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VACANCY-HYDROGEN DYNAMICS IN SAMPLES DURING LOW TEMPERATURE BAKING

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Abstract

The recent discovery of a modified low temperature baking process established an increased accelerating gradient of TESLA shaped cavities through reduction of surface losses. A possible explanation for the performance gain is the suppression of lossy nanohydrides via defect trapping, with vacancy-hydrogen (v+nH) complexes forming at the lower temperatures. Utilizing Doppler broadening Positron Annihilation Spectroscopy, Positron Annihilation Lifetime Spectroscopy and Nuclear Reaction Analysis, samples made from European XFEL niobium sheets and cavity cut-outs were investigated. The evolution of vacancies, hydrogen and their interaction at different temperature levels have been studied during in-situ and ex-situ annealing and in-situ cooldowns. Measurements of niobium samples and a correlation between RF, material properties, and v+nH distribution in cavity cut-outs have been carried out.

BAKING AND SRF PERFORMANCE

The influence of hydrogen on rf losses ('hydrogen Q-disease') of cavities and the need of outgassing cavities is known for quite some time. The operating temperature of superconducting accelerating cavities is 2-4 K, and while crossing the temperature range of 200-50 K during cool down, different phases of niobium hydride on the rf surface are forming, causing the increased losses. To prevent this, cavities are baked at 700 – 900° C at pressures below 10^{-6}mbar to purify the material. After the final electropolishing, an additional 120° C bake for 48 h has shown to reduce losses and cure the 'high field Q-slope' [1].
Lattice deformations, interstitials and vacancies are known to have high trapping potential for interstitials, especially hydrogen. Formation of so-called "nanohydrides" which are only weakly superconducting by proximity effect up to a certain threshold of applied field is assumed to be responsible for losses above the threshold causing the high field Q-slope [2]. The assumption is that the modified low T baking procedure [3] might influence the vacancy-density and their interaction with hydrogen in the relevant rf penetrated layer in a beneficial way to prevent formation of lossy nanohydrides. This new bake includes a 75° C step before the 120° C. At this temperature a $\beta \rightarrow \alpha'$ NbH phase formation takes place [4, 5] which potentially influences Nb-H dynamics during cooldown. So called vacancy-hydrogen (v+nH) complexes have been studied and found to play a role already in the standard 120° C bake [2, 6].

POSITRON ANNIHILATION (LIFETIME) SPECTROSCOPY

Positrons are easily trapped in vacancies and are very sensitive to their chemical environment. The positron annihilation spectrum (PAS) can be characterized in terms of the line shape parameter S and the wing parameter W which contain information of the low and high momentum part of the distribution, see Fig. 1. Those positrons annihilated with free electrons, which on average have a low momentum, will contribute to the S parameter. The higher the amount of vacancies, the more positrons will annihilate in vacancies with free electrons increasing the S parameter. The W parameter is the fractional area in the wing region and contains information of the annihilation of positrons with core electrons of the surrounding elements which on average have a higher momentum. Hence carrying information on the chemical loading of vacancies. At pulsed sources, the

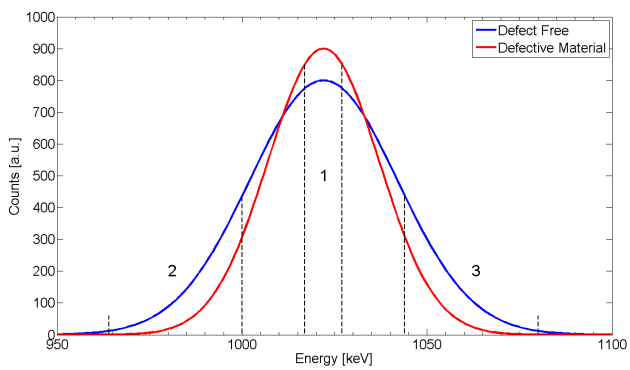

Figure 1: Annihilation spectrum of positrons in metallic material. The central area A_1 is used to quantify the S-parameter, while the areas A_2 and A_3 are used for the W-parameter.

lifetime of positrons depend as well on the density and types of vacancies (PALS). Deconvolution of the observed lifetime distribution will allow to identify the different contributions. In addition, when the energy of the annihilation photons is obtained, an energy shift ΔE can be observed (Coincidence Doppler Broadening (CDB) shift). This energy shift depends on the chemical surroundings of the annihilation site and also on the density and types of defects.

