POSITRON ANNIHILATION SPECTROSCOPY ON NIOBIUM SAMPLES

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Abstract

Since the "baking effect" discovery, a part of the Saclay R&D is dedicated to understand this effect and its correlated question about the High Field Q-slope origin. Complementary experiments on "fast baking" in Oxygen free atmosphere and SIMS analyses have shown that interstitial oxygen diffusion cannot be involved in baking physics.

Presence of niobium vacancy near the surface could contribute to explain such phenomenon. To explore this possibility, we have performed experiments on niobium samples by means of positron annihilation radiation Doppler broadening spectroscopy. For the first time, an increase after baking of vacancy sites is disclosed at the niobium sample surface. Vacancy-hydrogen complex dissociation could be involved. This modification is observed in 100 nm depth under the sample surface, an area where the superconducting RF layer is located.

INTRODUCTION

The "baking effect" concerns the benefit consequence observed on niobium superconducting RF cavity performances once cavity has been baked in a narrow range of temperature during a limited time. Baking is a necessary final stage in cavity preparation to reach high gradients. For the standard process [1], named "In-situ UHV Baking", the cavity is baked at 110-120 °C for 48-60 hours while its inner part is under Ultra High Vacuum.

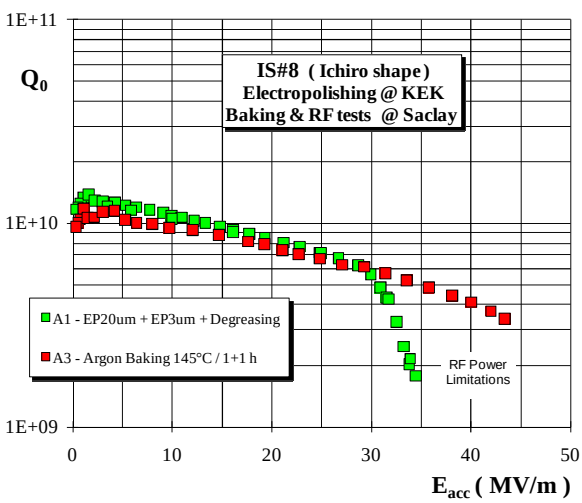

Figure 1: "Fast Baking" effect (145 °C / 2 hours) where SRF cavity is filled with argon gas (1 atm.).

An alternative less time consuming process, called "Fast Argon Baking" has also been proposed [2] and was successfully demonstrated on electropolished cavities [3]. In that case, thermal treatment is made at higher temperature (145°C) in oxygen-free atmosphere during 3 or even 2 hours (Fig.1).

Since the beginning [4] and due to the presence of interstitial oxygen at the Nb_2O_5-Nb interface, oxygen diffusion has always been suspected to play a role in the baking effect. Nevertheless later on, surface analyses by Secondary Ion Mass Spectroscopy (SIMS) achieved on Nb samples [5] have shown that no noticeable diffusion of interstitial oxygen can be observed after baking (Fig.2). Moreover RF cavity performances are deteriorated when baking is realized in air, instead of oxygen free atmosphere; in that case SIMS measurements show effective oxygen diffusion in material (black data in Fig.2). So the optimized couples of values for an efficient baking (120 °C / 48 h or 145 °C / 3 h) have to be considered as the upper limits before the undesirable oxygen diffusion in the RF layer occurs.

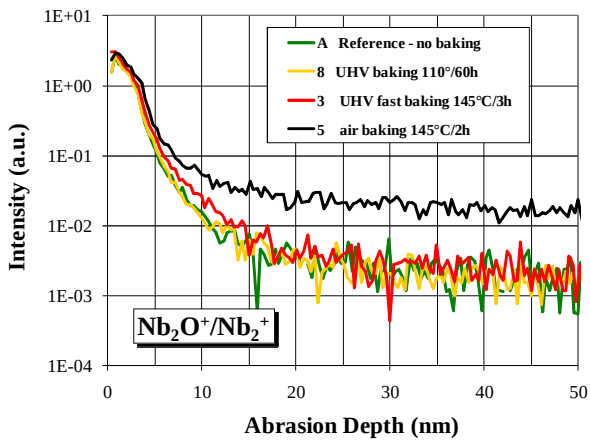

Figure 2: SIMS analyses of Nb samples [5]. Interstitial oxygen profiles before (green) and after baking (red and yellow).

