

STRUCTURE AND COMPOSITION OF Nb₃Sn DIFFUSION COATED FILMS ON Nb*

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Abstract

The structure and composition of Nb₃Sn films obtained by diffusion coating niobium coupons and SRF cavities were investigated by x-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS) and scanning electron microscopy (SEM) with energy-dispersive x-ray spectroscopy (EDS) and electron backscatter diffraction (EBSD), including native surfaces, depth profiles and cross-sections. We find that the native surface oxide is significantly tin-rich, we have measured depth profiles. We find that the grains apparent in the SEM images are individual crystallites having no evident relationship to the substrate or each other.

INTRODUCTION

Advanced particle accelerators are a critical tool for frontier science. Superconducting radio frequency (SRF) technology continues to grow as the choice for high-end machines because of cost and performance advantages over warm copper. Nonetheless, the initial cryoplant and ongoing electric powers costs of the presently-required 2 K operation are a significant burden for today's niobium cavity machines. Operation at 4.2 K instead would be a major benefit.

More than 40 years ago, accelerator science researchers exploring alternatives to pure niobium settled on Nb₃Sn as the most promising alternative. Their preferred embodiment was a few-micron thick layer formed by diffusion coating. Extensive R&D programs at Siemens and at the University of Wuppertal into the 1990's sought to achieve a readily deployable Nb₃Sn SRF cavity technology. Despite aggressive efforts to the contrary, the best and typical cavity performance featured quality factors in the mid 10¹⁰ to low 10¹¹ range at few MeV/m gradients, which fell sharply with increasing gradient. Meanwhile, the performance of pure niobium cavities continued to improve. While the cause was never clearly identified, the consensus view was that the slope is something inherent to Nb₃Sn and research activity declined.

Recently, however, performance results obtained by researchers at Cornell were essentially free of the slope, achieving gradients in excess of 10 MeV/m with diffusion-coated cavities.

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The prospect of success has thus re-emerged. Further, during the years since Wuppertal, the needs of microelectronics technology have driven development of an arsenal of powerful materials characterization tools that can wrest new insights from systems like Nb₃Sn diffusion coatings. Accordingly, Jefferson Lab and its university partners were motivated to undertake a research program aimed at diffusion coating. A diffusion coating facility, described elsewhere in these proceedings [1], was constructed to provide materials for research and coated cavities for performance studies. A goal for the present research was to explore what modern characterization tools might reveal about Nb₃Sn diffusion coatings, choosing the most effective for extensive investigation in the next program phase.

EXPERIMENTAL STUDIES

The material for the present study was 10 mm square coupons cut by electrical discharge machining from trimmings of the 3 mm thick niobium sheet used to make SRF cavities ("RRR grade"). Typical grain size was in the 50 μm to 100 μm range ("polycrystals"). The availability of large-grained sheet made possible to cut some coupons consisting of two grains with a single grain boundary lying side-to-side at the center ("bicrystals"). Coupons were prepared into conditions typical of cavity production: buffered chemical polishing (BCP), centrifugal barrel polishing (CBP) and electropolishing (EP). They were diffusion coated along with specially metallographically polished coupons ("nanopolished", NP). The details of the diffusion coating facility and its operation, the topography of the resulting coatings and its investigation by atomic force microscopy (AFM) are described in a companion paper in these proceedings.

The most widely applied surface analysis technique is X-Ray Photoelectron Spectroscopy (XPS), revealing the elemental composition and chemical state of the first few nanometers of a solid surface down to roughly a part per thousand [2]. Lateral resolution is 10 – 20 μm, somewhat depending on the sample. The XPS measurements were carried out in an ULVAC-PHI "Quantera SXM" instrument equipped with a monochromated aluminum anode. Surface analyses were collected at 50 W/15 kV using a 200 μm spot size, 45° take off angle. Survey scans were done using a pass energy of 280 eV, while high resolution scans used a pass energy of 26.00 eV. For depth profiles, sputtering was accomplished via an argon ion source at 5 kV over a 3 mm² area. Depth profile data was collected at 50 W/15kV with a spot size of 200 μm, 45° take off angle and 140 eV pass energy. Data were

collected at $t = 0$ and then at 1 minute sputter intervals. NP materials were always used to avoid confusing depth variation arising from underlying topography with other effects.

