EFFECT OF OXYGEN AND OTHER IMPURITIES ON COPPER COATING CONDUCTIVITY AT CRYOGENIC TEMPERATURES*

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Abstract

Theoretically, copper resistivity to a good approximation may be viewed as the sum of a term due to phonon-electron scattering, and a constant term. The electron-phonon term follows the Bloch-Gruneisen formula and goes to zero as T^5 at low temperature (at high T, →T). The constant term corresponds to scattering off defects and magnetoresistance. The defect part is due to impurities and finite crystal size. To minimize resistivity, the constant term should be kept as small as possible. Coatings of 10 µm thick copper films were deposited on stainless steel RHIC pipes; their RF conductivity measured. One deposition had RRR of 1.2, while another deposition resulted in RRR of 2.3. Multiple measurements (FIB, EDS, SEM TEM etc.) reveal that in both depositions copper purity was about 93%, which is surprising given the higher RRR. Additionally, grain structure and lattice defects look identical as well. The only difference between these copper depositions was in the miniscule quantity of oxygen contamination 0.125% versus 0.03% respectively; qualitatively consistent with predictions. Measurements, which are probably first conclusive results, showing the adverse effect of minute oxygen contamination on copper conductivity at cryogenic temperatures qualitatively are presented. The results are consistent with predictions for oxygen. Nevertheless, there are puzzling results for other impurities.

INTRODUCTION

High wall resistivity in accelerators can result in unacceptable levels of ohmic heating or to resistive wall beam instabilities [1]. This is a concern for the relativistic heavy ion collider (RHIC) machine, and even a larger concern future RHIC upgrades including the electron ion collider (EIC) as its vacuum chamber in the cold arcs is made from relatively high resistivity 316L stainless steel.

Present plan to reduce resistivity in EIC calls for copper coated cage insertion; copper coating the RHIC cold bore walls by a magnetron mole is a backup. In either case, the wall resistivity would be greatly reduced by having the accelerated beam exposed to oxygen-free high conductivity (OFHC) copper, whose conductivity is three orders [2, 3] of magnitude larger than 316LN stainless steel at 4 K.

A novel robotic plasma magnetron mole [4] with a 50 cm long copper cathode was successfully operated to copper coat an assembly containing a full-size, stainless steel, cold bore, RHIC magnet tubing connected to two types of RHIC bellows, to which two additional pipes made of RHIC tubing were connected for a total length of 20 m. The magnetron is mounted on a carriage with spring loaded wheels that successfully crossed bellows and adjusted for variations in vacuum tube diameter, while keeping the magnetron centered. Electrical power and cooling water were fed through a cable bundle. The umbilical cabling system is driven by a motorized spool. Excellent coating adhesion was achieved. Optimized process to ensure excellent adhesion was a especially developed discharge cleaning. Coating adhesion of 10 µm Cu passed all industrial tests (tape, nail) and even exceeded maximum capability of an industrial test fixture (pull machine) of $2.9x10^6$ N/m^2.

Previously, it was demonstrated [4] that deposition of even 5 µm of copper on RHIC tubing can result in room temperature conductivity, which is very close to solid copper. Room-temperature RF resistivity measurements [5, 6] were performed on 32 cm long RHIC stainless steel tubes coated with 2 µm, 5 µm, and 10 µm, thick OFHC with a folded quarter wave resonator structure. Q values were measured for eight resonant modes in the range of 180 MHz to 2 GHz, from which conductivity was deduced. Those measurements [5, 6] indicated that for the later 2 coatings conductivity was about 5 x 10^7 Siemens/meter or about 84% of pure copper. Since joints and connectors reduce the experimentally measured Q, the conductivity value of coatings may be even closer to pure solid copper. Additional details can be found in Ref. [5, 6]. Computations indicate [7] that 10 µm of copper should be acceptable for even the most extreme future scenarios.

