

THE OXIDIZING RESPONSES OF BAKED NIOBIUM EXPOSED TO VARIOUS GASES VIA IN-SITU NAXPS*

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Abstract

We carried out in-situ NAXPS (Near-atmospheric X-ray Photoelectron Spectroscopy) on SRF-cavity class niobium to observe its oxidizing responses when exposed to various gases. The niobium samples were baked at 800 °C until the peaks of niobium oxides disappeared in the spectrum. Then the revealed pure niobium samples were exposed to the air-proportion mixture of nitrogen and oxygen, pure oxygen, and pure water vapor respectively. And for the pure oxygen and water vapor group, we also carried out TOF-SIMS (Time-of-Flight Secondary Ion Mass Spectroscopy) measurements before and after the baking and oxidation experiments. We found that pure oxygen and water vapor could oxidize niobium at similar rate which was faster than the N₂/O₂ mixture. After re-oxidized by pure oxygen and water vapor, the niobium sample presented a significant increase of interstitial carbon and a moderate increase of interstitial oxygen in the magnetic penetration depth, while it showed a mild decrease of interstitial hydrogen.

INTRODUCTION

The tiny amounts of impurities in the magnetic penetration depth would influence the superconducting performance of SRF niobium cavities, including both non-magnetic impurities like carbon [1, 2], hydrogen [3-6], nitrogen [7-10] and oxygen [11-13], and magnetic impurities like iron, manganese, cobalt and titanium [14, 15]. The doping process of the impurities can hardly be completed without decomposing the niobium oxides layer at the surface, which serves as a safe guard for further intake of impurities [16, 17]. Among the impurities, oxygen and carbon released from the niobium oxides and the adventitious carbon at the surface during baking would diffuse into the deeper lattice and regulate the superconducting properties, while hydrogen from the environment could be actively absorbed into the niobium lattice when the oxide layer is removed by baking or polishing. One shall acknowledge that the more interstitial hydrogen inside the niobium lattice, the higher probability of niobium hydride precipitation with various sizes during cooling down, thus the lower the intrinsic quality and accelerating gradient of the cavities [18, 19].

High temperature baking around 800 – 1000 °C is usually used to degas hydrogen that results in less interstitial hydrogen in niobium lattice [20, 21], and baking above 200 °C has been enough for decomposing Nb₂O₅ [22, 23] which is the main component of the surface compounds.

However, after baking, the cavities with removal of surface oxide layer are usually exposed to air environment and go through high pressure rinsing afterwards, which are both highly possible for the hydrogen reabsorption by pure niobium before the oxide layer is completely reformed. Therefore, the pre-oxidization when niobium cavities are still in the baking furnace may suppress the reabsorption of hydrogen in the following industrial procedures effectively. So, we carried out in-situ near atmospheric X-ray photoelectron spectroscopy (NAXPS) to find out the oxidation responses of the pure niobium when exposed to mixed pure N₂/O₂, pure O₂, and pure H₂O vapor, which are available and economical supplies in laboratories and factories.

EXPERIMENT

We prepared 2 SRF-cavity class single crystal niobium samples with the size of around 1.5 mm × 5 mm × 8 mm with heavy buffered chemical polishing (BCP) and light electropolishing (EP) to obtain a flat and smooth surface of R_a = 10. We baked the first sample (Labeled as LGO22) at maximum temperature of 400 °C and then pumped in the air-proportion-mixed pure N₂/O₂ after cooling down to room temperature. The pressure inside the detection chamber was kept at about 200 Pa, which was the highest pressure the facility could withstand for in-situ observation, as shown in Fig. 1.

