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Effect of sheath material and reaction overpressure on Ag extrusions into the TiO_2 insulation coating of Bi-2212 round wire

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Abstract

In order to develop a high current density in coils, Bi-2212 wires must be electrically discrete in tight winding packs. It is vital to use an insulating layer that is thin, fulfils the dielectric requirements, and can survive the heat treatment whose maximum temperature reaches 890 °C. A thin (20–30 μm) ceramic coating could be better as the insulating layer compared to alumino-silicate braided fiber insulation, which is about 100 μm thick and reacts with the Ag sheath during heat treatment, degrading the critical current density (J_c). At present, TiO_2 seems to be the most viable ceramic material for such a thin insulation because it is chemically compatible with Ag and Bi-2212 and its sintering temperature is lower than the maximum temperature used for the Bi-2212 heat treatment. However, recent tests of a large Bi-2212 coil insulated only with TiO_2 showed severe electrical shorting between the wires after over pressure heat treatment (OPHT). The origin of the shorting was frequent silver extrusions that penetrated the porous TiO_2 layer and electrically connected adjacent Bi-2212 wires. To understand the mechanism of this unexpected behaviour, we investigated the effect of sheath material and hydrostatic pressure on the formation of Ag extrusions. We found that Ag extrusions occur only when TiO_2-insulated Ag-0.2%Mg sheathed wire (Ag(Mg) wire) undergoes OPHT at 50 bar. No Ag extrusions were observed when the TiO_2-insulated Ag(Mg) wire was processed at 1 bar. The TiO_2-insulated wires sheathed with pure Ag that underwent 50 bar OPHT were also free from Ag extrusions. A key finding is that the Ag extrusions emanating from the Ag(Mg) sheath actually contain no MgO, suggesting that local depletion of MgO facilitates local, heterogeneous deformation of the sheath under hydrostatic overpressure. Our study also suggests that predensifying the Ag(Mg) wire before insulating it with TiO_2 and doing the final OPHT can potentially prevent Ag extrusion.

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1. Introduction

$Bi_2Sr_2CaCu_2O_x$ (Bi-2212) is the only high temperature superconductor available in a round wire form that has a very high critical current density (J_c is around 10^5 A cm^{-2} up to 45 T) and irreversibility field (>100 T) at 4.2 K [1,2]. This round wire geometry is preferred by magnet designers and builders as it can be easily twisted and cabled into desired shapes. Thus Bi-2212 round wire is an attractive candidate for very high field applications that are beyond the range achievable by using Nb_3Sn and Nb-Ti technology [3–6]. In order to attain high J_c, the Bi-2212 round wire undergoes an overpressure heat treatment (OPHT) at 50 bar with a 1 bar oxygen partial pressure (PO_2) that prevents the formation of large gas bubbles that significantly degrade J_c in 1 bar processing[4, 7]. High superconducting intergrain connectivity is developed by the highly-aligned grains resulting from the strong quasi-biaxial texture that forms in a narrow filament cavity in the round wire architecture [8]. Bi-2212 wires are made with the Bi-2212 in contact with pure Ag because of the good chemical compatibility between them. But, pure Ag is weak (yield strength 45 MPa at 4.2 K after OPHT), so the wire is strengthened by using a stronger outer sheath that is typically a dispersion strengthened Ag-0.2 wt% Mg (hereafter Ag(Mg)) [9].

One of the essential components of any superconducting magnet is electrical insulation, which prevents electrical shorting while charging the magnet to the operating current or discharging during a quench. For Bi-2212, the insulation is applied to the as-drawn wire and it must survive being wound into a coil, as well as the heat treatment, which has a maximum temperature around 890 ^{0}C in an oxidizing environment. Also, it has to be chemically compatible with the Ag(Mg) sheath and with Bi-2212, and it has to have sufficient dielectric strength so that the thin layer of insulation provides adequate electrical standoff within the coil winding pack while maintaining a high conductor packing factor. The alumino-silicate braid Oxford Superconducting Technology has used to insulate Bi-2212 wires is quite thick and significantly reduces the winding current density in the coil. This insulation material also absorbs Ag from the sheath during the heat treatment, which reduces J_c by 15–20% compared to bare wire [10]. Considerable efforts have been made over the years to develop an effective insulation layer for Bi-2212 that is thin, chemically compatible, has good adhesive properties, and is viable for long length coating [11–15]. TiO_2 insulation developed by nGimat and by Kandel *et al.* appeared to be a successful solution for insulating Bi-2212 [16, 17]. The thin (10–30 μm) TiO_2 coating Kandel *et al.* developed has sufficient scrape resistance in both as-deposited and heat treated condition, is chemically compatible with Bi-2212 and Ag(Mg), and has high breakdown voltage and dielectric strength [17–19].

