

Influence of an Al₂O₃ capping layer on the thermal reduction of the native niobium oxide: An in situ x-ray reflectivity study

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Superconducting radio-frequency cavities, critical components of modern particle accelerators and quantum computing hardware, fundamentally rely on the surface properties of niobium. However, native oxide formation and impurity uptake in the near-surface region can degrade superconducting performance and increase radio-frequency losses during operation. In this study, we present a systematic *in situ* x-ray reflectivity investigation of (110) niobium single-crystal surfaces with and without an atomic layer deposited Al₂O₃ capping layer under ultrahigh-vacuum conditions up to 650 °C. Our results reveal a temperature-dependent reduction of the native niobium oxide layers in both capped and uncapped samples, with similarities in the overall behavior but clear differences in the reduction pathways. The Al₂O₃ capping layer modifies the reduction process, prevents oxide regrowth upon air exposure, and protects the niobium surface against impurity uptake during thermal treatment. These findings demonstrate that Al₂O₃ capping is an effective strategy to suppress native oxide formation during thermal cycling, offering clear benefits for the performance and operational lifetime of superconducting radio-frequency cavities and related quantum computing technologies.

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I. INTRODUCTION

Superconducting radio-frequency (SRF) cavities, the core components of modern particle accelerators and free-electron lasers like FLASH and EU-XFEL, underpin transformative advances in scientific research [1], medical diagnostics [2], and industrial applications [3]. Niobium, a weak type-II superconductor, is the preferred material for SRF cavities due to its unparalleled critical transition temperature T_c among pure metals, high lower critical magnetic field value H_{c1} , and favorable mechanical properties such as ductility and corrosion resistance [4]. These properties facilitate cavity production using standard machining and treatment techniques [5]. However, the performance of niobium cavities is highly sensitive to impurities, including hydrogen, oxygen, nitrogen, and carbon, particularly within the effective penetration depth of the RF layer (~ 100 nm). These impurities can alter superconducting properties by decreasing the electron mean free path [6], shrinking the energy gap [7], weakening flux pinning [8–10], or precipitating niobium hydrides during cooldown

to cryogenic temperatures [11–13]. Yet theoretical work indicates that carefully tailoring their concentration and spatial distribution can (1) optimize the mean free path and quasi-particle lifetime to enhance Q_0 [14,15], (2) shorten the mean free path within the London penetration depth to raise the superheating field [16–18], and (3) mitigate the high-field Q slope through engineered surface disorder [19,20]. Furthermore, it has been shown that the presence of 1 at. % of oxygen in niobium decreases T_c by 0.93 K [4]. Such sensitivity to impurities in niobium led to a strict annotation convention, specifying their content to be less than 50, 10, or 2 wt. ppm, depending on the atom (see Table 1 in [21]). Meeting the demands of next-generation accelerators—high electric accelerating fields, improved efficiency, and continuous wave operation—requires ongoing advances in niobium processing and impurity control to optimize the quality factor Q_0 and sustain high accelerating gradients.

Niobium-based SRF cavities are produced through a series of steps, including polishing cycles such as buffered chemical polishing and electropolishing, followed by high-vacuum heat treatments at 800 °C and subsequently at 120 °C [12,22] to reduce hydrogen content and relieve mechanical stress introduced during deep drawing [23]. In recent years, nitrogen doping and nitrogen infusion have been introduced to further enhance cavity performance. Nitrogen doping typically entails an annealing step at 800 °C for several hours, with nitrogen introduced briefly toward the end of the high-temperature hold (3–5 Pa). This is followed by electropolishing to

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remove the nitride layer, leaving a subsurface region enriched with interstitial nitrogen [24–27]. This approach can boost Q_0 by a factor of 3 at intermediate accelerating fields. Nitrogen infusion, in contrast, combines an 800 °C vacuum anneal with lower-temperature nitrogen exposure (120–200 °C) for 24–48 h. This process has yielded Q_0 values up to 6×10^{10} at low to moderate accelerating fields and has demonstrated accelerating gradients up to 45 MV/m [27]. While nitrogen doping has been successfully implemented in large-scale applications such as LCLS-II [28], nitrogen infusion remains more challenging to reproduce, owing to sensitivity to material parameters, inconsistent process conditions, and limited standard diagnostics [28–31]. Around the same period, titanium alloying via ultrahigh-vacuum (UHV) annealing at about 1400 °C tested on large-grain niobium cavities delivered Q_0 values exceeding 5×10^{10} at 2 K, offering a complementary impurity-based route to reduced surface resistance [32].

Mid-temperature (mid-T) baking, which involves treating cavities at approximately 300 °C for 3 h in vacuum better than 10^{-5} mbar, recently emerged as a promising alternative. Unlike earlier treatments, it has shown greater reproducibility across laboratories, although adjustments to parameters have been necessary. This approach has demonstrated the potential for substantial performance improvements, with reported Q_0 values in the range of $3\text{--}4 \times 10^{11}$ at $E_{\text{acc}} = 30$ MV/m and $T = 1.4$ K and approximately $3\text{--}4 \times 10^{10}$ at $E_{\text{acc}} = 5\text{--}15$ MV/m and $T = 2$ K, accompanied by reductions in both BCS and residual resistances [33,34]. A common ground for all treatments is the increase in the concentration of interstitial impurities (oxygen or nitrogen) within the first 100 nm of the cavity's near-surface region. These changes in surface composition are closely linked to the observed improvements in quality factors, highlighting the potential of such methods to enhance SRF cavity performance [35,36].

Superconductor-insulator-superconductor multilayers, first proposed by Gurevich, aim to push SRF cavities beyond the intrinsic limits of bulk niobium by covering the RF surface with alternating nanometer-scale superconducting and insulating films [37]. Typical designs pair higher- T_c nitrides, such as NbN and NbTiN, with chemically robust dielectrics like Al_2O_3 , applied by atomic layer deposition (ALD) to guarantee conformal coverage of the complex cavity geometry. As an intermediate step toward such multilayer architectures, the use of a single ALD-grown Al_2O_3 film has already shown performance improvements when applied prior to mid-T baking, making this passivation strategy a promising and independently relevant approach to optimizing SRF cavity function [38–40].