We baked the second sample (Labeled as LGO23) at the maximum temperature of 800 °C and used pure O₂ as oxidation gas at the same pressure, as presented in Fig. 2. In industrial production, the filtered air is pumped in when the cavities are about 70 °C to save waiting time. So, in the process of oxidization of this experiment, we raised the temperature from 25 °C to 70 °C to observe the difference. After exposing the second sample to air environment for 2 weeks, we re-baked it also at the maximum temperature of 800 °C but pumped in the pure H₂O vapor at the same pressure, as depicted in Fig. 3. We also carried out the time-of-flight secondary ion mass spectroscopy (TOF-SIMS) on the second sample before and after the oxidation experiments, and the relative concentration of C/O/H related impurities in depth are illustrated in Figs. 4, 5, and 6.

RESULTS

We focused on the Nb peaks during baking and oxidization during in-situ NAXPS experiments on both LGO22 and LGO23, and we compared the impurities of carbon, oxygen and hydrogen of LGO23 before and after the experiment. The results of the experiments and measurements are delivered as below.

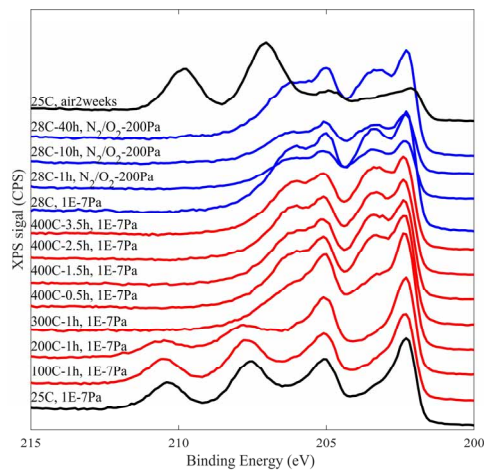
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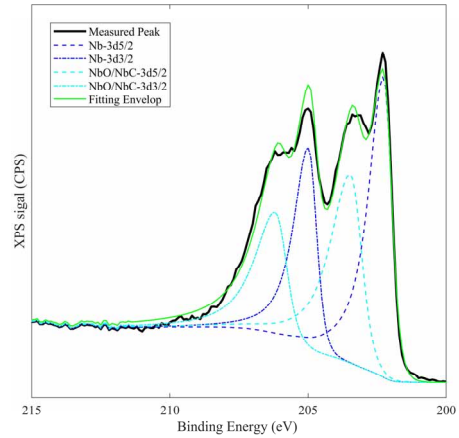
In-situ NAXPS

As presented in the curves in Fig. 1(b), 1(c) and 1(d), the double peaks of niobium present the chemical components of the niobium compounds. The peaks of the highest binding energy (far left) refer to Nb_2O_5 , and the peaks of the lowest binding energy (far right) refer to Nb, while the peaks of medium binding energy (middle position) refer to $\text{NbO}_2/\text{NbO}/\text{NbC}$. Comparing the results of Figs. 1, 2, and 3, we could obtain the information as below:

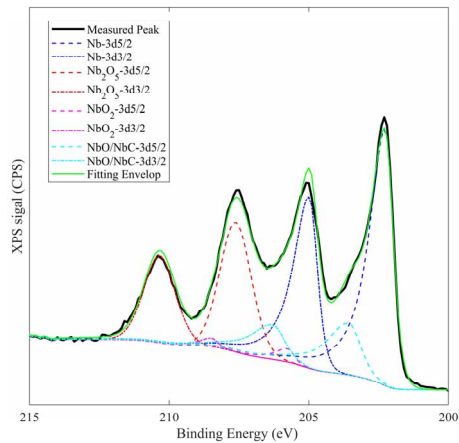
1. Baking at 300 °C for 1 h could adequately decompose the hypervalent niobium oxide and leave only the middle-valent niobium compounds, while baking at 800 °C for 2.5 h could decompose all the niobium compounds and leave only pure niobium.
2. Mixed air-proportion N_2/O_2 (LGO22, Fig. 1(a)) could have much slower oxidation rate than pure O_2 and pure H_2O under the same pressure. Although LGO22 only went through 400 °C baking and remained some middle-valent niobium compounds, its hypervalent niobium peaks did not appear after exposing to N_2/O_2 of 200 Pa for 40 h. As for LGO23 which went through 800 °C baking and remained no niobium compounds, its hypervalent niobium peaks appeared no more than an hour after exposing to O_2 and H_2O .
3. When exposing to pure O_2 at 70 °C for several hours, the curves of the Nb did not change very much compared to those at 25 °C, especially the hypervalent peaks. This means it would not change the oxide layer if breaking vacuum at 70 °C with 1 atm pure O_2 after baking, which would save the long period for naturally cooling the niobium cavities to room temperature. But it would require more time (10 hours for example) to get the protection layer formed completely.



