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# Microstructure of $MgB_2$ superconducting wire prepared by internal magnesium diffusion and in-situ powder-in-tube processes – Secondary phase intergrain nanolayers as an oxygen content indicator

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ABSTRACT

We analyzed microstructure of two undoped $MgB_2$ single core wires prepared by two different technologies – in-situ powder-in-tube (PIT) technology and internal magnesium diffusion (IMD) processes. Their microstructure showed mainly different densities of superconducting material, corresponding content of pores and the volume ratio of amorphous MgO phase. We observed a special microstructural feature – thin oriented secondary phase layers on grain boundaries of plate-shaped $MgB_2$ grains. The significant decrease of oxygen content in IMD wire was reflected in the presence of thin oriented Mg layers while in PIT wire thin oriented MgO layers were observed. The microstructure difference is reflected in increased critical current density $J_c$ of the IMD wire in comparison to the PIT one.



## 1. Introduction

Powder-in-tube (PIT) process is frequently used for the manufacture of superconducting $MgB_2$ wires [1–5]. Apparent in-field increase of critical current densities has been reached by different types of doping [6–9]. However, critical current densities of PIT $MgB_2$ wires do not meet requirements for practical use and need to be improved further. The main problem is high porosity of superconducting material due to low packing densities of $MgB_2$ grains in the case of ex-situ approach and due to apparent shrinkage of material during reaction between B and Mg in the case of in-situ technology [1]. To overcome the problem of high porosity liquid Mg diffusion [10] and later internal Mg diffusion (IMD) [11] methods have been proposed. They allow obtaining very dense $MgB_2$ structures. Dense C-doped $MgB_2$ layers prepared by IMD process exhibited critical current density $J_c$ of 1.07–$1.2 \times 10^5$ A cm$^{-2}$ at 4.2 K and 10 T and an engineering critical current density $J_e$ of about 1–$1.67 \times 10^4$ A cm$^{-2}$ [12,13].

Recently we presented IMD processed non-doped single-core and four-core $MgB_2$ wires [14,15].

The aim of this contribution is to analyze and compare microstructure of two single-core undoped $MgB_2$ wires made by PIT and IMD processes. We have chosen two wires, whose preparation was optimized from the point of view of high critical current density. Even though different barrier materials (Ti for IMD and Nb for PIT wires) were used, their effect on the $MgB_2$ cores becomes relevant at higher annealing temperatures than those used to prepare the studied wires [4].

TEM, EDS and XRD analyses were applied to the wires to investigate the basic properties of $MgB_2$ phase. Electrical properties of both $MgB_2$ wires are also measured and compared [16].

## 2. Experimental

To make an IMD wire a Ti-tube of inner/outer diameters of 5/7.5 mm with a coaxial Mg wire of 2.9 mm in diameter surrounded by B powder of 99% purity was rotary swaged to 6.5 mm and then inserted into a Cu tube of 6.7/9.15 mm. The assembled billet was hydrostatically extruded into a wire of 6.0 mm and then two-axially rolled to the wire size of $1.08 \times 1.08$ mm$^2$ [17]. A short piece of as-rolled wire was isostatically pressed by 1.9 GPa and finally annealed at 640 °C for 1 h in pure argon atmosphere.

A single-core PIT $MgB_2$ wire was produced by in-situ technique. Mg (purity 99.8%, size of particles 43 μm) and B (purity 99%, size of particles 200 nm) powders weighted in stoichiometric ratio were mixed in iron ball mill for 20 min in clockwise and counterclockwise directions at a rate of 280 rev/min. The wire was made by filling the Mg + B powder mixture into a Nb tube, then inserting the

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filled Nb tube into a Cu tube and subsequent rolling of the resulting structure into a rectangular shape of approximately $1 \times 1\ mm^2$. Afterward the sample was heat treated at 650 °C for 30 min in pure argon atmosphere.

Optical microscopy and Vickers microhardness measurements HV0.05 (5 g, 20 s) were performed on wire cross-sections.

XRD measurements were made using Bruker D8 DISCOVER diffractometer equipped with X-ray tube with rotating Cu anode operating at 12 kW (40 kV/300 mA). The measurements were performed in parallel beam geometry with parabolic Goebel mirror in the primary beam. Metallic covers of short wire pieces were peeled off and the superconducting cores or layers were crushed in an agate mortar.

Energy dispersive spectroscopy (EDS) measurements were performed on wire cross-sections prepared by accustomed dry grinding and polishing technique by JEOL JSM 7600F scanning electron microscope (SEM) equipped with Oxford Instruments energy dispersive X-ray spectrometer. All EDS experiments used 5 kV electron beam and internal standard method was used for quantitative analysis. As an $MgB_2$ standard we used a part of IMD wire where nearly pure $MgB_2$ phase was confirmed by transmission electron microscopy (TEM) [18]. TEM specimen was prepared using focused ion beam (FIB) technique using Dual Beam Helios Nanolab 600i device at IFW Dresden. TEM analysis was made using JEOL JEM 1200 EX conventional TEM.

