Microstructure - Critical Current Density Model for MgB$_2$ Wires and Tapes

B. Birajdar and O. Eibl
Institute of Applied Physics, University of Tübingen, Auf der Morgenstelle 10, D-72076 Tübingen, Germany
E-mail: balaji.birajdar@uni-tuebingen.de

Abstract. MgB$_2$ wires and tapes were prepared by the powder in tube method using different processing technologies and thoroughly characterised for their superconducting properties within the HIPERMAG project. Either pre-reacted MgB$_2$ (ex-situ) or a mixture of Mg + 2B (in-situ) were used as the precursor powders. In some wires the precursor powders were mixed with SiC. The critical current density ($J_c$) of these wires was found to differ by orders of magnitude, the highest $J_c$'s being $10^4$ A cm$^{-2}$ at 10.5 T and 4.2 K. A detailed understanding of the thermodynamics in Mg-B-O and Mg-B-Si-C-O system is necessary to control the phase and microstructure formation in these systems. Therefore, thermodynamical parameters like annealing temperature and annealing time used for the synthesis of the wires were systematically varied. The microstructure of these wires was investigated using advanced electron microscopy methods [1]: combined SEM, EPMA and TEM analysis with artefact-free sample preparation, elemental mapping and chemical quantification. Ex-situ wires show oxygen-free MgB$_2$ colonies (a colony is a dense arrangement of several MgB$_2$ grains) embedded in a porous matrix introducing structural granularity. The MgB$_2$ grains in the porous matrix are surrounded by MgSi$_x$O$_y$ layers yielding poor connectivity. In-situ wires are generally more dense, but show inhibited MgB$_2$ phase formation with significantly higher fraction of B-rich secondary phases in comparison to the ex-situ wires. SiC in the in-situ wires results in the formation of Mg$_2$Si secondary phases. The size of the MgB$_2$ grains varies between 20 – 1000 nm. A microstructure- critical current density model is proposed to explain the large, order of magnitude, differences in the $J_c$'s of MgB$_2$ wires and tapes. The model contains the following microstructure parameters: 1) colony size, 2) volume fraction of B-rich secondary phases, 3) oxygen mole fraction and 4) MgB$_2$ grain size.

1. Introduction
At the present stage, the $J_c$'s and resistivities of different MgB$_2$ superconductors, differ by orders of magnitude, the reasons for which are not fully understood.

Rowell in a review article [2] analyzed the resistivity of a large number of MgB$_2$ single crystals, bulk samples, thin films and one wire prepared by the diffusion of Mg into the B wire. Large variations were found in the residual resistivity (at 50 K) of these samples, the minimum being 0.4 $\mu\Omega$cm and maximum being 1560 $\mu\Omega$cm. Various models like reduction in the effective current carrying cross-sectional area of the sample and Josephson junction model of the grain boundaries, were proposed to explain the increase in resistivity and decrease in $J_c$. Transport $J_c$ (at zero field) of...
only one sample was discussed and the importance of more transport Jc measurements was underlined. MgB2 wires and tapes prepared by the technologically important PIT technique were not considered.

Eisterer et al. [3] studied the correlation of electrical resistivity on the Tc, Bc2 and Jc of MgB2 wires prepared in-situ by the PIT technique. The residual resistivity was increased by neutron irradiation, carbon doping or lower processing temperature, which led to increase in Bc2, which in turn was shown to be the main reason for the improvement in Jc. The effectively conducting cross section of the MgB2 filaments was found to be only one third of the geometrical cross section of filaments in pure MgB2 wires and one sixth of the geometrical cross section in SiC added MgB2 wires. The effect was attributed to the structural granularity, but the microstructure of these wires was not analyzed in detail.

In this paper we report the transport Jc’s of a large number of wires and tapes and their correlation to the microstructure, which was investigated using the advanced electron microscopy methods described elsewhere [1].

2. Experimental

The MgB2 wires and tapes were prepared by different variants of the powder in tube (PIT) technique. The deformation technique, precursor powders, annealing temperatures, superconducting transition temperature (Tc), upper critical field (Bc2) and critical current density (Jc) of samples 1-6 are given in Table 1. The synthesis of the samples and measurement of their superconducting properties was carried out by the partner institutes within the HIPERMAG project.