STUDY CONTEXT

Even if diffusion of interstitial oxygen is not observable at the 10 nm scale, a local diffusion leading to vacancy filling with complex formation cannot be excluded (as suggested in [2]).

Moreover during the 1980's, several papers [6-7-8] mentioned that for b.c.c. transition metals (Nb, Ta…) stage III annealing temperature, synonym of vacancy

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migration, is shifted to higher values than expected (between 250 and 420 K).

Already existing complexes in material, like vacancy-impurity or vacancy-hydrogen [8-9], are strongly connected to the stage III temperature shift.

For our purpose, vacancy filling, vacancy diffusion or vacancy-impurity complex dissociation are possible events occurring at the "baking effect" temperature range. For all these reasons we have decided to verify on Nb samples if baking can induce some modifications in the vacancy concentration profile.

POSITRON ANNIHILATION SPECTROSCOPY

Because positrons can easily get trapped in metal vacancy defects, positron annihilation is known to be very sensitive to detect this type of defects in solids and an excellent method to follow their population.

Description

When energetic positrons are implanted into a material, they are thermalized in a few picoseconds through inelastic collisions. Then positrons diffuse in material and annihilate with electrons producing two γ rays at 511 keV in opposite directions. Before annihilation with electrons, positrons can be trapped in open-volume defects (dislocations lines, voids, vacancies, vacancy clusters…) due to repulsion by lattice ions.

Positron Annihilation Spectroscopy (PAS) [10] is based on the detection of the positron annihilation radiation. Among the three most important PAS techniques, which measure the positron lifetime, the angular correlation or the γ-ray Doppler broadening, we will use the last one. Because of the centre of mass motion of the annihilating positron-electron system, gamma-rays will be Doppler-shifted; positron being thermalized, this broadening is only due to the electron momentum in the propagation direction.

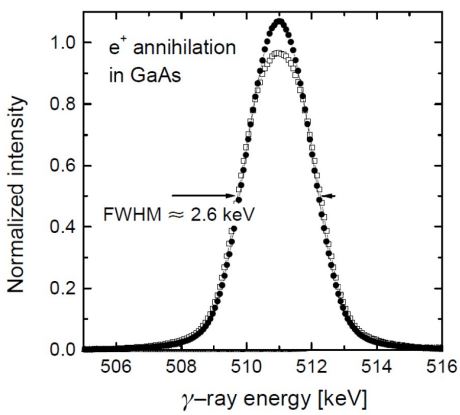

Figure 3: Doppler broadening example of positron annihilation radiation line. Dark dots correspond to a GaAs defect-rich sample and show a narrow line [11].

Positrons trapped in vacancies increase their lifetime and the annihilation is preferentially done with valence electrons (small momentum), due to a lack of core electrons (high momentum), giving a smaller Doppler shift and a narrow line (Fig.3). Two parameters S (sharpness) and W (wing) usually characterize the annihilation line shape. Although that annihilation line is a superposition of free and trapped positrons, S (W) plot gives specific information about a defect-rich sample (S↑, W↓).

Positron Beam Facility

The positron beam facility in Orléans [12] provides monoenergetic positrons with variable energy up to 25 keV.

To obtain a monoenergetic beam, positrons emitted by a ^{22}Na radioactive source have to go through a 4 µm polycrystalline W foil: the moderator. Meanwhile most positrons leave the moderator with a high residual energy or stop in the foil before annihilation, a very small fraction of them (0.05%) thermalises, diffuses and is spontaneously emitted by the moderator surface at very low energy (3 eV), due to the negative work function of tungsten.

