

# PROGRESS OF Nb/CU TECHNOLOGY WITH 1.5 GHZ CAVITIES

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## Abstract

The residual resistance of Nb/Cu cavities increases exponentially at high RF field. Two main possible causes have been investigated in detail: the hydrogen incorporated in the film during the sputtering process and the surface roughness induced by the substrate. The latter has been reduced with an optimised electropolishing technique, which couples laboratory analyses of the electrical characteristics of the bath with numerical simulations of the actual process. The hydrogen content of the film can be reduced by increasing the pumping speed during deposition, either in the form of a suitable getter underlayer or of an appendage getter pump. The main results from these studies will be presented, together with other minor developments.

## INTRODUCTION

The surface resistance of Nb/Cu cavities at 1.7 K increases with the RF field amplitude, and a reasonable empirical fit of the experimental data is given by the formula  $R_s [\text{n}\Omega] = a + b \exp(c \times E)$  [MV/m]. Typical values calculated for standard coatings on passivated copper substrates [1] for  $a$  vary from a few to a few tens of n $\Omega$ , which correspond to the usual range of variation of the zero-field surface resistance  $R_{\text{res}}^0$ . Values for  $b$  are in the range 1.5÷2.5 while  $c$  is in the range 0.18÷0.22. Depending on the cavity preparation method these values may have small variations, as will be discussed in the following sections. In bulk Nb resonators however the field dependence is much less pronounced, resulting essentially in a three to six times smaller  $c$  term.

The possible causes of the residual resistance increase for Nb/Cu cavities have been investigated at CERN for a few years, and the most likely sources had been singled out in [2]. The latest developments of the research on these topics are illustrated below.

## SUBSTRATE STUDIES

The influence of the substrate on the growth process of thin films is a classical topic in thin film technology, as already underlined in the case of Nb/Cu films for cavities [3]. Several aspects have recently been submitted to deeper scrutiny.

### Electropolishing

The electropolishing of copper has been in use at CERN for several years [4] and its first application to 1.5 GHz Nb/Cu cavities has allowed obtaining very promising RF performance [1]. However, it soon appeared that the operating conditions of electropolishing are not reliably reproducible in cavity geometry and that a

deeper understanding of the relevant processes was needed.

The standard electropolishing bath has a reference composition of 55% vol. of  $\text{H}_3\text{PO}_4$  and 45% vol. of n-butanol ( $\text{C}_4\text{H}_{10}\text{O}$ ). The polishing process is characterised by the current density – voltage ( $J - V$ ) curve of the bath (polarisation curve, see Fig. 1), and the optimum polishing conditions in terms of roughness are obtained at the plateau [2]. The polarisation curve, as measured in a reference laboratory system, depends only on the chemical process to solute the  $\text{Cu}^{++}$  ions taking place in the thin diffusion layer close to the anode, which is in turn responsible for the polishing effect. Care is taken to measure at the fixed temperature of 20 °C and to let a very long stabilisation time for the measurement, experiments having shown that the response time of the bath to a change in the applied current density is of the order of the minute. If the electropolishing of a cavity is performed at the plateau, the electrical resistance due to the diffusion process can be estimated at around 0.1  $\Omega$ . However, the bath possesses also an intrinsic electrical conductivity which, in the case of the reference composition, is about 30 mS/cm. This is a rather low value compared for example to the bath used for Nb electropolishing, based on very strong acids, where it can be one order of magnitude larger. As a consequence, the potential drop during the electropolishing of a Cu cavity is not only due to the diffusion layer, but also in large part to the main volume of the bath. In simple configurations, the spacing from the cathode to the cavity surface is not constant. The electrical resistance is then varying from point to point and so does the current, resulting in a variety of polishing