However, low temperature physical vapor deposition (PVD) of copper on stainless steel tubes does not have the same conductivity as copper tubing at cryogenic temperatures, since deposition of thick films could result in coatings with lattice defects and impurities, which at cryogenic temperature severely degrades conductivity. Even though this is covered in a number of books [8-12], clear evidence is not found in research papers. These phenomena are based on the following: room temperature copper, conductivity is dominated by conduction band electrons, while at

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cryogenic temperatures, lattice defects and impurities result in large conductivity reduction. Electrons are scattered off lattice defects and impurities, causing significant conductivity degradation. Straightforward deposition of thick films [13] could result in coatings with lattice defects and impurities, and columnar crystal and other microstructures, which [14] were observed in conventional PVD.

Furthermore, until very recent, it has been an "acceptable fact," based on Landolt-Bornstein's Physikalisch-chemische Tabellen that oxygen content must be > 0.1% in order to avoid adverse affect on Cu conductivity at cryogenic temperatures [15, 16]. Nevertheless, in the latest edition no reference to oxygen exists.

Additionally, a first-of-a-kind device for measuring the RF resistance of copper coated stainless-steel tubes at cryogenic temperatures over a range of 180 MHz to 2 GHz was developed and has been operating well [17].

COPPER COATING CRYOGENIC TEMPERATURE CODUCTIVITY RESULTS

In the coating setup described above (with the 50 cm-long cathode magnetron mole) 30-cm long RHIC stainless steel tubes coated with 10 µm, thick OFHC can be pulled out for performing various measurements and diagnostics, e.g., copper film adhesion, conductivity etc. Two 30-cm long RHIC stainless steel tubes coated with 10 µm, thick OFHC films were pulled out the system and their RF conductivity at 4 K was measured.

Conductivity enhancement at 4K of these copper coated RHIC tubes was measured. One tube had its conductivity of the copper coating was enhanced by a factor of 2.3 over its conductivity at room temperature; i.e. conductivity of 2.3 x 5.7 x 10^7 Siemens/meter, while the other tube had its copper coating conductivity enhanced by a factor of 1.2 over its room temperature conductivity; i.e. conductivity of 1.2 x 5.7 x 10^7 Siemens/meter. Although in both cases conductivity could be higher, since most likely there is contribution to resistivity from connectors (on the fact that a pure copper tube did not show the expected enhancement); nevertheless, the reason for the cryogenic temperature conductivity difference between the two was studied by examining crystalline structure and various contaminants in the copper films.

IMPURITIES, LATTICE STRUCTURE MEASUREMENTS

From each tube 2 samples were cutout from different locations. Each sample was 1 x 1 cm of 10 µm thick copper on RHIC stainless steel.

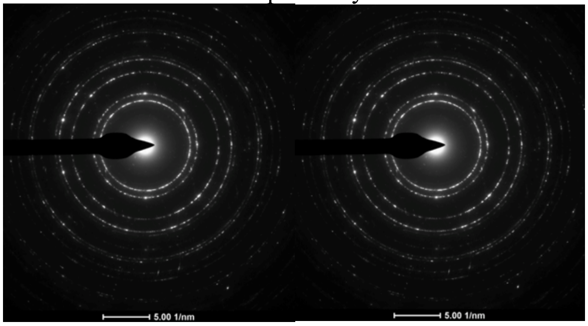
For impurity content, focused ion beam (FIB) 30 kV, 10 nm diameter, gallium ion beam was utilized to mill a cross-section across the thickness of the film with an area of ~ 80 x 40 µm^2, in a sample center, with a depth of ~ 5 µm. This was followed by EDS (Energy Dispersive X-Ray Spectroscopy) by injecting a 20 kV electron beam for excitation. From the energy spectra, the various atomic elements were determined.

To image lattice structure and defects, Transmission Electron Microscopy (TEM) was utilized. For determining lattice defects and crystalline structure an electron beam was transmitted through a thin specimen to form an image. An ultrathin section was cut with a laser. An image is formed from the interaction of the electrons with the sample as the electron beam passes through it.

All measurements were performed at the BNL CFN.

RESULTS

No difference in grain structure was found between the samples based on the transmission electron microscope measurements. In Fig. 1, for example, TEM diffraction is shown for samples taken from copper coated tubes whose RRR was 1.2 and 2.3 respectively.



