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# NITROGEN INFUSION SAMPLE R&D AT DESY

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*Abstract*

The European XFEL continuous wave upgrade requires cavities with reduced surface resistance (high Q-values) for high duty cycle while maintaining high accelerating gradient for short-pulse operation. A possible way to meet the requirements is the so-called nitrogen infusion procedure. However, a fundamental understanding and a theoretical model of this method are still missing. The approach shown here is based on sample R&D, with the goal to identify key parameters of the process and establish a stable, reproducible recipe. To understand the underlying processes of the surface evolution, which gives improved cavity performance, advanced surface analysis techniques (e.g. SEM/EDX, TEM, XPS, TOF-SIMS) are utilized. Additionally, a small furnace just for samples was set up to change and explore the parameter space of the infusion recipe. Results of these analyses, their implications for the cavity R&D and next steps are presented.

## LINE OF SIGHT PROTECTION DURING HEAT TREATMENTS

In this paper we focus on one parameter: The "line-of-sight"(LOS) protection that is used in the current nitrogen infusion recipe [1]. The recipe consists of a niobium surface heat treatment at 800°C for 3 h and ramping down to 120°C for 48 h while applying a partial pressure (25 mTorr) of nitrogen at 120°C. It has been discovered in [2] that niobium foils wrapped around the cavity flanges during annealing at and above 800°C act as a LOS protection and can help to avoid further post chemical treatment of a cavity without losing the performance benefits that come along. Contamination with hydrocarbons and titanium particles from the NbTi-flanges of the cavities inside the furnace was suspected to be the cause of cavity performance deterioration after heat treatments without any LOS protection.

In order to do a successful nitrogen infusion of a cavity, the avoidance of subsequent chemical treatment is a crucial factor. Cavity performance before and after the first N-infusion process w/o applying nitrogen, i.e heating at 800°C for 3 h under vacuum conditions followed by a ramping down to 120°C, and without subsequent chemical surface removal at DESY is shown in Fig. 1. The cavity preparation and testing is explained with further detail in [3]. Although niobium foils were used as a LOS protection for the treatments at

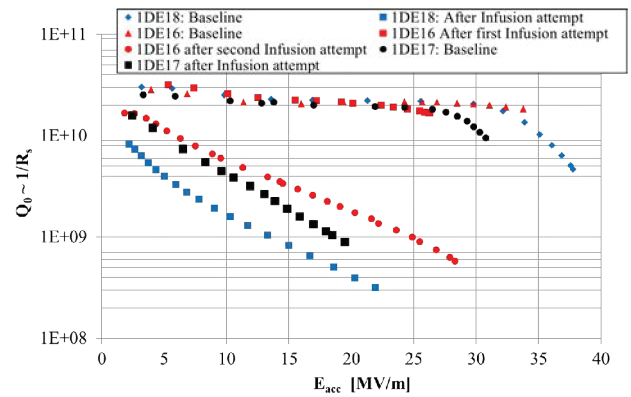


Figure 1: Cavity performance from the first attempts of nitrogen infusion and heat treatment without post chemical surface removal at DESY. For 1DE18 no nitrogen supply was given due controller failure. For 1DE16 and 1DE17 no Nitrogen was used on purpose to test our furnace vacuum environment for heat treatment and if Q degradation happens afterwards.

DESY, the cavity performance degraded as shown in Fig. 1 and look similar to ones observed in [2] when no LOS protection was used. During the heat treatment runs of

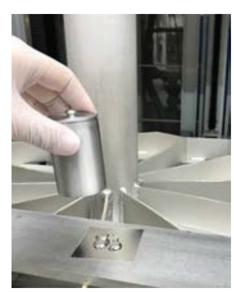

Figure 2: Coverage of cavity witness samples beneath a HOM coupler to mimic LOS protection of the caps.

the cavities labeled as 1DE16, 1DE17 and 1DE18, witness samples were placed under a niobium HOM coupler housing to mimic the LOS particle protection of the caps as shown in Fig. 2. Samples of all of these runs showed carbide formation on the surface. Although SEM images of star-shaped structures as in Fig. 3 look very similar to nitrides that occur under nitrogen doping [4], TEM analysis of fibbed lamellas and EDX mapping proved those to be carbides as shown in Fig. 4. A carbon-rich atmosphere beneath the HOM