XPS examination of the as-coated surface of a polycrystal (U4) and a bicrystal (B1-9) revealed Nb/Sn atoms ratio of 0.75 and 0.63 respectively, much lower than the nominal value of 3. Survey scans found only oxygen and adventitious carbon in addition; chlorine was not detected. High resolution scans found charge-corrected peak positions (Sn 3d 5/2, Nb 3d 5/2) consistent with the valence state of the individual native oxides formed upon exposure to the ambient atmosphere (4+, 5+).

Ion bombardment with suitable parameters (above) can be used to remove a chosen layer thickness. When alternated with analysis, a measurement of how composition varies with depth is obtained: sputter profile. Fig. 1a shows a profile of an as-coated NP polycrystal sample.

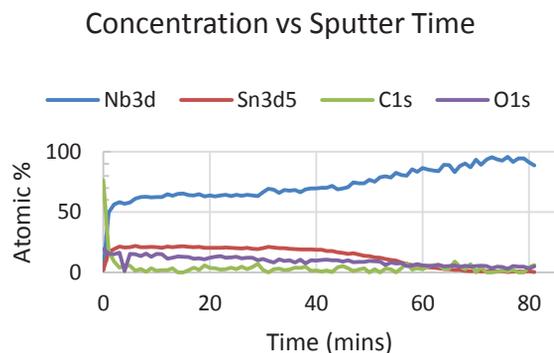


Figure 1a: Sputter profile of coated nanopolished coupon.

A first notable feature is immediate decrease of the carbon signal by a factor of 10, indicating that it is a surface contaminant, not a contaminant within the coating. A second is that the oxygen content, though small, is not insignificant and falls only slowly. Typical chamber pressures in the Quantera ($< 10^{-9}$ torr) still provide enough oxygen to react with the freshly exposed niobium metal surface. The tin concentration falls to baseline (but see later) after ~ 70 minutes sputter time; the 50% level is reached after about 50 minutes. Fig. 1b presents an expansion of interface sputter-through; the Nb is off-scale.

Calibrated SIMS measurements (see later) indicate a coating thickness of about $1.5 \mu\text{m}$. For the first half of the coating, the Nb/Sn ratio is approximately constant at the intended 3:1. A further example of the application of XPS may be found in the discussion of post-treatments later.

Concentration vs Sputter Time

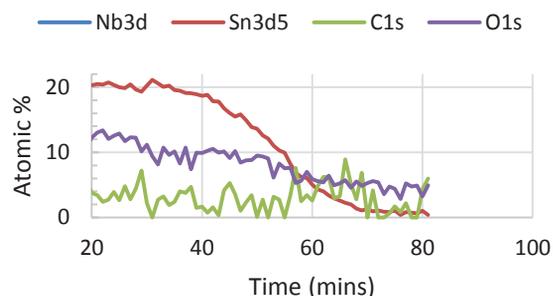


Figure 1b: Sputter profile of the base of the coating from the previous coupon.

Accurate measurements to lower concentration ($\sim\text{ppm}$) require secondary ion mass spectroscopy (SIMS), an approach widely applied in the microelectronics industry. SIMS analyses were collected on a CAMECA IMS-7f magnetic sector instrument. A Cs^+ primary ion beam was used and rastered over an area of $175 \mu\text{m}^2$. An impact energy of 5 kV was used with an incidence angle of 44° and current of $\sim 200 \text{ nA}$. Positive secondary ions of CsSn and CsNb were detected. For matrix level species the MCS^+ (CsSn^+ and CsNb^+) method has been shown to reduce or eliminate the matrix effects normally seen in SIMS analyses [3,4]. Data were collected at multiple locations on as-coated bicrystal coupon and polycrystalline coupons.