The Tc was determined by resistivity (ρ) versus temperature (T) measurements. The upper critical field (Bc2) was determined from the ρ(T) measurements carried out at different magnetic fields. The Jc’s were measured by transport measurements using the 1 µVcm-1 criteria.

Advanced electron microscopy techniques were used to study the microstructure of MgB2 wires and tapes. Advanced electron microscopy involves a combined SEM and TEM analysis with contamination free sample preparation, chemical mapping with good counting statistics and advanced chemical quantification as described in [1]. Schematic diagram of the steps involved in the microstructure analysis of MgB2 wires and tapes is shown in figure 2. These methods yield quantitative reliable data of the relevant microstructure parameters given in table 1. A more detailed explanation for the determination of the O mole fraction will be given elsewhere.

Table 1. Tc, magnetic field for 104 Acm-2 current density (B*), synthesis method, powder, annealing temperature and time/time (θ), colony size (S), volume fraction of B-rich phases (f), oxygen mole fraction and MgB2 grain size (g) of samples 1-6.

| #  | Tc (K) | B* (T) | Synthesis technique | Powder | θ (°C/h) | S (µm) | f (%) | O (at. %) | g (nm) |
|----|--------|--------|---------------------|--------|----------|--------|-------|-----------|--------|
| 1  | 36.5   | 9.6    | MA [4]              | Mg (gf)+2B (fluka) | 600/3    | -      | 1.4   | 3.75      | <50    |
| 2  | 32.5   | 9.7    | ,                   | Mg (gf)+2B (strem) | 650/3    | 1-35   | <0.5  | 9.34      | <50    |
| 3  | 33.7   | 9.0    | 4-fila.[5]          | Mg(aa) +2B (Geneva) +11.3 mol% SiC (aa) | 650/0.5  | -      | 2.7   | 10.4      | <50    |
| 4  | 35.5   | 6.5    | ,                   | Mg+2B+11.3 mol% SiC (oxford) | 650/0.5  | -      | 4.6   | 15.46     | <100   |
| 5  | 36.5   | 4.9    | 14-fila.[6]         | MgB2 (Lamia)       | 980      | 1-6    | ~0    | 14.57     | ~500   |
| 6  | 38.7   | HE[7]  | MgB2 (aa)+1.5 mol% SiC | 950/0.5 | 1-3     | 1.1    | 8.89  | ~200      |        |

notes: HE(Hydrostatic extrusion and two axial rolling); MA (Mechanical Alloying); 14-filament (see reference [4]); aa (Alpha Aesar); abcr (ABCR GmbH)

3. Results and discussion
3.1. Superconducting properties

The $T_c$'s of samples 1-6 is given in table 1. The $T_c$'s of the ex-situ samples 5-6 is higher than the $T_c$'s of in-situ and mechanically alloyed samples 1-4. Sample 6 has the highest $T_c$ (38.7 K) while sample 2 and 3 have lowest $T_c$'s of 32.5 and 33.7 K respectively.

$J_c(B)$ curves of samples 1-6 are shown in figure 1. Mechanically alloyed samples show the highest $J_c$ at high fields (> 5T) among the samples 1-6, which is about 3 times smaller than the $J_c$ of SiC added MgB$_2$ wires of Dou et al. [8]. A large scatter is observed in the $J_c$'s of different wires. At 7 T, the $J_c$ of sample 2 is about 100 times larger than sample 5. Similarly the field dependence of the $J_c$ varies from sample to sample. Sample 3 shows the best field dependence and. Sample 5 shows the most rapid decrease in $J_c$ with increase in magnetic field.

3.2. Microstructure analysis

The SE (secondary electron) images and the corresponding RGB (Mg-O-B) or RGB (Mg-Si-B) images of the SEM-EDX elemental maps are shown in figure 3. The volume fraction of B-rich secondary phases, size of MgB$_2$ colonies and O mole fraction summarised in table 1 were obtained by SEM analysis as described in [1]. TEM dark-field images (figure 3) yield the grain size of the MgB$_2$ filaments.

