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A study on the extent of Ag protrusions in different TiO_2-coated Bi-2212 wires

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Abstract. We report on the extent of Ag protrusions into the TiO_2 insulation layer on 9 different Bi-2212 wires after overpressure heat treatment. These wires were made with different powders and had different diameters and geometries, including aspected and twisted wires. To replicate coil heat treatments, we also studied whether increased time spent in the melt state affects the protrusions. We found that Ag protrusions are not universal and increasing the time in the melt state does not affect the protrusions.

1. Introduction
$Bi_2Sr_2CaCu_2O_x$ (Bi-2212) high temperature superconductor offers very high critical current density [1] and its irreversibility field is much higher than Nb_3Sn [2]. This high critical current density can be achieved in both round and aspected wires, which are multifilamentary and twistable. The round wire geometry of Bi-2212 enables employing the cabling technology developed for earlier generation Nb-Ti and Nb_3Sn superconductors, while twistability and multifilamentary geometry reduce AC loss. Also, the magnetic shielding current in Bi-2212 is much lower compared to REBCO coated conductors, which results in much reduced field uniformity errors [3]. Significant advances have been made in recent years that have put Bi-2212 on the verge of commercial applications and it is considered as a very attractive option for high field NMR and general purpose research magnets [4-10].

One of the key issues facing Bi-2212 superconducting magnet technology is the development of a suitable insulation material. In a wind-and-react coil fabrication process, the insulation has to be applied to the wire before coil winding, meaning that it has to withstand a heat treatment with a maximum temperature of around 890° C. The TiO_2 insulation developed in collaboration between the National High Magnetic Field Laboratory (NHMFL) and nGimat meets this criterion while offering a high winding current density due to its relative thinness compared to other available insulation materials [11-14]. However, while dip-coated TiO_2 insulation worked well in short samples, when used in a large coil it had severe electrical shorting after the overpressure heat treatment (OPHT). We found that this quiet unexpected shorting was caused by Ag protrusions through the TiO_2 layer. In our earlier work [15], we identified the combination of Ag- 0.2 wt.% Mg alloy (Ag(Mg)) sheath and overpressure heat treatment (OPHT) as the underlying reasons behind these Ag protrusions.

In this study, we wanted to investigate if all Ag(Mg) sheathed Bi-2212 wires with TiO_2 insulation have protrusions after OPHT. To do this we used 9 different wires produced between 2011 and 2018.

The diameter of the wires used varied from 0.8 to 1.3 mm and both round and aspected wires were used. We used the standard OPHT schedule (figure 1) and also heat treated some samples with increased time in the melt state to simulate the longer melt time that coils often seen compared to short samples due to their larger thermal mass.

2. Experimental procedure

The wires used in this study were fabricated by Bruker OST using the powder-in-tube method. Powders from three different manufacturers, Nexans, nGimat, and MetaMateria, were used. The nominal composition of all the powders was similar to $Bi_{2.17}Sr_{1.74}Ca_{0.89}Cu_{2.00}O_x$. The wires were all double restacked, with a pure Ag matrix in contact with the Bi-2212 and a Ag(Mg) outer sheath enclosing the restacked bundles. All the wires, except for one, were dip coated in-house at the NHMFL with a TiO_2 slurry. nGimat dip coated the other wire. Table 1 contains detailed information about the wires. Variation in coating thickness was observed between different wires and also along the circumference of the same wire.

Table 1: Brief description of the wires used in this study and results.

Wire No.	Powder[b]	Archi-tecture	Shape[c]	Dia or LxW (mm)	Insulation[d]	Twist (Y/N)	Results[e]
Pmm110106-2	Nex	85x18	R	1.2	nGi	N	NP, B
Pmm130125	Nex	121x18	A	1.38x0.98	I-H	N	NP, B
Pmm140328-2	Nex	55x18	R	1	I-H	Y	NP, B
Pmm140606[a]	Nex	55x18	R	1	I-H	Y	FP
Pmm151103	Nex	121x18	R	1	I-H	Y	NP, B
Pmm150227[a]	Nex	121x18	R	1.3	I-H	Y	EP
Pmm160301[a]	Meta	85x18	R	1	I-H	N	NP
Pmm180410[a]	nGi	85x18	R	1	I-H	N	NP
Pmm181004	nGi	55x18	R	0.9	I-H	N	NP, B

