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ELECTRICAL AND THERMAL PROPERTIES OF COLD-SPRAYED BULK COPPER AND COPPER-TUNGSTEN SAMPLES AT CRYOGENIC TEMPERATURES*

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Abstract

The development of high thermal conductivity coatings with pure copper or copper-tungsten alloy could be beneficial to improve the heat transfer of bulk Nb cavities for conduction cooling applications and to increase the stiffness of bulk Nb cavities cooled by liquid helium. Cold spray is an additive manufacturing technique suitable to grow thick coatings of either Cu or CuW on a Nb cavity. Bulk (~5 mm thick) coatings of Cu and CuW were deposited on standard 3 mm thick, high-purity Nb samples and smaller samples with 2 mm × 2 mm cross section were cut for measuring the thermal conductivity and the residual resistivity ratio. The samples were subjected to annealing at different temperatures and a maximum RRR of ~130 and ~40 were measured for the Cu samples and CuW samples, respectively.

INTRODUCTION

The development of metallic coatings with high thermal conductivity in liquid He temperatures may be beneficial for application to the superconducting radiofrequency (SRF) cavity technology [1]. The deposition of such bulk (a few millimeter thick) coatings on the cavity outer surface could result in niobium material cost saving, increased stiffness and increased heat conductance.

Recent research on SRF cavities cooled by conduction with a commercial cryocooler, instead of liquid He, utilized electroplating to grow a high-purity Cu layer on the outer surface of a Nb cavity with a Nb_3Sn film on the inner surface [2]. A drawback of the electroplating is the low deposition rate and the difficulty of achieving good bonding to the Nb substrate.

Cold-spray consists of accelerating solid powders with a carrier gas through a de Lavalle nozzle at high-enough speed such that the particles endure plastic deformation and adhere to the surface [3, 4]. This technique can be used to deposit many different types of materials. Cu and CuW were considered as candidate materials for cold-spray deposition in this study, aiming at producing samples with thermal conductivity of ~1 kW/(m K) at 4 – 7 K.

SAMPLE PREPARATION

The substrates used for this study were high-purity, fine-grain Nb plates cut from ~3 mm thick Nb used for SRF cavity fabrication. The cold spray was done at Concurrent Technologies Corporation, Johnstown, PA.

Copper Samples

For the Cu deposition, two 45 × 70 mm^2 and three 50 mm diameter Nb coupons were used. Cu powder with 99.95% purity and 325 mesh was used for the deposition. The substrate surface was grit blasted with aluminum oxide, followed by cleaning with isopropyl alcohol. A raster program was used to coat entire surface with a 1 mm step, speed of 200 mm/sec, and 1 inch standoff. The first 2 layers were applied with helium gas at 600 PSI and 400 °C. The next 4 layers were deposited with nitrogen gas at 950 PSI and 650 °C. The remainder of the deposition was done using nitrogen gas at 600 PSI and 400 °C to achieve a target thickness of ~3 mm. Helium gas was used for the first two layers as it allows for the Cu particles to be deposited at higher speed than nitrogen, therefore increasing the adhesion. The adhesion was measured to be ~33 MPa using a pull-off adhesion tester (PosiTest AT, DeFelsko), in accordance with ASTM D4541.

Figure 1 shows a picture of the samples, whereas Fig. 2 shows an optical microscopy image of the cross-section of a sample coated with similar deposition parameters as those used for this study. The microscopy images show some delaminations between the deformed Cu grains but a relatively small amount of coarse porosity.

The impurities content was measured on samples taken from the Cu powder and from the cold-sprayed coupon, as listed in Table 1. The concentration of Ag, Be, Cd, Co, Li, Mg, Mn, P, Pb, S, Se, V, Zn, and Zr was measured to be ≤ 1 ppm. The Cu concentration was measured to be 99.93% and 99.96% for the cold-sprayed and powder samples, respectively.

Samples 2 × 2 mm^2 in cross section were cut by wire electro-discharge machining (EDM) and were subjected to vacuum annealing in the temperature range 300 °C – 1000 °C for 3 h. The annealing of one sample at 900 °C and the one at 1000 °C was done in dry air, at ~10^{-2} Pa.

