Advanced electron microscopy methods for the analysis of MgB\textsubscript{2} superconductor

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Abstract. Advanced electron microscopy methods used for the analysis of superconducting MgB\textsubscript{2} wires and tapes are described. The 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. Microstructure analysis on µm to nm length scales is necessary to understand the superconducting properties of MgB\textsubscript{2}. For the MgB\textsubscript{2} phase analysis on µm scale an analytical SEM, and for the analysis on nm scale an energy-filtered STEM is used. Both the microscopes were equipped with EDX detector and field emission gun. Electron microscopy and spectroscopy of MgB\textsubscript{2} is challenging because of the boron analysis, carbon and oxygen contamination, and the presence of large number of secondary phases. Advanced electron microscopy involves, combined SEM, EPMA and TEM analysis with artefact free sample preparation, elemental mapping and chemical quantification of point spectra. Details of the acquisition conditions and achieved accuracy are presented. Ex-situ wires show oxygen-free MgB\textsubscript{2} colonies (a colony is a dense arrangement of several MgB\textsubscript{2} grains) embedded in a porous and oxygen-rich matrix, introducing structural granularity. In comparison, in-situ wires are generally more dense, but show inhibited MgB\textsubscript{2} phase formation with significantly higher fraction of B-rich secondary phases. SiC additives in the in-situ wires forms Mg\textsubscript{2}Si secondary phases. The advanced electron microscopy has been used to extract the microstructure parameters like colony size, B-rich secondary phase fraction, O mole fraction and MgB\textsubscript{2} grain size, and establish a microstructure-critical current density model [1]. In summary, conventional secondary electron imaging in SEM and diffraction contrast imaging in the TEM are by far not sufficient and advanced electron microscopy methods are essential for the analysis of superconducting MgB\textsubscript{2} wires and tapes.

1. Introduction
Electron microscopy and spectroscopy of MgB\textsubscript{2} wires and tapes is challenging because of the following reasons: i) carbon and oxygen contamination artefacts during sample preparation and under the electron beam in the microscope ii) low fluorescence yield of B-K\textsubscript{α} x-rays iii) B-K\textsubscript{α} and C-K\textsubscript{α} x-ray peak overlap in EDX iv) preferential absorption of B-K\textsubscript{α} x-rays in the sample v) formation of MgB\textsubscript{2} colonies and secondary phases (MgB\textsubscript{4+x}, MgB\textsubscript{2+x}, MgSi\textsubscript{x}O\textsubscript{y} and Mg\textsubscript{2}Si) yielding structural granularity on µm to nm length scale.

In this paper the methodology of the advanced electron microscopy analysis of MgB\textsubscript{2} is described and elemental mapping and quantitative elemental analysis is established for both the µm and nm scale. The limitations and strengths (in terms of the spatial resolution and accuracy) of the various
methods for the microstructure analysis of MgB₂ wires and tapes are discussed. The importance of these methods for the understanding of the thermodynamics of phase formation in MgB₂ as well as for improving the synthesis technology and the superconducting properties of MgB₂ wires and tapes is described.

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 1-5 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. Sample 1 and 2 are ex-situ monofilament wires prepared [2] using a mixture of MgB₂ and 1.5 mol. % SiC nano-particles. Sample 3 is a in-situ monofilament wire prepared [3] using a mixture of MgH₂+2B+6 mol % of SiC. Sample 4 is a commercial, 14-filament, ex-situ long length MgB₂ tape [4]. Sample 5 is a monofilament tape prepared using a mechanically alloyed [5] mixture of Mg +2B.

Table 1. Preparation technique, precursor powders, annealing temperature and time, Tc, Bc2 and Jc for samples 1-5.

| #  | Synthesis technique | precursor powder | Ann. Temp. / time | Tc (K) | Jc (Acm⁻²) |
|----|---------------------|------------------|-------------------|--------|------------|
| 1  | HE [2]              | MgB₂ (aa) +1.5 mol.% SiC | 950 °C/ 0.5 h    | 39.1   | 1.29 x 10⁴ (@4.2 K & 5 T) |
| 2  | HE+TAR             | MgB₂ (aa) +1.5 mol.% SiC | 950 °C/ 0.5 h    | 38.7   | 5.8 x 10³ (@4.2 K & 5 T) |
| 3  | HE+TAR [3]        | MgH₂ (abcr) +2B (Fluka) + 6 mol.%SiC | 670 °C/ 0.5 h | 36.0   | 1 x 10³ (@4.2 K & 9.5 T) |
| 4  | 14-filament       | MgB₂ (Lamia)     | 980 °C           | 36.5   | 2 x 10⁵ (@ 20 K & 1 T) |
| 5  | MA[5]             | Mg (goodfellow)+2B (fluka) | 600 °C/ 3 h    | 36.5   | 5.5 x 10⁴ (@ 20 K & 3 T) |