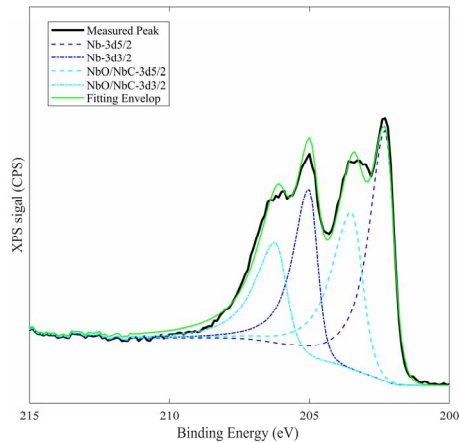
(a)



(b)



(c)



(d)

Figure 1: The Nb peaks during in-situ NAXPS 400°C baking and N_2/O_2 oxidization experiment. The black curves in (a) represent the situations at room temperature, and the red curves give information of the baking stages, while the blue curves show the process of oxidization. The peaking fitting results of (a) 25 °C before baking, (b) high vacuum baking at 400 °C for 3.5 h, (c) mixed N_2/O_2 oxidizing at 28 °C for 40 h are demonstrated respectively. The higher the binding energy, the higher the valence of Nb in the compounds, vice versa.

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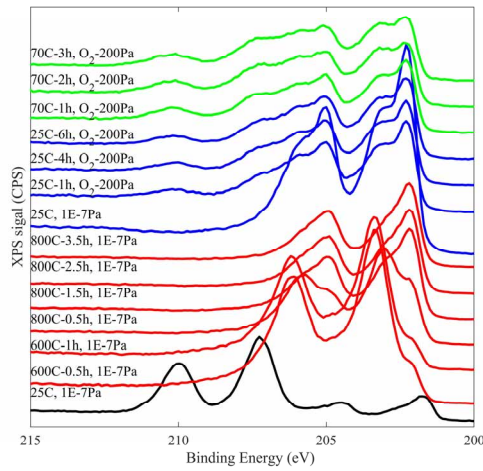


Figure 2: The Nb peaks during in-situ NAXPS 800 °C baking and O₂ oxidation experiment. The black curves represent the situations at room temperature, and the red curves give information of the baking stages, and the blue curves show the process of O₂ oxidation at 25 °C, while the green curves illustrate the oxidization variation when raising the temperature to 70 °C.

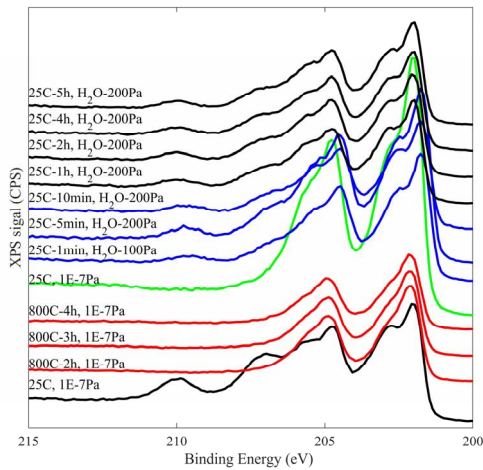


Figure 3: The Nb peaks during in-situ NAXPS 800 °C baking and H₂O oxidation experiment. The black curves represent the situations at room temperature, and the red curves give information of the baking stages, the green curve refers to the situation back to room temperature with high vacuum, while the blue curves show the process of H₂O oxidation at 25 °C.

