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Interstrand Resistance Studies of Oxidized Superconducting Wires

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Introduction

The current cables that are being fabricated for the SSC collider magnets are not suitable for the HEB magnets. Interstrand coupling leads to unacceptable losses and quench current degradation. There are many schemes to increase the interstrand resistance. One of them concerns the oxidation of the copper surface to increase the contact resistance. This may be achieved either by thermal or chemical methods. An example of a chemical method is the "ebanol" process which was used for the TEVATRON conductor [1] In this note I have reviewed certain aspects of copper oxidation in air and detailed the results of some special conductors that were deliberately oxidized to increase the contact resistance between the wires.

Oxidation of copper

A clean copper surface oxidizes very readily in air at 25°C. The process of oxide formation takes place by copper ion migration to the surface and the formation of Cu_20. The oxide layer growth is strongly influenced by temperature and the presence of certain impurities like sulphur dioxide in the atmosphere. Humidity also helps in promoting oxide growth. Table I summarizes the copper oxide thickness that have been observed at various temperatures.[2,5]

Table I

Temp °C	Type of oxide	Thickness (nm)
25°C	Cu_20	~2-5
90°C	Cu_20	~10
120°C/.30 mins	Cu_20	~20
120°/40 mins		~30-40
150°C/10 mins.	Cu_20	~30-40
170°C/20 mins.	mainly Cu0	>100 nm

For this study, one of the NbTi wire manufacturers, OKP [3], produced some specially processed RHIC wire, where in one case a final anneal was made in an in-line furnace with protective gas atmosphere (#394) and in the 2nd case the anneal was carried out in air (#395). Annealing in air produced a Cu_20 layer on the wire of ~50 nm as shown in the next section. The wire parameters are given in Table II.

Table II

SC0K 3600 Superconductor
Billet 41/91

Diameter	0.648 ± 0.0025 mm
Number of filaments	3546
Dia (fil)	6.0 μm
Filament spacing	1.0 μm
Twist pitch	13 μm
Twist direction	right
Cu/SC (nominal)	2.31

In the final phase the wires were processed as follows:

1. Spool #394, wire length 1100 m
   - Drawn to the final diameter 0.648 mm
   - Final annealing in protective gas
   - Immediately after annealing the wire surface is covered by paraffin oil

2. Spool #395, wire length 1190 m
   - Drawn to the final diameter 0.648 mm
   - Final annealing without protective gas (in air)

Estimating the thickness of the oxide layer.

The thickness of the oxide layer was estimated using Auger electron spectroscopy (AES). This spectroscopy can identify atomic species on the surface and can be used to obtain relative concentrations of the different species. For most wires we detected copper, oxygen and small amounts of carbon (from residues of cleaning) and chlorine and sulphur (from oil residues). To estimate the thickness of the oxide, Cu and 0_2 anger lines are monitored after periodic sputtering of the surface of the wire, till only Cu lines are observed with no observable 0_2 on the surface. The etching time is proportional to the thickness of the Cu_20 layer that is sputtered off. It was estimated that one minute of sputtering removed ~10nm of the oxide layer. Table III lists the AES estimation of the oxide thickness for several wires. The typically processed wire has a natural oxide layer of ~2.5nm. The wire #395 had a thermally oxidized layer of ~50nm.

Table III
AES Summary of SSC wires.

Sample	Time to clean surface (mins)	Estimated oxide thickness (nm)	Final anneal
#394	0.25	2.5	in inert atmos.
#395	5.0	50	in air
SSC-3-I-00054	0.25	2.5	no anneal
SSC-3-5-00022	0.25	2.5	no anneal
SC-12-0006	0.50	5.0	no anneal

Approximately 50' of cable was produced by NEEW [4] from wire #394 and #395. These were evaluated for I_c and the interstrand resistance. Standard I_c measurements showed that the final anneal had no effect on J_c.

Interstrand Resistance Measurements

Interstrand resistance measurements were made on double-stack samples after various temperature and pressure cycles as given below:

Table IV
Interstrand resistance in units of micro-ohm
Data shown are mean (sigma) of 10 readings

Steps	Cable # 394	Cable # 395
1. As RCVD	137 (21)	237 (45)
2. 135C "STD"	67 (10)	1575 (340)
3. 225C - III	1824 (279)	11980 (2740)
4. 135C @ 10 ksi	19 (9)	219 (57)
5. 170C @ 10 ksi	27 (3)**	31 (5)
6, After 135C in air	1100 (780)	40000 (13000)
7. 135C @ 10 ksi	137 (95)	7200 (3800)

** Pressure reduced to zero at 25C and then re-applied.

Step 1: The cables in the "as-received" condition.

