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NITRIC ACID SOAKING AFTER IMPERFECT FURNACE TREATMENTS

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Abstract

Annealings of niobium cavities in UHV or nitrogen atmospheres are crucial for the performance in the later cryogenic tests and operation. Recovery methods for imperfect annealing conditions have been discussed, and a more recent proposal, the so-called "nitric acid soak" has been studied here in detail. It shows surprising recovery potential, albeit the unclear origin of this improvement. We present our investigation on the several potential origins. For this, we used SEM, SIMS and XPS measurements of niobium samples to study the surface morphology and contaminations. We can reject the favored hypothesis on the origin of the improvement, and propose an alternative origin.

INTRODUCTION

As niobium (Nb) cavities are a key technology of linear collider, the properties of the inner surface play a crucial role to increase cryogenic performance of cavities [1, 2]. In such manner, different annealing treatments in UHV or nitrogen (N_2) atmosphere have been done on the surface of niobium [3-5] and different recipes have been presented to improve reproducibly of cavities [6, 7]. To reduce the impact of a pollution within the furnace, the usage of niobium caps during the anneal is now an established method [8, 9]. Moreover, Jefferson Lab reported using nitric acid (HNO_3) soak as an effective recovery method, even though the origin of the improvement is not clear yet [10]. Previous reports show that sulfur (S), titanium (Ti) and tin (Sn) contaminations are detrimental to the cavity performance [6, 11]. Nitric acid soak was already utilized to recover cavities which are polluted with indium (In) contamination [12]. The advantages of nitric acid are, that it does not dissolve the protective niobium pentoxide layer and is able to dissolve many metal contaminations [13]; hence this acid is a preferred candidate for a recovery of a Nb surface.

At DESY, we struggle with cavity deterioration after annealing procedures in sub-optimal atmospheres, causing formation of Nb carbides on the surface of cavities [3, 9]. Therefore, nitric acid soak as a recovery method is a potential interesting approach. This paper is organised as follows. We devote next sections to a discussion on hypotheses as possible origins of the cavity-performance improvement, our approach and, finally, the structural properties of Nb surface before and after using nitric acid soak, through SEM (scanning electron microscope), SIMS (Secondary-ion mass spectrometry) and XPS (X-ray photoelectron spectroscopy). Then we briefly report results of our study in the concluding section.

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ORIGIN OF THE IMPROVEMENT

In order to plan our study of the nitric-acid-soak effect on cavity performance, we discuss possible origins of the improvement. To this end, Nb carbides and metal contaminations are suggested as recommended nominees to deteriorate cavity performance during furnace treatment which are supposed to be removed by nitic acid soak [14, 15]. We also propose dissolving interstitial carbon as another possible origin based upon results in a preceding report [16]. Detail of hypotheses are given in the subsequent paragraphs.

Dissolving Niobium Carbides

As nitrogen infusion exhibit improvements of the performance for the Superconducting Radio Frequency (SRF) cavities, DESY tried to establish an appropriate nitrogen infusion recipe in an imperfect furnace [9]. Niobium carbide formation, star-shaped β-Nb_2C structures, were founded as the cause for the performance deterioration [8, 9]. Nb carbides are not only the origin of increased losses, but also cause the cavity to quench [9, 17]. Dissolving niobium carbides during nitric acid soak is the favoured assumption for the origin of the improvement. For this, we have studied sample surface with SEM before and after a nitric acid soak.

Dissolving Interstitial Carbon

SIMS results of a recent study, illustrate significant reduction of interstitial carbon concentration for nitric-acid-soaked samples [16]. A mechanism which can cause such a dissolution of interstitial carbon was not identified. To investigate this new hypothesis, we compared the carbon concentration before and after the nitric acid soak using SIMS.

Dissolving Metal Contaminations

Besides hydrocarbons and metallic contaminations in the furnace environment are detrimental to the performance of SRF cavities [6]. As Sn contamination is a considerable issue for Jefferson-Lab cavities after exposure to the furnace with and without caps [15], we have scanned our samples using XPS for such a contamination and plan a nitric acid soak for samples which showed such a contamination.

In the following section, we present the details of our samples used for this study.

OUR APPROACH

First, we identified 4 samples which are contaminated with Nb carbides from previous annealing studies (samples #1-4, see Table 1) to test the first assumption. To control

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for changes of surfaces, we did SEM measurements before and after the nitric acid soaking. Furthermore, we have chosen samples #1 and #2 to undergo a SIMS measurement before and after nitric acid soaking to test the second assumption. Moreover, we identified one sample to show Sn contamination using previous XPS measurements. Finally, one sample was found (sample #5, see Table 1). However, this sample was dropped in the cleanroom after annealing and we have to confirm that the source of the Sn contamination is a common furnace problem. Regardless of the origin, we can use this sample to investigate the effect of nitric acid soak on Sn contaminations as a third assumption.