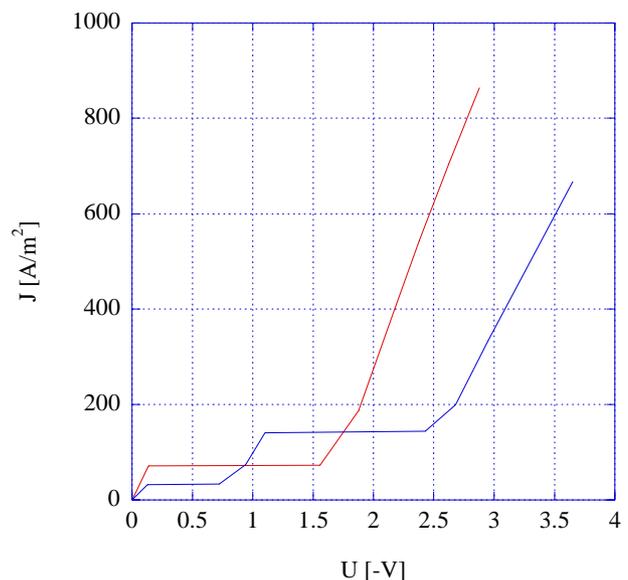


Figure 1: Polarisation curve measured for two different baths containing 4% (red line) and 10% (blue line) vol.  $\text{H}_2\text{O}$ . The conductivity is respectively 30 and 40 mS/cm.

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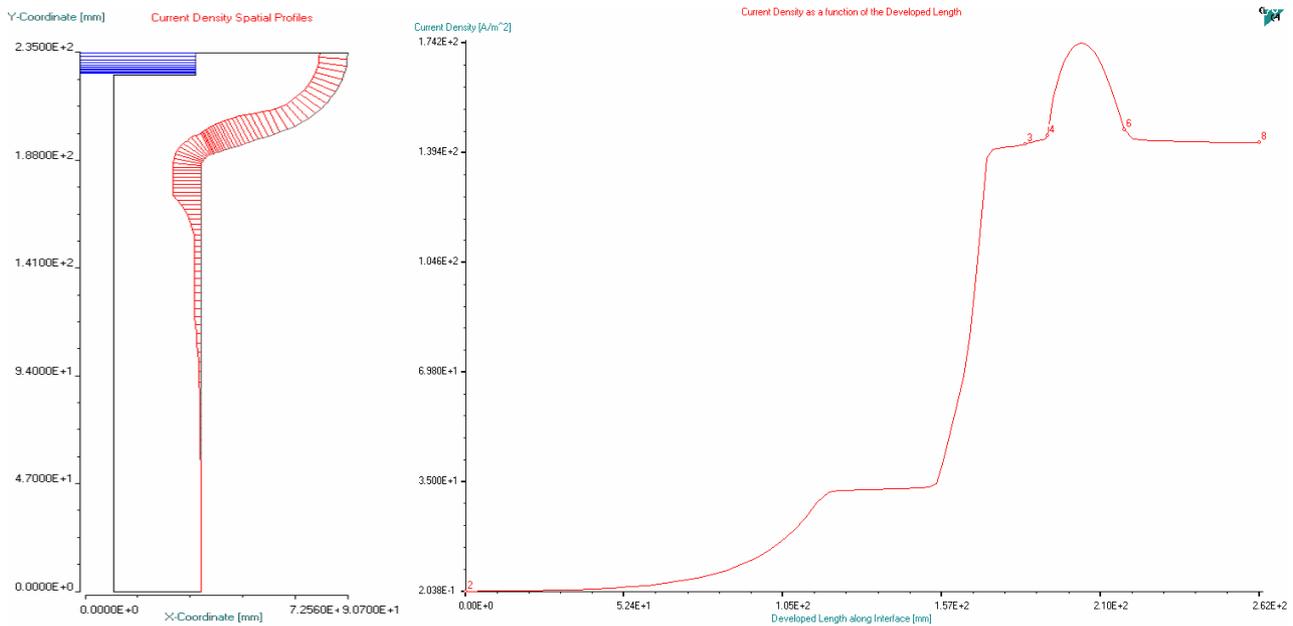


Figure 2: The same data for the polishing current distribution are plotted in different ways. (Left) The current density, equivalent to the width of the red stripe, is visualised along the cavity surface. The active region of the cathode is indicated in blue. (Right) Plot of the current density on a cavity meridian, as a function of the coordinate along the cavity axis. The total current to be applied is obtained by requiring that the region between iris and equator (from point 3 to 8) be polished at a current density equal to (or slightly above) the plateau value.

conditions along the surface. The electrical conductivity depends also on the water content of the bath, and since orthophosphoric acid is highly hygroscopic, water uptake may increase with time and reach very large proportions. For example, the conductivity has been measured to increase fourfold when water content is at 30% vol. A large variation of conductivity is also produced by the change of concentration of  $\text{Cu}^{++}$  ions in solution in the bath, which rises rapidly from the first use of the bath up to the saturation limit of about 15 g/l, limit that can increase when water is also present. Both the water and the copper content modify in turn the intrinsic polarisation curve by increasing the level of the plateau and reducing its width at very large concentrations. This is illustrated in Fig. 1, showing two polarisation curves measured for different water concentrations.