Unfortunately, a test coil at the National High Magnetic Field Laboratory (NHMFL) that used Ag(Mg) wire insulated with TiO_2 suffered from severe electrical shorting after OPHT, which prevented the magnet from charging. Post-mortem microstructural studies revealed that severe Ag extrusion through the insulation layer caused the shorting (figure 1). Here we report on a detailed investigation to determine the root causes of this Ag extrusion. We used Bi-2212 wires with both Ag(Mg) and pure Ag sheaths and did heat treatments at 50 bar (OPHT) and at 1 bar total pressure. Our results suggest that the combination of having a Ag(Mg) sheath that is coated with TiO_2, and the overpressure that is applied during the OPHT causes the Ag extrusions. We also found that Ag extrusions that penetrate TiO_2 can potentially be prevented by predensifying the Ag(Mg) wire before coating it with TiO_2 and then winding the coil and doing the final OPHT [20].

2. Experimental procedure

All the wires used in this study were fabricated using the powder in tube (PIT) method by Bruker-Oxford Superconducting Technology (Bruker-OST) using Bi-2212 powder with a composition of $Bi_{2.17}Sr_{1.}74Ca0_{.89}Cu_{2.00}O_x$ produced by Nexans. The wire architecture was a double restack with the Bi-2212 powder in contact with pure Ag. The outer sheath was either Ag-0.2wt%Mg (referred to as Ag(Mg) wire) or pure Ag to study the effect of different sheath materials. The as-drawn wires were dip coated with the TiO_2 slurry at the NHMFL, followed by a burn out heat treatment at 450 ^{O}C in 1 bar flowing O_2 to remove the organics from insulation layer [18].

The wires were then heat treated in a flowing gas system following the standard heat treatment procedure shown in figure 2 [21]. Heat treatments were carried out at both 1 bar and 50 bar (OPHT) total pressure. The 1 bar heat treatments were done in pure O_2 and the OPHT were done in a Ar-2%O_2 gas mixture at 50 bar total pressure, both of which maintained PO_2 = 1 bar during the heat treatment. 8 cm long samples were used because earlier observations showed that Ag extrusions occurred in these short samples. For the 1 bar heat treatment, the ends of the wires were kept open to allow gas (CO_2 and H_2O) that was present in the as-drawn wire to escape out the ends, thus avoiding swelling and degradation of the wire. In contrast, both ends of the wires that underwent OPHT were hermetically sealed using Ag.

To understand the effect of a predensification heat treatment on the formation of extrusions, a small coil with Ag(Mg) wire was heated to 820 ^{O}C for 2 h at 50 bar (1 bar PO_2) with a heating and cooling rate of 160 ^{O}C/h following the procedure in [19]. The coil was then unwound, the TiO_2 insulation coating was applied, followed by rewinding, organic burn out, and OPHT at 50 bar.

Cross-sections of the heat treated wires were dry polished using SiC papers to 800 grit, followed by final polishing in an automatic vibratory polisher (Buehler Vibromet 2) using a suspension of 50 nm alumina powder in methanol. A Zeiss 1540EsB scanning electron microscope (SEM) was used to observe the microstructure. We prepared thin lamellae for STEM observations using a focused ion beam (FIB) in the Zeiss 1540 EsB. A JEOL ARM200cF was used to perform high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) imaging.

