NbTiN SUPERCONDUCTING THIN FILMS PREPARED BY MAGNETRON SPUTTERING.

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Abstract

A prospective study of new materials for making superconducting cavities is presently undertaken at CEN Saclay. Coatings of the B1 intermetallic compound $Nb_{(1-x)}Ti_xN$ with $0.30<x<0.64$ have been elaborated by a reactive magnetron sputtering method. Structural, chemical and electrical characterizations of the deposits have been made in order to correlate the deposition parameters and the superconducting properties of the films. One of the main goals is to minimize the RF surface resistance of the coatings. For this purpose, a cylindrical TE011 cavity made out of massive niobium, with a dismountable end plate, has been developped in order to test the NbTiN films deposited on copper substrates . The best surface resistance of the deposit we have obtained at 4 GHz and 4.2 K is lower by a factor of 3 than for niobium.

Introduction

Superconducting cavities for electron accelerators are being studied in CEN Saclay. These cavities, usually made out of massive niobium, benefit of the knowhow accumulated over the years in many laboratories and display remarkable performances: quality factor $Q_0 \geq 10^{10}$ and accelerating field $\geq$15 MV/m for monocell cavities. The chosen frequency (1.5 Ghz) and the superconducting properties of Nb (Tc=9.2 K) dictate an operating temperature below 2 K in order to get a reasonable RF surface resistance (typically 20 nΩ).

In order to reduce the cost of fabrication of these cavities, as well as the cost of the cryogenic installation, it may be interesting to replace massive Niobium by thin films with better superconducting properties. The compound NbTiN is a good candidate for this purpose: first, its high critical temperature (Tc=17 K) should permit for cryogenics the use of boiling Helium at atmospheric pressure (i.e 4.2 K); second, previous results obtained by R. Di Leo et al [1] indicate that this material may have a low residual surface resistance; last, the elaboration technique (reactive magnetron sputtering) is compatible with the cylindrical geometry of the cavities [2]. It is thus possible to deposit the superconducting thin film inside the cavity made out of a good thermal conductivity material (copper), in

order to evacuate readily the dissipated power into the helium bath.

We present in this paper a prospective study of NbTiN thin coatings for RF applications. The first part is devoted to the description of the fabrication process in a planar geometry, and to the characterization of the films deposited on small samples. In the second part, we describe an experiment using a dismountable TE011 cavity to measure the RF surface resistance of the NbTiN deposits.

1- Elaboration and sample characterization of NbTiN coatings

1.1- Film Preparation.

The planar magnetron sputtering set up, developed in collaboration with the CEREM Grenoble, consists in a vacuum chamber, equipped with a turbomolecular pump (1500 l/s) enabling a 10^{-5} Pa residual pressure. A valve with a tunable aperture permits to control separately the pressure and the gas flow. Gas flows are regulated with the aid of massic flow-meters. The chamber pressure is measured with a membrane and a Bayard-Alpert gauges. Gas purity (Ar,N_2) is at least 99.995 %. The 210×90×5 mm NbTi target is mounted on a permanent magnet planar magnetron sputtering source. Different Nb to Ti composition ratios of the films have been obtained with the aid of 3 different magnetron targets: the first target was made out of the commonly used $Nb_{0.36}Ti_{0.64}$ compound. The second one was composed by a $Nb_{0.36}Ti_{0.64}$ plate in which were inserted several Nb inlets in such a geometry that we obtained a film composition varying from $Nb_{0.35}Ti_{0.65}N$ to $Nb_{0.45}Ti_{0.55}N$ as a function of the position in our 220×120 mm substrate. The third one was made out of a pure Nb plate in which were introduced Ti inlets in order to obtain an homogeneous $Nb_{0.70}Ti_{0.30}N$ film composition.