SE images of mechanically alloyed sample 1 and 2 show very few cracks and are dense. Sample 1 shows 1.4 % B-rich secondary phases (which appear blue in the RGB (Mg-O-B) image), indicating inhibited MgB$_2$ phase formation. Sample 2 shows dense and pure MgB$_2$ colonies embedded in an oxygen rich granular MgB$_2$ matrix. A colony is a dense arrangement of several MgB$_2$ grains.

SE images of in-situ samples 3 and 4 show a large density of cracks and voids on the 1-10 µm length-scale. RGB (Mg-Si-B) images show highest volume fraction (3.1 %) of Mg$_2$Si secondary phases and 2.7 % volume fraction of B-rich secondary phases. In sample 3. On the other hand, sample 4 has smaller volume fraction (1%) of Mg$_2$Si but highest volume fraction (4.6 %) of B-rich secondary phases. A TEM bright field image of the nanocrystalline SiC powder, used for the preparation of samples 3 and 4 is shown in figure 4a. These particles, originally thought to be incorporated as pinning centres, react with Mg to form µm sized Mg$_2$Si secondary phases (figure 4b). The carbon released during the formation of formation of Mg$_2$Si is doped into the MgB$_2$ matrix [8]. $T_c$ of sample 3 is suppressed because of the enhanced C-doping in this sample.
|   | Figure 3 (a) secondary electron images and (b) the corresponding RGB(Mg-O-B) or RGB(Mg-Si-B) images of samples 1-6. (c) TEM dark-field images showing MgB$_2$ grain size in samples 1-6. (note: dark-field image of sample 2 was acquired from a similarly prepared bulk sample) |   |
|---|---|---|
| 1 | ![Image 1](image1.png) | ![Image 2](image2.png) | ![Image 3](image3.png) |
| 2 | ![Image 4](image4.png) | ![Image 5](image5.png) | ![Image 6](image6.png) |
| 3 | ![Image 7](image7.png) | ![Image 8](image8.png) | ![Image 9](image9.png) |
| 4 | ![Image 10](image10.png) | ![Image 11](image11.png) | ![Image 12](image12.png) |
| 5 | ![Image 13](image13.png) | ![Image 14](image14.png) | ![Image 15](image15.png) |
| 6 | ![Image 16](image16.png) | ![Image 17](image17.png) | ![Image 18](image18.png) |
SE images of the ex-situ samples 5-6 and STEM dark-field image (figure 5a) of sample 5, show 2-6 μm large dense regions in a granular matrix with voids. RGB (Mg-O-B) image shows the dense regions to be MgB2 colonies and the granular matrix to be rich in oxygen. A schematic diagram of such a colony formation is shown in figure 5b and is found to be a universal feature of all ex-situ samples.

TEM dark-field images of samples 1-6 are shown in figure 4. The grain size of mechanically alloyed samples 1-2 and in-situ samples 3-4 is in the range of 15-100 nm. The grain size is of the order of the coherence length of MgB2 and yields reduction of Tc. The MgB2 grain size in ex-situ samples 5-6 is significantly larger (100-1000 nm) than in in-situ or mechanically alloyed samples.

Secondary phases on the sub-micrometer scale in samples 3-6 were studied using STEM-EDX and ESI elemental mapping as described in [1]. Sample 3 showed 50-400 nm large grains of crystalline Mg2Si and highest density of 100-200 nm large grains of amorphous B-rich secondary phases embedded in the MgB2 matrix. The granular matrix in sample 5 showed 200 nm wide oxide layers between the MgB2 grains. Sample 6 with SiC additives showed 50 nm wide oxide and MgSi2O3 layers between the MgB2 grains.

(a) TEM bright-field image of nanocrystalline SiC powder (b) RGB (Mg-Si-B) image showing Mg2Si secondary phase. Figure 4. (a) Schematic of the microstructure of ex-situ MgB2 (b) STEM dark-field image of sample 5

3.3. Jc-microstructure correlation model

Jc of MgB2 wires and tapes is influenced by Bc2 and microstructure (figure 6). Microstructure affects Jc because of the structural granularity and crystal defects on the coherence length scale of MgB2 namely grain boundaries, dislocations and precipitates, which can act as pinning centers [9]. The structural granularity arises due to inhibited MgB2 phase formation and due to the formation of secondary phases (B-rich secondary phases, Mg2Si) and oxide layers at grain boundaries.