3. Results

3.1. Effect of external pressure

To investigate the effect that external pressure during the heat treatment has on Ag extrusions, samples of Ag(Mg) wire were heat treated at 1 and 50 bar total pressure. As seen in the longitudinal cross-section in figure 3, the Ag(Mg) wire that underwent OPHT has frequent Ag extrusions through the TiO_2, but there are fewer extrusions than in the shorted coil shown in figure 1. We observed a section of the interface between the sheath and the insulation that was about 4.5 cm long, and found that the Ag extrusions were randomly distributed along the entire length. The Ag extrusions were irregular in shape and size, and most of them did not penetrate the entire thickness of the insulation layer. Previous studies in our lab showed that cracks and porosity formed in the insulation layer during the sintering of TiO_2 particles [17, 18]. Thus, the Ag extrusions did not crack the insulation, rather they grew into the pre-existing gaps and pores in the TiO_2 insulation.

In contrast, there were no Ag extrusions in the Ag(Mg) wire heat treated at 1 bar (figure 4), even though there were lots of cracks and much porosity in the TiO_2 layer of this wire, just as in the OPHT sample (figure 3). The interface between the sheath and insulation was well defined.

3.2. Effect of sheath material

We also did OPHT on wire with a pure Ag sheath to understand what role the composition of the sheath plays in Ag extrusion. Figure 5 shows there were no Ag extrusions and that there was a well-defined interface between the Ag sheath and the TiO_2 insulation layer. This was identical to the behavior of Ag(Mg) wire heat treated at 1 bar (figure 4).

3.3. HAADF-STEM images

The HAADF-STEM image of figure 6(a) shows the distribution of MgO in two adjacent grains in the Ag-Mg sheath at a depth of ~8 μm from the surface of the bare wire (this wire was not coated with TiO_2 insulation) in a OPHTed Ag(Mg) wire. It is apparent from the figure that the density and distribution of MgO varies significantly between the two grains, one of them being devoid of MgO while the other had a uniform distribution of spherical MgO precipitates. In general, we found that the density of MgO particles is significantly lower near the wire surface than in the middle of the Ag(Mg) sheath. Figure 6(b) shows the HAADF-STEM image of a Ag extrusion in the TiO_2. Interestingly, the Ag extrusion appeared to be completely devoid of MgO precipitates. A sharp interface was observed between the Ag and TiO_2, which indicates no chemical reaction occurred between Ag and TiO_2, confirming that they are chemically compatible.

3.4. Effect of predensification

As figures 7 (a, b) show, no Ag extrusions were observed in the TiO_2 insulation layer when the Ag(Mg) wires were predensified at 820 ^{O}C for 2 h, followed by coating with TiO_2, and then OPHTed at 50 bar. However, small, smooth, regularly-spaced, undulations on the surface of the Ag(Mg) sheath were observed. We have also checked the microstructure of Ag(Mg) wires without insulation that had been predensified separately and did not undergo OPHT (figure 7 (c, d)). They showed undulations of similar shape but smaller size and shorter periodicity.

4. Discussion

The Ag(Mg) sheath is used for Bi-2212 wires, because, when the alloy is oxidized, MgO precipitates form in the Ag that strengthen the Ag sheath. It was expected that the MgO particles in the heat-treated wires would be distributed uniformly; however, we found a non-uniform MgO particle distribution in the Ag(Mg) after the OPHT. In particular, the MgO density is significantly reduced and nonuniform near the wire surface. This nonuniform distribution of MgO likely causes a local variation in mechanical properties between different regions in the sheath. We expect the regions with higher MgO content to be stronger and harder than regions with lower MgO content. Our hypothesis is that, while the external pressure provided by the isostatic gas pressure during OPHT is isotropic, the regions with different MgO content respond differently to this applied pressure, causing MgO free Ag to be squeezed through the insulation. We expect that the MgO-poor, weaker regions in the Ag(Mg) form the extrusions, which is based on the lack of MgO precipitates in the Ag extrusions shown in figure 6(b). At this point, we do not know what causes this variation in MgO distribution. The wire with the pure Ag sheath that was OPHTed had no MgO, so we expect the mechanical properties of the sheath to be uniform, so there was no extrusion.

For 1 bar processed Ag(Mg) wire, there is no external pressure gradient to cause extrusion. We confirmed the need for a pressure gradient to form extrusions by doing OPHT on a Ag(Mg) wire with open ends at 50 bar. With open ends, a pressure gradient could not form between the outside and inside of the wire. As with the 1 bar processed Ag(Mg) wire, no extrusions formed even with 50 bar total pressure.