[a]Wire used for extended time in the melt study -- [b]Nex = Nexans; Meta = MetaMateria; nGi = nGimat -- [c]R = round; A = aspected -- [d]nGi = nGimat; I-H = in-house -- [e]EP = extensive protrusions; FP = few protrusions; NP = no protrusions; B = blob

8 cm long samples were used with each end hermetically sealed with a Ag-bead using a torch before the heat treatment. All the wires first went through a burnout heat treatment with a maximum temperature of 450° C in flowing oxygen to remove the organic binders and plasticizers in the TiO_2 slurry. The heating rate was 10° C/h to avoid ignition of the organics. After that, the wires underwent the OPHT processing heat treatment at 50 bar overpressure (1 bar O_2 + 49 bar Ar). Two slightly different OPHT schedules were used. In one, the standard OPHT was carried out (figure 1) in which the wires took about 1 hr to cool down from 888° C (the maximum temperature) to 878° C. For the other OPHT, this cooling time was extended to 3 hrs.

Longitudinal sections of heat treated wires were mounted in conductive epoxy using a mounting press. The wires were dry polished using SiC papers up 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 SEM was used to observe the microstructure of the TiO_2- Ag(Mg) interface. About 6 cm of this interface was examined for each wire.

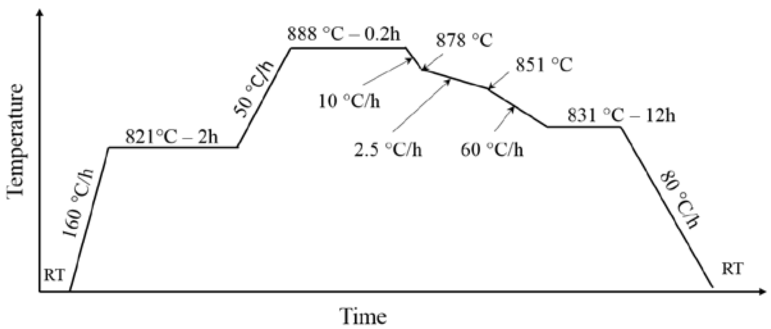

Figure 1. Standard heat treatment schedule for Bi-2212. For increased time in the melt samples, the cooling rate between 888 °C and 878 °C was reduced to 3.3 °C/h. The figure is not to the scale.

3. Results

3.1. . Standard OPHTed wires:

3.1.1. Pmm150227. This is the wire that was used for the large coil that shorted. Similar to the coil, the short sample showed a lot of Ag protrusions into the insulation layer (figure 2a, 2b) which varied in size, some almost penetrating through the whole 20 µm insulation layer. The distribution of the Ag protrusions was not homogenous; there were areas where they were significantly more abundant. The wire also showed reduced roundness, which is a common feature for twisted wires. In addition to the large Ag protrusions, there were many Ag particles distributed in the portion of the insulation close to the wire surface. We suspect that these discrete Ag regions are actually part of the large Ag protrusions.

3.1.2. Pmm110106. The TiO_2 on this wire was dip coated by nGimat and the composition of the TiO_2 slurry was possibly different as the insulation was brown instead of the usual bright white colour of in-house coated wires. Almost no Ag protrusions were observed in this wire (figure 2c). There were some Ag "blobs" on the wire surface (5 or 6 blobs along the 6 cm of interface that was examined). The size of the blobs was less than 5 µm and none of them penetrated the 12 µm thick insulation layer. These Ag blobs are a common occurrence in the Ag(Mg)-sheathed wires and can be seen in bare wires too. We refer to them as blobs because their shape and size are distinctly different from the Ag protrusions. Also, the insulation had very few of the Ag particles that we saw in Pmm150227 (figure 2a, 2b).

3.1.3. Pmm130125. This wire was rolled into an aspected geometry from a round wire. The insulation thickness was around 14 µm. The microstructure (figure 2d) was similar to Pmm110106, with only 5-6 Ag blobs along 6 cm of interface. The blobs were mostly smaller than 5 µm, with one reaching about 8 µm.

3.1.4 Pmm140328. The insulation thickness for this wire was about 16 µm. Its microstructure (figure 2e) was similar to Pmm110106 with very few Ag blobs.

3.1.5. Pmm140606. The wire lacked roundness like most of other twisted wires. The insulation thickness, which was on average around 15 µm, also varied due to the unevenness of the wire surface and was considerably thinner at some places. This wire and Pmm150227 were the only wires that had Ag protrusions (figure 2f) that were as large as the insulation layer thickness. However, the number of protrusions was significantly less compared to Pmm150227, with only 10-12 protrusions observed along the 6 cm of interface examined. Like Pmm150227, there were randomly distributed Ag particles in the insulation layer in contact with the Ag.