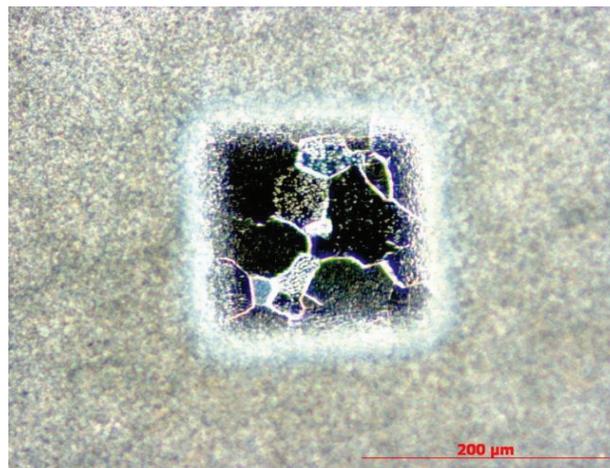


Figure 2: Crater after removal of 8 microns from polycrystal.

Figure 2 shows digital optical microscope image of the crater on the polycrystal; note the grain boundaries visible. No structure was visible on the bicrystal. Profilometer measurement of the crater depth was used to calibrate the sputter rate. Fig. 3 presents the SIMS sputter profile of the polycrystal.

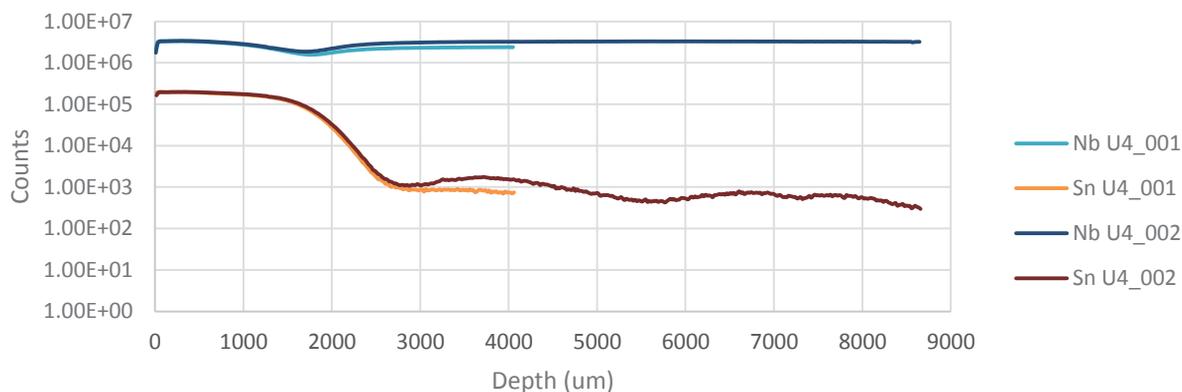


Figure 3: SIMS sputter profile just through the coating (001) and several microns depth (002).

The profiles obtained from two locations on the bicrystal are almost identical, falling to baseline at 3 μm . In contrast, the polycrystal profile is not at baseline, even at 8 μm . The question of enhanced grain boundary transport arises. An approach could be to collect a profile in the single crystal region of the bicrystal and at the grain boundary. The lateral resolution of our SIMS is not sufficient for grain boundary material to dominate the data. Other approaches are being investigated. In the XPS profiles presented above, absolute photoionization cross-sections provide a basis for quantitation.

The SIMS process is more complex at the atomic level, so that quantitation requires known standards, as may be prepared by implanting the ion of interest in the matrix of interest in the concentration range of interest.