Figure 1: Picture of Nb coupons with 3 mm Cu deposited by cold spray.

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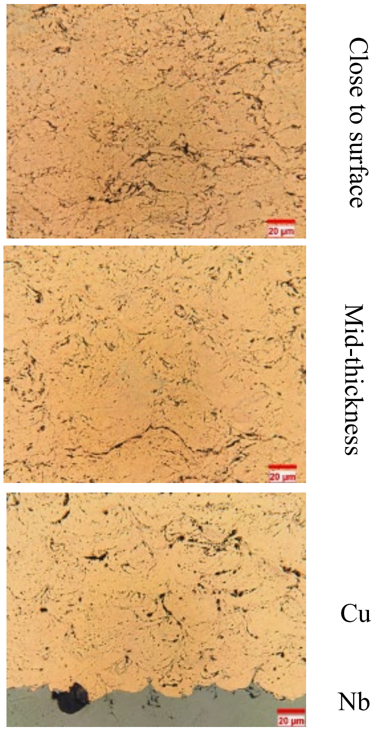

Figure 2: Optical microscopy of the cross-section of cold-sprayed Cu on Nb sample.

Copper-Tungsten Samples

A powder mix with 85 wt.% W and 15 wt.% Cu (99.95% pure) sized at -270 +625 mesh was used for the cold spray of CuW. The first 2 layers were applied with helium gas at 650 PSI and 400 °C. The remainder of the deposition was done using nitrogen gas at 950 PSI and 600 °C to achieve a target thickness of 3.7 mm. Figure 3 shows a picture of the CuW coupon. The adhesion to the Nb was measured to be ~36 MPa. The impurity content was measured on a sample from the CuW coupon, and the composition was found to be 60.1 wt.% W and 39.7 wt.% Cu. Other major impurities were 905 wt.ppm of Si, 760 wt.ppm of O, 330 wt.ppm of Cr and 219 wt.ppm of Zn.

Samples 2 × 2 mm^2 in cross section were cut by wire electro-discharge machining (EDM) and were subjected to vacuum annealing in the temperature range 300 °C – 800 °C for 3 h.

Figure 3: Picture of W40Cu deposited on a Nb sample by cold spray.

SAMPLE MEASUREMENTS

The residual resistivity ratio (RRR) was measured on all Cu and W40Cu samples, whereas the thermal conductivity as a function of temperature was measured on three Cu samples and two W40Cu samples. The RRR was measured with the standard DC 4-probes method [5, 6]. The thermal conductivity was calculated from the steady-state temperature difference along the sample as a function of DC power supplied to a heater on side of the sample, with the other side cooled by liquid He. Figure 4 shows a plot of the RRR as a function of the annealing temperature for all samples. Figure 5 shows a summary of $\kappa(T)$ data. The values of RRR and κ(4.3 K) measured on the same samples are listed in Table 2.

The thermal conductivity as a function of temperature was measured also on a bi-metallic NbCu sample after annealing at 900 °C/3 h in vacuum and the data are also shown in Fig. 5.

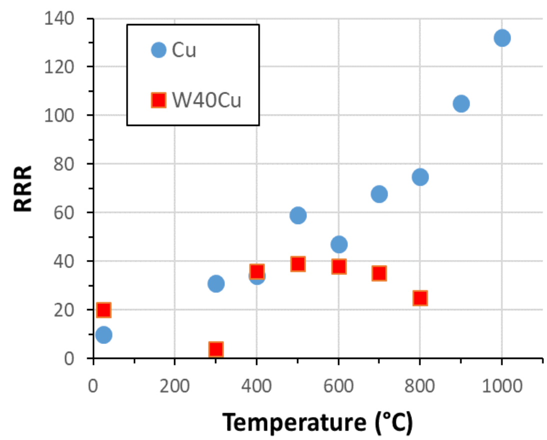

Figure 4: RRR as a function of annealing temperature for cold-sprayed Cu and W40Cu samples. Annealing at 900 °C and 1000 °C were done in dry air.