3.1.6. Pmm151103. This wire showed the least number of Ag blobs (figure 2g), only 1-2 that were all less than 5 µm in size. Surprisingly, this twisted wire was fairly round.

3.1.7. Pmm160301. The microstructure of this wire (figure 2h), which was made with MetaMateria powder, was quite clean and there were almost no Ag protrusions observed in the microstructure checked.

3.1.8. Pmm180410. This wire showed very little to no sign of Ag protrusion (figure 2i).

3.1.9. Pmm181004. The microstructure (figure 2j) was similar to Pmm110106, with only 5-6 blobs that were around 5 µm in size.

3.2. Increased time in the melt

We choose 4 wires to study the effect of increased time in the melt. These were the two wires that showed significant protrusions after the heat treatment (Pmm150227 and Pmm140606), which were made with Nexans powder, and one made with nGimat and one with MetaMateria powder, Pmm180410 and Pmm160301, respectively, which did not show any protrusions. No significant change in the protrusions were observed with longer time in the melt for any of the wires.

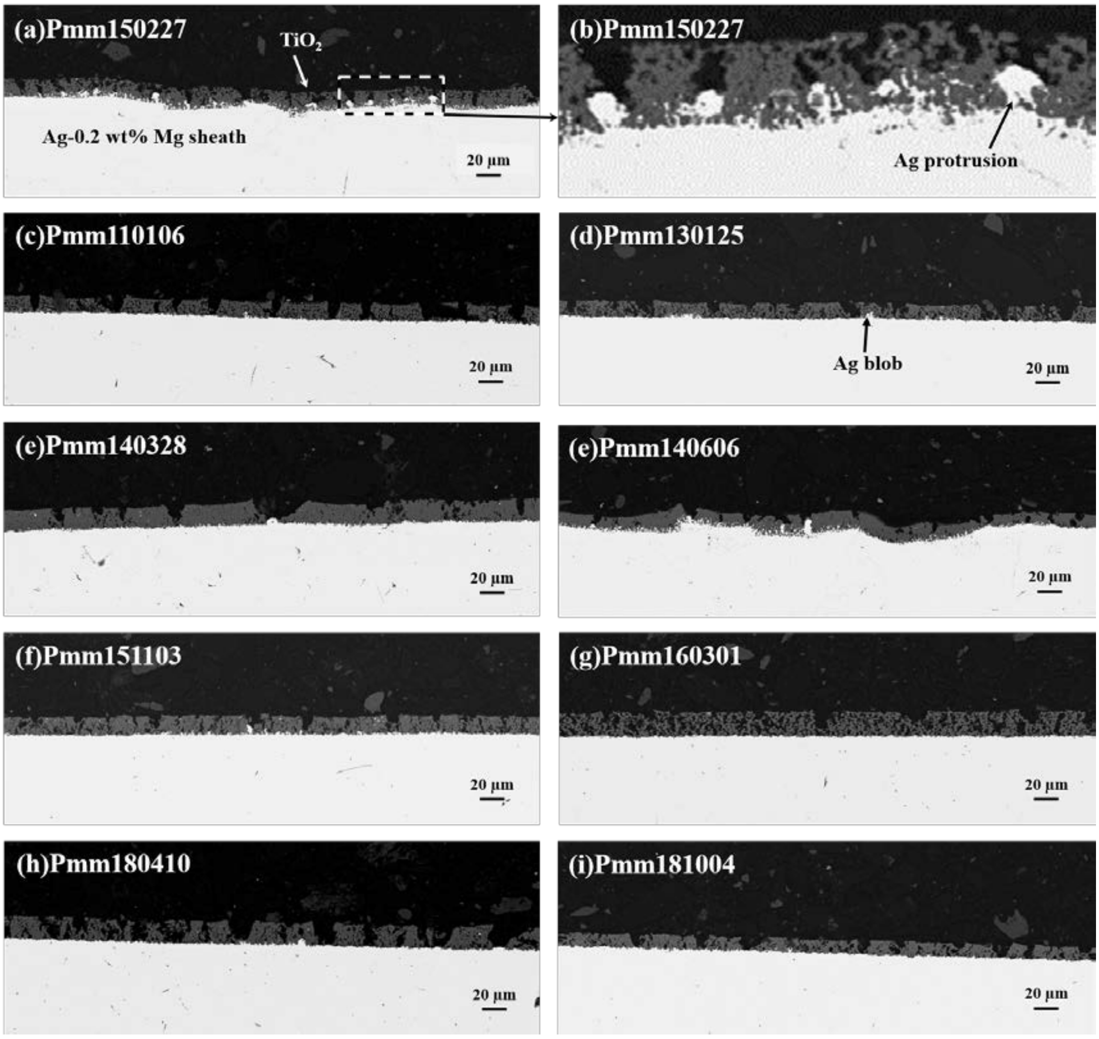

Figure 2. Longitudinal cross sections of different wires that underwent standard OPHT. A section of (a) is magnified in (b) for better demonstration of Ag protrusion. In (d), an arrow points to a Ag "blob".

4. Discussion

The wires used in our earlier study [15] showed extensive protrusions, leading to our concern that all Bi-2212 wires with a TiO_2 insulation layer would form protrusions after OPHT, thus defeating the essential purpose of TiO_2 as an insulation. An important observation of this subsequent study is that the broad range of wires studied displayed a wide range of behavior, ranging from extensive protrusions (Pmm150227) to essentially no protrusions. There is no apparent correlation between the wire properties listed in Table 1 and whether the wire had protrusions. For example, the two wires that had extensive protrusions were twisted, but the two other twisted wires did not have extensive protrusions. Unsatisfactory though it is, it presently appears that the only way to tell if a wire will form protrusions is to test it.

One positive result is that we did not find that increasing the time in the melt affected the development or extent of protrusions. This relives one of our concerns for continued use of TiO_2 for coil insulation, since coils tend to spend a longer time in the melt than optimised short samples of low thermal mass.