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The samples used for this study were cut out of niobium sheets from the European XFEL cavity production. The sheets were produced by Tokyo Denkai Co. Ltd. ('Tokyo Denkai' - samples with numbers above #50) or Ningxia Orient Tantalum Industry Co. Ltd. ('Ningxia' - samples with numbers below #50), and material certificates with the mechanical and chemical properties are available. The samples are of flat-conical design, with a base diameter of 12 mm, a top diameter of 10 mm and a thickness of 2.8 mm. They were cut with a water jet cutter and turned to the final design. The sample preparation followed closely the standard cavity preparation and the cleaning and rinsing was carried out in a ISO 4 cleanroom environment.

VACANCY EVOLUTION AS A FUNCTION OF TEMPERATURE

The DB-PAS measurements of sample 17 is shown in Fig. 2. The figure shows the S-parameters as a function of the positron energy which translates into penetration depth. For all samples, the observable changes happen in a layer of

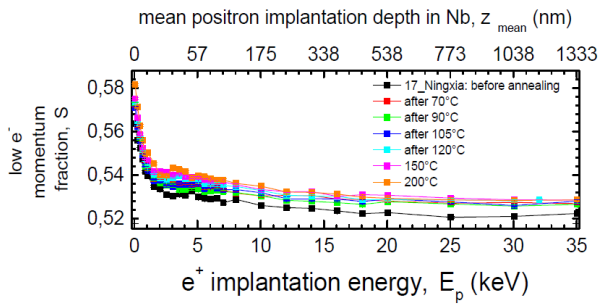

Figure 2: S-parameter vs. positron energy measured on sample 17 for different temperatures. The vacancy density which is proportional to the S-parameter increases with temperature while baking for 4h up to 200° C

about ≈ 170 nm. This is sufficient to influence the rf performance, since the London penetration depth λ_L is 40-50 nm for clean niobium at 2 K. All samples showed an increase of the S-parameter during the baking for 4 h up to 200° C. Above that temperature the overall defect concentration decreases shown in Fig. 3. There, the S-W-plot for an energy of incident positrons of 1.5 keV or mean positron penetration depth of ≈ 18 nm is shown. Assuming that that only two states (defect and nondefect) contribute to the annihilation, the measured S and W represent a superposition of these states and have a linear dependency

$$(S - S_{bulk}) = R \cdot (W - W_{bulk})$$

with a defect specific slope R [7]. All S-W values are on the same line up to 200° C where a strong clustering occurs. The 25° C and 70° C measurement show no significant change. Only annealing at 80° C or higher has a significant influence This is in agreement with the literature as mentioned above, that 74° C is an important temperature for the Nb-H system.

The change in the offset at 250° C is a consequence of the combination of the reduction of the vacancy density and a change of the surface states which is further confirmed by the $3\gamma 2\gamma$ ratio (not shown here).

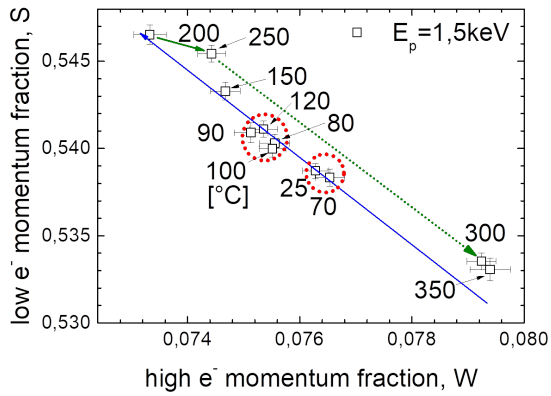

Figure 3: S-W plane at a fixed energy of 1.5 keV of sample 64. All data points up to 200° C are on the same line, hence the defect type does not change, only the density increases. At 250° C the defect type starts to change and the defect density decreases.