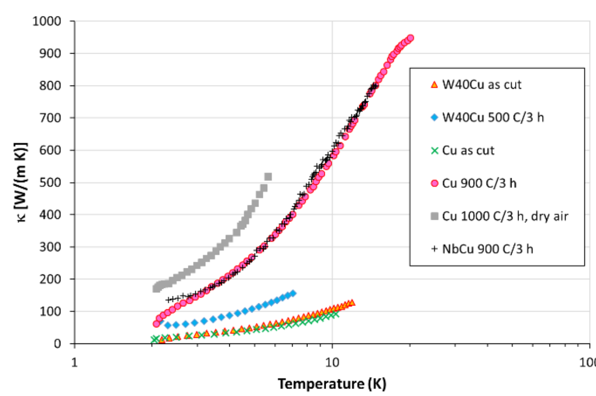

Figure 5: Thermal conductivity as a function of temperature measured on cold-sprayed Cu samples, W40Cu samples and a Nb sample with cold-sprayed Cu.

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Table 1: Impurities Content Measured on Copper Powder and Cold-Sprayed Cu Coupon

Element	Cu sample (wt.ppm)	Cu powder sample (wt.ppm)
C	39	8
O	565	362
N	7	<5
H	29	6
Al	7	<1
As	2	2
Bi	3	5
Ca	6	5
Cr	2	<1
Fe	4	1
Ni	8	8
Sb	3	1
Si	10	1
Sn	2	1
Te	5	5

Table 2: RRR and Thermal Conductivity at 4.3 K Measured on Cu and W40Cu Samples

Sample	Annealing	RRR	κ(4.3 K) [W/(m K)]
Cu	None	10	36
Cu	900 °C	n/a	233
Cu	1000 °C, dry air	132	345
W40Cu	None	20	43
W40Cu	500 °C	39	94

DISCUSSION

He gas allows achieving a higher particle impact velocity, therefore it was used for the deposition of the initial layers for best adhesion to the Nb. The carrier gas was switched to N_2 for the remainder of the coating in order to reduce cost.

A high-purity (~99.99% Cu) copper powder with the mesh size suitable for cold-spray is not readily available on the market and the one used in this study has about two orders of magnitude higher oxygen concentration than specified for oxygen-free copper. The presence of a high density of lattice defects and porosity also contributes to the low electrical and thermal conduction of the as-deposited samples. Annealing allows increasing the RRR and thermal conductivity of cold-sprayed Cu samples [7]. In particular, annealing at 1000 °C for 12-92 h in a dry oxygen atmosphere was shown to enhance the RRR by about one order of magnitude [8], which was confirmed on our sample. However, the Cu cold-spray is intended to be applied to a Nb cavity coated with a Nb3Sn film and post-annealing of the cavity with the cold-sprayed Cu layer above ~950 °C may cause significant tin sublimation, resulting in degraded superconducting properties of the Nb_3Sn film. Therefore, we decided to limit the annealing temperature to 900 °C. The thermal conductivity at 4.3 K of a NbCu sample annealed at this temperature for 3 h was about a factor of three higher than that of the RRR ~ 300 Nb substrate.

Annealing has less of an impact in improving the low-temperature electrical and thermal conductivities of the W40Cu alloy. The increase in RRR at temperatures below 500 °C can be attributed to the inhomogeneous grain growth of copper and tungsten components [9, 10]. At 500 °C, the copper-tungsten sample exhibited the highest RRR-value, which can be attributed to the maximum structural stability at this temperature [11]. Above this temperature, the grain growth of tungsten occurs causing more porosity in the sample which decreases the RRR.

CONCLUSION

Different samples of cold-sprayed copper and copper-tungsten were prepared and annealed at various temperature ranging from 300 °C to 1000 °C in order to improve the thermal conductivity at liquid helium temperature. The largest RRR achieved was for a Cu sample annealed at 1000 °C in dry air, however the annealing temperature should be limited 900 °C if Cu was cold-sprayed on an SRF cavity which has a Nb_3Sn film. The thermal conductivity at 4.3 K of a cold-sprayed Cu sample annealed at 900 °C/3 h in vacuum was about a factor of three higher than that of the Nb substrate.

We plan on depositing a thick Cu layer onto the outer surface of a Nb single-cell cavity with a Nb_3Sn film by cold-spray and post-anneal it at 900 °C/3 h, in preparation for an RF test of the cavity cooled by conduction with a cryocooler.

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