The history of the samples which are used in this study are summarized in Table 1. All samples are conical fine-grain RRR300 Nb samples made from European XFEL sheets. They have been soaked in nitric acid with a 65% concentration for 30 minutes.

Table 1: Summary of Used Samples

Sample	Treatment	Measurements
#1	N_2 infusion @120C in Nb box in furnace	SEM, SIMS
#2	N_2 infusion @160C in Nb box in furnace	SEM, SIMS
#3	N_2 infusion @160 in furnace	SEM
#4	2h @800C in Nb box in furnace	SEM
#5	N_2 infusion 48h @120C in furnace	XPS

RESULTS

In this section, we separately report the results of the beforementioned measurements and discuss them.

SEM Measurement

As we mentioned in the preceding section, to have a comparable result, we did measurements before and after nitric acid soaking at the DESY NanoLab [18]. SEM measurements for 4 samples with different history of treatment are illustrated in Fig. 1. Left images belong to before nitric acid soaking and right images belong to after nitric acid soaking. In these images, the star-shaped crystals are β-Nb_2C structures which formed on the surface, but protrude the material up to 200nm. When we carefully compare before and after images, we cannot find any differences due to nitric acid soak, even for sample #4 which was saturated by the contaminations. There is no difference in size, concentration and shape of Nb carbide structures. Hence, we reject the hypothesis of dissolving Nb carbides with nitric acid.

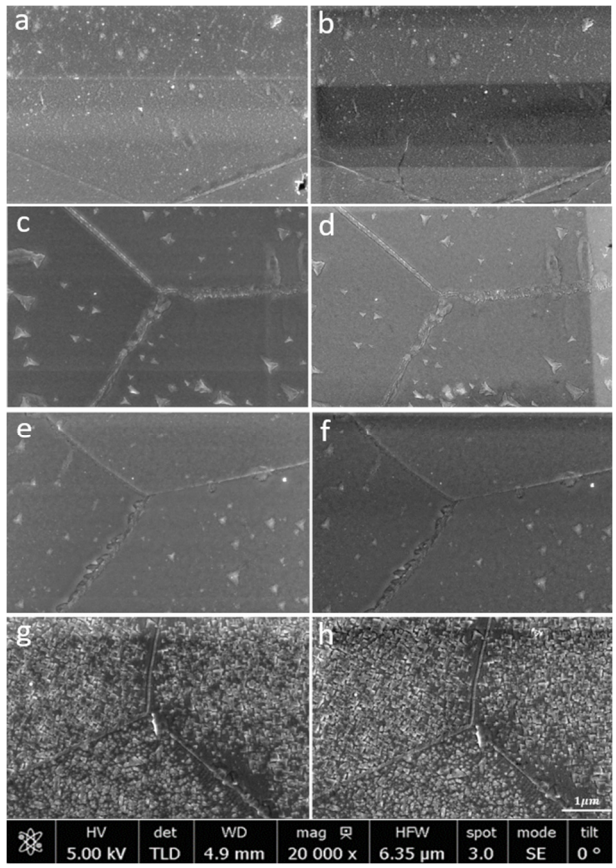

Figure 1: SEM measurements (a), (c), (e) and (g) before, (b), (d), (f) and (h) after nitric acid soaking for samples #1, #2, #3 and #4, respectively from top to bottom.

SIMS Measurement

To make a comparison between the interstitial carbon concentration before and after the nitric acid soak, results of the SIMS measurement for samples #1 and #2 is depicted in Fig. 2 parts (a) and (b), respectively. It is noted from this figure that there are negligible changes after nitric acid soaking and dissolving interstitial carbons is not confirmed. But, as it is shown on the figure, some carbon removal appeared in the first 2 nm on the surface of Nb samples. If the surface of a cavity is not saturated with carbon, as it is the case for our samples, can this carbon removal be significant enough to be the origin of the observed cavity improvement?

XPS Measurement

To investigate the composition of elements on the surface of Nb samples before nitric acid soaking, we present the corresponding XPS measurement in Fig. 3. To prove Sn removal, after nitric acid soaking, we sent this sample for the second XPS measurement and the result is pending.