The first step to circumvent the problems listed above has been to carry out numerical modelling of the cathode with the specialised simulation software package Elsy2D/3D [5], in order to find its best shape for cavity electropolishing. The optimisation, carried out in several iterations of design and computer modelling, was based on the criterion of achieving the most uniform current density distribution on the cavity surface. It has appeared early that such a distribution cannot be obtained both in the cell and in the cut-off tubes with an equipotential cathode surface. In the final design it has been chosen to polish only the cell surface, where a uniform current density is achieved from equator to iris, while the cut-off tubes are not polished (Fig. 2). The polishing is then performed by applying between cathode and cavity a current calculated with the simulation program, in

floating voltage mode. This design choice has proved to be correct, allowing very good RF performance and an excellent repeatability of the process, provided that the bath characteristics are monitored regularly and the operating set-point for cavity electropolishing are adjusted in consequence. For this purpose the bath composition is regularly analysed in order to monitor changes in water and copper concentration, and the optimum working point is routinely re-calculated using as input for the simulation program a numerical representation of the polarisation curve and the conductivity.

The cavities are polished in vertical position and completely filled with acid. Although electropolishing was in the past performed in horizontal configuration with the cavity half-filled and in rotation, this has been abandoned because of the long stabilisation time of the electropolishing process at the location where the surface enters in contact with the liquid. The new cathode shape allows homogeneous polishing at plateau conditions to be achieved, minimising the regions with a higher current density where gas bubbles are produced, and which were the main argument against the vertical configuration.

### Microstructure of Copper Substrate

Although electropolishing allows obtaining very low roughness on uniform surfaces, it has little effect on curing localised defects. This had already been underlined in [1], where SEM micrographs of electropolished surfaces showed the existence of localised defects. There is evidence that these defects are already present in the matrix of the OFE copper of the cavities. In Fig. 3(b) is

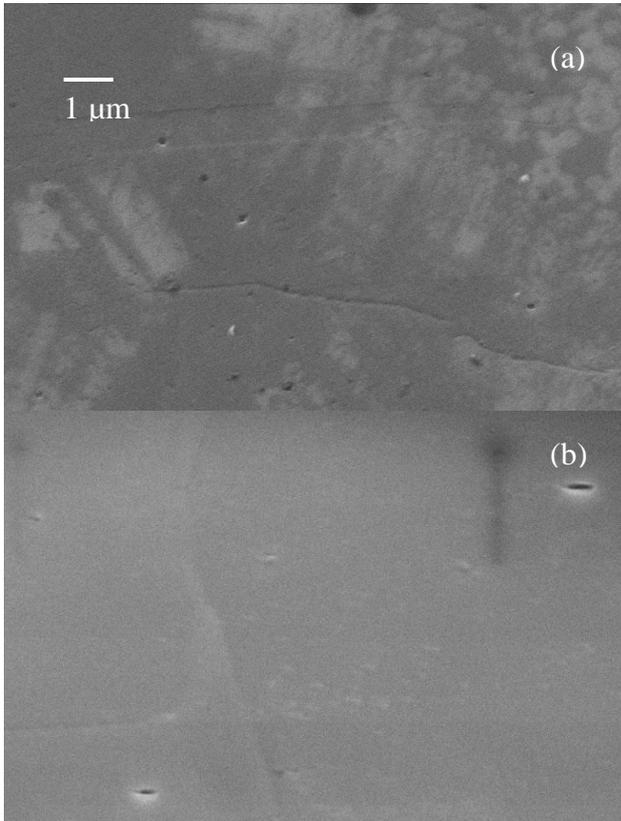


Figure 3: (a) Plan view of an electropolished copper surface (from [1]). (b) Cross sectional view of a cavity copper matrix.

illustrated a cross-section of the copper cut from a real cavity, where are clearly visible voids and defects whose spacing is not much larger than the one observed in plane view. This means that voids are equally distributed in the copper volume, and since the cut cavity shown had undergone a total copper surface removal of the order of 500  $\mu\text{m}$ , it can be excluded that they are located in a cortical layer. It is at present still unclear whether they are originated by the spinning process or if they are already present in the copper OFE sheets used for manufacturing. It can however be safely excluded that these voids originate from gas bubbles produced by the electropolishing process, as earlier suggested.