Matras *et al*. showed that 50 bar OPHT reduces the diameter of Bi-2212 round wires by around 4% [22]. They found that about 80% of this diameter reduction occurs while holding for 2 h at 820 ^{o}C, which is below the melting point of Bi-2212, during the standard heat treatment. Figures 7 (a, b) showed no extrusions in the sample that was predensified at 820 °C before being insulated with TiO_2, and then given a full OPHT. The quasiperiodic undulations on the surface of this initially predensified wire (figures 7 (a, b)) appeared underneath the insulation layer. In addition, the predensified Ag(Mg) wire without insulation shows similarly shaped (although smaller size) undulations (figure 7 (c, d)). These observations suggest that the surface undulations were formed during the predensification step where the majority of densification takes place.

Based on our observations, we propose that the following conditions are needed to form Ag extrusions: (1) a sheath made from Ag(Mg) (2) the wire has to be coated with TiO_2 insulation before the majority of the densification due to overpressure takes place. Our results suggest that it may be possible to limit Ag extrusions by predensifying the Ag(Mg) wire before applying the TiO_2 insulation, followed by full OPHT.

5. Conclusions

We studied the formation of Ag extrusions through the TiO_2 insulation layer in Bi-2212 round wires using two different sheath materials and under various heat treatment conditions. Our results suggest Ag extrusions occur only in Ag-0.2 wt% Mg sheathed wires during heat treatment under a substantial overpressure. HAADF-STEM observations showed non-uniform distribution of MgO in the Ag(Mg) sheath near the surface of the wire, which would lead to local variations in mechanical properties in different regions of the sheath, which is the root cause of Ag extrusion during OPHT. Our study suggests that predensifying Ag(Mg) wire below the Bi-2212 melting temperature before applying the insulation and doing a full OPHT may be an effective way to limit Ag extrusion into the TiO_2 insulation layer.

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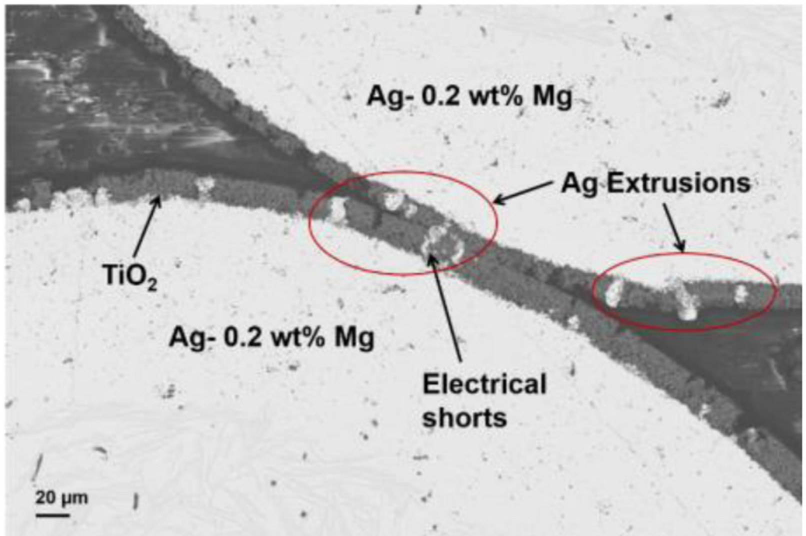

Figure 1.

Transverse cross section from the shorted coil. The circled regions show Ag extrusions (white) in the TiO2 insulation. Some of the extrusions shown in the middle of the figure connect adjacent Bi-2212 wires, producing the electrical shorting.