Enhanced thin-film coatings, such as those based on Al_2O_3 , not only improve the performance of niobium-based superconducting resonators but also have significant implications for quantum computing. Niobium resonators are affected by two-level system (TLS) defects originating in their native oxide layers [41–45]. Moreover, Nb/ Al_2O_3 interfaces are central to superconducting quantum interference devices and other modern qubit architectures, where oxide defects can severely limit coherence times [46–49]. ALD deposition of a 10 nm Al_2O_3 layer on a niobium resonator, followed by annealing at approximately 650 °C, where the niobium surface is largely free of Nb_2O_5 , was shown to significantly reduce TLS losses

by modifying the niobium oxide interface, likely reducing oxygen vacancy density and stabilizing defect-related charge fluctuations. This reduction in TLS losses enhances the quality factors of niobium resonators in low-field quantum regimes [40,42]. The encapsulation of niobium-based transmon qubits with thin films that suppress the formation of native Nb_2O_5 has likewise been shown to significantly extend coherence times [50]. Furthermore, the air-stable protective properties of Al_2O_3 facilitate handling and characterization, supporting the development of reliable and scalable quantum technologies.

While significant progress has been made in improving cavity performance, insights into the surface state during and after cavity treatments remain limited. Model systems, such as single-crystal niobium surfaces, provide a controlled platform for studying surface phenomena and could bridge the gap between fundamental understanding and practical cavity applications. Knowledge gained from these systems could contribute to the design of new treatments aimed at pushing the performance limits of SRF cavities, which not only are essential for accelerator technology but also play a key role in quantum computing applications, where surface properties influence coherence and stability.

Here, we present a study investigating, both *in situ* and *ex situ*, the near-surface structural evolution of mechanically polished Nb(110) single crystals with and without an Al_2O_3 capping layer to thoroughly explore its influence on the processes at play. The samples were subjected to a series of temperature steps up to 650 °C under ultrahigh-vacuum conditions. X-ray reflectivity (XRR) measurements, carried out at each temperature and upon cooling to room temperature, were employed to characterize the near-surface region. Complementary measurements were performed in air immediately after extraction and 2 weeks later to study the regrowth of the native oxide layer. This systematic approach allows us to probe the effects of thermal processing and the presence of the Al_2O_3 layer on the morphology and stability of the niobium near-surface region.

II. EXPERIMENTAL METHODS

A. Sample description

Two different mechanically polished niobium (110) single-crystal samples (10 mm diameter, 2 mm height) oriented to better than 0.1° were utilized for this study. One of the samples was coated with a 32 nm thick Al_2O_3 layer using ALD at 120 °C over a total duration of 17 h. ALD is a sequential chemical vapor deposition technique involving alternating exposures to two precursors. Each cycle consists of surface adsorption of the first precursor, followed by a purge, then exposure to the second precursor and a second purge. This sequence results in the deposition of one atomic layer per cycle. The deposition temperature critically influences precursor reactivity and film uniformity. To minimize unintended annealing of the niobium substrate, the process was carried out at the lowest possible temperature that still ensured conformal, homogeneous coverage. The selected parameters follow those used for three previously coated and successfully tested SRF cavities, as detailed in Ref. [39]. The full set of ALD process parameters is summarized in Table I.

TABLE I. ALD process parameters used for the deposition of an Al_2O_3 layer.

Material	Pulse (ms)	Exposure (s)	Purge (s)
Trimethylaluminium (TMA)	500	60	120
H_2O	500	60	120

B. Characterization techniques and experimental steps

For all further mentioned studies, the samples were mounted in a dedicated UHV setup with an initial pressure of 10^{-9} mbar, permitting direct XRR measurements at elevated temperatures. XRR is a widely employed technique for characterizing thin-film structures and multilayered materials, enabling precise determination of layer thickness, interfacial roughness, and electron density profiles [51]. As an x-ray beam is directed at a sample at very shallow angles, some of the x rays reflect off the sample surface, while others penetrate and reflect off the interfaces between different layers within the sample. The reflected x-rays from different interfaces interfere with each other, producing a pattern of oscillations in the measured intensity. The reflected intensity is primarily determined by the optical properties of the investigated material, which are directly related to its electron density, as well as by layer thickness and interfacial roughness. The behavior of reflected intensity across multiple interfaces was analyzed by Parratt, who established a recursive formalism to accurately account for these effects [52].

Throughout the experiment a six-circle diffractometer with a Cu $K\alpha$ source and a two-dimensional detector at DESY Nanolab were used [53]. Each sample was studied separately both before it entered the UHV furnace at room temperature (RT) and throughout a wide range of temperature steps (100–400 °C, 650 °C). The sequence of temperature points was chosen to cover in detail all important thermally assisted processes in niobium up to 650 °C, the upper limit of the furnace used. For each temperature, a reflectivity curve was recorded both in a heated state and after returning to room temperature. A detailed bar chart containing all relevant information regarding the heating time for each experiment step is given in Fig. 1. As a last step, the samples were extracted from the furnace and measured in air again immediately, as well as 2 weeks later, to observe the potential regrowth of the native oxide layer.