TOF-SIMS

From the 3 groups of baking and oxidation experiments on 2 single crystal niobium samples described above, one could tell it would be more effective to use pure O₂ or pure H₂O to re-grow the oxide layer after baking the niobium cavities. But it is reported that H₂O would react actively with Nb and lead to heavy load of hydrogen reabsorption along the oxidization process [24]. We wanted to have a qualitative understanding of the hydrogen reabsorption, so we carried out the TOF-SIMS measurements on LGO23 before and after the baking and oxidation experiments, as presented in Figs. 4, 5, and 6. To be honest, it would be better to have another measurement between the O₂ and H₂O oxidation experiments, but the TOF-SIMS facility was not available at the gap when the NAXPS facility was available. One could summarize the information from Figs. 4, 5 and 6 as below:

1. The interstitial carbon increased over a magnitude after the experiment while the NbC and NbC₂ compounds remained at the same level.
2. The interstitial oxygen deeper than 3 nm increased slightly after the experiment while the Nb₂O₅, NbO₂, and NbO compounds remained at the same level.
3. The interstitial hydrogen deeper than 2 nm decreased slightly after the experiment even with LGO23 exposing to pure H₂O in the second round, while the NbH compound remained at the same level.
4. There was an apparent doping effect of interstitial carbon and oxygen after baking, and the pure O₂ oxidization did have very promising effect of suppressing hydrogen reabsorption after high temperature baking.

CONCLUSION

We carried out in-situ baking and oxidization experiments on SRF-class niobium samples via NAXPS. The results showed that the pure O₂ and pure H₂O could oxidize pure niobium at similar rate which was much faster than that of the air-proportion mixture of N₂/O₂. Besides, after two rounds of baking and oxidization experiments, the niobium sample presented decreased interstitial hydrogen with increased interstitial carbon and oxygen, even with the use of pure H₂O vapor. This suggested that we could try to pump in 1 atm pure O₂ to break vacuum after baking the niobium cavities in order to get the niobium oxide layer effectively re-grown. Furthermore, it is advised to break vacuum when the cavity temperature is naturally cooling down to around 70 °C to save time in industrial production, but it requires several hours for the niobium cavities exposing to pure O₂ in the furnace to get fully oxidized.

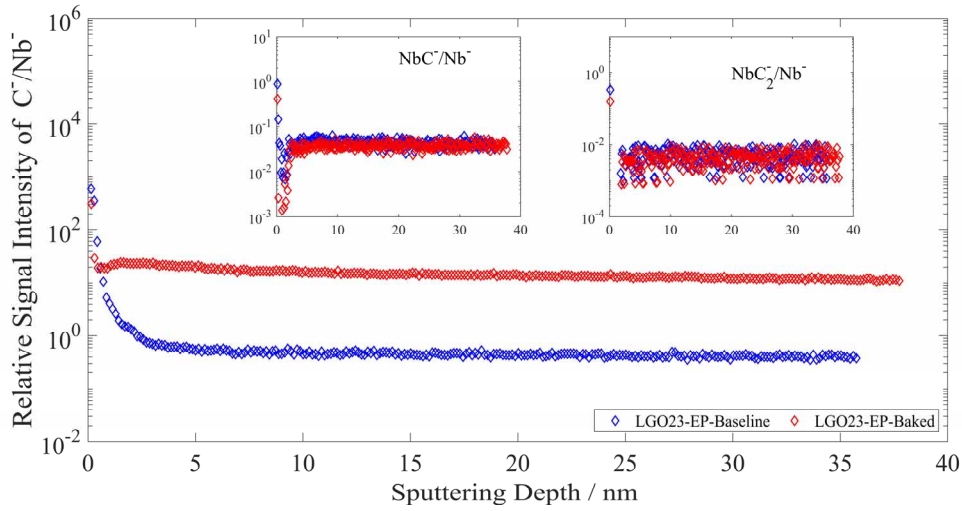


Figure 4: The relative concentration in depth of carbon related impurities of niobium sample LGO23 before (blue curve) and after (red curve) in-situ baking and oxidization experiments.