These monoenergetic slow positrons are then extracted, accelerated and magnetically guided towards the sample-holder target (Fig.4); at this point, diameter of positron beam is 2 mm.

To detect the γ-ray Doppler broadening at 511 keV, the experimental chamber is equipped with a high purity Germanium detector.

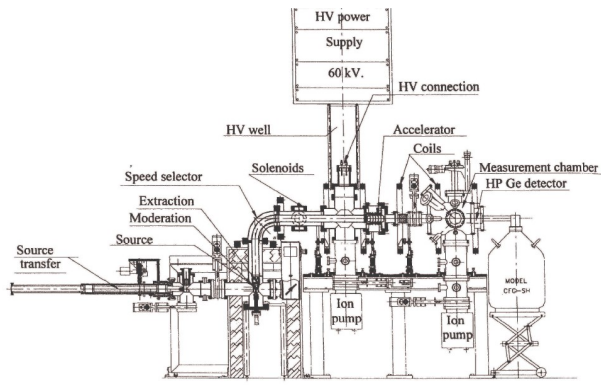

Figure 4: Schematic view of slow positron beam facility in Orléans [12].

The formula (1) below allows calculating the positron implantation profile after thermalization and before particle diffusion in material:

$$P(z,E) = \frac{2z}{z_0} e^{-(z/z_0)^2} \qquad (1)$$

where $$z_0 = \frac{A\,E^{\alpha}}{\rho\,\Gamma(3/2)} \equiv \frac{z_m}{\Gamma(3/2)}$$

Parameters A and α are material dependent; ρ is the mass density and Γ the gamma function. Makhov profiles for niobium (see Fig.5) are calculated with A=2.95 $\mu g/cm^2.keV^{-\alpha}$, α=1.7 and ρ=8.57 g/cm^3.

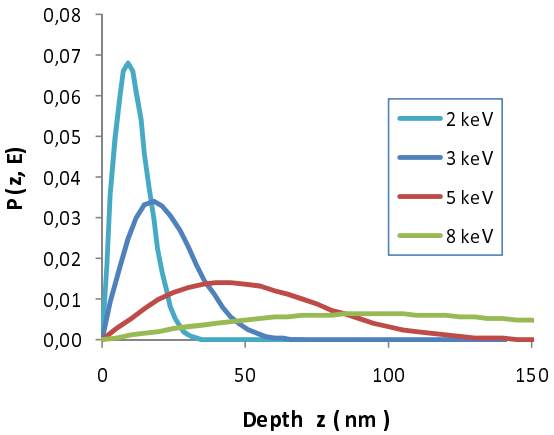

Figure 5: Makhov profiles of positron penetration in niobium for different beam energies.

NIOBIUM SAMPLES

Two types of niobium samples (8 mm diameter, 1 mm thickness) are tested in this experiment:

- Samples 1, 2, 3 and 4 are made from a single crystal (*SC*) provided by DESY, corresponding to the "beam-aperture offcut" of a large grain Nb sheet (Heraeus - RRR 500)
- Samples B, C and G are made from a fine grain (*FG*) niobium piece (Tokyo Denkai - RRR 200).

Samples are cut out to the right diameter using a water jet technique with abrasive garnet sand.

Table 1: Recap of Nb sample treatments

Sample	Nb	Chemistry	Cutting	Annealing 800 °C 1.10^{-7} mbar	Chemistry	Baking Argon – 1 atm.
1 & 2	Single Crystal	-	Water Jet	4 hours	BCP 100 µm	-
3 & 4						145°C / 2 hours
B	Fine Grain	EP 500 µm	Water Jet	2 h 30 mn HF rinse before & after	-	-
G					-	145 °C / 2 hours
C					BCP 120 µm	-

Figure 6: *FG* samples (∅ 8 mm) cut by water-jet; Nb sheet (140 x 10 mm) was electropolished first.