III. RESULTS AND DISCUSSION

Figure 2 shows the x-ray reflectivity curves obtained at each stage of the heat treatment, with measured data represented by gray dots. Figure 2(a) corresponds to the uncoated Nb sample, while Fig. 2(b) shows results for the Nb sample capped with an Al_2O_3 layer. All curves begin with a high-intensity plateau at low 2θ angles, characteristic of total external reflection below the material-specific critical angle. This is followed by a sharp decline in intensity around $2\theta \approx 0.7^\circ$, corresponding to the critical angle of niobium. In Fig. 2(b), a second, earlier drop in intensity is visible, marking the lower critical angle of the Al_2O_3 layer due to its lower electron density. In both plots we observe large-period

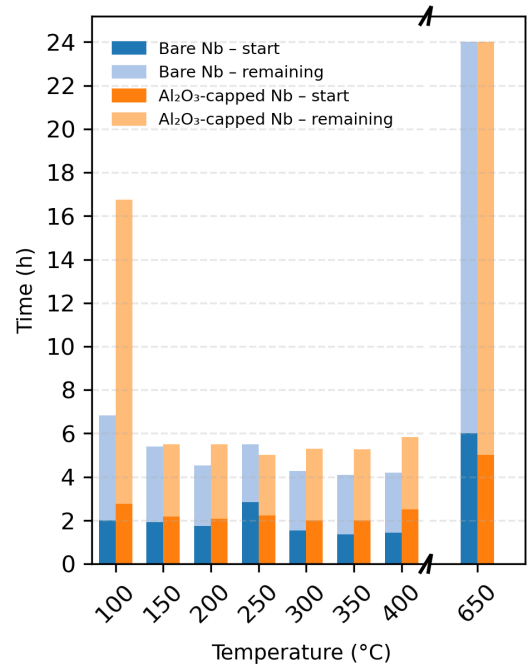


FIG. 1. Cumulative time spent by both samples at elevated temperature for each experiment step. Dark blue bars represent the time spent at each temperature by the uncoated niobium sample prior to the start of the XRR measurement, while the light blue bars add up the time at temperature during the XRR measurement and prior to cooldown. Dark orange bars indicate the time spent at each temperature by the Al_2O_3 -capped niobium sample prior to the start of the XRR measurement, and the light orange bars add up the time at temperature during the XRR measurement and prior to cooldown. Thus, the total height of each bar stands for the total time a sample spent at a certain temperature before being cooled down.

oscillations in the reflected intensity, the so-called Kiessig fringes, which correlate with the thickness values of the native oxide layers on top of the niobium bulk material: the larger the oscillation period, the thinner the layer. A good comparison to the more widely spaced fringes originating from the native oxide layer (~ 5 nm thick) is the more closely spaced oscillations presented in Fig. 2(b), which correspond to the 32 nm thick Al_2O_3 layer. Observing the curves from bottom to top, representing progressively higher temperatures, a gradual increase in fringe spacing is evident. This change reflects a decrease in the thickness of the native oxide layer as it is thinned by the heat treatment. The XRR data were analyzed by fitting structural parameters using the GenX software [54], which is based on the Parratt formalism mentioned above. The fits are represented by the colored curves overlaid on the measured gray data points. The most accurate agreement with the experimental XRR data was achieved by assuming a gradient in electron density increasing from the surface toward the oxide/metal interface, consistent with increasing oxygen concentration across the oxide layer [35,36]. This gradient reflects the sequential arrangement of Nb_2O_5 , NbO_2 , and NbO phases atop the Nb substrate, whose corresponding bulk electron densities follow the trend $\text{Nb}_2\text{O}_5 < \text{NbO}_2 < \text{NbO} < \text{Nb}$. The resulting electron density profiles derived from the fitted reflectivity curves are shown in Fig. 3. Modeling the Al_2O_3 overlayer presented additional challenges, as indicated by