This change of defect type and surface states starting at 200° C can be explained by the gradual dissolving of natural oxide layers on the niobium surface which starts around 120° – 130° C for Nb_2O_5 and NbO_2 and is finished at 300° C. The results of the PALS measurements from MePS for sample 78 are shown in Fig. 4. The lifetime τ_1 of the decay

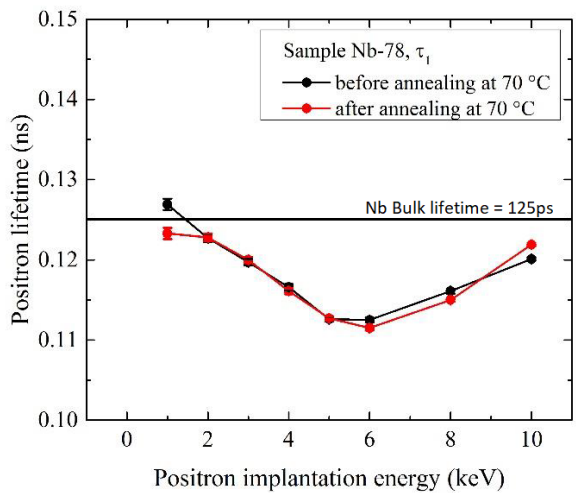

Figure 4: τ_1 lifetime component vs. positron energy measured in-situ for sample 78 before and after annealing at 70° C.

curve for the sample 78 in Fig. 4 is shorter than the bulk positron lifetime for niobium of 125 ps. Hence another contribution with a lower lifetime on the order of 110-130 ps is expected. This result has been found in the cavity cut-outs as well. From these results and the results in [8], it can be

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concluded that within the first 200 nm of the niobium, v+nH complexes with 4-6 hydrogen atoms attributed to a vacancy or vacancy clusters exist in this surface layer since these lifetimes matches the observed additional contribution.

VACANCY CONCENTRATION AND V+NH FORMATION DURING BAKING

Figure 5 shows an increase of the vacancy concentration for short baking durations but a decrease for the longer baking. Although there is a clear difference between samples 6 and 73 the overall behavior is similar. To better analyze

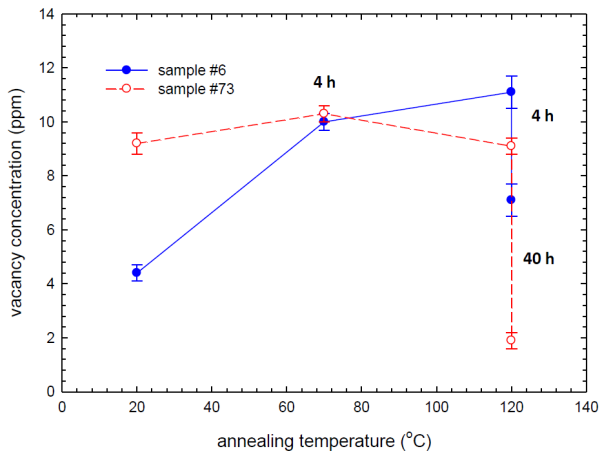

Figure 5: Vacancy Concentration calculated from PALS data using two state positron trapping model vs. annealing temperature at a fixed energy for samples 6 and 73.

the interaction of the vacancies with the hydrogen in the samples, the CDB measurements in the bulk were done. The measurements on sample 73 are shown in Fig. 6. The measurements show the CDB signal normalized to a pure Nb annealed reference sample at a 1000° C and hence exhibiting a defect- and interstitial-free lattice. Two CDB curves of reference samples containing vacancy-hydrogen (v+H) pairs and vacancies associated with 4 hydrogen atoms (v+4H) are shown in the figure as well.

Forming of v+nH complexes is visible after the first baking steps for both samples 6 and 73 but they are close to the detection limit after the longer baking time. The initial measurement at room temperature for both samples prior any baking shows a difference in the shape of CDB ratio curves reflecting different chemical environment of positron annihilation sites due to different amount of impurities and loading of vacancies for the two different material suppliers.