SC samples are treated like SRF cavities by annealing under vacuum (800°C – 1.10^{-7} mbar) during 4 hours to remove hydrogen, and then by BCP chemical etching (100 µm).

To test in this experiment both chemistries and to ensure a small surface roughness on fine grain samples, these are treated by electropolishing (EP). For practical reasons, due to the samples dimensions, EP took place before water jet cutting (Fig.6). To prevent any grain growth at the surface, samples were annealed during only 2.5 hours. Nevertheless, hydrofluoric acid (HF) treatments have been applied on *FG* samples before and after annealing to suppress any surface contamination (see Table1).

At last, all samples underwent high pressure rinse with ultra pure water and air drying in clean room class 100. Moreover some of them (samples 3, 4 and G) were baked during 2 hours according to the "Fast Argon Baking" process.

EXPERIMENTAL RESULTS

The maximum positron beam energy (25 keV) corresponds to a mean implantation depth (z_m) around 820 nm, deep enough to explore the superconducting RF layer of niobium (~50 nm).

Single Crystal Samples

Low and high momentum annihilation fractions, S and W respectively, are recorded versus the incident positron energy in Fig. 7 and 8.

The parameter variation between surface and bulk is more important for W compare to S one; this is probably due to the most important W sensitivity to chemical surrounding of the annihilation sites. Moreover, we can clearly observe that baked *SC* samples (3 and 4) have higher S and lower W parameters than unbaked ones (1 and 2).

This increase of vacancy number, after baking, rules out the scenario of a local diffusion of interstitial oxygen (or impurity) with a complex creation. Vacancy migration cannot be detected either. As consequence,

only the third scenario, vacancy-impurity dissociation followed by the impurity diffusion could be considered as realistic.

The baking effect on positron trapping is mainly visible up to 8 keV which corresponds to 120 nm of mean positron penetration depth, wide overlap of the superconducting RF layer. In this way, vacancy-impurity complexes could be involved in non quadratic losses at high fields.

Hydrogen atom could be a good candidate to be this impurity, because of:

- its high diffusion coefficient at typical baking temperatures ($D \sim 2.10^{-5}$ cm^2/s) and
- the inevitable contamination of Nb by absorbed hydrogen coming from aqueous species during BCP and EP chemistries,

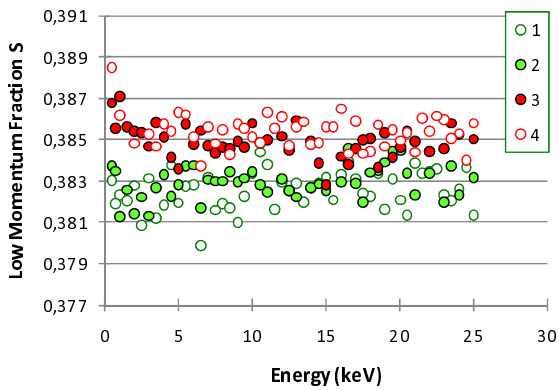

Figure 7: Low momentum annihilation fraction S vs. positron energy. Red / green data correspond to baked / unbaked single crystal Nb samples.

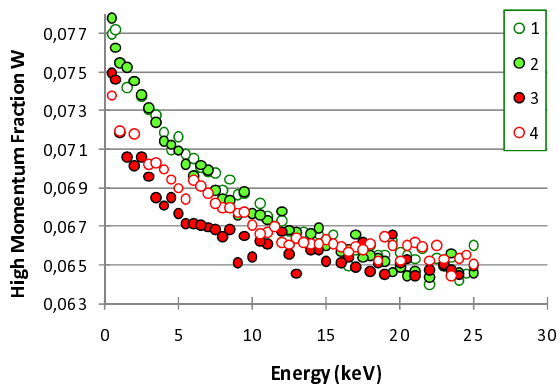

Figure 8: High momentum annihilation fraction W vs. positron beam energy. Red / green data correspond to baked / unbaked single crystal Nb samples.