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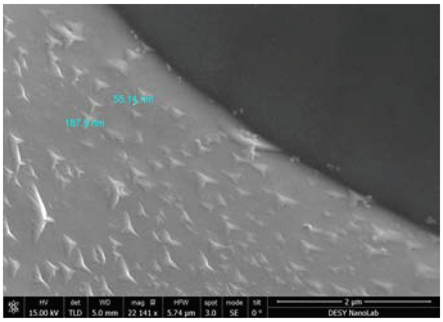

Figure 3: SEM of witness sample from heat treatment with one of the degraded cavity shown in Fig. 1. Precipitates were found on samples of each run and identified as carbides via TEM EDS. The optical appearance is very similar to those of nitrides.

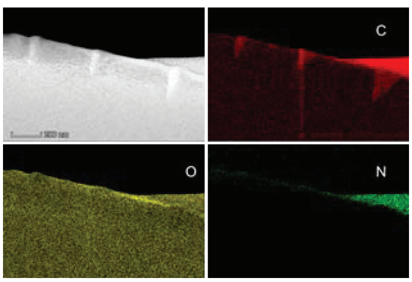


Figure 4: TEM EDS of cross section from niobium sample growing precipitates during heat treatment with a cavity from Fig. 1. Star shaped precipitates have been identified as carbon enriched and as possible hexagonal $\beta-Nb_2C$ phase.

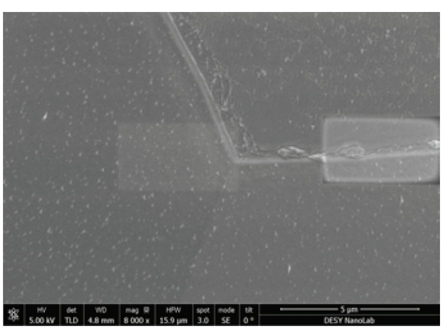

Figure 5: SEM image of a cutout sample from cavity 1DE16. Star shaped precipitates are observed on the surface. A more detailed analysis of their size distribution compared from hot to cold spots is discussed in [5].

coupler might have caused the precipitation of star-shaped hexagonal $\beta-Nb_2C$ during annealing. The contamination could have come from the furnace walls or anything that was in the furnace, such as one of the cavities, the caps or the HOM coupler itself. The final source of the contamination is unclear. Cut-out samples were taken from cavity 1DE16 after the second treatment. SEM images as in Fig. 5 shows star-shaped precipitation on the surface. A correlation between hot and cold spot is observed and is discussed with further details in [5]. For some of the next nitrogen infusion

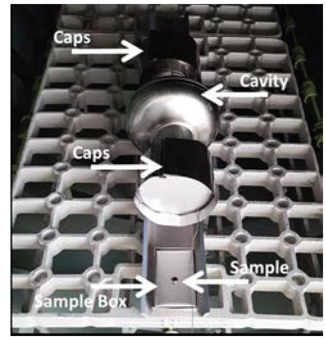


Figure 6: Picture of the inside of the vacuum furnace with the cavity 1DE27. Niobium foils are wrapped around the flanges as protection from LOS particles inside the furnace. A niobium box is placed in front of the cavity to mimic the LOS protection for the samples. One sample is placed on top of the box to have a comparison between with and without LOS protection.

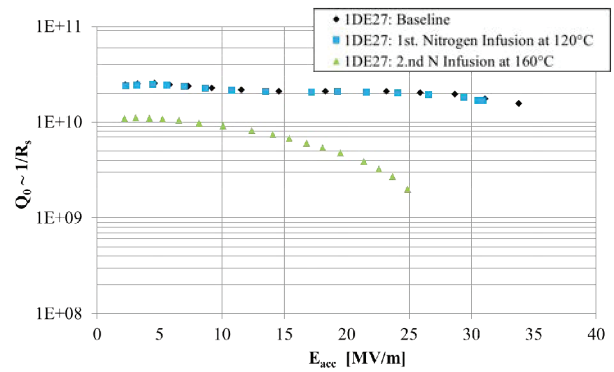


Figure 7: Cavity performance of 1DE27 before and after nitrogen infusion treatment at two different temperatures without post chemical surface removal at DESY. There was no chemical surface removal between the two nitrogen infu-sion's.