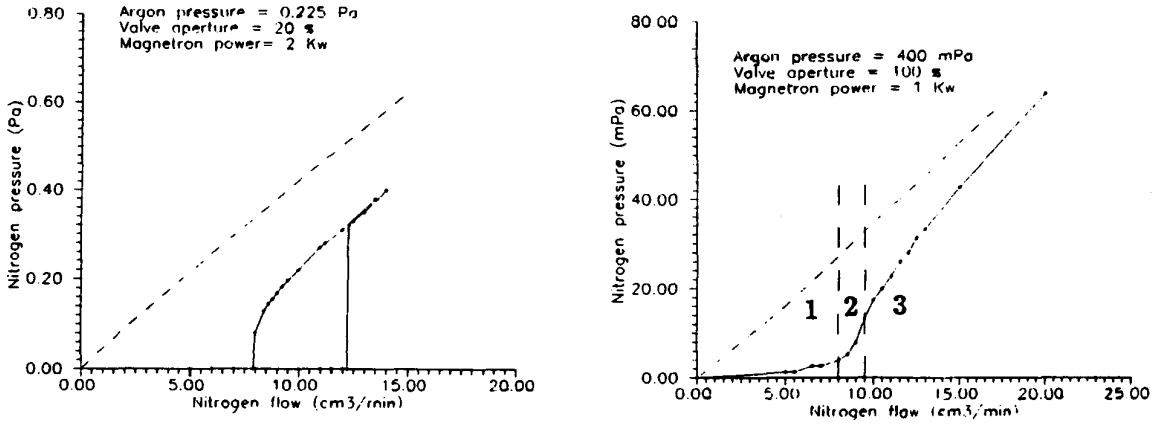
1.2- Sample Characterization.

The thickness measurement is made with a Taly-Step gauge. The chemical analysis uses an electron microprobe and ion beam techniques (RBS, NRS)[3]. X Ray diffraction, using a $(\theta - 2\theta)$ goniometer, enables the determination of the cristallographic structure of the surface (phase, texture). Resistivity and superconducting critical temperature measurements are performed with the "4 points" methode.

The superconducting behaviour of the films was also investigated by a.c. susceptibility measurements at low frequency (35 Hz). The excitation field is parallel to the sample plane with intensity ranging from 1 to 30 Oe. This type of investigation allows to measure the critical temperature onset by considering the first negative deviation occuring on the χ'(T) curve when the temperature decreases, and to identify the presence of different superconducting phases by the number of χ"(T) peaks which develop in the superconducting transition.

1.3- Results and Discussion

The first step of the study consisted, with the first magnetron $Nb_{0.36}Ti_{0.64}$ target, in the determination of the sputtering parameters which gives the best superconducting properties of the films. In the second step, with the two other targets, we analyzed the influence of the Nb to Ti composition ratio on the film properties.



1.a 1.b

Fig.1. Partial pressure of nitrogen $P(N_2)$ as a function of the nitrogen flow rate $F(N_2)$ for a low value of the pumping speed (fig.1.a). and for the maximum pumping speed (fig.1.b)

1.3.1- Reactive Sputtering Parameters.

It is well known that the elaboration parameters leading to the optimum properties of the coatings depend strongly on the sputtering facility characteristics (geometry, pumping speed, magnetron target surface...). Accordingly, we first made a parametric study of the sputtering set up itself.

The two main operating parameters enabling the process control are the nitrogen flow consumed by the reaction and the magnetron target voltage [4,5]. A qualitative description of the reactive sputtering process may clarify the role of these parameters:

When no electrical power is applied to the magnetron, the nitrogen partial pressure $P(N_2)$ is proportional to the total nitrogen flow $F(N_2)$. When electrical power is applied, the curve obtained at low pumping speed displays a hysteretic behaviour, and is characteristic of the $P(N_2)$-$F(N_2)$ curves relative to the TiN and NbN systems [4,6]. Three domains can be distinguished in the $P(N_2)$ vs $F(N_2)$ curve (Fig 1.a):

1) For the small values of $F(N_2)$, all the introduced nitrogen reacts, either on the magnetron target, or on the deposit. Here, $P(N_2)$ is close to zero, and the target voltage U_t is independent of the nitrogen flow rate. In this case, the nitridation rate is smaller than the erosion rate.

2) P(N_2) and U_t rise suddenly when F(N_2) reaches a critical value proportional to the applied power. This intermediate domain is believed to correspond to the total target nitridation.
3) For the high values of F(N_2), the P(N_2) vs F(N_2) curves follow asymptotically a straight line parallel to the one obtained at zero power level.

The hysteresis phenomenon is generally attributed to the denitridation of the target [4]. For high pumping speeds (fig 1.b), the pressure and target voltage variations are more progressive, and the hysteresis disappears. In this case, the operating conditions are very stable and reproducible [7]; it is then possible to investigate the evolution of the deposit characteristics in the transition zone.

The general shape of the P(N_2)-F(N_2) curves does not depend on the composition of the target.

1.3.2- Sample Characterization.