RRR = 1.2 RRR = 2.3

Figure 1 TEM diffraction patterns in samples having RRR 1.2 (left) and 2.3 (right). In both samples the inner two diffractions rings represent a D-spacing of 2.13 Angstroms and 1.80 Angstroms, respectively.

While there was no difference in crystalline structure between the copper films that can account for the RRR difference between the copper coated RHIC tubes, contaminates measurements using focused ion beam followed by energy dispersive X-ray spectroscopy revealed significant difference in oxygen content between the samples.

Table 1 summarizes concentrations of the various elements as revealed by the FIB and EDS measurements.

RRR	direction	Cu	Fe	Cr	Ni	C	O
2.3	axis	93.25	3.7	0.8	0.8	0.95	0.03
2.3	90^0	92.1	3.6	0.8	0.7	0.9	0.03
1.2	axis	92.35	3.7	0.75	0.7	0.8	0.12
1.2	90^0	93.15	3.6	0.8	0.8	0.9	0.13

Table 1 displays the results of focused ion beam energy dispersive X-ray spectroscopy measurements that were performed on samples that were cutout from the copper coated RHIC tubes.

The first column, in Table 1, displays the RRR of each copper coated RHIC tube, from which the 1x1 cm samples were cut out. The second column shows the direction, from which the x-rays were measured whether along the tube axis or at 90^0 to the tube axis. Third to sixth columns display the percentage of each atomic element in each sample based on the energy spectra. Following the second row for example, the tube with RRR = 2.3, from the x-ray spectrum measurements along the tube axis, element concentrations are 93.25% Cu, 3.7% Fe, 0.8% Cr, 0.8% Ni, 0.95% C, and

0.03% oxygen. Surprisingly, the copper concentration was only about 93%. Consistency of x-ray emission (on axis or at 90^0) could be an indication of deposition uniformity. It's important to note, in Table 1, that the iron concentration is a factor of about 122 higher than oxygen for RRR = 2.3, and a factor of about 29 in the case of RRR = 1.2. As it is shown in the discussion below, iron contamination might be the biggest contributor the conductivity reduction.

DISCUSSION

Data in the Landolt-Bornstein tables until very recent indicated that oxygen content must be less than 0.1% to avoid adverse affect on Cu was taken seriously [15]; basically the adverse-affect is on or off whether the oxygen concentration is >0.1% or <0.1% (newest edition of the tables oxygen was taken out). Nevertheless, the Table 1 data RRR = 1.2 with oxygen level is 0.125% > 0.1%, while for RRR = 2.3 oxygen level = 0.03%, is consistent with that assertion.

In the NIST monograph [18], there is a formula, based partially on empirical data (containing 7 constants), which seems consistent with Bloch-Gruneisen as well as [19].

Although oxygen in copper increases electrical resistivity more than any other element (0.53 nΩm per 10 ppm), based on Table 8.1 on page 8.2 in the NIST monograph [18], the iron concentration of 3.65% with resistivity increase of (0.099 nΩm per 10 ppm) contributes a resistivity increase factor of 22.8 higher than oxygen for RRR = 2.3 and 5.5 higher for RRR = 1.2. Additionally, based on Table 8.1 [18], contributions from chromium and nickel also add to conductivity reduction. The 7 constants in RRR complex formula in the NIST monograph [18] do not show element dependence, hence the puzzling results.

But, the NIST data (in Table 8.1) is for "impurity element present in a solid solution." None of the contaminant shown in Table 1 form molecular compounds with copper except for oxygen, which forms CuO and Cu_2O. Is it possible that during deposition, copper-oxygen compounds formed and imbedded in the deposited copper?

A mistake, which was made during deposition, was utilizing the same magnetron for both discharge cleaning and deposition: contaminates, which were deposited on cathode during discharge cleaning, mixed with copper during deposition. Future copper coating should be performed with two magnetrons: one for discharge cleaning the other for coating at an UHV base pressure. Further studies of the copper conductivity degradation by oxygen should be done with controlled oxygen leak during deposition generating many samples. Additionally, highly pure copper, which has two orders of magnitude lower resistivity than OFHC, should be utilized.

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