In-situ studies of Fe$_2$B phase formation in MgB$_2$ wires and tapes by means of high-energy x-ray diffraction

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Abstract. The phase transformations occurring in the ceramic core of Fe-sheathed MgB$_2$ wires and tapes prepared by in-situ reaction of Mg and B precursor powders, have been studied by means of high-energy x-ray diffraction. In particular, the time evolution of the Fe$_2$B phase, forming at the interface between the sheath and the ceramic, was studied at different sintering temperatures. The reactivity of the sheath towards Fe$_2$B formation is strongly dependent on powder pre-treatment. In wires produced with commercial Mg and B powders without additional mechanical activation, the Fe$_2$B phase starts forming around 650°C. In contrast, in tapes produced from a mixture of Mg and B powders subjected to high-energy ball milling, the interfacial Fe$_2$B layer forms readily at 600°C. The increase of Fe$_2$B volume fraction is linear to first approximation, showing that the interfacial layer does not act as a diffusion barrier against further reaction between the sheath and the ceramic core. If the ceramic core is converted to MgB$_2$ at a temperature, which is low enough to avoid Fe$_2$B formation, the interface is stable during further annealing at temperatures up to 700°C at least. However, too high annealing temperatures (T > 800°C), would result in formation of Fe$_2$B, probably following the partial decomposition of MgB$_2$.

1. Introduction

The majority of MgB$_2$-based conductors are presently manufactured in association with iron, either as a single sheath material or as a protective layer between the superconducting ceramic core and an external sheath material such as Cu [1,2]. This choice results from the stability of Fe towards reaction with MgB$_2$ in comparison with other metals [3,4]. However, Fe is not totally inert during high-temperature treatments, especially when a mixture of Mg and B powders are loaded in the tube instead of pre-reacted MgB$_2$. An interface reaction layer consisting of Fe$_2$B may form and reduce the actual cross-section of the ceramic core carrying the superconducting current. Depending on the manufacturing process, the thickness of this layer can reach up to several micrometers, setting serious limitations to the size of the MgB$_2$ filaments in multi-core conductors.

The formation of the interface reaction layer can be followed in-situ by X-ray diffraction in transmission geometry, using a high-energy synchrotron beam. We compare here the behavior of two kinds of Fe-sheathed conductors prepared either with a “standard” mixture of micrometer-sized Mg and B powders or using nanometer-sized precursors mechanically alloyed by high-energy ball milling.
2. Experimental

For the “standard” wires, commercial Mg (= 30 μm) and B (= 1 μm) powders (Alfa Aesar) were mixed in proper ratio and homogenised by ball milling for 10 min. The powder was packed in a Fe tube, which was then deformed by rotary swaging followed by two-axial rolling into rectangular wires of 1.24 mm x 1.24 mm [5].

For the preparation of the samples with mechanically activated precursor powders, the Mg and B powder mixture was mixed in a high-energy ball-mill for 50h. After loading in an Fe tube, the composite was deformed by drawing and rolling to flat tapes [6]. 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 [7]. Short pieces of wires or tapes (2 cm length) were clamped in a steel holder inserted in a quartz tube. The sample holder assembly was placed in a high-temperature furnace equipped with a stainless steel heat shield. The samples were maintained in a flow of Ar (≤ 0.5 ppm residual O₂) during the runs. Small pieces of Ta foil were placed on the bottom of the sample space to act as an oxygen getter. A heating rate of 200°C h⁻¹ was used to reach the annealing temperature. A thermometer was situated close to the samples and the temperature was stable within 0.5°C during the 3h long dwell at 600°C, 650°C, 700°C or 780°C.

A beam cross-section of 1x1 mm² was chosen to probe the ceramic core throughout the width of the samples. Diffraction patterns were recorded on a two-dimensional image plate and evaluated using the fit2d software package [8]. The intensity of the signal was normalised to the X-ray beam current value, which varies with time during the experiment.

3. Results and discussion

Figure 1 shows the interface reaction layer formed in a “standard” wire after 3h sintering at 780°C. It can be unambiguously identified as Fe₂B. Other Fe-borides that may form in this area [9] were not detected in the diffraction patterns during the present investigations.

Figure 2 presents a compilation of data on the sintering-temperature dependence of the interface reaction layer thickness. For the samples prepared from Mg and B powder mixtures (in-situ process), the thickness increases with temperature in a rather consistent way. Deviations from a linear dependence are mostly attributable to differences in processing variables like sintering time for...