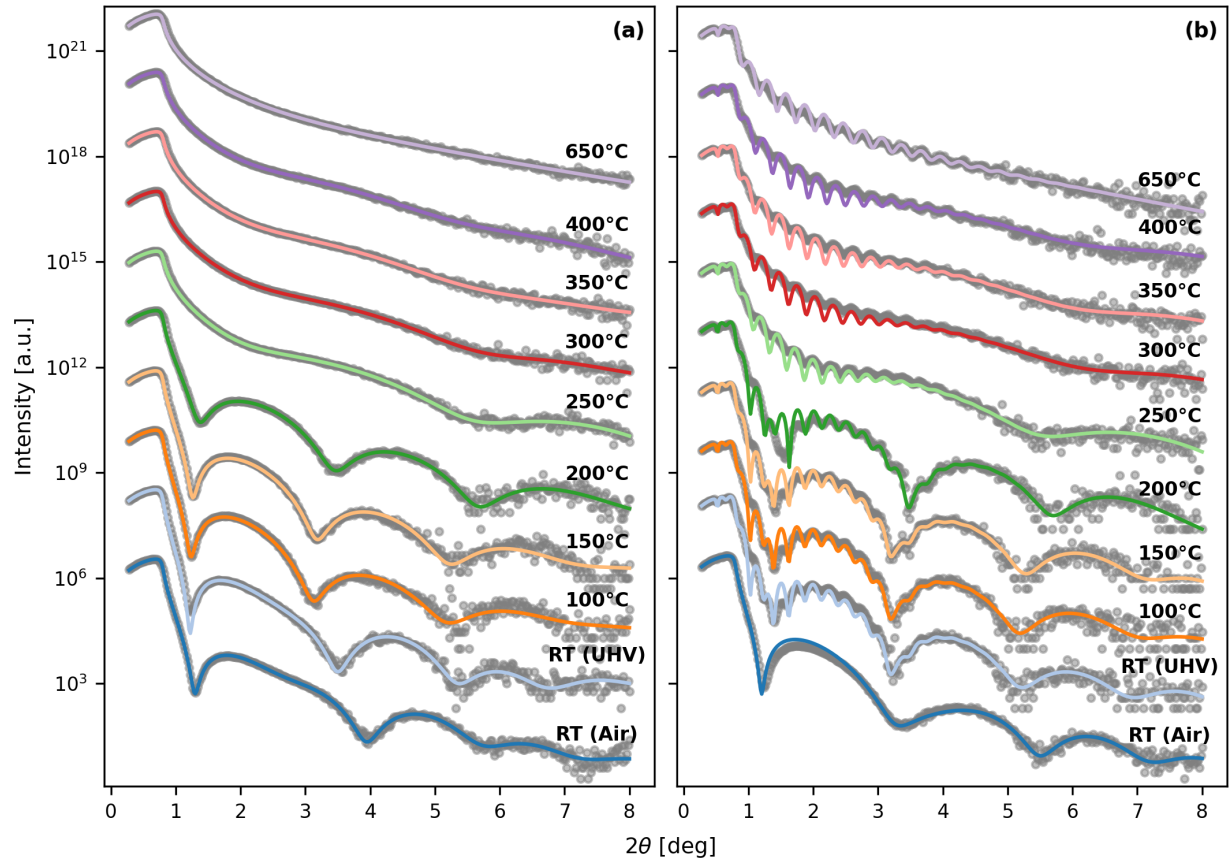


FIG. 2. XRR curves measured between room temperature and 650 °C for (a) the uncoated sample and (b) the Al_2O_3 -capped sample. Gray dots indicate the measured data; colored curves represent the model fits. All data were recorded at room temperature after each respective heat treatment step. The curves are offset for clarity. See Tables S1 and S2 in [67] for detailed fit parameters.

discrepancies between the measured data and the calculated reflectivity in the region of the corresponding interference fringes. Several modeling approaches were evaluated for the Al_2O_3 layer, all yielding differences within 10% of the final adopted model. Ultimately, a simplified description was used, treating the deposited Al_2O_3 as an amorphous, homogeneous layer with a constant electron density value. Although this approximation does not fully capture the fine structure of the Al_2O_3 oscillations, it was deemed sufficient given that the primary focus of this study is on the niobium substrate and its native oxide layers, which were prioritized during model refinement.

As an initial qualitative observation, the reflectivity curves in Fig. 2 exhibit similar temperature-dependent trends for both samples across the studied range. To enable a more quantitative comparison of the thermal evolution, Fig. 4 presents a bar chart summarizing the composition and thickness of the native niobium oxide layers throughout the experiment. In their initial state, prior to any thermal treatment or coating, both samples show the characteristic native oxide structure, composed of Nb_2O_5 , NbO_2 , and NbO , with a total thickness of approximately 5 nm. Slight differences in the individual sublayer thicknesses can be noted: the uncoated sample comprises roughly 3 nm of Nb_2O_5 , 0.5 nm of NbO_2 , and 1.6 nm of NbO (with an estimated error of ± 0.1 nm [35]). In contrast, the sample to be coated with Al_2O_3 shows a thicker Nb_2O_5 layer (3.6 nm), a similar NbO_2 layer (0.5 nm), and a

thinner NbO layer (1 nm). Such slight discrepancies in initial oxide composition between the samples are not unexpected and can be explained by small differences in air exposure time after polishing. At room temperature in UHV, the total oxide thickness differs by about 1 nm between the two samples. This discrepancy can be attributed to differences in surface exposure following the initial XRR measurement: the uncoated sample remained under ambient conditions, allowing further native oxide growth [55], while the other was promptly capped with Al_2O_3 , effectively halting oxidation. Additionally, the prolonged ALD process at 120 °C led to a partial reduction of Nb_2O_5 to NbO_2 in the coated sample, a transformation that was also observed in the uncoated sample during subsequent annealing steps between 100 and 150 °C.

At 200 °C, both samples exhibit nearly identical native oxide compositions: 2.5 nm of Nb_2O_5 , 1.3 nm of NbO_2 , and 0.5 nm of NbO . This indicates that regardless of the presence of a capping Al_2O_3 layer, a measurable thinning of the oxide layers occurs already within the low-temperature range of 100–200 °C, consistent with earlier reports [36,56,57]. This general trend reflects the progressive chemical reduction of the oxide layers, involving oxygen depletion from NbO and redistribution of oxygen from Nb_2O_5 to NbO_2 toward the substrate. Although the two samples differ in initial oxide structure and thermal history as they enter vacuum conditions, they converge to a similar native oxide composition at 200 °C. This observation points to the onset of a

