

ATMOSPHERIC SURFACE TREATMENTS FOR IMPROVING THE Q-VALUE OF 6 GHz NIOBIUM CAVITIES

V. Palmieri*[§], A. Rossi*, K. Atroshchenko*, A. Camacho Romero^{§*}, S.Yu. Stark*

*Istituto Nazionale di Fisica Nucleare– Legnaro National Laboratories, Italy

[§]University of Padua, Padua, Italy

Abstract

A new technique for nitriding niobium cavities has been discovered and tested on 6 GHz resonators. The reduced size of the resonator at such a frequency allows to fabricate, surface treat, process and RF test at low temperature a high number of resonators at low cost and in a reduced time. The nitridation process is performed at temperature close to the Niobium melting point, for a few minutes, in Nitrogen stream and without the use of vacuum technology. Results are encouraging since the low field Q-factor is increased up to five times. The field gradient is instead reduced by the presence of a non-stoichiometric nitride under-layer that acts as a thermal barrier. Current research is developed in order to increase the superconducting properties of the superconducting top nitride layer and to decrease the thickness of the insulating under-layer.

INTRODUCTION

The Q-value of superconducting resonators is inversely proportional to Surface Resistance. The BCS contribution to the Surface Resistance will decrease exponentially with the Superconducting Critical Temperature T_c , while it will increase with the square root of the dc resistivity in normal state.

Superconductors with T_c higher than that of Niobium are then interesting for achieving at 4,2K the Q-values that Niobium reaches at 1,8K [1]. Worldwide efforts have been spent in order to find superconductors different than Niobium with higher T_c . The requirement is that the candidate material will be as much as possible metallic in normal state and will have as high as possible critical fields. Materials that have been applied up to now to fabricate cavity prototypes are the following: Mo-Re alloy, B1 compounds (NbN, NbTiN) and A15 compounds (Nb₃Sn). Q-values even higher than those of Niobium have been applied. However none of the above mentioned materials gave an accelerating field comparable with the values achieved with Niobium. The used experimental techniques were mainly based on Sputtering and/or on Thermal Diffusion. In any case both technologies require ultrahigh vacuum.

What we propose in the following is a new technique, that does not require vacuum technology, and it is suitable for preparing superconducting thick films for RF applications. The achieved results on 6 GHz cavities show the possibility to increase even of a factor 5 the Niobium Q-value at low field. Unfortunately first attempts gave low accelerating field values, but results are under continuous improvement.

There is one severe limitation to the research historically done on B1 and A15 compounds for SRF: the fact that the investigation performed on samples is not always meaningful and scalable to a resonator. On the other side samples are useful because working with a real accelerating cavity prototype is time and resource consuming, due to the big dimensions of the cavity itself.

Working with 6 GHz cavities is a particularly convenient choice, since it is well known that the BCS component of surface resistance scales with the square power of frequency. Therefore 6 GHz cavities are an extremely powerful tool for the full comprehension of physics under RF superconductivity [2]. Moreover 6 GHz cavities, in the way they are produced at Legnaro National Laboratories of INFN, are intrinsically inexpensive because they: i) are fully seamless; ii) require a little amount of Niobium; iii) need short fabrication times. In addition to that, other advantages consist in: i) fast and low cost BCP and EP treatments; ii) inexpensive Cryogenics; iii) quick RF measurements.

The SRF scientific community includes three different classes of experimentalists: i) those mainly involved in sample production and characterization; ii) the ones focused on methods for the measurement of Surface Resistance; iii) those mainly busy with real size cavity production and testing.

Certainly, the final goal of acceleratorists is the production of a nine cell resonator, and the sample production phase (surface morphology and microstructure analysis, Resistive and Inductive Measurement of T_c , Measurement of H_{C1}) is of course a mandatory step, but it is also the farthest from the world of production.

In terms of scalability the surface resistance measurement methods (Pillbox cavities, etc: Calorimetric Methods; Differential methods for Surface Resistance Measurements; microstrip resonators) are already closer than samples to the final goal, but still far from it.

From the final goal, 6 GHz monocell prototypes are the lowest step among all cavity choice (6 GHz cavities; 1,5 and 1,3 GHz monocells. 1,3 GHz 3-cell cavities, 1,3 GHz 9-cell cavities), but they interface the simplicity of samples with the technologies used for treating and testing a cavity.