Niobium films grown on oxide-free copper surfaces, obtained either by sputter cleaning or by sputter coating a copper underlayer, grow hetero-epitaxially [2, 3] with an average grain size corresponding to the copper grain size, contrary to films grown on standard passivated substrates, which are nanocrystalline. Oxide-free Nb films have been shown to have larger RRR, less dislocations and less gas content than standard films. However they consistently display inferior performance compared to standard films [2]. This phenomenon is enhanced in cavities that have undergone in their lifetime long bakeouts at 350  $^{\circ}\text{C}$  for various reasons. In Fig. 4 is illustrated the dependence of the surface resistance versus accelerating field at 1.7 K

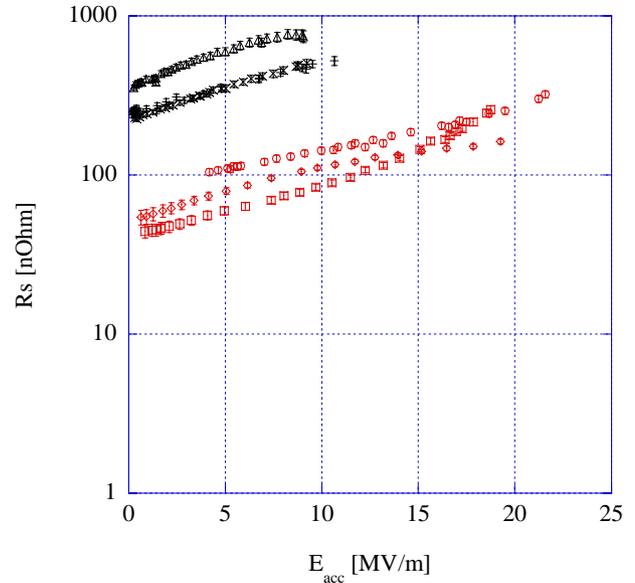


Figure 4: Examples of surface resistance at 1.7 K for oxide-free films, measured up to high accelerating field, deposited on standard spun copper substrates (red) and deposited on annealed ones (black). For the latter is indicated the maximum spread among five cavities. The performance was not correlated to the polished method applied, as mentioned in the text.

for a few typical cases. Fitting the data with the exponential formula previously mentioned results in several times larger  $b$  coefficients than for standard coatings, accounting for the global upward shift of the  $R_s(E)$  curves, as well as increased  $a$  coefficients. As a consequence the fit of the  $c$  parameter suffers from a very large uncertainty, having nevertheless values that can be one-half those of standard coatings.

One of the cavities heated at 350  $^{\circ}\text{C}$  has been cut in order to analyse its structure. It has been observed by optical microscopy that such cavities undergo a slight recrystallisation of the copper. In particular, cutting the cavity along a meridian and observing the cross-section, it has been seen that several grains are larger than the average size observed in standard cavities, and no longer show the elongation which is a consequence of the spinning process. The RRR of the Nb film (sputtered with Kr), measured after dissolving the copper with the usual technique, has a value of  $44 \pm 2$ . The measured value for an analogue Ar-sputtered film was  $29 \pm 1$ , which corrected for the know contribution due to gas implantation would result in a value of  $35.5 \pm 1$ , still much lower than the value presently measured, and supporting the hypothesis of an RRR increase due to a larger grain size. The origin of poor RF performance is still uncertain, but is likely linked to a larger mobility of the hydrogen present in the film [2]. Since a few cavities chemically polished present the same behaviour, it can be excluded that this phenomenon is due to a poor control of the electropolishing conditions.

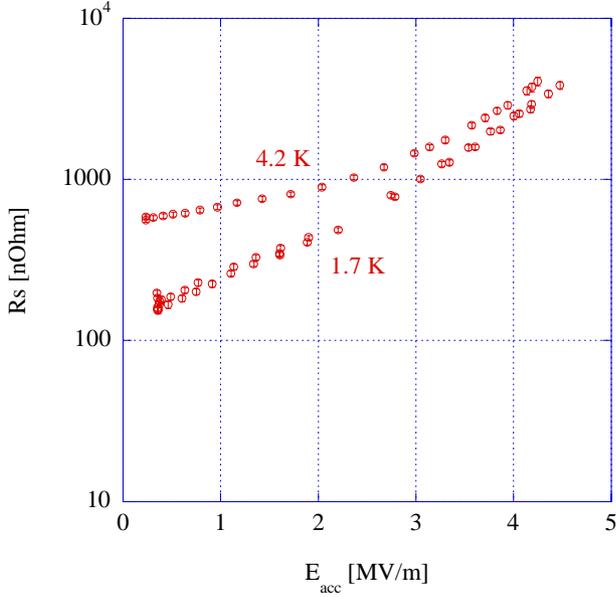


Figure 5: Surface resistance for a spun ultra-pure aluminium cavity at 4.2 K and 1.7 K.