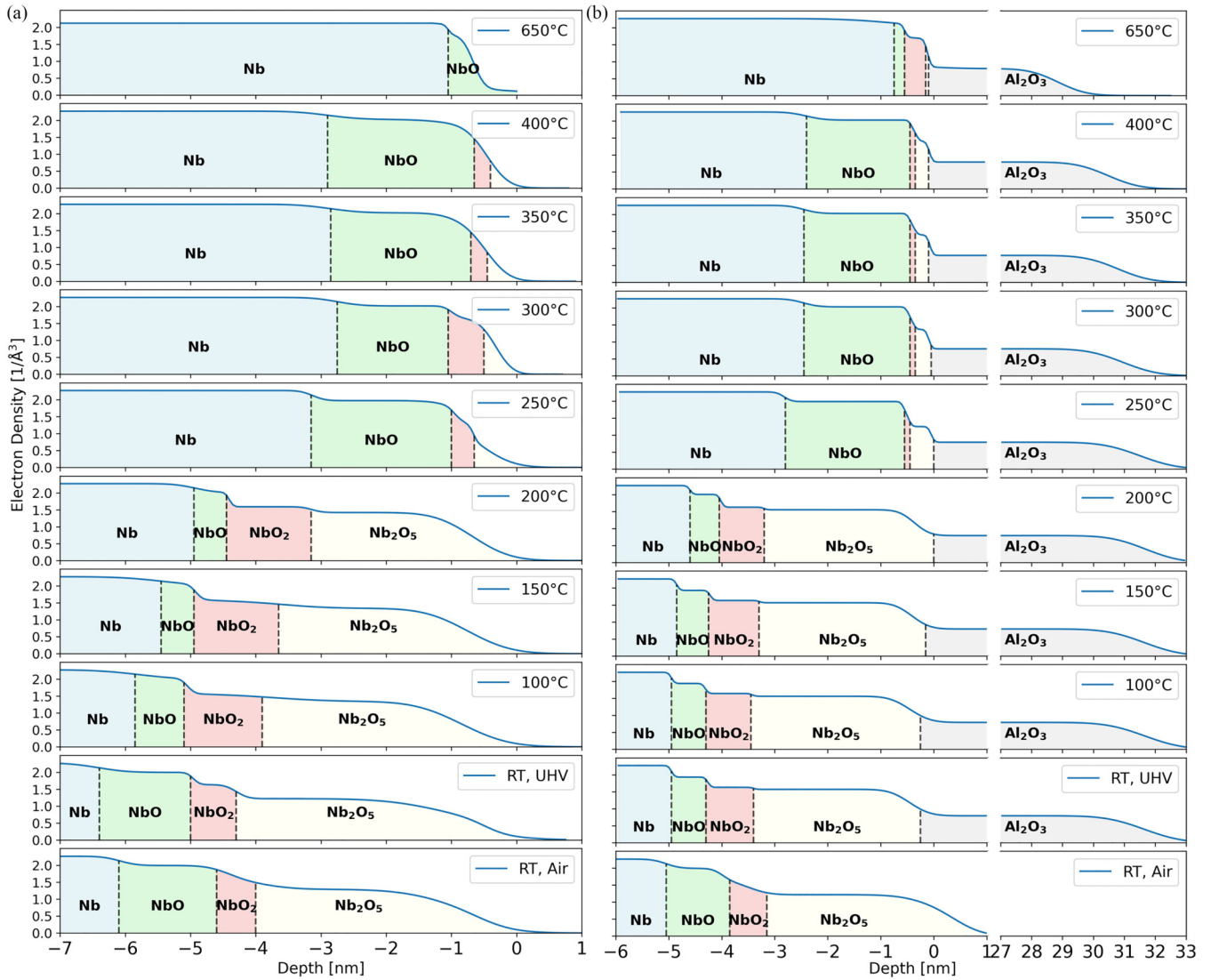


FIG. 3. Electron density profiles from model fits between room temperature and 650 °C for (a) the uncoated sample and (b) the Al_2O_3 -capped sample. Layer assignments by color: bulk niobium, blue; NbO, green; NbO_2 , red; Nb_2O_5 , yellow; and Al_2O_3 , gray.

temperature-dependent saturation level beyond which further chemical reduction does not proceed, in line with findings by Yu *et al.*, who reported a stronger dependence of oxygen diffusion on temperature than on baking time in this regime [58]. The uncoated sample exhibits a total thickness decrease of 1.3 nm, compared to 0.9 nm for the capped sample. Since the capped surface can facilitate only inward oxygen diffusion, the additional thinning observed in the uncapped sample may suggest that part of the oxygen is released outward into the vacuum.

The temperature region around 300 °C in the thermal treatment of niobium, typically spanning 250–350 °C, is commonly referred to as the mid-T bake range and marks the onset of pronounced chemical reduction of the oxides [35,36,57]. This transition becomes clearly observable in the present data, with structural changes intensifying near 250 °C. Figures 5 and 6 present detailed results for both samples at 200 and 250 °C, measured both at temperature and after cooling. A pronounced thinning and chemical reduction of the native

oxide layer are observed in both cases, resulting in a surface composition dominated by NbO. Based on the model in which Nb_2O_5 hosts a TLS that contributes to surface losses at low fields and cryogenic temperatures, the observed removal of the native Nb_2O_5 layer is consistent with reports of reduced surface losses in SRF cavities annealed *in situ* at 350 °C [33,49]. Although the measurements conducted in this study are not time resolved, the observed temperature-dependent structural changes reflect the slow kinetics typically involved in the reduction of niobium surface oxides. In the uncoated sample, a thickening of the NbO_2 layer at the expense of Nb_2O_5 is evident at 250 °C, indicating inward oxygen transport. After cooling, further redistribution toward NbO is observed, with the total oxide thickness decreasing to 2.5 nm. For the Al_2O_3 -coated sample, a similar reduction pathway is apparent, although the transformation progresses more directly toward NbO, with less pronounced intermediate formation of NbO_2 . In this case, the reduction in overall oxide thickness proceeds more gradually, reaching 2.8 nm at 250 °C and 2.4 nm at

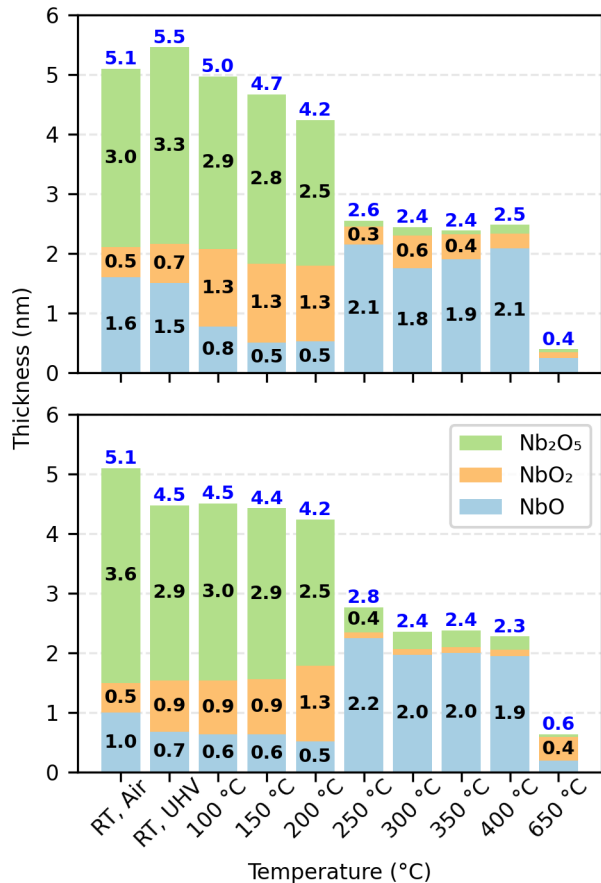


FIG. 4. Oxide layer composition between room temperature and 650 °C for the uncoated sample (top) and the Al₂O₃-capped sample (bottom). All data were acquired at room temperature following each heat treatment step. The estimated uncertainty in layer thickness is ± 0.1 nm.