runs, a niobium box as shown in Fig. 6 was used as LOS protection for samples. The niobium box underwent a BCP, ultrasonic cleaning and de-ionized water rinsing in our clean room [6] before each run. Figure 6 shows cavity 1DE27 with the usual niobium foils wrapped around the flanges. It underwent a nitrogen infusion at 120°C and second one at 160°C without any chemical treatment in between. In those particular runs, a additional witness sample was also placed on top of the niobium box, thus directly exposed to the furnace vacuum. The performance test result of 1DE27 after each treatment are shown in Fig. 7. SEM images of those samples are shown in Fig. 8. In both runs, carbide precipitation occurred on samples inside the box only. Dif-ferent from before the contrast of precipitates here is darker then the background. This effect is reversed if focused with the SEM as illustrated in Fig. 9 and therefore appears as a small window that appears less dark in Fig. 8 (b). This could be a charging effect from the SEM although usually a darker contrast appearance is given after focusing what is

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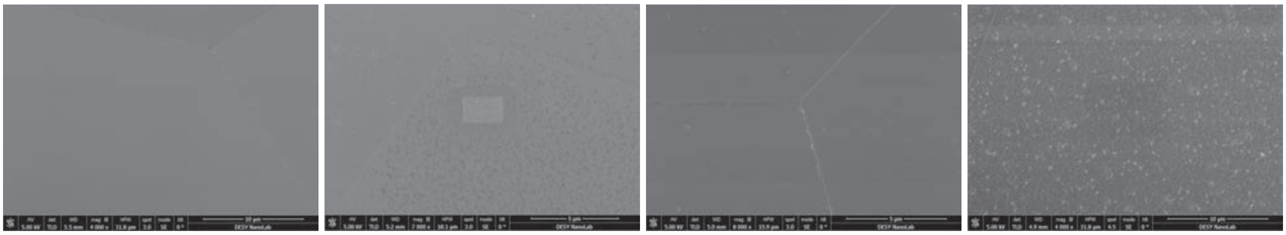

(a) Witness sample from first nitrogen infusion at 120°C outside the niobium box.
(b) Witness sample from first nitrogen infusion at 120°C inside the niobium box.
(c) Witness sample from second nitrogen infusion at 160°C outside the niobium box.
(d) Witness sample from second nitrogen infusion at 160°C inside the niobium box.

Figure 8: SEM images of samples inside and outside a niobium box during the nitrogen infusion treatments of 1DE27. In both cases carbide precipitation occurred on samples inside the box, only.

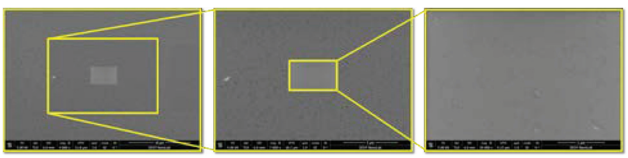

Figure 9: SEM image of a sample with different magnifications.

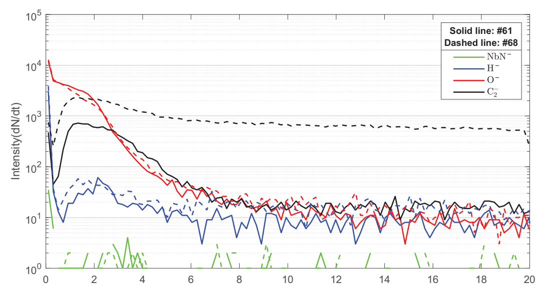


Figure 10: SIMS measurement of samples inside (dashed line) and outside the (solid line) niobium box from the 1.st infusion of 1DE27 at 120°C. A clear difference in the carbon signal is observed.