## THERMAL EXCHANGE

The origin of the residual resistance increase at high field may simply be a poor thermal exchange between the film and the helium bath. Although unlikely, this possibility has been explored in several ways.

### Aluminium Substrate

A cavity made of 99.999 % pure aluminium has been shaped by lathe spinning at INFN-LNL. High purity aluminium has a better thermal conductivity than OFE copper [6] and can help reduce possible limitations in the overall heat transfer. Tests on samples had already shown that films having usual  $RRR$  values could be produced on Al substrates. Tests [3] of Al underlayers deposited on Cu before Nb deposition indicated that the behaviour of the Nb film is similar to films grown on oxidised copper substrate, with the exception of a lower  $T_c$  which is equal to the bulk Nb value. This phenomenon is due the absence of stress in the film, probably because the expansion coefficient of Nb and  $Al_2O_3$  are similar and the supporting Al substrate may easily flow following the deformation of the oxide.

The surface of the cavity was found to be heavily damaged after the spinning process, with long and deep longitudinal cracks clearly visible by naked eye. In copper cavities these are usually removed by intensive polishing. In this case however the reduced thickness of the cavity wall prevented their complete elimination, since mechanical stability calculations suggested not reducing the cavity thickness below 1 mm at the iris to avoid implosion. The cavity has been chemically polished using a solution of  $H_3PO_4$  40% vol.,  $CH_3COOH$  40% vol. and  $HNO_3$  10% vol. in pure  $H_2O$ , developed by INFN-LNL. Total material removal amounted to 130  $\mu m$ . Endoscope

observations still showed the presence of cracks after polishing. However, since the cavity was fitted with UHV flanges welded via a friction-bonded s.steel/Al transition, the risk of developing vacuum leaks at the transition region was a further reason not to insist with chemical polishing. The coating was carried out with the standard procedure, taking care of blocking the cavity flanges with temperature-controlled thick Al bars to prevent collapse. The result is presented in Fig. 5. The value of zero-field BCS surface resistance is reasonable at  $430 \pm 20$  n $\Omega$ , however the residual resistance shows a steep increase with RF amplitude already at very low fields. The main conclusion that can be drawn from this result is that the surface quality is predominant in determining the performance of Nb-film cavities, as already known. Nothing can unfortunately be inferred about the effect of the higher thermal conductivity of the substrate.

### Thermal Impedance at the Film/Substrate Interface

It has been shown [2] that if the surface resistance increase at high accelerating field is attributed only to a temperature increase of the film, the dependence of  $\Delta T$  on the power flux is not linear, as expected for Kapitza-like impedance or for heat flow across a solid material. Nevertheless, it has been judged important to carry out a direct test on samples [7] in order to clarify this point. Electropolished copper ( $RRR=100$ ) and niobium ( $RRR=180$ ) discs, with and without coating on one side, have been mounted between two separate superfluid helium baths, one pressurised and the other saturated. The latter acts as a large heat sink, while the former can be heated with a controlled heat flux, and the temperature difference between the two baths is used to calculate the total thermal conductance. Care is of course taken to control all sources of uncertainty in the experimental apparatus. The main results are reported in Table 1. The presence of a Nb film reduces slightly the overall thermal conductance both for Cu and Nb discs, but this effect is within the experimental uncertainty. It is however largely negligible when compared to the poor overall thermal conductance of the solid niobium disc. The intrinsic thermal conductivity of the niobium used in the experiment has not been measured and is certainly lower than for the high-purity annealed niobium used for cavity manufacturing. Calculating with literature data [8], the latter would in the present geometry have an overall

Table 1: Measurements of thermal conductance for Nb and Cu discs, with and without a Nb coating

Sample type	Overall thermal conductance [ $Wm^{-2}K^{-1}$ ]
Cu electropolished	$4300 \pm 250$
Cu EP + 1.5 $\mu m$ Nb	$4100 \pm 250$
Nb electropolished	$1200 \pm 200$
Nb EP + 1.5 $\mu m$ Nb	$1000 \pm 200$