300 °C, a value comparable to that of the uncoated sample at the same temperature. This slower decrease in oxide thickness for the coated sample likely results from restricted, unidirectional oxygen diffusion into the bulk, whereas the uncoated sample additionally allows for outward oxygen release into the vacuum.

Between 300 and 400 °C, the Al₂O₃-coated sample shows no further significant changes in its oxide composition, while the uncoated sample continues to exhibit gradual reduction of Nb₂O₅ and NbO₂ toward NbO, consistent with the trend observed at lower temperatures. During UHV conditions, no regrowth of the native oxide layer is observed across all investigated temperatures, regardless of whether the surface is capped or measured at elevated temperature or after cooling. This is clearly demonstrated by the example of the mid-T threshold region in Figs. 5 and 6. The consistent decrease in overall oxide thickness across all conditions suggests that oxygen incorporated into the bulk does not diffuse back to the surface to regenerate the native oxide layer, an observation supported by diffusion calculations from by Ciovati *et al.* [59] that were further refined by Lechner *et al.* [60].

Prior to exposure to the highest-temperature step in this experiment, both samples exhibit comparable native oxide thicknesses. The uncoated sample consists of 0.15 nm Nb₂O₅,

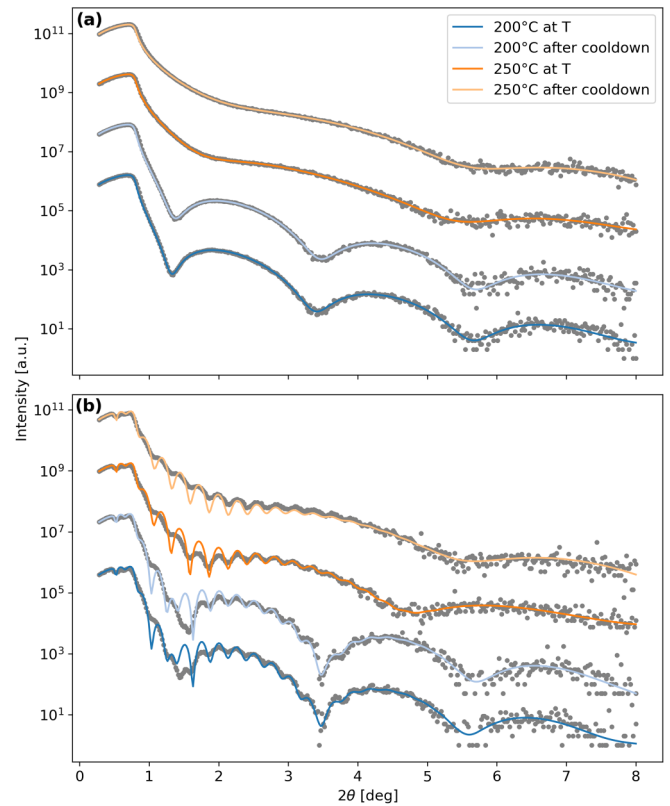


FIG. 5. XRR curves measured between 200 and 250 °C for (a) the uncoated sample and (b) the Al₂O₃-capped sample. The gray dots represent the measured data, while the colored curves correspond to the calculated reflectivity based on the refined model parameters. Data were collected both in a heated state and after cooling to room temperature. The curves are offset for clarity. See Tables S3 and S4 in [67] for detailed fit parameters.

0.25 nm NbO₂, and 2.1 nm NbO, while the coated sample comprises 0.25 nm Nb₂O₅, 0.1 nm NbO₂, and 1.95 nm NbO (it should be noted that the individual thickness values for Nb₂O₅ and NbO₂ fall within the estimated fitting uncertainty of ± 0.1 nm [35] and must therefore be interpreted with appropriate caution). This observation contrasts with Ref. [57], in which only a single monolayer of NbO is reported on fine-grain niobium after annealing at 400 °C for 3 h under UHV conditions. At 650 °C, a further overall decrease in oxide thickness is observed for both samples. For this thermal step, measurements were performed after approximately 5–6 h at temperature and again after 24 h, revealing differences in the evolution of the remaining oxide layers. Under the Al₂O₃ overlayer, most of the oxide thinning occurs within the first few hours, resulting in a residual thickness of 0.7 nm that remains stable upon prolonged annealing. This behavior is consistent with the findings of Kalboussi *et al.* [40]. In contrast, the uncoated sample shows a more gradual thinning: after 6 h at 650 °C, 1.4 nm of oxide remains, and only after 24 h does the thickness decrease further to 0.4 nm. One possible explanation for this difference is the presence of surface impurities or carbide phases in the uncoated sample, potentially introduced from the furnace environment, which may hinder further oxygen migration toward the bulk or into the vacuum [57,61–63]. The layer breakdown at this stage