Step 2: Stacks molded using the standard Fiberglass Kapton cure cycle at 135°C.

Step 3: Stacks molded using the modified cure cycle III for all Kapton insulation at 225°C.

Steps 4 through 7: represent cycles made on the same pair of samples from cable #394 and #395 which were mounted in a special holder that allows molding at elevated temperatures and pressure and then permits low temperature R_I measurements without removing the samples. All low temperature measurements were made under 10 ksi loading. Table IV summarizes the interstrand resistance that were observed after certain temperature and pressure cycles as indicated in the table. These data are also graphically shown in Fig. 1.

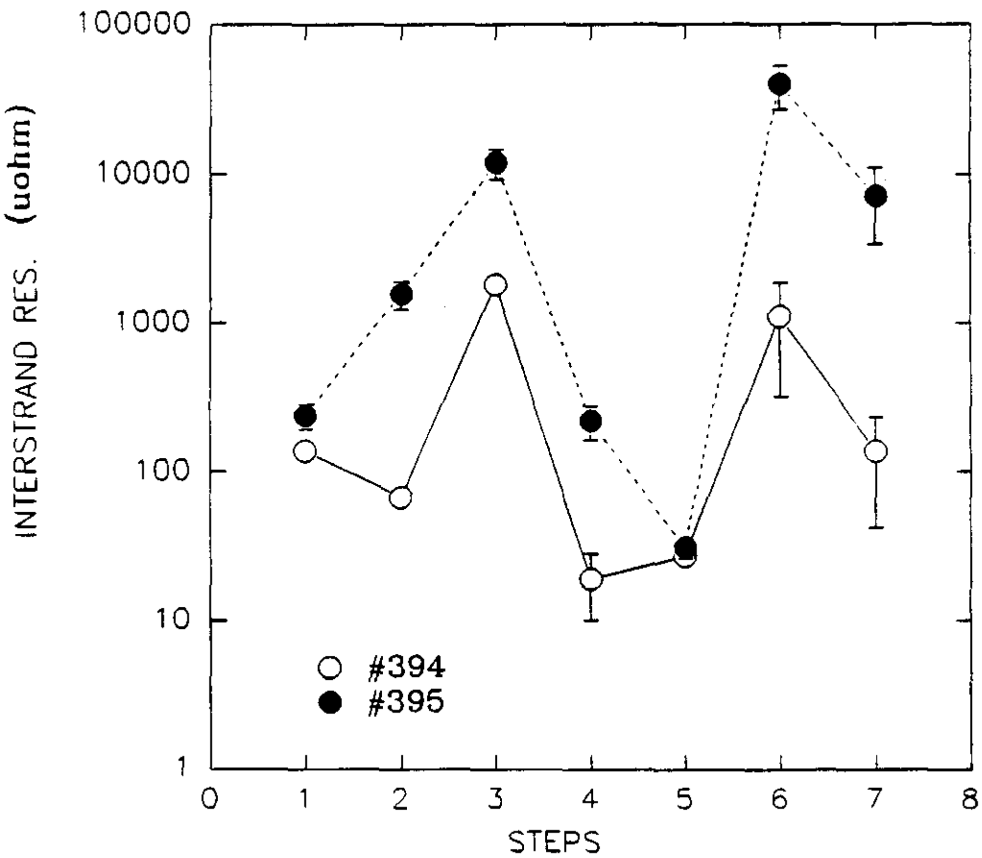

Fig 1. Int^rstrand resistance after various steps

Discussion

The interstrand resistances of the "as-received" cables are not markedly different despite the oxide on the wire #395. This is due to the fact that during cabling the Cu_2O oxide layer which is not hard is probably broken. However when cured at elevated temperatures the pre-oxidized wire readily re-oxides at the contact surface. During the simulated magnet coil cure cycles the pressure on the cables are released at certain stages. At these times the copper surface has a chance to oxidize. The standard cure cycles are shown in Fig. 2 for the different insulation schemes.

