Filament and interface structure of \textit{in-situ} MgB$_2$ wires

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\textbf{Abstract.} The structure of MgB$_2$ filaments and interface areas of \textit{in-situ} made composite MgB$_2$/Ti/Cu/Monel wires sintered at temperatures 650-850°C were studied by polarized light optical microscopy and Vickers microhardness. The microhardness can be used for the filament density evolution and also for the sensitive detection of sheath contamination. The temperature dependent MgB$_2$/Ti and Ti/Cu interface reactions were studied. The presented results give useful information above how the applied composition and annealing can affect the core density, $J_c$ and interface diffusion/reaction.

1. \textbf{Introduction}

The evaluation of powder density is important for MgB$_2$ composite superconductors made by powder-in-tube (PIT) process, where deforming routes, tool geometry and all composite elements play an important role. Vickers microhardness has been used many times for the composites containing filaments made by PIT [1-5]. Detailed studies of variable BSCCO filament densities in Ag matrix were performed [3-4]. The density of ‘as-deformed’ \textit{ex-situ} MgB$_2$ wires has also been tested by the Vickers microhardness [5]. The highest hardness was measured for large MgB$_2$ grains and an increased density has been observed for a mechanically reinforced sheath. Beilin et al. have shown the relation of Vickers microhardness in MgB$_2$ with current density for \textit{ex-situ} Ni sheathed wire [6]. It was found that microhardness data gave valuable information about MgB$_2$ and metal sheath hardening, which is influenced by the applied deformation and by wire composition as well. Very high hardness values indicated undesirable phases created by inter-diffusion and/or inter-reaction among B, Fe and Cu, which was confirmed also by microprobe analysis [7].

Recently, titanium as a sheath material has been used for MgB$_2$ wires [8-9]. Alessandrini et al. have fabricated Ti sheathed single-core MgB$_2$ wire and they did not observe any reaction or diffusion up to 900°C [8]. Kovac et al. observed some chemical reaction of MgB$_2$ with the Ti barrier and with the Cu stabilizer at annealing temperatures above 800°C [9].

The aim of this contribution is to show the capability of the Vickers microhardness test to analyze the sheath interactions of MgB$_2$/Ti/Cu/Monel \textit{in-situ} wire subjected to variable heat treatments.

2. \textbf{Experimental}

Four-core MgB$_2$/Ti/Cu/Monel composite wires were prepared by an \textit{in-situ} process using so called rectangular wire-in-tube technique (RWIT) [9-10]. The final rectangular wire cross-sections (1.2 mm x 1.2 mm) contained 6.6% of MgB$_2$+10wt%SiC filament area, 14% Ti-barrier, 24% of OFHC copper stabilizer and 55.4% of Monel Alloy 400 outer sheath. Short samples were heat treated in argon atmosphere at following temperatures ($T_s$): 650°C, 700°C, 750°C, 800°C and 850°C for 0.5 hr.
Transport critical current densities of differently treated samples were measured at 4.2K in a 5 T external magnetic field by a standard four-probe technique with $I_c$ criterion of 1 $\mu$V/cm. Annealed samples were polished and etched by 30% nitric acid solution to allow better resolution by optical microscopy (OM). An Olympus BX51M microscope equipped with polarized light was used for the interface area observations. Figure 1 shows the etched cross-section annealed at 850$^\circ$C. The Vickers microhardness HV 0.01 (10g/10s) and HV 0.05 (50g/10s) were measured in MgB$_2$ cores as well as in the composite elements and interface areas of the as-deformed and heat treated wires. The indentation size was averaged using approximately 10 measurements for HV 0.01 and HV 0.05.

![Figure 1](image1.png)

**Figure 1.** The cross-section of the etched MgB$_2$/Ti/Cu/Monel wire annealed at 850$^\circ$C.

![Graph](image2.png)

**Figure 2.** The filament microhardness HV 0.05 and transport current densities at 5 T and 4.2 K.
3. Results and Discussion

3.1. MgB$_2$ filaments and metallic sheaths

The averaged HV 0.05 values for MgB$_2$ filaments are plotted in Figure 2 together with the filament critical current densities ($J_c$) measured at 5 T. While an initial hardness HV 0.05 = 170 was measured for the as-deformed Mg+B filaments, MgB$_2$ phase creation leads to an apparent increase of HV 0.05 > 400 and it continued to increase with annealing temperature. The highest value HV0.05 = 535 is measured for the sample annealed at 850 $^\circ$C. The $J_c$ also increases with temperature and increases by 40 % between 800 $^\circ$C and 850 $^\circ$C (from 73 kAcm$^{-2}$ to 92 kAcm$^{-2}$). This $J_c$ improvement cannot be explained by the small filament density increase between 800 $^\circ$C (510) and 850 $^\circ$C (535). The filament density is also influenced by the mechanical strength of the sheath material, which is proportional to averaged strength (hardness) of individual composite components. The strengthening of Ti barrier for $T_s > 700$ $^\circ$C was measured [9]. The increased hardness of titanium barrier can be caused by possible diffusion/reaction of elements from MgB$_2$ filaments on the one side and with Cu stabilizer on the opposite side.