![Figure 1](image1.png)

**Figure 1:** Optical micrograph showing the interface reaction layer formed after 3h at 780°C.

![Figure 2](image2.png)

**Figure 2:** Thickness of the interface reaction layer versus annealing temperature for in-situ and ex-situ preparation processes.
example. On the other hand, the samples prepared from pre-reacted MgB₂ powders (*ex-situ* process) show a clearly different behaviour, the interface reaction taking place at higher temperatures.

The evolution of the amount of Fe₂B phase in the “standard” wires is plotted in Figure 3 for two different sintering temperatures. The equivalent thickness of the interface layer can be related to the diffraction intensity by comparison with a polished cross-section of the samples at the end of the *in-situ* studies. The interface reaction takes place from $T \approx 655^\circ$C during the heating stage. In another high-temperature run performed with a sintering temperature of 650°C, the intensity of the Fe₂B diffraction lines was hardly higher than the background noise level, even after 3h at high temperature.

In contrast, the Fe₂B phase readily forms at lower temperatures in the samples prepared with mechanically activated precursors (Figure 4). The difference is most probably related to the higher reactivity of the smaller B particles present in the ball-milled powders. In both cases, we observe that the increase of the Fe₂B volume is approximately linear, suggesting that the interface layer does not act as a diffusion barrier against further reaction between boron and the Fe-sheath. The sintering temperature dependence of the Fe₂B formation kinetics is also clearly illustrated and explains in part the data presented in figure 2.

Ball-milled Mg and B precursor mixtures have an extremely high reaction rate that may result in the formation of MgB₂ already during annealings performed in the course of the tape deformation process. In such a case, the formation of Fe₂B is prevented during further heat-treatments provided the final sintering is not performed at a temperature high enough to induce partial decomposition of MgB₂.

**Figure 3**: Evolution of the amount of Fe₂B phase in wires prepared with “standard” commercial Mg and B powders. O: 780°C, ▲: 700°C.

**Figure 4**: Evolution of the amount of Fe₂B phase in tapes prepared with Mg and B powders mixed using high-energy ball-milling.

### 4. Conclusions
Fe₂B is easily detected by hard X-ray diffraction without need for destroying the samples. The detection limit for Fe₂B corresponds to a layer thickness of 150 to 200 nm, making synchrotron radiation a very interesting tool for the non-destructive examination of the interface reaction layer in Fe-sheathed MgB₂ wires and tapes after heat treatment, also in long conductors.

The formation kinetics of Fe₂B is strongly temperature and powder characteristics dependent. The Fe₂B layer does not appear to act as a diffusion barrier against further reaction between the sheath and the ceramic core.

Besides Fe₂B, *in-situ* synchrotron investigations enable to follow the development of several other phases involved in the processing of MgB₂-based wires and tapes.

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References
[1] Bhatia M, Sumption M D, Tomsic M and Collings E W 2004 Physica C 407 153
[2] Glowacki B A, Majoros M, Vickers M, Evetts J E, Shi Y and McDougall I 2001 Supercond. Sci. Technol. 14 193
[3] Jin S, Mavoori H, Bower C and van Dover R B 2001 Nature 411 563
[4] Zhou S, Pan A V, Ionescu M, Liu H and Dou S X 2002 Supercond. Sci. Technol. 15 236
[5] Ková P, Hušek I, Melišek T and Štrbík V 2005 Supercond. Sci. Technol. 18 856
[6] Fischer C, Rodig C, Hässler W, Perner O, Eckert J, Nenkov K, Fuchs G, Wendrock H, Holzapfel B and Schultz L 2003 Appl. Phys. Lett. 83 1803
[7] Poulsen H F, Frello T, Andersen N H, Bentzon M D and von Zimmermann M 1998 Physica C 298 265
[8] Hammersley A P, Svensson S O, Hanfland M, Fitch A N and Häusermann D 1996 High Pressure Research 14 235
[9] Lezza P, Gladyshevskii R, Suo H L and Flügler M 2005 Supercond. Sci. Technol. 18 753
[10] Pachla W, Presz A, Ková P, Hušek I and Diduszko R 2004 Supercond. Sci. Technol. 17 1289
[11] Grovenor C R M, Goodsrin L, Salter C J, Ková P and Hušek I 2004 Supercond. Sci. Technol. 17 479
[12] Goldacker W, Schlachter S I, Obst B, Liu B, Reiner J and Zimmer S 2004 Supercond. Sci. Technol. 17 8363
[13] Fischer C, Hässler W, Rodig C, Perner O, Behr G, Schubert M, Nenkov K, Eckert J, Holzapfel B and Schultz L 2004 Physica C 406 121
[14] Xu H L, Feng Y, Xu Z, Li C S, Yan G, Mossang E and Sulpice A 2005 Physica C 419 94