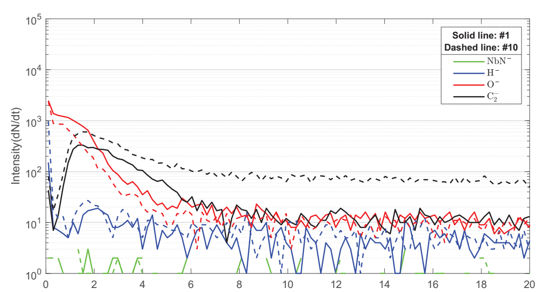


Figure 11: SIMS data of samples inside (dashed line) and outside the box (solid line) from the second infusion of 1DE27 at 160°C. The relative difference in the carbon signal between the two samples here is less pronounced compared to the first infusion run. Furthermore the amount of oxygen is lower for the sample inside the niobium box compared to the sample outside.

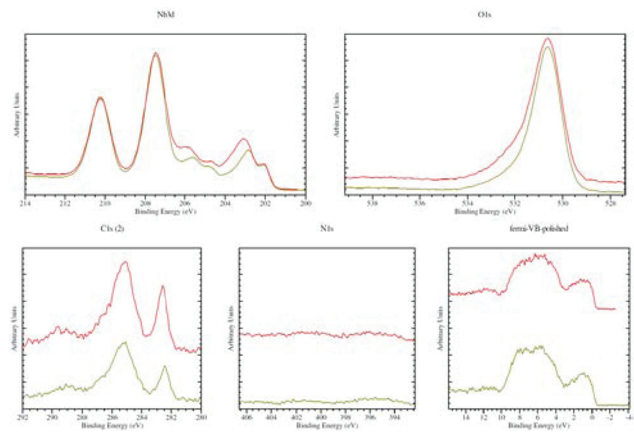

Figure 12: XPS measurement on sample 68 (green curve) from the 120°C nitrogen infusion and sample 10 (red curve) from the 160°C nitrogen infusion. Both samples were treated inside of the niobium box. A higher amount of oxygen and carbon is present for sample 10 which has been infused at 160°C. No nitrogen signal is present for either sample. The curves of C, N and O are offset in the vertical direction.

exactly the other way around then we observe here. This might also suggest a very thin carbon layer on the surface is present. Samples outside the niobium box showed no carbide precipitation. SIMS data of the samples from the 120°C infusion run are shown in Fig. 10 and from the 160° C infusion run in Fig. 11. The carbon signal is higher for the sample inside the niobium box compared to the sample out-side the box in both cases. The sample outside the box from the 160°C infusion run shows a higher oxygen level then the sample inside the box. The weaker relative difference in the carbon signal between samples inside and outside the box from the 160°C infusion compared to the 120°C infusion is a hint that more interstitial carbon contamination happened for the 160°C infusion run. This assumption is confirmed by the XPS data from the samples of both infusion runs that were inside the box shown in Fig. 12. The data shows a higher oxygen and carbon amount for the sample from the 160°C infusion compared to the 120°C infusion. Another 160°C nitrogen infusion was done with cavity 1DE7. The performance before and after the treatment is given in Fig. 13.

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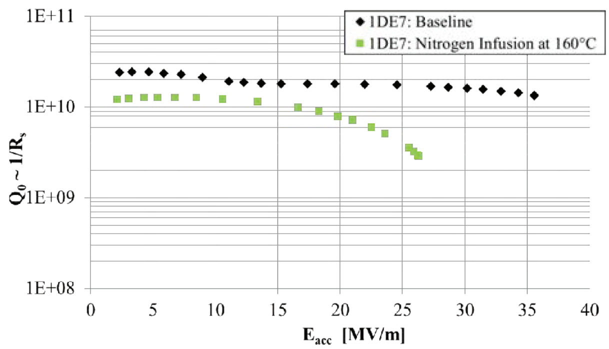


Figure 13: Cavity performance before and after nitrogen infusion at 160°C without post chemical surface removal at DESY.

Figure 14: Illustrated cavity installation for the nitrogen infusion of 1DE7. To mimic the line of sight protection a dummy cavity (instead of the niobium box) is used shown on the left picture. The sample "outside" is placed on a ceramic plate to make sure to have a clean underground for the sample.