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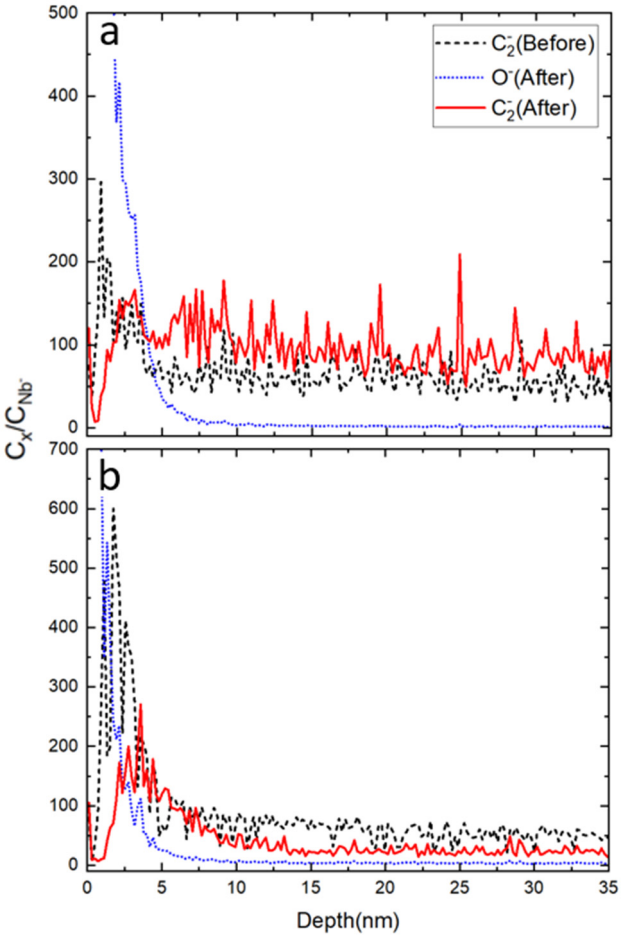

Figure 2: SIMS measurement of (a) sample #1 and (b) sample #2. Shown in the interstitial concentration, normalized to the Nb signal as a function of depth for carbon before (black dashed line) and after (red solid line) the nitric soak. The blue dotted line depicts the oxygen signal, to help identify the transition between the surface and native niobium oxides and the metallic bulk niobium.

CONCLUSION

Nitric acid soak improves the performance of cavities; however, the reason is still unknown. The present article is concerned with hypotheses behind improved performance of imperfect-treated cavities due to nitric acid soak as a recovery method. The SEM measurements in Fig. 1 demonstrate that, in our samples, Nb carbides are not removed after 30 min nitric acid soaking which was a favoured origin of the improvement. SIMS measurements before and after nitric acid soaking are presented in Fig. 2, indicate that interstitial carbon contamination is not changed, while the carbon concentration in first 2nm decreased after recovery. One has to be noted that the majority of the SIMS carbon signal comes from amorphous carbon, as the density of Nb carbides was sparse on the surface. We cannot say certainly, that this amount of removal is enough to be the origin of the improvement. But with a less severe carbon polluted cavity surface, because of a better furnace pressure, it is reasonable to assume that

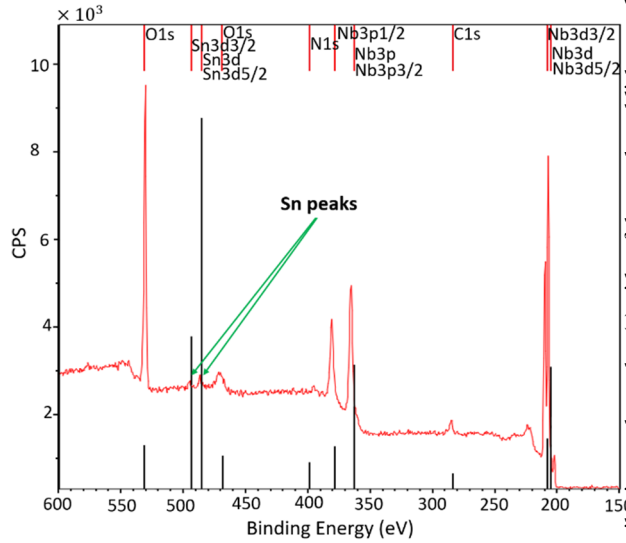

Figure 3: XPS measurement of sample #5. The two peaks at 458 and 495 eV are due to a Sn contamination of the niobium surface.

the previous amount of carbon is detrimental to the cavity performance. And that the removal of the amorphous carbon, not forming Nb carbides, certainly would recover the performance. Hence, the SIMS measurement is not in contradiction with the SEM measurement, as the amorphous carbon is simply not visible this way. Furthermore, the XPS measurement (Fig. 3) of one Nb sample presents Sn contribution, similar to the results from [6]. We used this sample to study dissolving of Sn contamination due to nitric acid soaking and the result after the treatment is pending. As the beneficial of using nitric acid soak on the cavity performance has been proved before [10], we will continue this study to convincingly find out an origin or origins of the improvement.

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