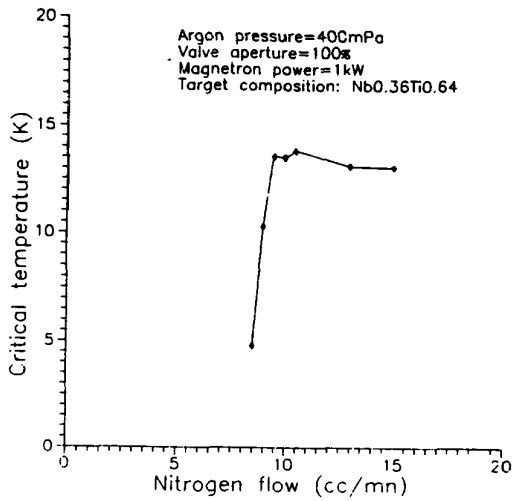


Fig.2 Critical temperature of the coatings as a function of the nitrogen flow rate for the maximum pumping speed and with the $Nb_{0.36}Ti_{0.64}$ target composition.

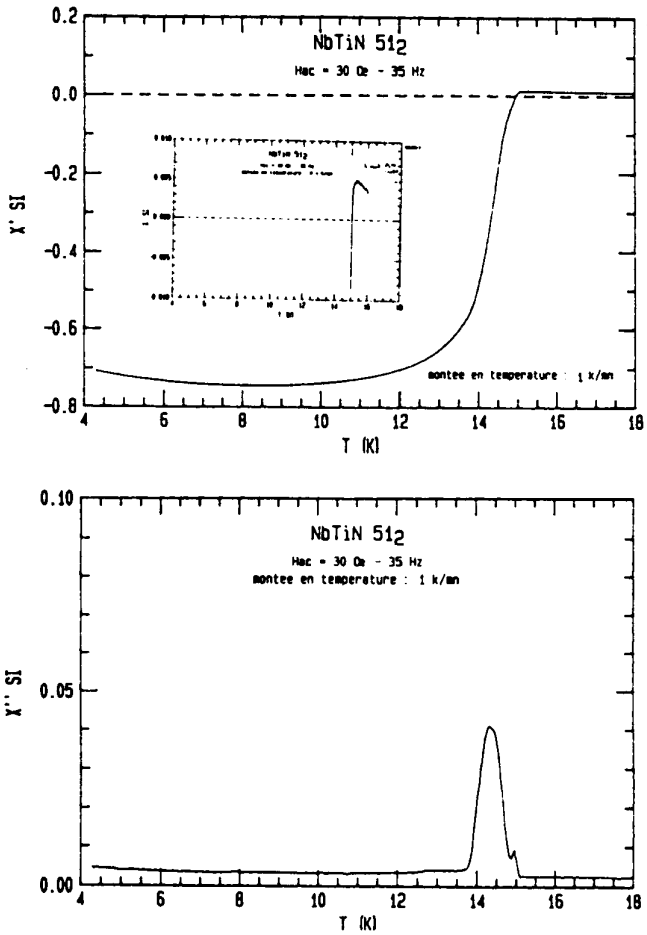
All the deposits were prepared at room temperature, and their thicknesses were comprised between 1 and 3 μm. The deposit rate was between 1 and 3 nm/sec.

For the low values of the nitrogen flow, i.e before the transition, the deposits always have the bcc structure of the niobium. It is possible to incorporate high nitrogen concentrations (up to 30 % at) while keeping a supersaturated solid solution. The lattice parameters calculated perpendicular to the substrate surface from the (110) diffraction peak are comprised between 0.329 nm (for zero nitrogen content) and 0.308 nm. The samples are highly textured along the axes [110] and [200]. When the nitrogen content increases, the [200] texture component decreases, and the diffraction peaks are broadened. This feature may reflect either a decrease of the crystallite size or an increase of the lattice microdeformations [8].

The transition zone (denoted by 2 in fig 1.b) corresponds to higher nitrogen contents (between 30 and 50 % at), and a highly textured [200] fcc structure is now obtained. Here, the broadening of the Xray diffraction peaks is very large.

The samples elaborated in the region 3 of the curve have a nearly stoechiometric Nitrogen content, and the material becomes less textured. The crystallographic structure is now of the fcc NaCl type, which corresponds to the superconducting phase, and the lattice parameter is about 0.431 nm. This structure is also obtained by using lower pumping speeds , at the top elbow of the P(N_2)-F(N_2) hysteresis curve for decreasing N_2 flow (fig 1.a).

The superconducting critical temperature is directly correlated with the structure evolution as it is shown on figure 2.



3.a

Tc onset is defined by magnifying the χ' component

3.b

Fig.3 χ'(T) and χ"(T) responses of a NbTiN film 2.7 μm thick with an excitation field of 30 Oe. The signal is normalized by the volume of the film and the components χ'(T),χ"(T) are expressed in S.I. units. Note that the slight raise of the χ' component near 4.2 K is probably due to a magnetic contribution of the substrate.