With the same amount of Niobium required for a ninecell 1,3GHz cavity, we have instead produced 200 monocell 6 GHz resonator prototypes. Moreover due to the tiny sizes of such small resonators we can treat and measure up to 4 cavities per day. Obviously if our purpose was the optimization of the engineering of a ninecell cavity inside a cryomodule, the 6 GHz research

would be useless. But, if our purpose is instead either the comprehension of RF superconductivity or the search for alternative superconductors to Niobium, working on 1,3 GHz ninecell cavities would be a financial suicide. In any case our daily laboratory experience on 6 GHz seamless cavities make us sustaining the following statement: "Low research budget → Large amount of cavities".

The possibility to do quick and costless measurements allowed us to open a totally unexplored road in the way of considering superconductors with T_C higher than that of Niobium: the use of temperature over 2000°C for preparing cavities of Niobium Nitride by thermally diffusing a 6 GHz resonator in a Nitrogen flux at atmospheric pressure, in a few seconds and without the need of vacuum technology. Due to the NbN superconducting critical temperature of 16.8K, an immediate increase of the Q-factor at low field has been observed. It has been also observed a direct correlation between the Q-factor increase and the quality of superconducting transition of the Niobium Nitride samples fabricated with the same parameters.

Following the scientific debate and literature on SRF technology, there is an attempt to codify a cavity fabrication protocol that fixes experimental procedures in order to fast achieve reliable results. This is a good method whenever the goal is a cavity production, but it is self-limitation when looking for new ideas in search of a breakthrough in technology. If the goal is to achieve a robust production of cavities that guarantee 25MV/m on the largest possible number of produced pieces, a codified protocol is compulsory. But, if the goal is the search for superconductors that could maybe in future achieve 100MV/m, many codified assumptions risk to be dogmas.

In our experience and in our case, the list of dogmas are the following: 6 GHz cavities are not representative; any other flange, that is not Nb-Ti, is not reliable; Kapton joints are not reliable; 2000° C is a too high temperature because contamination from crucibles will arise and the dimensional control will be lost; vacuum technology is mandatory for not contaminating Niobium; among A15 materials those suitable for SRF applications are only those that can be prepared at T around 900°C. For what we are going to discuss further, the above mentioned assumptions are just dogmas and not necessarily true.

EXPERIMENTAL TECHNIQUE

The experimental apparatus is the simplest conceivable. It consists in a quartz tube containing the bulk Niobium 6 GHz cavity immersed in a nitrogen flux at atmospheric pressure. Heat is simply provided by induction heating at 70 KHz and a maximum power of 15 KW. Nothing else; vacuum is not needed. The idea is to bring the Nb cavity close to the melting point and to do a surfacial thermal nitridation of a few minutes. The process is fast, cheap, and simple. Figure 1 displays a photo of a 6 GHz cavity during the treatment.

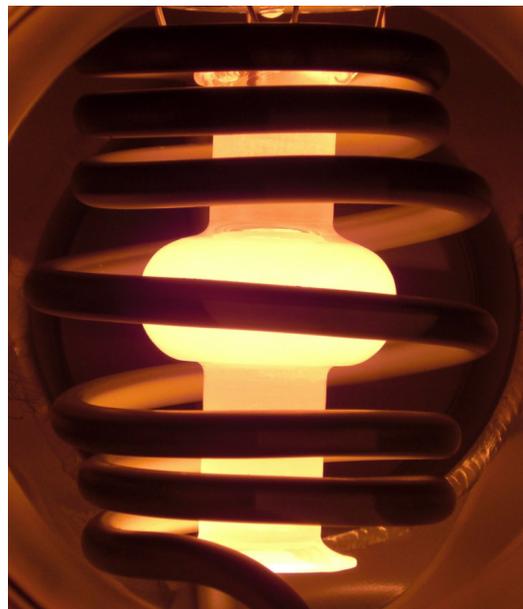


Figure 1: – A Nb 6 GHz cavity heated at a temperature close to 2000°C.

The nitridation process has three important steps: the heating ramp, the Niobium Nitridation in mushy state, the cooling step. Clearly the most important step is the central one. The key parameter, that more than others regulates the diffusion mechanism, is the homologous temperature θ , i.e. the temperature of a material as a fraction of its melting point temperature using the Kelvin scale, in other words the ratio between the operational temperature and the melting temperature both expressed in Kelvin

$$\theta = T[\text{K}]/T_m[\text{K}]$$

The homologous temperature is a fundamental parameter for a metallurgist, since at same values of θ , the majority of metals exhibit approximately the same behavior. Therefore at high θ -values, there are two regimes, that are almost unexplored for niobium, but that can reserve nice surprises for SRF experimentalists, for their extraordinary properties. These two regimes are the mushy state and the premelting region.