Transition temperature $T_c$ and critical current density $J_c$ were investigated by magnetic measurements on 3 mm long samples using the VSM option of a 9 T PPMS from Quantum Design. Transition temperature $T_c$, defined as the onset of diamagnetism, was determined from zero field cooled measurements at 10 mT. In the temperature range 4.2–36 K (2 K steps) hysteresis loops between −2 and +9 T with constant field sweep of 6.3 mT/s were recorded. Using Bean's critical state model [19] current densities $J_c$ were determined.

## 3. Results and discussion

### 3.1. Microstructure

Both investigated wires have comparable outer dimensions of about $1 \times 1\ mm^2$, but they have different $MgB_2$ core geometry (see the insets in Fig. 1). The PIT wire has relatively large inner core with the area of $0.234\ mm^2$ and $MgB_2$ occupies 22.2% of the wire cross-sectional area. In the IMD wire $MgB_2$ layer occupies only 9.4% of the cross-sectional area and 11.7% is occupied by a central hole. The central hole is a result of Mg diffusion into B powder during annealing. The created IMD $MgB_2$ layer is very compact without any visible pores when analyzed by optical microscope, SEM (Fig. 1b) and TEM [18]. In PIT wire there are pores distributed through the whole superconducting core. They reach dimensions from sub-micrometer size up to several μm (Fig. 1a). Observed pores have often shapes prolonged in the direction of wire extension (Fig. 2). They were created due to Kirkendall process during Mg diffusion into boron and original Mg powder particles were prolonged due to wire deformation by rolling.

The difference in pore volume ratio in both wires is in accord with the different average microhardness of $MgB_2$ prepared by PIT or IMD. While average microhardness in the range of HV0.05 = 350–500 MPa was measured for in-situ PIT $MgB_2$ wires annealed at temperatures between 650 and 800 °C [20], the presented $MgB_2$ layer prepared by IMD after heating at 640 °C had average microhardness HV0.05 = 1600 MPa.

#### 3.1.1. Composition

The SEM images in Fig. 1 show many dark-gray secondary phase grains more or less uniformly distributed throughout the gray $MgB_2$ in the both wires. In IMD wire the large dark-gray grains correspond to B-rich phase with the B/Mg atomic ratios ranging from 87/13 to 91/9 (estimated using EDS analysis). TEM analysis showed that they consisted of amorphous or nanocrystalline mixture of boron, $MgB_4$ and possibly some other $MgB_x$ phases with $x > 4$ [18]. In the PIT wire, dark particles are also amorphous (as proved by TEM) and have the B/Mg atomic ratios ranging from 90/10 to 95/5. The B-rich grains are regions with small content of oxygen (below 1 at %) in the both wires.

The majority of superconducting core or layer has gray contrast in SEM, which is homogeneous in IMD wire but variable in PIT wire (Fig. 1). TEM analysis of IMD wire showed that the superconducting layer besides large B-rich grains consisted mainly of $MgB_2$ phase with very small volume ratio of pure Mg [18]. This made it possible to use a selected part of $MgB_2$ layer near the Ti sheath as an internal standard for EDS analysis. The method of internal standard gives more accurate quantitative characterization of low atomic number elements than using fabric standards.

The variable contrast of the PIT wire in Fig. 1a is a result of inhomogeneous phase distribution, where the brighter regions correspond to regions with higher oxygen content. Because of the aforementioned inhomogeneity the core composition was measured from areas of about $30 \times 30\ \mu m^2$ from different parts of the $MgB_2$ core. The average B/Mg atomic ratio was estimated as 73/27. Point analysis of only gray regions (excluding the dark-gray B-rich grains as well as the brighter oxygen rich regions) gave average B/Mg atomic ratio of 69/31. This value could not be regarded as the exact atomic ratio in $MgB_2$ phase because the average volumes with dimensions larger than $MgB_2$ grain size observed by TEM (see Section 3.1.2) are measured. Casino software

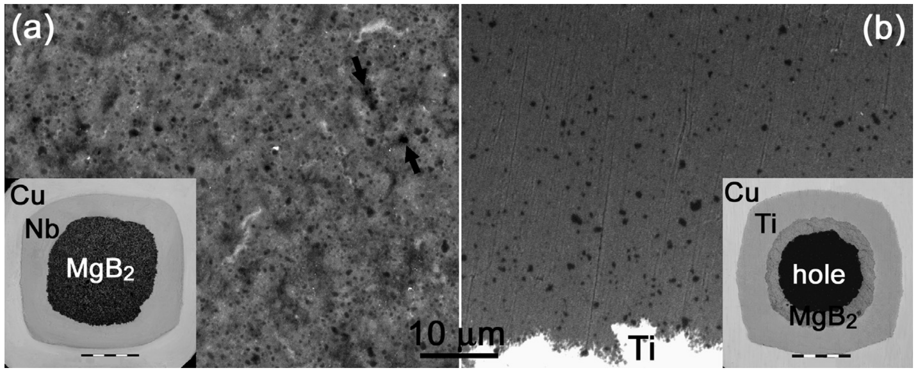


**Fig. 1.** SEM images of PIT (a) and IMD (b) samples. Two larger pores are marked by the black arrows. On the insets there are the corresponding images of whole polished cross-sections in optical microscope. The markers in the insets correspond to 300 μm.