It has a similarity with the curve of 1DE27 after the second infusion at 160°C. In this run a dummy cavity instead of a niobium box is used as a LOS protection for the witness samples. The cavity and sample installation inside the furnace is illustrated in Fig. 14. SEM images of the witness samples are summarized in Fig. 15. Precipitation occurred on both samples inside and outside the dummy cavity. However the sample without LOS protection also has grains completely free of precipitates as for example shown in Fig. 15 (c). Such free spots could not be found on the sample with LOS protection. Already for samples from the first heat treatments in Fig. 1 as for example Fig. 3 a dependence of the growth on crystal grains was observed. Hexagonal $\beta$–$Nb_2C$ carbides might only grow on certain niobium crystal-lattice orientation. Surprisingly that also accounts for the shadow like structures that we stated as thin carbon enriched layer as can be seen e.g. in Fig. 8 (b) and in the upper left corner of Fig. 15 (a).

## SUMMARY

Several samples have been investigated for surface changes after heat treatments without any subsequent chemi-cal cleaning. Star-shaped precipitates were found on samples as well as cavity cut-outs as shown in Fig. 5 and are sus-pected to be a source for cavity performance deterioration. Contrary to prior expectations this study shows a strong cor-relation between carbide precipitation and the use of LOS

Table 1: Summary of so-far observed carbides on witness samples during heat treatment with and without a LOS protection. A "✓" means carbides were observed and "✗" no carbides were observed.

| Cavity | perf. | w. LOS | w/o LOS |
|---|---|---|---|
| 1DE18 | degr. | ✓ | n.a. |
| 1DE17 | degr. | ✓ | n.a. |
| 1. 1DE16 | same | ✓ | n.a. |
| 2. 1DE16 | degr. | ✓ | n.a. |
| 1DE9 | degr. | ✗ | n.a. |
| 1DE10 | degr. | ✓ | n.a. |
| 1DE11 | degr. | ✓ | n.a. |
| 1. 1DE27 | same | ✓ | ✗ |
| 2. 1DE27 | degr. | ✓ | ✗ |
| 1DE7 | degr. | ✓ | (✓) |
| 1. 1DE3 | degr. | ✓ | n.a. |
| 2. 1DE3 | same | ✓ | n.a. |

Table 2: Summary of so-far observed carbides on witness samples treated without cavities in the sample furnace (see Fig. 16) and the big DESY cavity furnace. More details about the cavity furnace can be found in [3].

| Heat treatment | w LOS | w/o LOS |
|---|---|---|
| 180°C N-Inf sample furnace | n.a. | ✗ |
| 800°C cavity furnace | ✓ | ✗ |
| 800°C sample furnace | n.a. | ✗ |
| 800°C sample furnace | n.a. | ✗ |
| 800°C sample furnace | n.a. | ✗ |
| 800°C sample furnace | n.a. | ✓ |

protection (e.g. niobium foils or boxes as shown in Fig. 6) during heat treatment. However, cases are observed were carbides grew without LOS protection and can be attributed to other sources too. A summary of when precipitation with and without LOS protection occurred is given in Table 1 and 2. For the cavities 1DE18, 1DE17, 1DE16 and 1DE9, no nitrogen has been used but the same heat ramping to 800°C for 3 h and then 120°C for 48 h in $p<10^{-5}$ mbar. The assumption is that, in order to have carbide precipitation on a niobium surface, a sufficiently high partial pressure of carbon-enriched atmosphere must be present [7, 8]. The LOS protection can serve as a trap for the carbon-rich at-mosphere, thus not being pumped away. SIMS and XPS measurements of the 1DE27 witness samples show more carbon contamination during the second infusion treatment where the cavity started to deteriorate. The SIMS data in Fig. 10 and 11 show this by the relative comparison of each run between samples outside and inside the box. The higher in-fusion temperature of 160°C could lead to a slightly higher carbon contamination. The fact that 1DE16 and 1DE27 did not deteriorate after the first infusion treatment while carbides were still found on a sample with LOS protection seems to contradict the assumption that niobium carbides are supposed to deteriorate the cavity performance. This

