

# Electrodeposition of copper on niobium for cryocooler application

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**Abstract.** The electrodeposition of copper onto niobium using commercial acidic and alkaline electrolytes was tested. The continuous dense polycrystalline copper films were successfully obtained in aqueous alkaline-type bath containing copper sulphate, sodium hydroxide and sodium gluconate. The effect of benzotriazole and sodium lauryl sulphate additives on the morphology and crystal structure of the deposited copper was investigated by optical and scanning electron microscopy, and X-ray diffraction. No copper oxides were found in the grown films. Copper films had moderate adhesion properties that would be insufficient for cryocooler application. We are currently exploring different compositions of electrolyte baths for obtaining the coatings on niobium with improved adhesion.

## 1. Introduction

One of the ways to make superconducting rf accelerators more compact and affordable for industrial application is to replace the liquid helium refrigerator operating at 2 K with compact cryocoolers operating at 4.2 K or above [1, 2]. In this case, a high- $T_c$  alloys have to be used as material for accelerating structures. Most commonly, these structures represent niobium cavities with films of  $Nb_3Sn$  or  $NbTiN$  on their inner rf surface [3]. For sufficient removal of power dissipated during operation, copper deposition onto the outer cavity surface is required. Copper electrodeposition is the simplest technique for such a purpose as compared to other techniques like physical vapor deposition, chemical vapor deposition and sputtering techniques [3, 4]. For copper deposition acidic solutions with sulphate or alkaline cyanide-based baths are commonly used. Because of toxicity and environmental issues, alkaline non-cyanide Cu-plating electrolytes have become more preferable in recent years [5].

Success of the electrodeposition process in terms of obtaining a uniform dense coating with good adhesion depends on numerous factors. Specifically for niobium which undergoes the galvanic displacement reaction with Cu, such film with good adhesion in aqueous solution would represent a challenge. Considering the background of copper plating on steel which similarly to niobium has a high reactivity, one can think over the following approaches. The first, the simplest one, is using acidic or alkaline sulphate bath with various additives that were successful for Cu-plating of steel substrates. The second is pre-plating niobium with less active metal or alloy (Ni, Sn, etc.) followed by plating using commonly used electrolytes. Alternatively, the electrodeposition using ionic liquids is also promising. We launched our investigation of Cu-plating onto Nb owing to the advantages of the first approach. In particular in this paper we present our results on copper electroplating onto niobium

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using the acidic and alkaline copper(II) sulphate electrolytes that were successfully used for copper plating of steel.

## 2. Experimental details

High-purity oxygen-free copper and fine-grain niobium (RRR 300) electrodes with the dimension of 35×10×2.8 mm were used as an anode and a cathode, respectively. Prior electroplating, copper electrodes were mechanically polished with grinding paper (grit 800), cleaned in soap solution in ultrasonic bath, and rinsed with acetone. Niobium electrodes were etched chemically in a solution of HNO<sub>3</sub>:HF:H<sub>3</sub>PO<sub>4</sub>=1:1:2 and thoroughly washed in ultra-pure water. For our study we used two acidic-type commercial electrolytes:  $\mu$ Chem520 by Surtec Suisse GmbH and the high-speed bright copper electroplating solution by Sigma-Aldrich (see table 1). These electrolytes are meant to be used on a wide variety of substrates including semiconductor, glass, polymers, et al.

**Table 1.** Composition of the Acidic Electrolytes.

| Component                            | $\mu$ Chem 520 | Sigma-Aldrich |
|--------------------------------------|----------------|---------------|
| Cu basis                             | 25 g/l         | 65.0 g/l      |
| H <sub>2</sub> SO <sub>4</sub> basis | 230 g/l        | 8.0 g/l       |
| chloride basis                       | 60 mg/l        | 40 mg/l       |
| organic additives                    |                | 600 mg/l      |

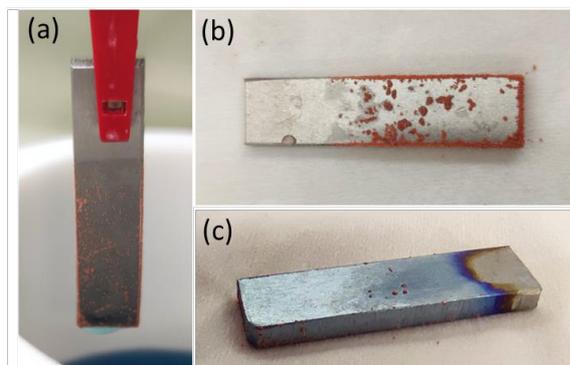
The compositions of alkaline electrolytes were adopted from the work [6] in which copper electroplating on steel substrates was studied. In particular, three electrolyte baths were prepared. Bath A: water solution of copper sulphate (50 g/l), sodium hydroxide (125 g/l), sodium gluconate (100 g/l). Bath B: the composition of bath A with the addition of 1,2,3-benzotriazole (0.5 g/l). Bath C: the composition of bath B with the addition of sodium lauryl sulphate (0.05 g/l). The temperature of the electrolyte was maintained at 25 °C for all electrochemical tests (also 50 °C for  $\mu$ Chem 520). The electrodeposition was carried out using the two-electrode set-up and current densities in the range 0.1–7 A/dm<sup>2</sup>. The morphology of the copper deposits was examined visually, by optical microscopy (Zeiss Axio), scanning electron microscopy (SEM, Zeiss Merlin), energy-dispersive analysis (EDX, Ultim Extreme, Oxford Instruments) and X-ray diffraction (XRD, Bruker D8 Advance with Cu K $\alpha$  anode,  $\lambda$ =1.5105 Å).