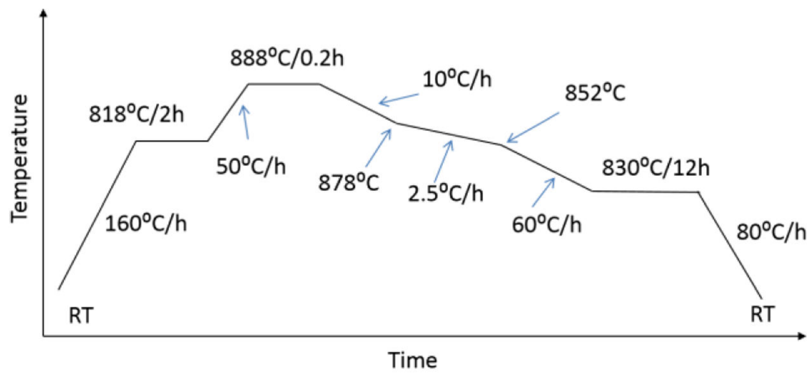

Figure 2.
Standard heat treatment schedule for Bi-2212. This heating schedule was used for the 50 bar OPHT and for the 1 bar heat treatment.

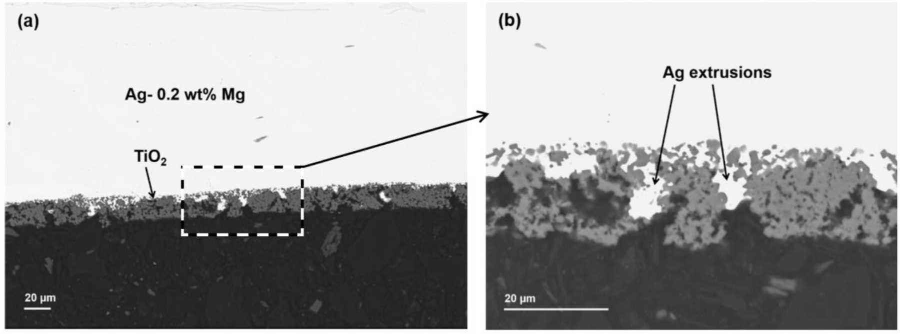

Figure 3.

(a) SEM image of the interface between the Ag(Mg) sheath and the TiO2 insulation in a Ag(Mg) wire after 50 bar OPHT. (b) Higher magnification image of a region in (a).

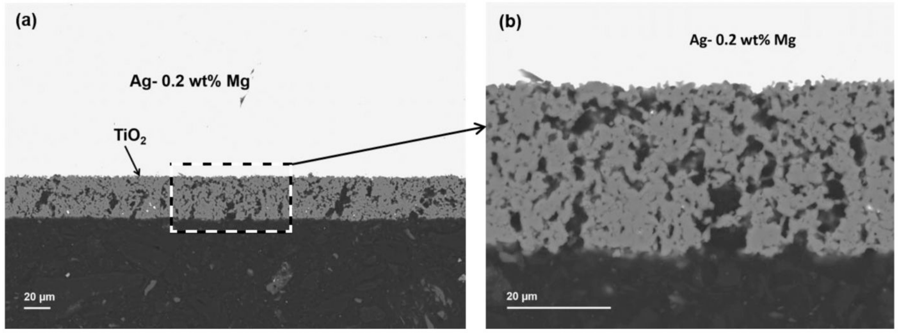

Figure 4.

(a) SEM image of the interface between the Ag(Mg) sheath and the TiO2 insulation in a Ag(Mg) wire after 1 bar processing. (b) Higher magnification image of a region in (a).

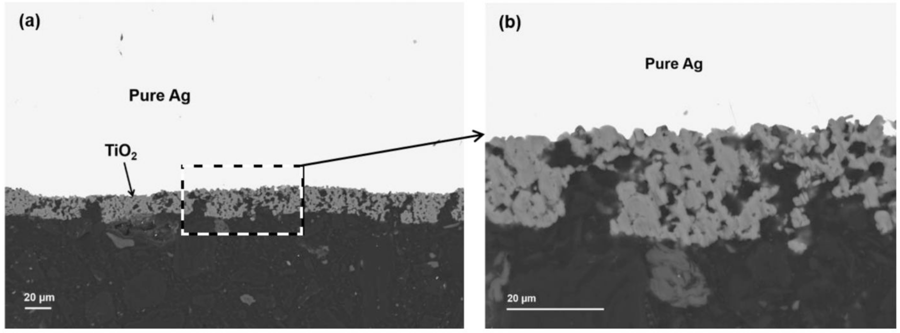

Figure 5.