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

For the preparation of SEM samples, MgB₂ tapes (samples 4 and 5) were glued to Si-wafers [4] and the cross-section surface was polished using diamond foils. In the case of MgB₂ wires (samples 1-3) the lateral section of the wire was polished using diamond foils in a manner similar to TEM sample preparation (Fig. 1a). After polishing, the SEM samples were cleaned by ion etching for 30 minutes by 4 kV Ar⁺ ions incident at an angle of 12°. The carbon contamination in SEM samples was drastically minimised using this modified sample preparation method (Fig. 1a and 1b). TEM samples were prepared by a conventional TEM sample preparation procedure described elsewhere [4]. After ion etching, the electron microscopy samples were immediately transferred to the electron microscopes to minimise the artefacts due to oxidation. The SEM used for the microstructure analysis is described in Table 2. For TEM analysis energy filtering was used in a Zeiss 912 Ω (LaB₆, 120 kV) and a Libra 200FE STEM (FEG, 200 kV).

Table 2. Intensity of the signal (s) and the relative statistical error (σ) in the quantitative analysis of MgB₂ using different electron microscopy methods.

| Method               | Microscope description                                      | Signal name               | s    | σ (%) |
|----------------------|------------------------------------------------------------|----------------------------|------|-------|
| EPMA-WDX             | Jeol Superprobe 8900 RL                                    | B-K integrated x-ray cts. | 25000| 0.6   |
| SEM-EDX              | Same as for SEM-EDX mapping                               | B-K integratedx-ray cts.  | 4820 | 1.4   |
| TEM-EDX              | Zeiss 912 Ω with Si(Li) EDX detector (Oxford), 120 kV       | B-K integratedx-ray cts.  | 5300 | 1.4   |
| SEM-EDX mapping      | JEOL 6500F with field emission gun & Si(Li) EDX detector (Oxford) | Mg-K x-ray cts per pixel | 600  | 4.1   |
| STEM-EDX mapping     | Zeiss Libra 200FE with Si(Li) EDX detector (EDAX), 200 kV  | Mg-K x-ray cts per pixel | 100  | 10.0  |
| EFTEM-ESI            | Same as for STEM-EDX mapping                              | B-K edge intensity per pixel | 700  | 3.8   |
3. Results and discussion

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 of point spectra. A schematic diagram of the steps involved in the microstructure analysis of MgB$_2$ wires and tapes is shown in figure 2a.

Carbon contamination is a common artefact introduced mainly during sample preparation. It causes serious problems for the quantitative boron EDX analysis in MgB$_2$ samples because of the B and C peak overlap and for C analysis in SiC added MgB$_2$ wires and tapes. The problem of C contamination was significantly minimized by avoiding the use of organic resin during SEM sample preparation as described in the experimental section.
Structural granularity in MgB$_2$ arises not only from the cracks and voids, but also due to formation of colonies and secondary phases. Chemical mapping techniques are essential to study these phenomena related to thermodynamics.

The lateral resolution and the accuracy (in terms of the error in the quantitative analysis) of the different electron microscopy and spectroscopy techniques are given in figure 2b. In the MgB$_2$ analysis, the accuracy in the quantitative analysis is related to the statistical error in the electron or x-ray counts in elemental maps and spectra. (Table 2). It is seen from figure 2b, that an accurate chemical analysis of MgB$_2$ wires and tapes on different length scales is not possible with a single electron microscopy technique and therefore a combination of electron microscopy techniques is essential.

A RGB overlay of Mg(Red), O(green) and B(Blue) SEM-EDX elemental maps (henceforth referred to as RGB(Mg-O-B) image) of sample 1 is shown in figure 3b. It shows O free MgB$_2$ colonies (a colony is a 3-10 µm large dense arrangement of MgB$_2$ grains) and B-rich secondary phases, embedded in a granular oxygen-rich MgB$_2$ matrix. Colony formation is found to be a universal feature of all ex-situ MgB$_2$ samples [4,6], but the colony size and density vary strongly. From the Si SEM-EDX elemental map (not shown here) Si was found to be inhomogenously distributed in the MgB$_2$ matrix.

A RGB(Mg-Si-B) image of sample 3 is shown in figure 3f. It shows Mg$_2$Si and B-rich secondary phases, embedded in a MgB$_2$ matrix. The volume fraction of the B-rich secondary phases is however higher than in sample 1. The oxygen in the matrix of in-situ samples is concentrated at the voids or cracks, probably arising from the oxidation of unreacted Mg on contact with air. These features indicate incomplete formation of MgB$_2$ phase in the in-situ samples like sample 3.

Figure 3. (a) secondary electron image and (b) corresponding RGB(Mg-O-B) image of sample 1, showing MgB$_2$ colonies (1), B-rich secondary phases (2) and granular matrix (3). RGB(Mg-O-Si) image of STEM-EDX elemental maps and (c) RGB (B-C-O) image of ESI elemental maps, acquired from the granular matrix (a region similar to the one marked by rectangle in figure 3b) of sample 2. (e) Secondary electron image and (f) the corresponding RGB (Mg-O-B) image of sample 3.