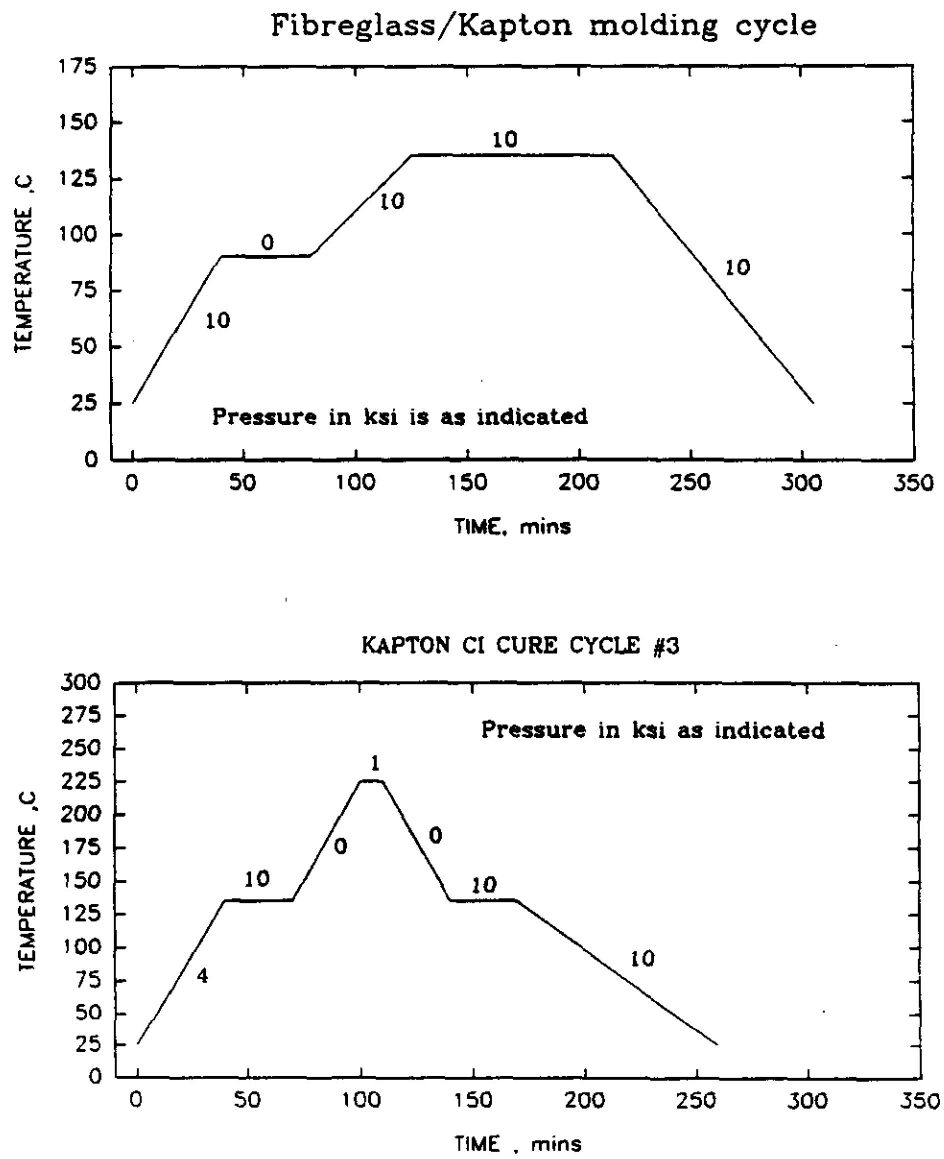

Fig. 2. Molding cycles used to simulate magnet coil molding for the two different insulation schemes.

Step 4 is a cure cycle to 135°C under constant 10 ksi for 90 mins. Since the pressure was not released during this cycle, the R_I values are low reflecting the improved contact surface area. Step 5 is a subsequent cycle to 170°C for 90 mins. without relaxing the pressure. At these temperatures the copper yields under the high pressure exerted at the crossover regions thereby further improving the contact area. Subsequent to Step 5, the pressure was relaxed to zero at 25°C and then annealed at 135 in air. (Step 6) Both cables seem to get oxidized, however cable #395 was seen to have very high R_I values. This would be the range of R_I values for wires which have a substantial layer of oxide. Step 7 is a subsequent heat treatment to 135°C for 90 mins. under 10 ksi pressure. The clean sample's R_I is decreased to values comparable to Step 2 but that of cable #395 is still quite high at 7200μΩ. Reclamping to 10 ksi does not seem to break the oxide layer on cable #395. It is not known whether the surface now has Cu_20 or Cu0 which is a harder oxide of copper.

These experiments indicate that pre-oxidized wires have their oxide layer damaged during cabling. However, subsequent heat treatment restores the oxide layer and produces a high R_I as seen in steps 2 and 3. Preoxidiation of wire and subsequent reoxidiation after cable fabrication is a potential way of increasing the interstrand resistance of current SSC conductor. Controlling the processes that guarantee a high reproducibly R_I needs to be examined.

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