CONCLUSIONS

Virgin samples contain interstitial hydrogen and v+nH complexes and locally exceeding maximum solubility in bcc lattice leading to formation of hydride precipitates. Annealing at 70 – 80° C will cause nanohydrides to decompose and hydrogen atoms are gradually released and diffuse into the lattice and form v+nH complexes. Annealing at 120° C results in gradual disappearance of v+nH complexes over time in the bulk. Near-surface lifetime measurements, shown in Fig. 4 and from cavity cut-outs, show strong contributions with large vacancy clusters paired with hydrogen even after annealing reducing the positron lifetime [8]. These near surface v+nH cluster have been further confirmed by cavity cut-outs measurements. At 250° C the oxide layers Nb_2O_5 and NbO_2 are dissolved into the bulk [9] and start to change the vacancy types. The vacancy-hydrogen interaction with the niobium lattice at baking temperature and cryogenic temperatures has been the scope of research for quite some time. The results presented here shows that the dynamics of the formation of v+nH complexes is of importance, and that an influence of the baking temperature and duration plays a crucial role in the dynamics.

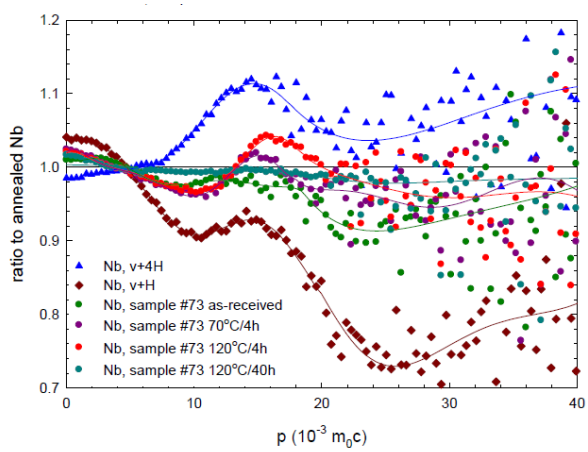

Figure 6: CDB ratio related to pure Nb (annealed at 1000° C) vs. momentum of the annihilating pair for sample 73. Two reference curves for Nb with v+H and v+4H complexes are shown for comparison. While for as-received, some hydrogen is associated to vacancies. v+nH complexes form at 70° C and are stable up to 120° C with short annealing time. After full annealing at 120° C no v+nH complexes are observed.

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REFERENCES

[1] G. Ciovati *et al.*, "High field Qslope and the baking effect: Review of recent experimental results and new data on Nb heat treatments", *Phys. Rev. Accel. Beams*, vol.13, no.2, p:22002, 2010.

[2] A. Romanenko *et al.*, "The effect of vacancies on the microwave surface resistance of niobium revealed by positron

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annihilation spectroscopy", *Appl. Phys. Lett.*, vol. 102, no.23, p. 232601, 2013.

[3] A. Grassellino *et al.*, "Unprecedented quality factors at accelerating gradients up to 45 MVm^{-1} in niobium superconducting resonators via low temperature nitrogen infusion", *Supercond. Sci. Technol.*, vol. 30, no 9, p. 094004, 2017.

[4] C.K. Gupta and A. K. Suri, "Hydrides"in Extractive metallurgy of niobium, Routledge, 2017, p. 147.

[5] M. W. Stanley and Z.C. Szkopiak, "The α and β peaks in cold-worked niobium", *J. Mater. Sci.*, vol. 2, no.6, p. 559-566, 1967.

[6] B. Vienstin *et al.*, "Involvement of hydrogen-vacancy complexes in the baking effect of niobium cavities", *Phys. Rev. Accel. Beams*, vol. 13, no. 5, p. 052002, 2010.

[7] P. Hautojarvi and C. Corbel, "Positron Spectroscopy of Defects in Metals and Semiconductors"in Positron Spectroscopy of Solids, A. Dupasquier and A. P. Mills, Jr., Ed., IOS Press, Amsterdam, 1995, p. 491.

[8] J. Cizek *et al.*, "Hydrogen-induced defects in bulk niobium", *Phys. Rev. B*, vol. 69, no.22, p. 224106, 2004.

[9] M. Delheusy*et al.*, "X-ray investigation of subsurface interstitial oxygen at Nb/oxide interfaces", *Appl. Phys. Lett.*, vol.92, no.10, p. 101911, 2008.