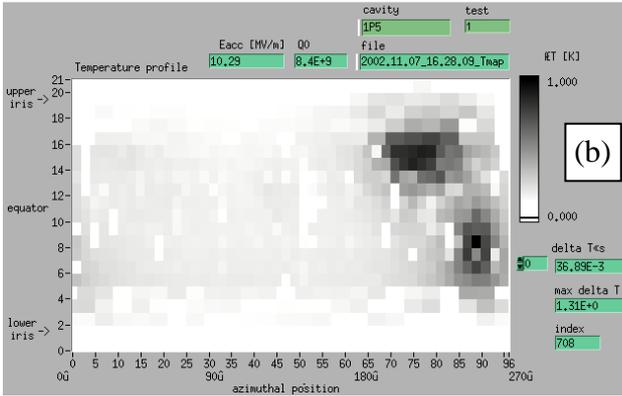
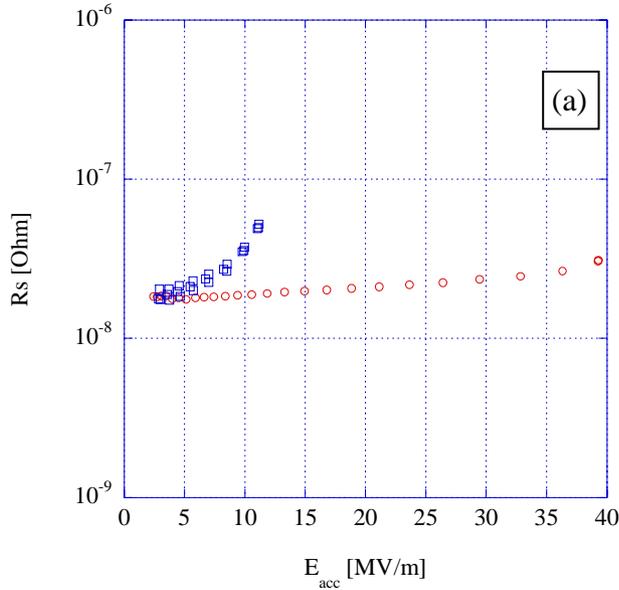


Figure 6: (a)  $R_s$  value measured at 1.8 K for cavity 1P5 (spun) after EP and mild bake-out (red dots) and after 1.5  $\mu\text{m}$  Nb coating (blue dots). (b) Temperature map in subcooled He at field level slightly below quench for the Nb/Nb film. The quench region is the bottom black one, while the upper heated region is probably due to a slight deformation of the cell geometry.

thermal conductance of  $2500 \text{ Wm}^{-2}\text{K}^{-1}$ , dominated by Kapitza impedance. This value is still lower than what measured for Nb/Cu, thus proving that the thermal impedance is not the limitation factor for the performance of Nb/Cu cavities.

A further element of information arises from Nb coatings that have been performed on single-cell bulk Nb 1.3 GHz TESLA cavities. The results obtained on a cavity manufactured by spinning (1P5) are illustrated in Fig. 6. This cavity had excellent performance before coating, and suffered severe degradation when a Nb film was applied. The effect is too strong, and too similar to what happens in Nb/Cu cavities, to be attributed to additional thermal impedance at the Nb/Nb interface. The maximum field is limited by a quench, and T-maps performed at DESY confirm that the source of heat is a localised defect, while and increased thermal impedance would have generated

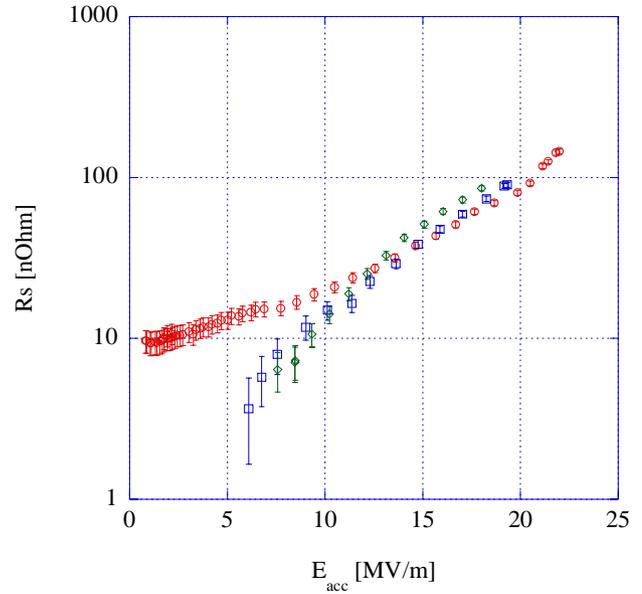


Figure 7: Surface resistance at 1.7 K for electropolished copper resonators. Standard coating (red), with added NEG pumping in the coating system (blue), and three times thicker coating (5  $\mu\text{m}$ , green). The difference at low field is an artefact of the RF measurement.