Figure 5. (a) Schematic diagram of the factors affecting Jc.

The Jc-microstructure correlation model is used to explain the order of magnitude differences in the Jc of samples 1-6. The model consists of 1) colony size, 2) volume fraction of B-rich secondary phases, 3) oxygen mole fraction and 4) MgB2 grain size, which are summarized in table 1 for samples 1-6.

The high Jc of mechanically alloyed tapes (samples 1-2) is attributed to their small MgB2 grain size and dense microstructure. The improved field dependence of Jc can be attributed to the enhanced grain
boundary pinning. The \( J_c \) is likely to be further enhanced by reducing the volume fraction of B-rich secondary phases in sample 1 and increasing the volume fraction of MgB\(_2\) colonies in sample 2.

Sample 3 shows the best field dependence of \( J_c \), which can be attributed to the enhanced grain boundary pinning due to small MgB\(_2\) grain size and enhanced B\(_{c2}\) due to carbon doping. Besides its favourable effect of MgB\(_2\) doping with C, addition of SiC contributes significantly to the formation of Mg\(_2\)Si and B-rich secondary phases [5], yielding structural granularity, which limits \( J_c \) enhancement in SiC-added MgB\(_2\) wires.

Sample 5 shows high \( J_c \) at low fields, because of the large 6 µm colonies (figure 5a) yielding good connectivity. The rapid decrease in \( J_c \) of sample 5 with increase in B is explained by poor grain boundary pinning, due to large MgB\(_2\) grain size (figure 3c) [6].

The low \( J_c \) of samples 6 is attributed to the large volume fraction of the oxygen rich granular matrix (figure 3b). MgB\(_2\) grains in the MgB\(_2\) matrix are surrounded by about 50 nm wide oxide or MgSi\(_x\)O\(_y\) layers yielding poor connectivity. The field dependence of \( J_c \) is however improved in comparison to sample 6 because of enhanced grain boundary pinning due to smaller (about 200 nm) size of MgB\(_2\) grains (figure 3c).

**Acknowledgement**

Authors are thankful to the following partners within the Hipermag consortium for providing samples and for the measurement of their superconducting properties (\( T_c \) and \( J_c \)): W. Haessler of IFW Dresden for samples 1-2, P. Kovach of IEE Bratislava for samples 3-4, V. Braccini of INFM Genova for sample 5, and W. Pachla and A. Morawaski of IHPP Warsaw for sample 6. This work was supported by the EU-FP6 Specific Targeted Research Project HIPERMAG (STRP 505724-1).

**References**

[1] Birajdar B and Eibl O 2007 *Advanced electron microscopz methods for the analysis of MgB\(_2\) superconductor* (accepted as poster presentation in EUCAS 2007, to be published in *Journal of Physics: conference series*)

[2] Rowell J M 2003 *Supercond. Sci. Technol.* 16 R17-R2

[3] Eisterer M, Müller R, Schöppl R, Weber H W, Soltanian S, Dou S X 2007 *Supercond. Sci. Technol.* 20 117-12

[4] Haßler W, Birajdar B, Gruner W, Herrmann M, Perner O, Rodig C, Schubert M, Holzapfel B, Eibl O and L Schultz L 2006 *Supercond. Sci. Technol.* 19 512

[5] Kovac P, Birajdar B, Husek I, Holubek T, Eibl O *MgB\(_2\) rectangular wires in tube:influence of precursor powders and sheath materials* (communicated to *Supercond. Sci. Technol.*)

[6] Birajdar B, Braccini V, Tumino A, Wenzel T, Eibl O, Grasso G 2006 *Supercond. Sci. Technol.* 19 916

[7] Pachla W et al. 2005 *Supercond. Sci. Technol.* 18 552-556

[8] Dou S X et al. 2007 *Phys. Rev. Letters* 98 097002

[9] Birajdar B et al. 2007 *Physica C* 460-462 1409