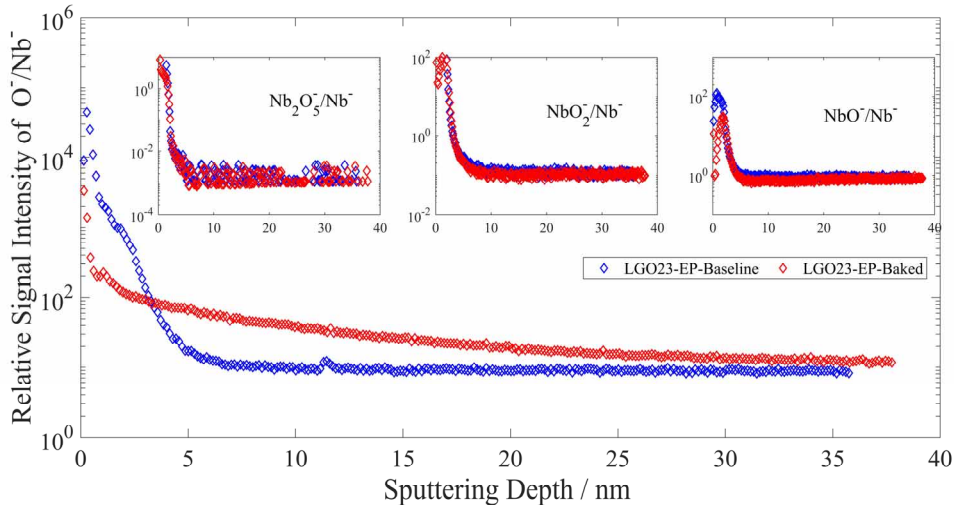


Figure 5: The relative concentration in depth of oxygen related impurities of niobium sample LGO23 before (blue curve) and after (red curve) in-situ baking and oxidization experiments.

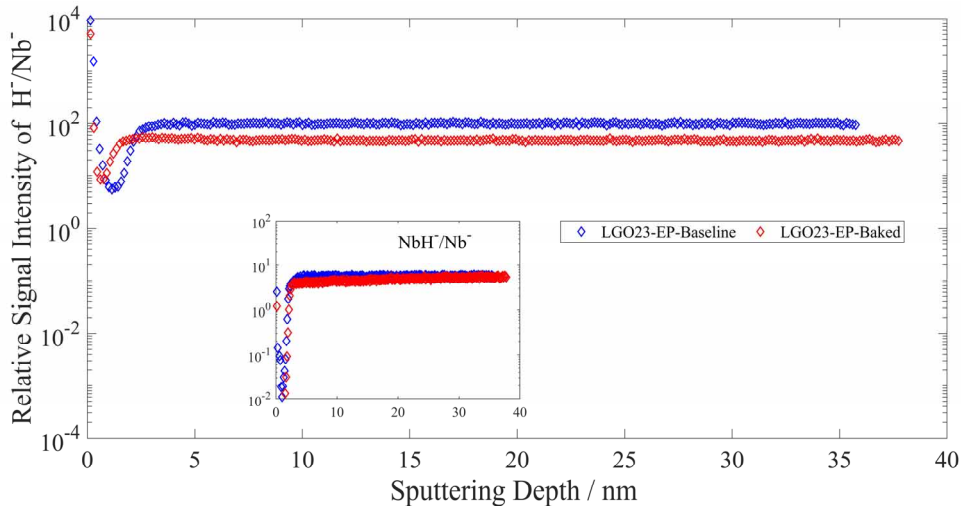


Figure 6: The relative concentration in depth of hydrogen related impurities of niobium sample LGO23 before (blue curve) and after (red curve) in-situ baking and oxidization experiments.

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