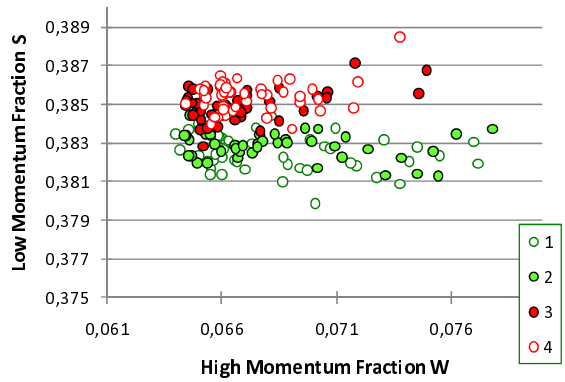

Figure 9: S vs. W plot for *SC* samples (red data correspond to baked samples).

Fine Grain Samples

Experimental results on fine grain samples B and G are very different (see Fig.10). A possible surface contamination could explain this fact because after cutting, no efficient surface cleaning does exist for *FG* samples compared to the BCP chemistry of *SC* samples (see Table 1).

As proof, an additional BCP chemistry, applied on *FG* sample C, induces data regrouping with *SC* results (Fig.10). More trapping sites are observed in sample C, compared to *SC* samples; it is probably due to the difference of surface roughness (Fig.11) with a vacancy excess at the interface structures and grain boundaries.

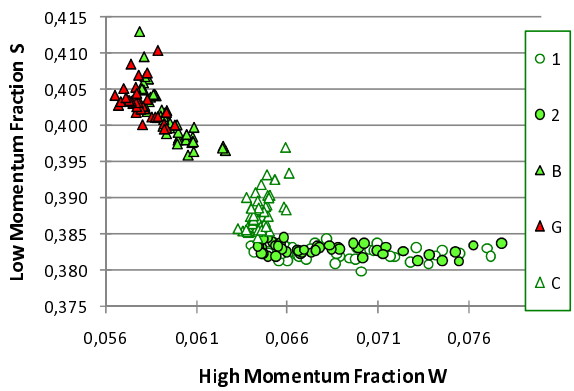

Figure 10: S versus W plot for *SC* and *FG* samples (red data correspond to baked sample).

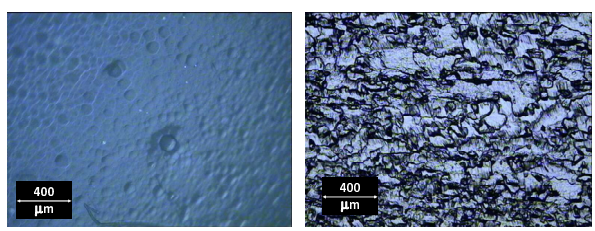

Figure 11: Optical microscope pictures of Nb samples after BCP chemistries (sample 1 on right and C on left).

Nevertheless to confirm the coherence of these *FG* results, we plan in the next experiments to retreat B and G samples by an additional BCP chemistry followed by the baking of one of them.

CONCLUSION

Preliminary experiments have been performed on Nb samples to define a possible impact of vacancies in "Baking Effect". Single crystal and fine grain samples have been analyzed by Positron Annihilation Spectroscopy through the radiation Doppler broadening method.

On baked single crystal samples, no vacancy migration is detected and for the first time an increase of vacancy sites is clearly observed in a 100 nm depth under the surface. A possible scenario to explain these results could be the dissociation by baking of vacancy-hydrogen complexes, followed by the hydrogen diffusion. The zone concerned by the vacancy site increase, covers thickness of the superconducting RF layer.

Similarly to niobium hydrides, involved in RF losses at low accelerating fields (Q-disease), vacancy-hydrogen complexes could be involved in non quadratic losses at high fields (Q-slope).

To confirm first results on vacancy increase after baking, experiments will be pursued on fine grain samples. Complementary studies on Nb samples by Elastic Recoil Detection Analysis (ERDA) will be also plan to understand if hydrogen can be involved in the assumed scenario.

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