## 3. Results and discussion

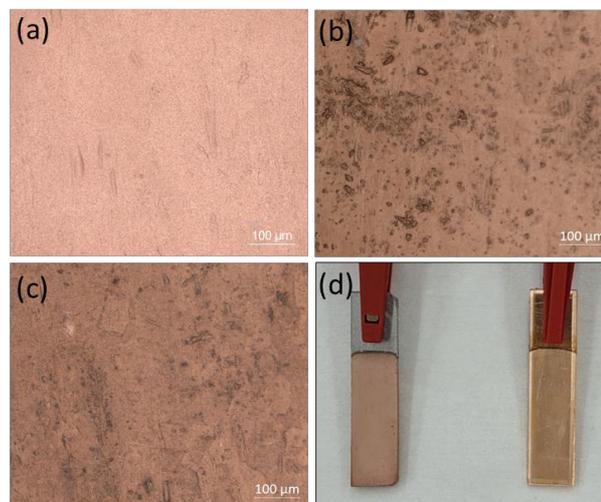
Electroplating using the acidic-type electrolytes did not result in a formation of a continuous copper film on niobium. Particularly for  $\mu$ Chem 520, no deposit was formed at current densities below 0.5 A/dm<sup>2</sup>, at 0.9–1.3 A/dm<sup>2</sup> copper islands were formed, and above 1.5 A/dm<sup>2</sup> the anode degraded (oxidized). Increasing the bath temperature from 25 to 50 °C allowed the electroplating to be conducted at higher current densities up to 7 A/dm<sup>2</sup> without degradation of an anode (figure 1(a,b)).

Modification of a cathode surface by anodization did not affect noticeably the obtained result (figure 1(c)). As to the plating using the electrolyte by Sigma-Aldrich, no good results were obtained either within the range of experimental parameters. It was found that copper anode degraded by formation of copper chlorides CuCl and Cu<sub>2</sub>O revealed by XRD, and thus was subsequently considered unusable for this bath.

In figure 2 the photograph of the both electrodes after the electrodeposition procedure are shown as an example as well as optical images of the films deposited using baths A, B and C. All the films were obtained at current density of 0.15 A/dm<sup>2</sup>. The deposition rate estimated by mass was equal 2.3  $\mu$ m/h



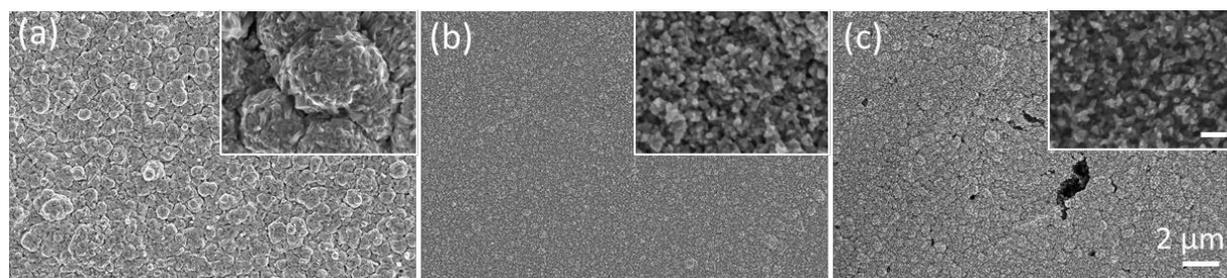
**Figure 1.** Visual appearance of the Nb electrodes after the Cu deposition in  $\mu\text{Chem}$  520 bath at  $50^\circ\text{C}$ : (a)  $0.65 \text{ A/dm}^2$ ; (b)  $6.5 \text{ A/dm}^2$ ; (c)  $0.65 \text{ A/dm}^2$ , pre-oxidized Nb.



**Figure 2.** Optical microscopy images of Cu films deposited in bath A (a), bath B (b) and bath C (c). (d) Visual appearance of the electrodes after the Cu deposition in bath A.