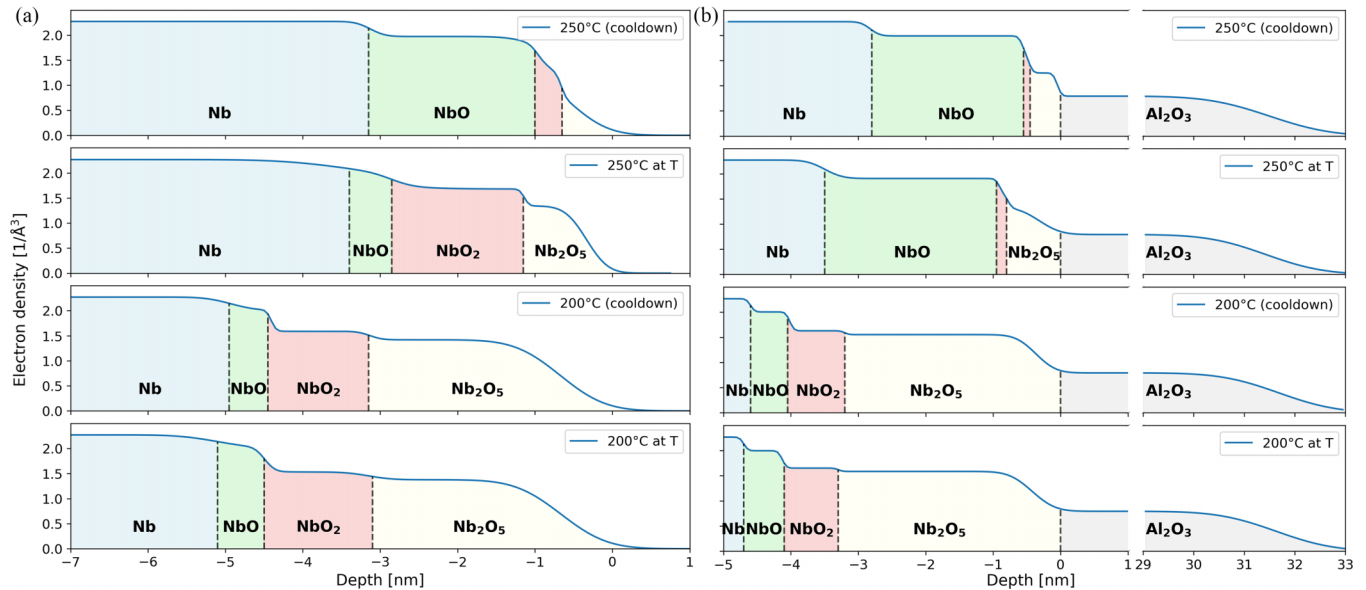


FIG. 6. Electron density profiles derived from reflectivity curve modeling for the temperature steps between 200 and 250 °C for (a) the uncoated sample and (b) the Al_2O_3 -capped sample. For each case, results are shown both at temperature and after cooling. Layer assignments by color: bulk niobium, blue; NbO, green; NbO_2 , red; Nb_2O_5 , yellow; and Al_2O_3 , gray.

is 0.05 nm Nb_2O_5 , 0.1 nm NbO_2 , and 0.25 nm NbO for the bare niobium sample and 0.05 nm Nb_2O_5 , 0.4 nm NbO_2 , and 0.2 nm NbO for the Al_2O_3 -capped sample. It is important to note that the Al_2O_3 overlayer exhibited a thickness decrease of about 4 nm during annealing up to 650 °C. This thinning of the Al_2O_3 capping layer is likely associated with densification and structural homogenization processes within the amorphous film. However, no crystallization was detected, consistent with previous studies placing the onset of crystallization for ALD-grown Al_2O_3 around 800–900 °C, depending on layer thickness and deposition parameters [64–66]. (As mentioned above, the Al_2O_3 layer was modeled as an amorphous, homogeneous layer with constant electron density, and this approximation was retained throughout the analysis to maintain the focus on the evolution of the niobium surface oxides.)

After completing the thermal treatment, both samples were exposed to atmospheric conditions for 2 weeks and subsequently remeasured using XRR. The results, shown in Fig. 7, reveal a clear reoxidation of the uncoated sample, with the native oxide layer consisting of 2.25 nm Nb_2O_5 , 0.6 nm NbO_2 , and 0.5 nm NbO. In contrast, the capped niobium remained unchanged, showing no signs of oxide layer regrowth. To rule out the possibility of delayed reoxidation, the Al_2O_3 -coated sample was remeasured periodically over the course of 1 yr. No changes in oxide thickness were observed, confirming the impermeability of the Al_2O_3 layer and its effective passivating role in protecting the underlying niobium.

IV. CONCLUSIONS

In this study, we carried out a systematic *in situ* XRR investigation of (110) niobium single crystals over a wide temperature range under UHV conditions, comparing samples with and without an ALD-deposited Al_2O_3 capping layer. The

results indicate that, up to 200 °C, both samples evolve toward a similar native oxide composition and thickness, irrespective of their initial state or annealing duration. This convergence suggests the presence of a temperature-limited equilibrium in the early stages of oxide decomposition, beyond which no further structural changes occur. In the mid-temperature range, we reported distinct reduction pathways for the two samples. While the Al_2O_3 -capped sample shows a more direct transformation to NbO with limited intermediate formation of NbO_2 , the overall decrease in oxide thickness progresses more slowly, reaching 2.4 nm at 300 °C. In contrast, the uncoated sample already reaches a comparable thickness of 2.5 nm at 250 °C, following a sequential reduction through distinct suboxide phases. At elevated temperatures (650 °C), a more persistent NbO layer is observed in the uncoated sample, with 1.4 nm remaining after 6 h and thinning to 0.4 nm occurring only after 24 h. In contrast, the capped sample reaches a stable oxide thickness of 0.7 nm after approximately 5 h. The slower progression in the uncoated state may be attributed to surface contamination or impurity phases originating from the oven environment, that appear to delay the chemical reduction process. Across the entire investigated temperature range, no evidence of oxide regrowth is detected under UHV conditions, indicating that oxygen diffused into the near-surface region does not return to the surface. Reexposure to ambient conditions results in oxide regrowth only for the uncoated sample, while the Al_2O_3 -capped sample remains unchanged. The amorphous overlayer stays chemically stable up to 650 °C in UHV, demonstrating its effective passivating function after air exposure and its utility in shielding the niobium surface from environmental influences, which is particularly relevant in the context of impurity uptake during cavity processing, as highlighted by Prudnikava *et al.* [57]. By systematically comparing capped and uncoated niobium