Electron microscopy offers the advantages of nm-scale lateral image resolution with approximately part per thousand sensitivity for elemental analysis. Lateral resolution for elemental analysis is only in the micron range, however, as discussed in an accompanying paper in these proceedings. Still another capability of the scanning electron microscope (SEM) is to obtain structure information by electron back-scatter diffraction (EBSD). An example of EBSD data is the orientation image map (OIM). In OIM, EBSD data are collected at a series of points covering the area of interest in a manner similar to the pixels comprising a SEM image raster. With investigator guidance as to what structures are present, here Nb and Nb_3Sn , the data system uses the diffraction data to determine what crystal structure is present in each pixel, and how the lattice is oriented in space. The usual presentation is an image in which grains are assigned colors relating their orientation to a stereographic triangle for that phase.

Figure 4 presents an EBSD image in which both phases are shown, with their orientations. Locations where the data system could not determine a confident solution, typically at phase boundaries, are blacked out. The dominant feature is that the Nb_3Sn layer is chiefly single grains from the top to the bottom of the film, with no evident relationship to the film or each other.

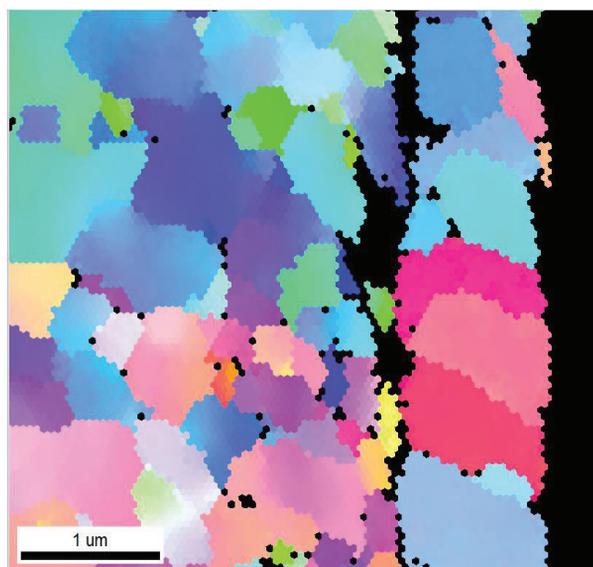


Figure 4: EBSD OIM of cross-section of coated nanopolished polycrystal. The grains in the line on the right side are Nb_3Sn . Those on the left are Nb. Diffraction patterns not shown.

While this is only an initial result and much more work is needed, it is clear that EBSD may be expected to contribute useful insights. The contributions of SEM imaging and EDS elemental analysis are discussed in the accompanying paper.

The post-treatment of coated coupons affords an example of the combined use of some of the techniques just discussed. Rinsing with hydrofluoric acid is understood to dissolve niobium oxide, leading some investigators to employ it for clean-up. Summarizing briefly, coated coupons were placed in bottle-strength HF at room temperature for 0, 1, 5 or 60 minutes, removed and rinsed. XPS surface analysis yielded Nb/Sn ratios of 2.38, 1.64, 1.57 and 1.54 respectively. The last three values are close enough that further effort would be needed to establish that they truly are different. More detail will be presented in the future. Nonetheless, it seems clear the HF rinsing has only modest impact on the surface chemistry.

Anodization in ammonia solution is another post-treatment process. It may be combined with HF rinsing as oxy-polishing in which the HF removes oxide formed during anodization. The present experiments used equal parts of 50% ammonium hydroxide solution and de-ionized water. DC voltages of 10, 20, 30, 40 or 50 volts were applied for sufficient time for current to fall to 10 mA. To obtain an initial view of the resulting oxide layer thickness, a platinum protective layer was applied to the surface of the coupon anodized at 50 volts and a cross-section through the coating was cut by focused ion beam (FIB). A scanning electron microscope image of the cross-section appears in Fig. 5, affording opportunity to directly measure the coating thickness at several locations. These values were used to calibrate the XPS sputter profiles appearing in Fig. 6. The effectiveness of the combination is evident.