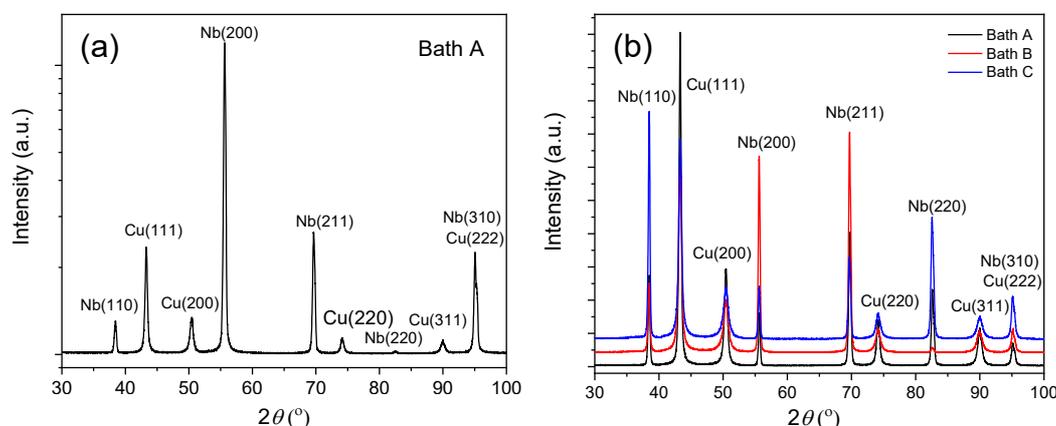
for bath A, and  $1.8 \mu\text{m/h}$  for baths B/C. When the current density reached  $1 \text{ A/dm}^2$ , a black deposit was formed on the cathode surface, and it easily peeled off.

The morphology of the as-deposited copper films is presented in figure 3(a-c). It represents dense evenly distributed deposits in all the experiments, but it is different for bath A as compared to baths B/C. In the first case the copper nucleated and grew forming larger particles as compared to the latter. Thus, benzotriazole additive affected significantly the morphology of the grown copper films, which agrees with [6, 7]. For bath C, the residue of surfactant was also found (figure 3(c)). Unlike in the work of R. Sekar [6] devoted to copper plating on steel, the effect of surfactant on the morphology or crystal structure of copper formed on niobium was not identified. The EDX elemental mapping revealed Cu, O, C and N (not shown).



**Figure 3.** SEM micrographs of the Cu films deposited onto Nb: (a) bath A; (b) bath B; (c) bath C. The insets show magnified views (the scale bar is equal to  $200 \text{ nm}$  and is valid for all insets).

The crystal structure of the copper deposits was studied with XRD. In figure 4(a) the diffractogram of the sample obtained using bath A measured in Bragg-Brentano focusing geometry is presented as an example. Apart from niobium, reflexes indexed as (111), (200), (220), (311) and (222) of face-centered cubic crystal lattice of Cu were revealed (PDF 03-065-9743). The intensity of Cu(111) plane was more dominant as compared to other reflexes which is in agreement with the standard diffraction data. The calculated texture coefficients for each peak diffracted on copper represents the degree of deviation of the relative intensities with respect to those reported for Cu powder [8]. The values of this



**Figure 4.** XRD patterns of copper deposits obtained upon electrodeposition using baths A, B and C: (a) Bragg-Brentano geometry ( $2\theta/\omega$  scan); (b) SAXS geometry,  $\omega=3^\circ$ .

parameter were increased for the reflexes with higher-order  $hkl$ -indexes, (220) and (311). No evidence of any of the copper oxides was detected even when the measurements were performed in Göbel mirror geometry at fixed angles of primary X-rays (Small-Angle X-ray Scattering, SAXS),  $\omega=0.5\text{--}5^\circ$ . As an example, the diffractograms measured at  $\omega=3^\circ$  (the corresponding probing depth,  $d$ , in copper is approximately  $1.2\ \mu\text{m}$ ) are presented in figure 4(b). Since the reflexes from the niobium substrate are visible, thickness of the films is less than  $d$ . The estimated by mass copper deposition rate varied in the range  $1.8\text{--}2.3\ \mu\text{m/h}$ , which corresponded to copper deposit thickness of  $0.6\text{--}0.8\ \mu\text{m}$ . The crystallite sizes calculated with the Debye–Scherrer equation [9] are 22.9, 16.4 and 16.3 nm for bath A, B and C, correspondingly.

Unlike in [6], no copper oxides were observed with XRD. One can assume that this is related to the fact that in the mentioned work slightly higher current densities were used. As we increased the current density, the film adhesion suffered significantly, so the crystallite size dependence on current density was not investigated. The decrease of the crystallite size when benzotriazole/surfactant are present, agrees with [6] and is probably related to the higher degree of adatoms saturation and increase in nucleus densities.

The films adhesion was ranked as 2A/3A according to the adhesion tape test performed after ASTM D3359, Test Method A (X-cut Tape Test), so the copper adhesion was unsatisfactory even when low current densities were used for plating.

#### 4. Conclusion

We tested several electrolytic baths both the acidic and alkaline in nature for electrodeposition of copper onto niobium. Uniform continuous Cu-films were obtained on niobium substrates using the alkaline-type electrolyte with and without additives. It was revealed by electron microscopy that the morphology and the crystallite size are affected if the benzotriazole additive is present. Unlike the similar experiments with steel substrates, no copper oxides were observed by XRD. Adhesion-tape test showed that the bonding of the obtained films may be insufficient for some applications, such as cryocoolers. We are working on electrodeposition procedure which would provide a better adhesion of the copper coating on niobium to fulfil our goals.

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