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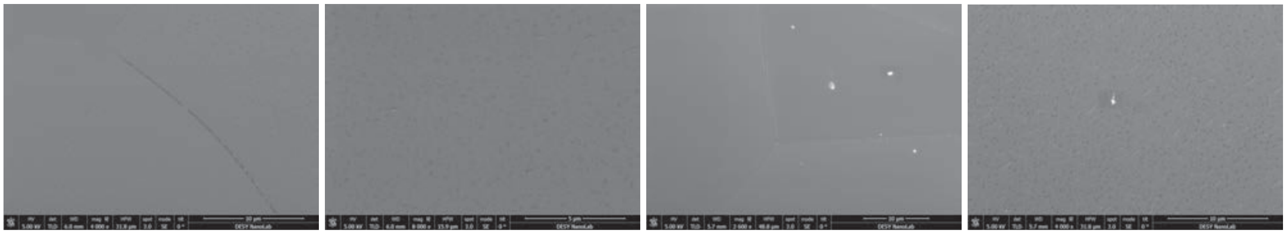

(a) Witness sample inside the dummy cavity. (b) Witness sample inside the dummy cavity. (c) Witness sample on a ceramic plate. (d) Witness sample on a ceramic plate.

Figure 15: SEM images of witness samples from 160°C nitrogen infusion of the cavity 1DE7. (a) and (b) are images from the sample infused inside the dummy cavity and show star shaped precipitation. (c) and (d) show the sample on the ceramic plate which also shows precipitation on some grains but none on others.

Figure 16: Image of the small sample furnace. The furnace has a ceramic tube with a diameter of 80 mm. A Residual Gas Analyzer and a mass-flow controller for nitrogen inlet is installed. The maximum achievable, stable temperature is 1350°C. The pump system is completely oil free and achieves $p<2 * 10^{-7}$ mbar. The furnace has been setup for dedicated nitrogen-infusion studies on samples.

could be explained by the fact that the formation does depend on the purity of the caps, the inside furnace and the conductance depending on the tightness between caps and cavity flange. One of these factors might have affected only the second try for the cavity but already on the first try for the samples. So far cut-out samples were only taken of one cavity after the second. The witness samples of a cavity infused with nitrogen at 160°C show carbides inside and outside the protection but the sample outside the dummy cavity also has precipitate-free grain spots as shown in the SEM images from Fig. 15. This leaves the assumption that less precipitation happened on the sample outside the cavity. In this case two cavities were baked simultaneously which also provides more sources of carbon out-gassing. The cavity performance after the nitrogen infusion has a similar characteristic deterioration for 1DE7 and 1DE27 but differ from the first attempts without nitrogen of 1DE16, 1DE17 and 1DE18. In contrast to the first attempts, precipitates also appear in a darker contrast due either charging effects or perhaps a thin carbon layer on the sample surface.

## CONCLUSION

Heat-treated samples w/o LOS protection mostly do not give rise to carbide formation. Our findings strongly suggest that carbides are the cause for the degradation shown in Fig. 1 provided they are available in sufficient number and concentration. Since carbides seem to be avoided without LOS protection, it might be interesting to infuse a cavity without caps. However it was also found that more dust contamination occurred on samples without LOS protection although the furnace was charged and uncharged under local clean-room conditions. A further advantage would be that witness samples in such a run would offer a better compari-son between sample and cavity inner surfaces. Another way would be to modify the caps to prevent LOS contamination while still having a defined conductance between furnace and cavity vacuum as a pathway for desorbed gases. This would be superior to the current system of flanges and cap fingers which differ every time they are installed.

## NEXT STEPS

Another test is scheduled where two niobium boxes will be used. Each will undergo a BCP beforehand while only one of them will be annealed above 800°C. This should give an insight about the importance of the pre-treatment of LOS protection itself. If the focusing effect in Fig. 9 really is due charging effect or due a thin carbon layer that accumulated on the surface will be further investigated. New fabricated caps with interleaved holes, giving a defined vacuum conductance between the interior of the cavity and the furnace will be used as LOS protection. This will allow a comprehensive investigation of the recipe parameter space.

## ACKNOWLEDGMENTS

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