The mushy state starts at an homologous temperature values of 0.8 and it is a quasi-solid state characterized by the melting of grain boundaries, while the grains remain still solid. The mechanical yield strength collapses, while the intergrain diffusion coefficient diverges.

The premelting, or surface melting, instead describes a common phenomenon for crystalline materials consisting in the appearance of a surfacial quasi-liquid film that can be observed on a crystalline surface just below the material melting point T_m , being a common attribute of the solid state that the melting process begins at the surface. The thickness of the quasi-liquid film is temperature dependent.

The melting temperature of Niobium is 2467°C. The mushy state starts at $0.8 \cdot \theta$ corresponding at 1924°C. Table 1 reports a few values of the homologous temperature of interest for the nitridation of Niobium.

Table 1: Conversion of the homologous temperature to the centigrade values for Niobium close to melting point.

θ	T[°C]	
0.80	1924	Mushy state
0.90	2196	
0.96	2357	
0.98	2412	
0.99	2440	Close to Premelting
1.00	2467	Melting

The Nitrogen diffusion inside polycrystalline Niobium has two components: the inter-granular (across grain boundaries), and the intra-granular (inside grains). The inter-granular component is order of magnitudes higher than the intra-granular. However both increase exponentially with temperature. A thermal diffusion around 2000°C indeed results in a nitridation of Niobium for a thickness of the order of the millimeter.

Of course at the melting point the Niobium lattice constant value diverges because the crystal bonds are annihilated. The Niobium lattice parameter depends on temperature. The closer to the melting point Niobium will be heated, the higher it will be the lattice parameter. In the premelting zone the Niobium lattice parameter will increase up to it will diverge. The lattice parameter of Niobium is 3.303Å. That one of Niobium nitride is 4.385Å. Therefore it is clear that at high temperature of nitridation, the thermally expanded niobium lattice constant will become closer to the Niobium nitride lattice constant.

The cooling phase, after the nitridation temperature, is also of extreme importance, since in this phase all the spurious phases are formed. Moreover from the rapidity of cooling, it also depends the thickness of non-stoichiometric Nitride that separates the surface superconducting layer from the bulk Niobium. This layer not only has poor superconducting properties, but it is also a bad thermal conductor. So this intermediate layer will be an undesired layer, since it is a thermal barrier from the good surface layer to the unreacted Niobium. The thickness of this layer, that is practically a thermal insulator, is therefore directly responsible for the actual limit of the technique that is the low accelerating field achieved up to now. Such a thickness should be as thin as possible, so the cooling phase should be rather fast. However if this step is too fast, it is possible that, due to the different thermal expansion coefficients, the NbN layers will contract differently. As a consequence mechanical fractures parallel to the top superconducting layer can appear.

RESULTS AND DISCUSSION

The superconducting transition of a typical reacted niobium nitride sample is reported in the Fig. 2. The superconducting transition has been inductively measured, so that the double phase is a clear sign of the presence of at least two overlapped layers with two different critical temperatures.

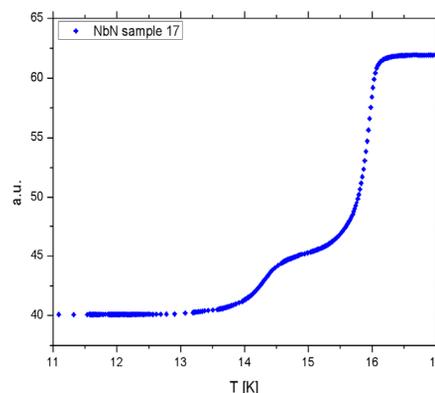


Figure 2: The critical temperature of a typical NbN reacted around 2000°C, where it is visible a double transition at 16K and at 14.3K.

From Literature [3] it is well known that in thermally diffused NbN the different phases occurring are the following. Their thicknesses being dependent on pressure of Nitrogen and temperature and time of nitridation.