The volume fraction of the B-rich and Mg$_2$Si secondary phases was quantitatively determined using the Mg-B and Mg-Si concentration-histograms (CHI) [7]. The chemical composition of the B-rich and Mg$_2$Si secondary phases was confirmed by acquiring EDX point spectra. The oxygen mole
fraction in the sample was determined from spectra acquired from the total area of the image during elemental mapping and will be discussed in more detail elsewhere.

Many of the microstructure features relevant for the synthesis technology are on the micrometer scale and can be efficiently studied by SEM analysis which includes SE imaging, EDX elemental mapping and EDX spectroscopy. Additionally SEM analysis is less demanding in terms of efforts and time and thus suitable for the analysis of a large number of samples, in order to optimize the synthesis technology to produce wires and tapes with higher critical current density. However, chemical analysis by SEM-EDX is limited by the lateral resolution of the method, which is about 1 µm.

Chemical mapping in TEM using EDX (STEM) and energy filtering (ESI :Electron Spectroscopic Imaging) is essential for the analysis of secondary chemical phases on the sub-µm scale. A RGB(Mg-O-Si) image of STEM-EDX elemental maps and RGB(B-C-O) image of ESI elemental maps, acquired from the granular MgB$_2$ matrix of sample 2 i.e. from a region similar to the one indicated by rectangle in figure 3b, is shown in figure 3c and 3d respectively. The MgB$_2$ grains appear red in the RGB (MgOSi) image (figure 3c). At the grain boundary about 50 nm thick, Si rich and O-rich phases appear. Since, the EDX detector used in the STEM was not able to fully detect B, it remained open whether the grain boundary phases contained boron. However, the RGB(B-C-O) image (figure 3d) of ESI elemental maps shows the grain boundaries to be deficient in boron. These 50 nm wide non superconducting MgSi$_x$O$_y$ phases at MgB$_2$ grain boundaries yield poor connectivity between grains which limits the $J_c$ of ex-situ samples like 1 and 2.

Diffraction contrast imaging in TEM is essential for the analysis of the MgB$_2$ grain size and crystal defects like grain boundaries, dislocations and precipitates which are comparable to the coherence length of MgB$_2$ (5-10 nm) and can act as pinning centers. TEM dark-field images in figure 4 show 20-50 nm, 100-300 nm and about 1000 nm large MgB$_2$ grains in sample 5, 2, and 4 respectively.

Quantitative B analysis by EDX has been established for SEM and TEM analysis [8]. Here we will concentrate on TEM. Quantitative boron analysis using TEM-EDX is essential to identify B-rich secondary phases and MgB$_2$ matrix. A series of TEM-EDX spectra were acquired at positions of increasing sample thickness in MgB$_2$, indicated in the bright-field image (figure 5a) of a colony of sample 4. B-K$_\alpha$ x-ray peaks of these spectra, after normalisation at the Mg-K$_\alpha$ peak are shown in (figure 5b). The height of the B-K$_\alpha$ x-ray peak decreases with increasing sample thickness because of the preferential absorption of the B-K$_\alpha$ x-rays in the sample which needs to be corrected. The absorption was corrected using a parameterless method [9] which does not require the absolute knowledge of specimen thickness and mass absorption coefficients of B-K$_\alpha$ x-rays.

The B mole fraction of sample 5, with and without B-K$_\alpha$ x-ray absorption correction is plotted as a function of sample thickness (in units of Mg-K$_\alpha$ x-ray counts) in figure 5c. Without absorption
correction the B mole fraction decreases exponentially with increasing sample thicknesses, where as with absorption correction, the B mole fraction is independent of the sample thickness.

Figure 5. (a) TEM bright field image of sample 4 . (b) TEM-EDX spectra acquired at points of increasing sample thickness marked in (a) . (c) Quantitative B analysis of sample 5 using TEM-EDX, with absorption correction (●) and without absorption correction (o) of B-Kα x-rays.

Using the advanced electron microscopy methods, the following microstructure parameters were extracted: 1) colony size, 2) volume fraction of B-rich secondary phases, 3) oxygen mole fraction and 4) MgB$_2$ grain size. Using these microstructure parameters a $J_c$-microstructure correlation model is established to explain the large variation of $J_c$ of MgB$_2$ wires and tapes, which will be presented elsewhere [1].

Acknowledgement
Authors are thankful to the following partners of the Hipermag consortium for providing samples and for the measurement of their superconducting properties ($T_c$ and $J_c$): W. Haessler of IFW Dresden, P. Kovach of IEE Bratislava, V. Braccini of INFM Genova, W. Pachla and A. Morawski of IHPP Warsaw, and S. Schlachter of FZK Karlsruhe. Authors are thankful to Fr. I. Meissner for assistance in sample preparation. Assistance by W. Sigle and C. Koch in using the 200kV Zeiss Libra FEG at the Max Planck Institute for Metals Research in Stuttgart is gratefully acknowledged. This work was supported by the EU-FP6 Specific Targeted Research Project HIPERMAG (STRP 505724-1).

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