![Figure 3. MgB$_2$/Ti/Cu area with Vickers indentations after annealing at 850 $^\circ$C.](image3)

![Figure 4. MgB$_2$/Ti interface layer (1) created after annealing at 850 $^\circ$C/30min.](image4)
3.2. Ti barrier

A more detailed analysis has been done by polarized light optical microscopy (POM) and localized HV 0.01 measurements at both Ti interfaces. Figure 3 shows POM picture of the MgB$_2$/Ti/Cu area with Vickers indentations made after annealing at $T_s = 850$ °C. One can see that the size of the indentations in the Ti barrier is dependent on their distance from the MgB$_2$ filament and also from the Cu stabilizer. It means that some inter-diffusion/reaction took part at both sides of the Ti barrier leading to the creation of multiphase layers. More selective etching and POM allowed finding the reactive layer at MgB$_2$/Ti (see Fig. 4) and the Ti/Cu interface which consisted of several separated layers (Fig. 6). Therefore, HV 0.01 measurements across the Ti barrier and also in the separate layers 1 (at MgB$_2$/Ti) and 2, 3 and 4 (marked from Ti to Cu side) have been done for all temperatures.

![Figure 5. Ti-B binary diagram [11].](image)

The hardness of layer 1, with an average thickness of 4.5 and 10 μm had a linear increase between 650°C and 800°C and nearly one order of magnitude increase (from 350 to 2200) between 800 °C and

![Figure 6. Ti/Cu interface layers (2, 3 and 4) after annealing at 850 °C/30min.](image)
The Ti-Mg binary diagram [11] indicates diffusion of Mg into Ti is possible at relatively low temperatures ( > 650°C) and α-Ti phase can be present for 0-1.6 at% of Mg. The diffusion of magnesium increases with temperature and a higher content of α-Ti can lead to increased hardness. A sharp increase of HV 0.01 measured at $T_s > 800°C$ cannot be attributed to α-Ti phase, but most probably to some reaction of Ti with boron (titanium boride) or with free oxygen present inside the filaments (titanium oxide). Figure 5 shows possible phases of Ti-B, where the probable phase is α-Ti for B < 0.2 at% B. Our results show that Ti is not inert and reaction and/or diffusion with MgB$_2$ filaments occur at temperatures 750 – 850°C which was not observed by Alessandrini et al.

The layers 2, 3 and 4 observed at Ti/Cu interface (see Fig 6) have a microhardness in the range of 130 – 580 and their thickness as well as HV 0.01 values increase with $T_s$. These layers are created by inter-diffusion between Cu and Ti. Layers 2 and 3 of 1.0 - 5.5 μm thickness are well separated one from another and they are harder (HV 0.01 = 250 - 580) than layer 4. The thickness of the less uniform layer 4 (close to Cu) is ranging from 10 to 15 μm (for 650 – 850 °C) and the hardness is lower (HV 0.01 = 130 – 300), which corresponds probably to Ti diffusion into copper. The binary Ti-Cu diagram [11] allows predicting what possible phases can be present in layers 2, 3 and 4. For the low Cu content (0-1.6 at%) only α-Ti phase is created in layers 2 and 3 at temperatures below 850°C and coexistence of α-Ti + Ti$_2$Cu is possible up to 33.3 at% of Cu. Other side of the Ti-Cu binary diagram shows the existence of (Cu) up to 8 at%Ti between 500 °C and melting temperature of copper and βTiCu$_4$+αCu for Cu content above 81 at% and temperatures 500-885 °C. If Cu concentration is larger than 5 at%, it is not possible to use $T_s \geq 875$ °C due to Ti-Cu eutectic (L + (Cu) ↔ βTiCu$_4$ at 875 ±10 °C Eutectic). Therefore 885 °C is the temperature limit for the application of Ti barrier with Cu.

### 3.3. Cu stabilizer

Oxygen free high conductive copper is used as the stabilizer in presented wire, which should be protected from the reaction with magnesium and boron by Ti barrier to keep the high thermal and electrical conductivity. As shown above, some reaction with Ti took place during the final heat treatments, which contaminated the Cu into some depth depending on the applied $T_s$ (see Fig. 6). It means that the reacted Cu area will not have sufficient thermal and electrical conductivity after sintering, which should be taken into account for the MgB$_2$ wire design using a Cu stabilizer protected by a Ti barrier. The Cu/Monel interface area was also analyzed by POM. Figure 7 shows the very sharp interface between copper and Monel indicating no inter-diffusion after sintering at the highest temperature $T_s = 850$ °C.

![Figure 7. POM picture of Cu/Monel interface after annealing at $T_s = 850$ °C.](image-url)
Fine grain Monel structure consists of the mixture of dark and light grains of average size \( \approx 4 \mu m \). The area of dark grains corresponds to 28-34 % of total area, which correlates well with the content of copper in the used Monel 400 alloy.

4. Conclusions
Polarized light optical microscopy and Vickers microhardness were used to analyze the composite elements and interface areas of MgB\(_2\)/Ti/Cu/Monel wire annealed between 650-850 °C. It was found that HV 0.05 data gave valuable information about the MgB\(_2\) filament density and metal sheath hardness after annealing. Localized HV 0.01 measurements done at the MgB\(_2\)/Ti and Ti/Cu interface areas showed that titanium is not inert and some reaction and/or diffusion with MgB\(_2\) filaments occurred at 750-850 °C. Much more pronounced inter-diffusion was observed at the Ti/Cu boundary. The reacted Cu area is not effective for thermal stability, which should be taken into account in the case of a Cu stabilizer protected by Ti barrier.

Due to a Ti-Cu eutectic, Ti can be used as barrier only if \( T_s < 875 \) °C.

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