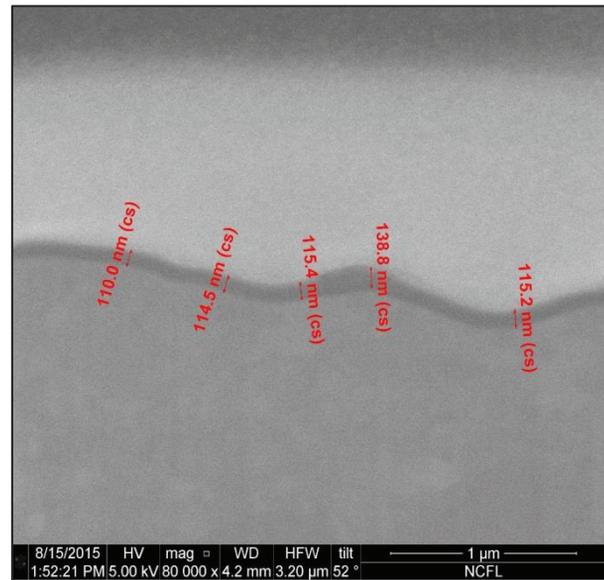


Figure 5: SEM image of a FIB cross-section through the surface oxide obtained by anodization at 50 volts.

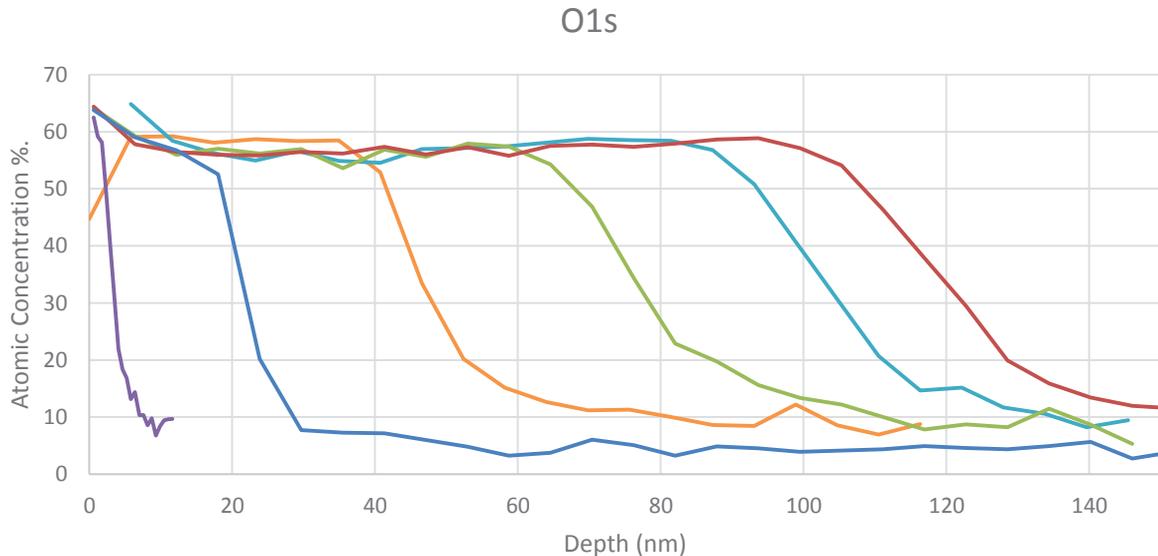


Figure 6: XPS sputter profiles of oxygen to indicate the oxide layer thickness obtained by anodization at 0, 10, 20, 30, 40 or 50 volts, left to right respectively.

SUMMARY

The power of modern materials characterization to reveal important information about Nb₃Sn coated niobium is clear. The challenge will be to use it incisively to gain the insights needed to move the technology forward.

ACKNOWLEDGMENT

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