Combined X-ray and electron microscopy study of MgB$_2$ powders, wires and tapes

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Abstract. MgB$_2$ wires, tapes and bulk samples produced within the EU-funded HIPERMAG project have been studied by a combination of X-ray diffraction and electron microscopy. The reaction layers forming at the interface between the ceramic core and Fe or Ni sheaths can be studied with both methods. The complementary techniques enable to study both the microstructure and the formation kinetics of the interface layers. Grain sizes can be determined either by direct observation or by analysis of the shape of X-ray diffraction peaks. Electron microscopy can detect B-rich secondary phases and phases present in small fractions that are not accessible by x-ray diffraction. On the other hand, synchrotron diffraction provides a fast and non-destructive method for the study of the main phases and their development during in-situ, high-temperature investigations. The combination of the two techniques is a very valuable tool for the optimisation of MgB$_2$-based superconducting material.

1. Introduction
The technological relevance of MgB$_2$-based metal-sheathed composites has induced a tremendous activity in all aspects relating to the optimisation of the performances of these materials. Careful investigations of the ceramic core microstructure are vital for understanding the influence of processing parameters on properties like the critical current density and the irreversibility field. The use of hard X-rays produced by a synchrotron source enables the non-destructive investigation of the phases present in the samples in transmission geometry. However, the weak scattering power of magnesium and boron sets limitations to the detection of the boron-rich magnesium borides. In contrast, electron microscopy coupled with selected area diffraction and compositional analysis is a powerful tool to identify and localise such phases as well as amorphous phases and precipitates that may be too small to produce a detectable diffraction pattern. Combining these two investigation techniques and taking advantage of the strength of each of them provides a detailed picture of the microstructure of the MgB$_2$-based samples. The phase evolution of compounds yielding detectable
diffraction intensities can also be followed during in-situ synchrotron studies under conditions similar
to those used during manufacture.

Technologically important aspects like MgB2-sheath interface, compactness and phase composition
of the MgB2 filament, active pinning defects like grain boundaries, precipitates and dislocations were
investigated using either SEM (scanning electron microscopy) and EPMA (Electron probe
microanalysis) or TEM (Transmission electron microscopy) depending on the length scale of the
feature under study.

2. Experimental

Samples with different characteristics produced within the EU-funded project “HIPERMAG” have
been used throughout these studies. We refer to specific publications for descriptions of the
preparation processes. The samples included multi-filament tapes [1], single-filament tapes [2], wires
with SiC additions [3] and bulk pellets sintered by hot isostatic pressing [4].

The high-energy X-ray diffraction measurements were conducted at the DESY-HASYLAB
synchrotron facility on beamline BW5 with a 90 keV incident beam in transmission geometry. Details
on the experimental set-up and data analysis can be found in a previous publication [5]. For high
temperature in-situ studies, short pieces of wires of tapes are clamped in a steel holder inserted in a
quartz tube. The samples are maintained in a flow of Ar (≤ 0.5 ppm residual O2) during the runs. Small
pieces of Ta foil are placed on the bottom of the sample space to act as an oxygen getter.

A Jeol JSM 6500F SEM with a field emission gun and a JEOL 8900 RL EPMA with a LaB6 gun
were used for electron microscopy analysis on the micrometer scale. For TEM analysis a LEO 912
transmission electron microscope operated at 120 kV and equipped with an EDX detector and Omega
energy filter is used. Special care had to be taken during sample preparation to avoid carbon
contamination, which severely affects the analysis of boron. Therefore SEM samples were not
prepared by embedding in resin. Instead the sample surfaces were polished directly using diamond
foils and subsequently cleaned using 4 kV Ar+ ions for 30 minutes. In SEM-EDX spectra acquired
from MgB2 wire samples prepared by the conventional method, the boron peak is dominated by the
neighbouring carbon peak, whereas no such artefact is found with the modified method. More details
of the applied methods and results are summarized in [6].

3. Results

3.1 Multi-filamentary tapes

A fourteen MgB2 filaments tape comprising a Cu core, an Fe protective layer and a Ni matrix was
studied. MgB2 colonies of sizes varying from 0.5 µm to 6 µm were observed by SEM. In this sample,
the presence of three different metals in the sheath results in a large amount of intense diffraction
peaks covering a non-negligible area of the diffraction patterns.