(a) SEM image of the interface between the Ag sheath and the TiO2 insulation in a wire with a pure Ag sheath after OPHT. (b) Higher magnification image of a region in (a).

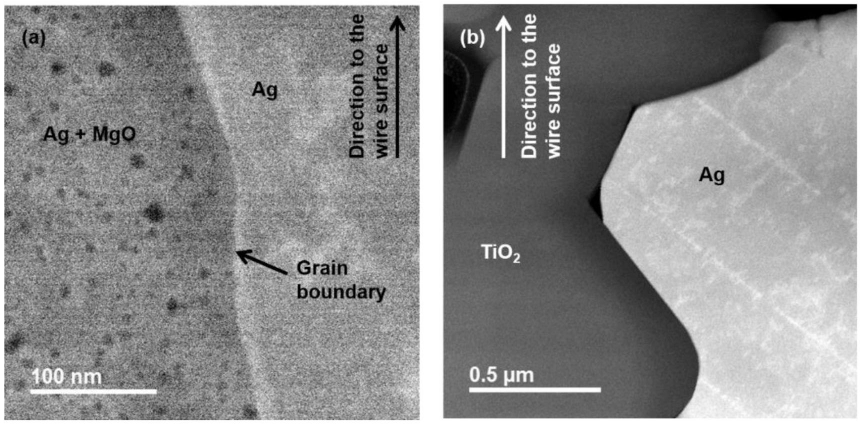

Figure 6.

HAADF-STEM images of (a) grains within the Ag(Mg) alloy sheath. The darker round shaped particles are MgO. (b) Ag extrusion in the TiO2 insulation layer. The brighter contrast inside the Ag is due to defects introduced by the Ga ion beam during sample preparation by using focused ion beam.

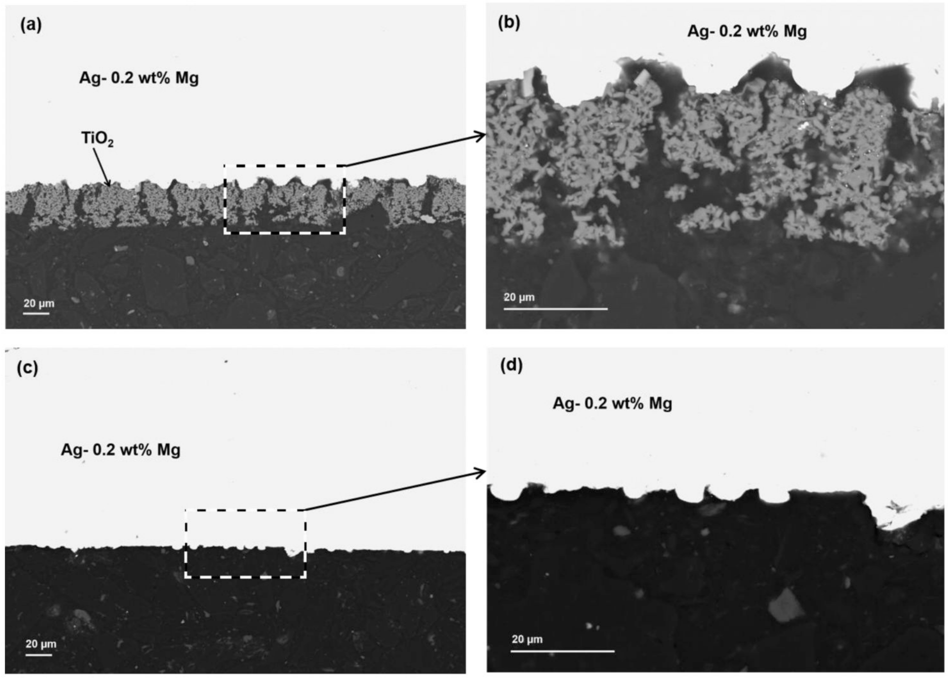

Figure 7.
(a, b) SEM image of the interface between the Ag(Mg) sheath and the TiO2 insulation in a sample that was predensified, coated with TiO_2, and then OPHTed. (c, d) The surface of the Ag(Mg) sheath in a sample that was only predensified and was not coated with TiO2.