In our earlier study [15], we found one curious result which was that Ag protrusions were devoid of the MgO particles that provide precipitation hardening of the sheath. We did not do TEM studies in the current investigation, but suspect that the protrusions in wire Pmm140606 were also devoid of MgO. Our working hypothesis was that the Mg or MgO is mobile during the highest temperature portion of the heat treatment and that the thermodynamic stability of MgO is greater at the surface where it has access to 1 bar O_2. Protrusions can then be viewed as a form of extrusion of the purer and weaker Ag into the interstices in the TiO_2 layer. The variability of this result suggests either that the quality of the Ag(Mg) alloy used in the sheath matters or perhaps that the quality of the oxidation matters.

As part of this work, we also heat treated wire Pmm150227 at 1 bar pressure and found that it did not show any Ag protrusions. This confirms our observation [15] that OPHT is required to form the protrusions. A working hypothesis is that the hydrostatic pressure of the gas in the furnace can actually produce a non-hydrostatic response in the Ag sheath if there are local variations in the strength of the wire caused by variations in the local MgO concentration. Thus 50 bar can provide a driving force for protrusion formation, while 1 bar total pressure cannot.

We changed the insulation strategy we use for Bi-2212 coils after the extensive protrusions in wire Pmm150227 electrically shorted the large coil. Now we use two insulation layers: first the dip-coated TiO_2 layer in direct contact with the Ag(Mg) sheath and then an alumino-silicate braid that prevents shorting if protrusions occur. This alumino-silicate braid does however react with Ag, meaning that we do require the TiO_2 layer to physically separate the braid from the Ag(Mg) sheath. Unfortunately the alumino-silicate braid is much thicker (150 μm) than our preferred 20-30 μm TiO_2 layer thickness, meaning that we do lose winding current density. This study suggests that it is worth further effort to understand how protrusions form in some wires and not others. We should point out however, that the braid helps epoxy penetrate the coil and strengthens it after curing, meaning that we are not yet ready to go back to single layer TiO_2 insulation.

5. Conclusion
We examined the extent of Ag protrusions in 9 different Bi-2212 wires coated with TiO_2. Our findings showed that the extent of Ag protrusions varies strongly among different wires and indeed that most of the wires did not show Ag protrusions. Samples that spent 3 hours longer in the melt state did not show any change in the overall amount or size of Ag protrusions. We speculate that Ag protrusion are related to variations in the particular Ag(Mg) alloy used or its oxidation heat treatment, allowing us optimism that we may be able to control and avoid protrusions with better understanding of the state of the Ag(Mg) sheath.

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