- Nb_5N_6 ; N_4N_3
- δ -NbN_{1-x}; η -NbN (hexagonal);
- δ' -NbN (hexagonal);
- β -Nb₂N (hexagonal); γ -Nb₄N_{3-x}
- α -Nb (N) (bcc solid solution)
- Niobium

The overstoichiometric phases Nb_5N_6 and N_4N_3 are unstable. The δ -phase is the desired superconducting phase with a critical temperature up to 17,2 K, but it is metastable and it can be created only by high pressure or by non equilibrium processes, like for example sputtering. The critical temperature of g-Nb N is lower, in the range 12–15 K but it can be interesting for our application as well. As the phase transformation from δ -NbN to γ -Nb₄N_{3-x} is a very fast, quasi-continuous transition, it cannot be avoided by quenching.

Over 14 prototypes of 6 GHz cavities have been fabricated cleaned, processed and RF tested at 4,2 K in less than one month of work and the results are reported in the Fig 3.

The lowest curve is that of Niobium. For all the cavities the q-limitation was due to a kind of global heating. From the plot it appears that there are two families of curves: those limited around 2.5MV/m and those limited at 4MV/m. The difference in treatment is mainly the temperature of treatment that for the former was around the 2000°C and for the latter over 2300°C.

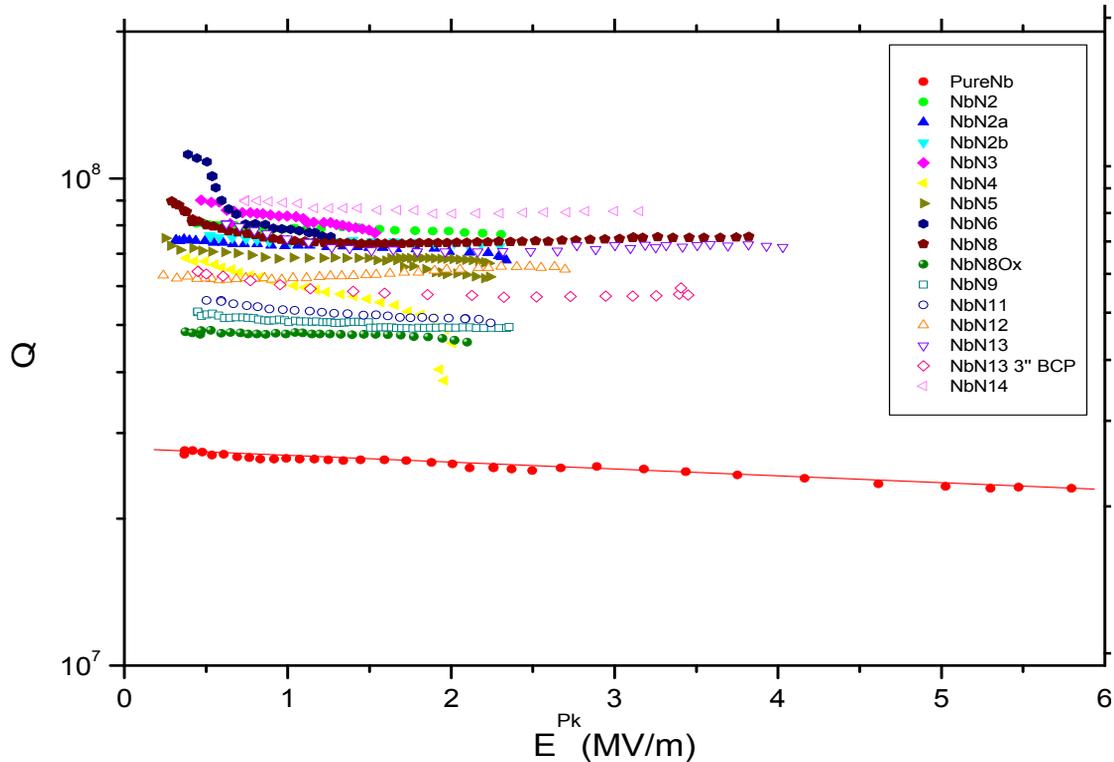


Figure 3: The Q-factor versus peak electric field for the 14 different Nitrided 6 GHz Niobium cavities. The lowest curve (Red dots) refers to the pure Niobium, while all the others are nitrided cavities at temperatures over 2000°C. All curves refer to 4,2 K.