It is therefore difficult to estimate the coherent crystalline size of the sub-grains forming the colonies
by means of peak shape analysis. Nevertheless, as shown in figure 1, it is possible to detect several

![Figure 1: Detail of an XRD pattern showing various phases including MgNi_2B_2.](image1)

![Figure 2: SEM picture showing the various areas of the interface reaction layer.](image2)
phases and to identify a ternary compound, MgNi$_{2.5}$B$_{2}$. This is the only ternary compound detected by diffraction. However, SEM/EPMA investigations reveal two distinct reaction layers (figure 2). The composition of the inner reaction layer was found to be MgNi$_{2.9}$B$_{2}$. This is likely to correspond to the MgNi$_{2.5}$B$_{2}$ composition found in XRD patterns. At the farthest edges of the filament, the composition is MgNi$_{2.0}$B$_{0.6}$. The outer reaction layer has a homogenous chemical composition of MgNi$_{1.0}$B$_{3.3}$.

Performing \textit{in-situ} studies under real heat-treatment conditions would enable to determine the threshold temperature for the appearance of this reaction layer and study its formation kinetics.

3.2 Single filamentary tapes
Performing \textit{in-situ} diffraction studies on un-reacted single-filament tapes with an Fe sheath, it was possible to determine the interface reaction formation kinetics, which in this case consists of Fe$_{2}$B. As shown in figure 3, the amount of this phase contributing to the diffraction pattern increases during the whole duration of the heat-treatment at 600°C. The very high reactivity of the precursor powders used for the manufacture of this sample is reflected in the low onset temperature for the formation of MgB$_{2}$ ($T \approx 400\,^\circ\text{C}$). This feature should be carefully taken into consideration if intermediate annealing steps are performed during the deformation stage of the preparation process.

Figure 3: Evolution of selected phases during a high-temperature run at 600°C.

Figure 4 shows a SEM image of a similar tape after 3h annealing at 600°C. Besides the reaction layer, many dark grains are evidenced within the ceramic core. EPMA analyses show that these consist in B-rich Mg borides, which are not detected by X-ray diffraction. The size of these precipitates was found to be proportional to the annealing temperature.

3.3 Wires with additives
A SEM cross section image of a wire containing a mixture of MgB$_{2}$ and 1.5 at.% SiC prepared by hydrostatic extrusion and two axial rolling is shown in figure 5. Approximately 30 nm sized SiC inclusions are visible. This size is similar to the initial SiC powder size. The MgB$_{2}$ core of the wire is compact. No reaction layer is seen at the interface.

3.4 Hot-pressed ceramics
The macroscopic grain size of these samples, as determined by SEM observations, was lying in the 0.5 to 100 µm range. Based on the \textit{shape} of diffraction peaks (figure 6), the \textit{size} of the coherent crystalline domains of the MgB$_{2}$ phase has been determined. This size ($\approx 400$ nm) was found to be sample independent, showing that this parameter was not influenced by the heat-treatment conditions. The residual strain, determined by the same method, is quite small ($\approx 0.04\%$) and similar for all samples. The temperature used for the synthesis of the samples ($900\,^\circ\text{C} – 1000\,^\circ\text{C}$) is in fact high enough for releasing the strain present in the powders during the initial stages of processing.
4. Discussion and conclusions
The development of the major phases in MgB₂ ceramics, wires and tapes could be successfully tracked during in-situ synchrotron studies. In specific cases, X-ray absorption in the metal sheath can hamper the observation of relevant diffraction peaks. The low scattering power of B imposes restrictions on the detection of boride compounds, especially when composite sheaths or metals with strong scattering power (Nb, Ta, etc) are used. In such cases, specially prepared samples with very thin sheaths would be more suitable for model studies aiming at determining the threshold temperatures for reaction between the ceramic core and the sheath material.

Lower fluorescence yield of B-K X-rays, their rapid absorption in the sample and proximity of C-K X-ray peak to B-K X-ray peak are the difficulties encountered in the x-ray microanalysis of MgB₂ wires and tapes. However the present day EDX detectors allow peak to background ratios of > 10 for B in SEM-EDX. Thus, if the carbon contamination during sample preparation is eliminated, quantitative chemical analysis (including B) of MgB₂ tapes and wires is possible.

The grain size, dislocation density and density of precipitates of the MgB₂ matrix is an important parameter and can only be determined reliably by TEM. For multi-filamentary tapes grain sizes were determined as 0.5 - 1 μm, and dislocation densities up to \(10^{10}\) cm\(^{-2}\) were found. Reaction layers are formed at MgB₂-Ni and MgB₂-Fe interfaces and their chemical composition was determined by EPMA. For single-filament tapes low sintering temperatures (500°C) yielded considerable fraction of B-rich Mg-borides. With 600°C sintering temperature the phase fraction of higher borides decreased. The upper critical field was found to increase from 6 T (500°C reaction) to nearly 12 T (600°C) [7]. The critical current density of MgB₂ wires can be enhanced by nanometer sized SiC inclusions. These inclusions can be imaged by TEM analysis.

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References