global heating. A second Nb cavity (1B4) manufactured by the usual welding technique was coated with a Nb film, and displayed the same behaviour. After a further EP the original performance before coating was recovered, thus proving that the coating procedure did not have deleterious effect on the bulk of the niobium.

## EFFECT OF HYDROGEN

The results presented in [2, 9] have spurred a programme to test several methods for reducing the hydrogen concentration in the film.

A NEG pump made with a TiVZr-coated s.steel tube having a pumping speed for hydrogen of approximately 800 l/s has been added to the vacuum system used for cavity coating. Furthermore a st707 getter strip has been wound in the part of the coating system where the sputtering gas is injected. The residual hydrogen pressure before coating was improved by a factor of three compared to standard conditions, while water and other major impurities gases decreased by one order of magnitude. A similar improvement for hydrogen is observed also while monitoring the overall gas composition during sputtering. No change has been observed in the RF performance at high field, as shown in Fig. 7 where one such a cavity is compared to a standard coating, the only significant difference in the fit parameters being an almost zero  $a$  coefficient.

A further test has been carried out performing a few coatings keeping an almost static flow of discharge gas (Kr) by throttling the main turbomolecular pump. Vacuum quality was also in this case guaranteed by a NEG pump, the purpose of the exercise being excluding that some

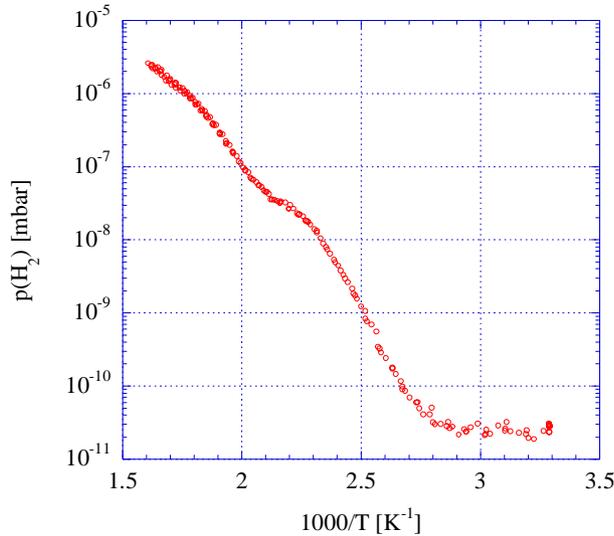


Figure 8: First heating cycle for a Nb film deposited onto a Ti film. The inflexion at about 180 °C (value 2.2 in the x-coordinate) clearly indicates activation of hydrogen from trapping sites in niobium.

hydrogen might come from the flow of the gas. No improvement could be observed, the performance being similar to that obtained under standard sputtering conditions.

If hydrogen is coming from a source having a finite quantity, which is released during the coating, diluting it in a thicker film might result in a decrease of concentration in the film. A test with a 5  $\mu\text{m}$  thick coating showed no improvement (also in Fig. 7), the difference in the fit of the RF results being again a zero  $a$  coefficient.

The latter result would be expected, in the hypothesis that hydrogen is really affecting the performance at high field, if the hydrogen is produced by some source having a constant flow. Outgassing from the vacuum system and the flow of discharge gas are likely excluded by the first tests mentioned above. A third potentially strong source of hydrogen is copper, as already shown in [3], with an outgassing that depends on the cavity fabrication method and on the cavity history. A few cavities have thus been coated with the two cathode coating system by first depositing a 1.5  $\mu\text{m}$  thick Ti underlayer, followed without exposing to air by the usual 1.5  $\mu\text{m}$  thick Nb film. Titanium would have in this case the double function of blocking whatever hydrogen may come from the copper, and act also as a sink for the hydrogen that might be released by other sources during the coating process, and that might diffuse through the niobium film. The performance is unchanged compared to standard cavities in term of the  $a$  and  $c$  parameters, however  $b$  is slightly larger.