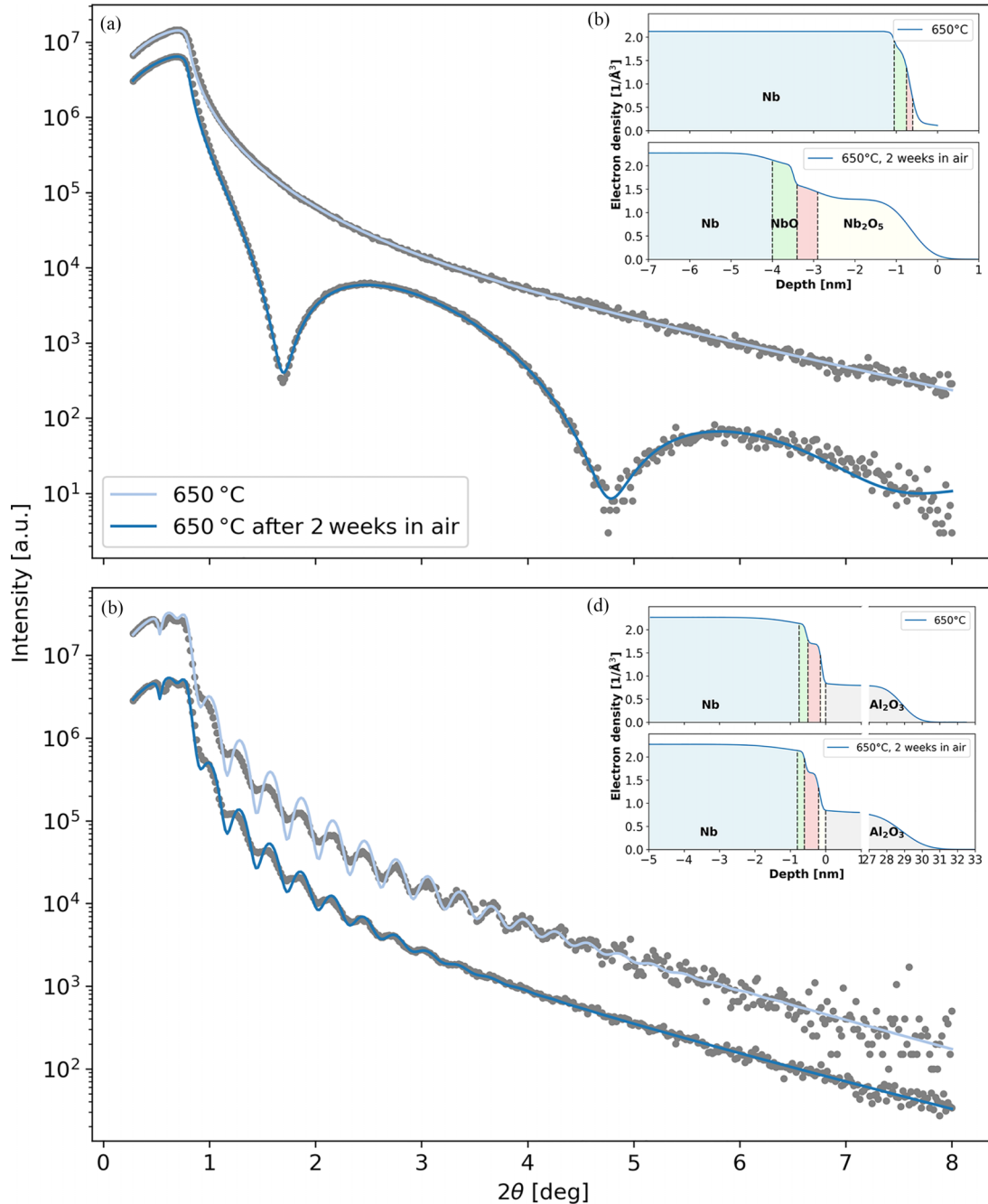


FIG. 7. XRR curves measured directly after cooling down from the 650 °C thermal treatment (light blue) and after 2 weeks in atmospheric conditions (dark blue). (a) shows the uncoated sample, while (b) corresponds to the sample coated with Al_2O_3 . Gray dots represent the measured reflectivity data, and the overlaid colored curves show the corresponding simulated reflectivity based on the fitted structural models. All data were collected at room temperature after the final heat treatment step. The curves are offset for clarity. Electron density profiles derived from the reflectivity fits for (c) the uncoated sample and (d) the Al_2O_3 -coated sample. Layer assignments by color: bulk niobium, blue; NbO, green; NbO₂, red; Nb₂O₅, yellow; and Al₂O₃, gray. See Tables S5 and S6 in [67] for detailed fit parameters.

surfaces under thermal treatment, this study demonstrates the potential of Al_2O_3 capping layers to facilitate improved control over near-surface oxygen interactions, particularly within the RF penetration depth, a region critical for SRF cavity performance. By stabilizing the surface oxide environment, such capping strategies can contribute directly to optimizing superconducting properties critical for advanced technologi-

cal applications. Future experiments should build upon these findings by employing complementary characterization methods, such as grazing-incidence x-ray diffraction (GIXRD), to more precisely investigate structural and compositional changes within the niobium near-surface region. This study highlights the necessity of gaining deeper insights into oxygen diffusion and incorporation mechanisms, processes

particularly accessible through GIXRD analysis, to further optimize heat treatment protocols. Additionally, targeted investigations of the $\text{Al}_2\text{O}_3/\text{Nb}$ interface under diverse environmental and operational conditions, coupled with performance assessments of capped SRF cavities, could provide valuable understanding of the long-term effectiveness of such surface modifications. These directions promise substantial enhancements of the reliability and efficiency of niobium-based technologies integral to particle accelerator and quantum computing applications.

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DATA AVAILABILITY

The data are available from the authors upon reasonable request.

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