With the first composition $Nb_{0.36}Ti_{0.64}N$ the highest Tc value obtained is 13.9 K and the lowest resistivity at room temperature is 41 $\mu\Omega$.cm. The critical temperature of the coatings increases with the niobium concentration, as it is reported in [1], and the maximum value we have obtained is 16.08 K for $Nb_{0.70}Ti_{0.30}N$ films. For this last composition, resistivity at room temperature is about 90 $\mu\Omega$.cm.

Whereas crystallographic analysis reveals only one single superconducting phase (fcc NaCl type), susceptibility measurements identify different phases with different critical temperatures as it is shown on figure 3. For this sample the critical temperature onset is 15.33 K (fig.3.a), but the χ"(T) component of figure 3.b displays clearly two χ" peaks (T_{peaks}=14.2 and 15 K), and a third one of very low intensity ($T_{peak}\approx$13 K). Intergranular coupling may also generate χ" peak but in the present case more refined investigations are needed to identify such phenomenon.

This contradiction between X rays cristallographic analysis and susceptibility measurements is perhaps due to strong heterogeneities of the cristallographic structure (local variations of the lattice parameter due to variations of composition or strains) which have already been observed in TiN and Mo magnetron sputter deposited coatings [9,10]. Further X rays diffraction analysis of the cristallographic texture and of the lattice strains is in progress to verify such an hypothesis.

2- RF Characterization of the Superconducting Films

We use a cylindrical TE011 niobium cavity with dismountable end plate to determine the RF surface resistance of superconducting coatings [11,12]. We also obtain their critical temperature and penetration depth (if the film is thick enough) from quality factor and resonance frequency measurements as a function of the temperature in the 10 K to 17 K range.

2.1- Cavity Design.

The main body of the cavity is made out of high purity Niobium (RRR=180). The diameter of the removable disc, 126 mm, has been chosen to fit in a SEM apparatus. The inner diameter of the cavity is 110 mm; its length is 66 mm . Sealing is achieved by an 1 mm Pb gasket located in a groove machined in the disc itself. A peripheric groove in the fixed end plate has been designed to shift away the degenerate TM111 mode by 50 Mhz. Finally , a variable coupling on the incident port with a possible loop displacement of 25 mm gives a 10^5 to 3.10^{11} Q_{ext} range.

The resonance frequencies of the TE011 and the TE012 modes on which we operate are respectively f_1=4.04 GHz and f_2=5.66 GHz. The corresponding geometric factors are G1=722 Ω and G_2=853 Ω for the overall cavity, G'_1=3298 Ω and G'_2=2254 Ω for the only end plate. The maximum magnetic field is situated on the half diameter of the end plate (and simultaneously on the half length of the cylindrical wall for the TE011 mode).

2.2- Thermometry.

In order to localize defects of the coated disc in superfluid helium, we use sensitive fixed thermometers developped at IPN Orsay [13]. Forty probes, 10 mm in diameter, are mounted and pressed with a thermal bonding agent on the plate under test. The temperature mapping is performed by a scanning technique using HP 44705 relay multiplexers and a HP 3458 voltmeter. A particular bath temperature sensor is scanned after each other one in order to correct the bath temperature variation during the test sequence. The resolution of the RFon-RFoff differential temperature measured is better than 0.1 mK. We have checked its response and linearity as a fonction of the power density $\frac{1}{2}R_sH^2$. These results are reported in [13].

2.3- RF Experiments.

The quality factor Q of the cavity is measured by the usual decrement method. A preliminary test is first carried out with a RRR=180 Nb end plate in order to determine the surface resistance of the cavity main body. Then, from the test performed with the coated disc, we obtain the surface resistance of the coating by substracting the contribution of the cavity body.

The validity of this methode is based on the invariance of the surface resistance of the niobium cavity from one test to another one. In order to check this reproducibility after disassemblings and reassemblings without any treatmement of the cavity, the first experiments were carried out with niobium discs. For three consecutive tests with different end plates chemically treated, the residual surface resistance at T=1.6 K and f=4 GHz was R_{res}= 100, 130, and 105 nΩ. For three other tests performed with the same Nb disc we obtained successively R_{res}=50, 70, and 70 nΩ. Then, in the conditions of our experiment R_{res} remains relatively insensitive to exposure to atmosphere. No chemical treatment of the cavity is needed between two successive tests.

In order to reduce uncertainties, tests with niobium discs are systematically carried out after 2 consecutive tests with coated discs. For the test with the coated disc, the niobium R_s(B) curve adopted, results from an interpolation of the preceding and following smoothed Nb measurements.