It is worth mentioning that one such cavity was used for several measurement cycles of the hydrogen equilibrium pressure, up to 350 °C. Two cycles have been performed after Ti deposition, resulting in an average binding energy for H of  $0.44 \pm 0.04$  eV/at. No signatures of activation or release of hydrogen from trapping sites have been

identified at the first temperature increase. Conversely, at the first heating of the Nb film deposited on the Ti film, a drastic change of binding energy happens at around 180 °C, as shown in Fig. 8. The binding energy decreases from  $0.58 \pm 0.02$  eV/at at low temperature to  $0.42 \pm 0.02$  at high temperature, similar to the value for pure Ti. It should be noted that  $0.34 \pm 0.01$  was measured for Nb alone [1]. This energy does not show further changes at subsequent cycles. Moreover, the equilibrium value of the  $\text{H}_2$  pressure is about a factor 50 less than what had been measured for Nb films alone.

For testing further the influence of the copper substrate, several coatings have been performed on electropolished copper strips, some annealed at 800 °C for 4 hours and finally chemically polished, and others that did not undergo the annealing step. The samples have been coated in a stainless steel 500 MHz dummy cavity. The hydrogen content has then been measured in a dedicated system by Thermal Desorption Spectroscopy up to 700 °C. Plain copper strips prepared in the same way have also been measured, and the corresponding hydrogen background has been taken into account when calculating the amount of hydrogen released by the niobium films. The hydrogen content of niobium films on annealed copper turns out to be about 0.3% at., and about 0.4% at. for films on un-annealed copper. The difference is likely due to some effect of the annealed copper on the growth properties of the film. The hydrogen quantity released by films is in fact about ten times more than the quantity released by the copper substrates alone, both annealed and not. This suggests that copper is probably not the source of the hydrogen contained in these niobium films.

The above result can be translated to cavities only under the assumption that they are manufactured by a comparable material and process, which is probably the case for the standard spun cavities. This assumption is supported by the fact that the outgassing of cavities up to 350 °C had given a total hydrogen quantity of about 0.2% at.. In TDS measurements, the hydrogen peak is between 350 °C and 400 °C, and up to these temperatures the integrated hydrogen quantity released is also about 0.2% at., both for annealed and un-annealed copper substrates.

## CONCLUSION

Several possible limiting factors for the high-field performance of Nb/Cu cavities have been studied in detail. It has been shown that this limit is not of thermal origin, and that decreasing the hydrogen content of films does not significantly increase the RF performance.

Further studies will be concentrated on the reduction of the intrinsic roughness of the films, eventually by bias sputtering, and on the study and optimisation of the oxidation of the films after coating.

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## REFERENCES

- [1] C. Benvenuti, S. Calatroni, P. Darriulat, M. Peck, A.-M. Valente, C. Van't Hof, *Physica C* 351 (2001) 421
- [2] C. Benvenuti, S. Calatroni, M. Hakovirta, H. Neupert, M. Prada, A.-M. Valente, *Proceedings of the 10<sup>th</sup> Workshop on RF Superconductivity*, S. Noguchi Ed. (KEK, Tsukuba, 2003) p. 252
- [3] C. Benvenuti, S. Calatroni, P. Darriulat, M. Peck, A.-M. Valente "Influence of the nature of the substrate on the growth of superconducting niobium films" CERN Internal Report CERN-EST-2000-005-SM
- [4] S. Calatroni et al., *Proceedings of the 6<sup>th</sup> Workshop on RF Superconductivity*, R. Sundelin Ed. (CEBAF, Newport News, 1994) p. 687
- [5] [www.elsica.be](http://www.elsica.be)
- [6] C. Benvenuti, V. Palmieri, R. Vaglio, *Proceedings of the 4th Topical Symposium on Superconductivity and Superconducting Materials Technologies*, P. Vincenzini Ed. (Techna, Faenza, 1994) p. 637
- [7] L. Dufay, J.-M. Rieubland, G. Vandoni – CERN Internal Note Cryolab Note 10-00
- [8] J. Amrit, M.X. Francois, *J. Low Temp. Phys.* 119 (2000) 27
- [9] W.R. Frisken, L.N. Hand, *Proceedings of the 9<sup>th</sup> Workshop on RF Superconductivity*, B. Rusnak Ed. (LANL, Los Alamos, 2000) p. 312