Even it happened that the cavity 8, meanwhile nitrided over 2000°C, was exposed to the air by accident. The cavity was measured as well, and the Q was lower than the usual Q-value for NbN cavities. However surprisingly the Q-factor remains still over the Q-factor of Niobium. The authors explanation is that at those temperatures the Niobium oxides decomposes, being the Nb₂O₅ melting point equal to 1512°C and even the Evaporation temperature is around 1700-1900°C.

The final RF test at low temperature will depend so on two variables: the quality of the top superconducting NbN layer and the insulating sub-nitride layer. The quality of this second layer will depend on time of nitridation and on time and rate of cooling. The superconducting quality of the top layer Niobium nitride instead depends on temperature and time of nitridation and pressure of Nitrogen. Moreover it has been seen on several cavities that the initial status of the surface is absolutely crucial for the nitridation. Maintaining the same process parameters, electropolished cavities perform better than BCP treated cavities. Even for little simple, two samples one bared and one chemically polished, treated in the same moment and at the same conditions display two superconducting transitions that differ of even 1 K. A surface treatment is beneficial and the same effect has been noticed both for samples and for 6 GHz cavities.

A chemical polishing after the nitridation lower the Q-factor, proving that the good superconducting layer is the most external. A cavity annealing also does not work. We have tried several times an annealing after the 2000-

2300°C nitridation. Both annealings in Helium and in Nitrogen has been performed and the results are displayed in Fig. 4. In both cases the Q degrades. In the case of N₂ annealing, the results are even worse than in He.

The post-annealing then seems to not work. Even the Q factor becomes lower than that of Niobium. The authors hypothesis consists in the fact that once the superconducting layer is formed, any further action will only diffuse the nitrogen from the top superconducting layer to the wall interior.

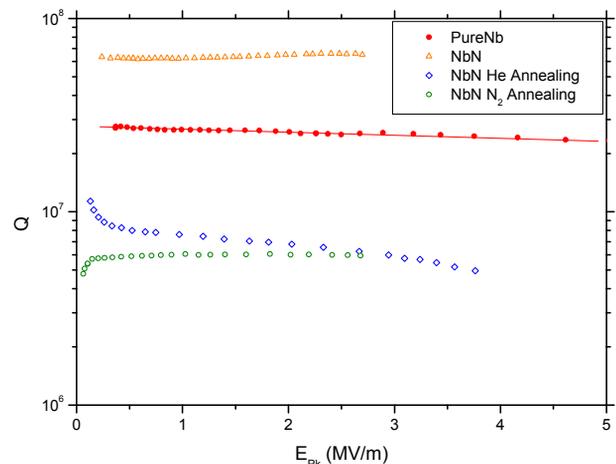


Figure 4: Q factor versus peak field at 4,2 K for 6 GHz cavities, for bulk niobium (full red dot); for NbN (red empty triangles), for a nitride cavity annealed in Helium (blue empty raster); for a nitride cavity annealed in Nitrogen (green empty raster).

CONCLUSIONS

The fabrication, surface treatment and test of a 1,3 GHz ninecell cavity in an optimistic vision takes around one month of work of several operators. Moreover such a cavity is not suitable for investigating fundamental properties. 6 GHz cavities instead allow a fast and dense statistics.

The nitridation at temperature over 2000 °C allows to increase the Q-factor up to a factor 5 at low temperature. The peak electric field is instead limited by the thermally insulating layer of not stoichiometric NbN between the good superconducting layer at the top and the niobium.

The process parameters that for the moment appear to play a key role for the improvement of RF performances, besides the process temperature, are the initial status of surface, the time of process and the flux of nitrogen.

REFERENCES

- [1] C. Benvenuti, V. Palmieri, R. Vaglio, "Construction Materials for Superconducting RF accelerating cavities", P. Vincenzini ed., *Advances in Science and technology 8, Superconductivity and Superconducting Materials Technologies*, Techna publ. Faenza (1995), pp. 637-648.
- [2] L. Badan, C. Durand, V. Palmieri, R. Preciso, S. Stark, F. Stivanello, W. Venturini, "RF Characterization of small scale cavities", *Particle Accelerators*, vol 62, (1998), pp. 637-643.
- [3] V. Buscaglia, F. Caracciolo, M. Ferretti, M. Minguzzi, R. Musenich, "Effect of pressure on the composition and superconducting Tc value of NbN prepared by combustion synthesis", *Journal of Alloys and Compounds* 266 (1998) 201–206.