesting behavior. The peak value of hardness for these samples is observed at the center of each specimen and decreases with distance from the center. The hardness at the edges of the samples increases significantly as the soaking time is increased in the IG process, while the maximum hardness at center remains the same. This probably suggests that the superconducting phase first forms at the center of the sample, while the edges are partially transformed during the initial 2 hour processing period.

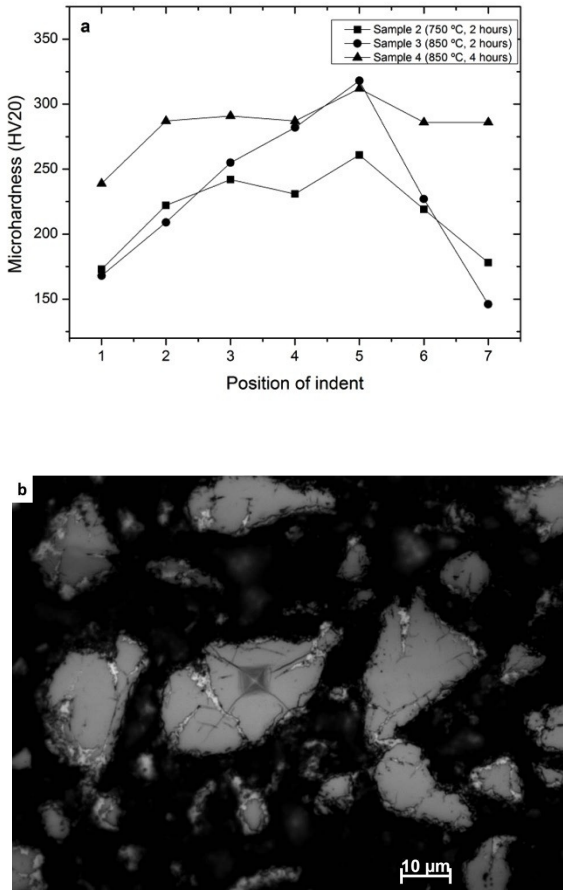

Fig.5. Hardness of MgB_2 samples (a) Semi-microhardness of samples 2, 3 and 4 measured along the cross section Load= 20 kg, dwell time= 10 sec and (b) Microhardness performed on sample 4 with load= 0.1 kg, dwell time= 5 sec.

Finally, the microhardness of individual MgB_2 particles was measured on sample 4. After the indentation, the cracks invariably formed along either side of both diagonals in all measurements and propagated towards the surface of the particle as shown in Fig 5(b). The calculated average value of hardness over 4 particles was 33 GPa, although this might be underestimated due to the formation of cracks upon application of the load. Maximum hardness in MgB_2 samples is reported as 35 GPa [10], which is in good agreement with our measurements. Presence of Mg_2B_{25} phase inside the larger

MgB_2 grains is reported to be the reason for such high hardness [10]. As expected, the hardness measurements across the Mg veins inside MgB_2 particles show a reduced value of 20 GPa.

E. Critical Current Density:

The variation of critical current density as a function of externally applied field is shown for sample 4 (850 ºC, 4 hours) in Fig 6. J_c up to 400 kA/cm^{2}at 5 K and 280 kA/cm^{2}at 20 K was achieved. This value is significantly higher than that observed in our earlier studies where maximum J_c of 260 kA/cm^2 was measured [8]. This is likely to be due to the very low fraction of MgO in the sample and to the presence of 20-50 nm fine particles that enhance flux pinning in the bulk material.

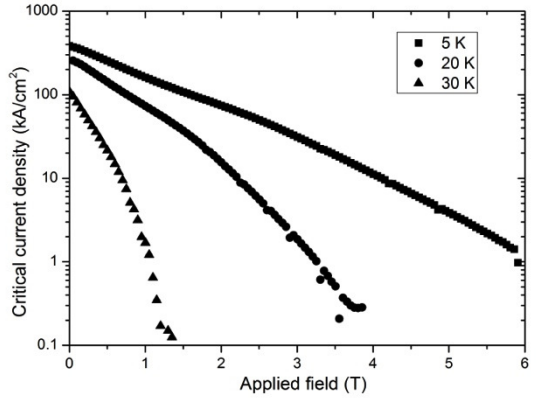

Fig 6. Critical current density of bulk MgB_2 as a function of applied magnetic field.

IV. Conclusion

In summary, we have fabricated bulk MgB_2 superconductors by a modified infiltration and growth process using varying time-temperature heating cycles. X-Ray diffraction shows the presence of a considerable amount of the lesser-known Mg_2B_{25} intermediate phase in samples processed at low temperature. Samples fabricated above 750ºC, however, exhibit a strong diamagnetic signal with superconducting transition temperature (T_c) onset at 37.4 K. The width of the transition (ΔT_c) is found vary systematically with the reaction parameters, which is attributed to the reaction kinetics that control the rate of phase transformation. SEM images reveal a dense microstructure in each sample. A bimodal grain size distribution observed is associated with a similar distribution in the B precursor powder. Excess Mg in the bulk superconductor is observed in the form of continuous channels and veins inside individual MgB_2 particles. 20-50 nm sized precipitates are observed in the inter-particle area, which are potential flux pinning sites in MgB_2. Finally, the hardness measured in samples show an increasing trend from the surface to the interior of the sample, indicating that MgB_2 first forms at the centre and finally at the sample edges. The measured critical current density of the material in self-field is quite high, which is attributed to low MgO content inside the MgB_2 bulk superconductor.

V. References

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