With such precautions (repetitive measurements, averaging, smoothing), we estimate the Q measurement error at ±4%.

At T=1.6 K the major part of the error on the coating R_s is determined by the uncertainty on the R_{res} of Nb i.e ±20nΩ at 4 GHz, and ±50 nΩ at 5.7 GHz.

At T=4.2 K the R_s error results from the Q errors on each of the two measurements with Nb disc and with coated disc. It becomes very important when the coating surface resistance is lower than the Nb one.

2.4- Results obtained for 10 significant tests.

2.4.1- Surface resistance at zero field

-At f=4.04 GHz and T=1.6 K
R_{res}=400 to 1600 nΩ (mean value 900 nΩ)

with $\Delta R_{res} = \pm 80$ to ± 100 nΩ

- At f=4.04 GHz and T=4.2 K
  R_s=1600 to 5800 nΩ (mean value 4000 nΩ)
  with $\Delta R_s = \pm 1120$ to ± 1240 nΩ

-At f=5.66 GHz and T=1.6 K
  R_{res}=800 to 2600 nΩ (mean value 1600 nΩ)
  with $\Delta R_{res} = \pm 90$ to ± 140 nΩ

-At f=5.66 GHz and T= 4.2 K
  R_s=3000 to 9400 nΩ (mean value 6000nΩ)
  with $\Delta R_s = \pm 1070$ to ± 1270 nΩ

-Frequency influence on the residual resistance

For the two frequencies f_1=4.04 GHz and f_2=5.66 GHz, $(\frac{f_2}{f_1})^2$=1.96, we obtained a ratio $\frac{R_{res}(f_2)}{R_{res}(f_1)}$=1.3 to 2.2 (mean value: 1.9). From this results,it seems that the residual resistance varies as the square of the frequency.

2.4.2- Penetration depth

With a program based on a model developped by H. Safa in [14], the values obtained for λ_L : 180 to 360 nm (mean value 290 nm) are higher than the predicted value of 151.5 nm [1]. S. Calatroni at CERN, for NbTiN films at f=500 MHz, has also obtained values comprised between 210 and 316 nm [15].

2.4.3- Surface Resistance dependence on the magnetic field

- For all the tested coatings we observe a large increase of the residual surface resistance with the field level, whereas R_{res} of Nb keeps a constant value of about 70 nΩ up to the quench at 50 mT (fig.4). This R_{res}(B) slope, which depends strongly on the elaboration parameters of the deposits, has been observed for all superconducting coatings deposited by a sputtering method. It might be related to a granular superconductivity phenomenon [16].

- We also notice the same R_s variation with the field level at T=4.2 K and T=1.6 K (fig. 4 and 5). The residual surface part is therefore very important on the R_s at 4.2 K.

R_s(T) curves measured for some discs show that R_s is nearly constant below 2.5 K. In spite of the fact that we have got only few experimental points with large errors between 4.2 K and 2.5 K, it seems that we cannot correctly fit them with the BCS resistance computed by Halbritter's code [17]. This is probably related with the granular structure of the NbTiN films.

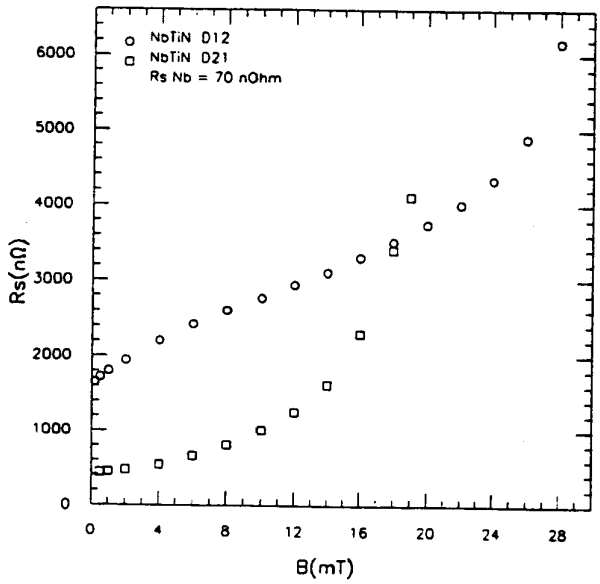


Fig.4 Residual surface resistance of the D12 ($Nb_{0.36}Ti_{0.64}N$) and D21 ($Nb_{0.70}Ti_{0.30}N$) coatings as a function of the magnetic field at f=4 GHz and T=1.6 K.

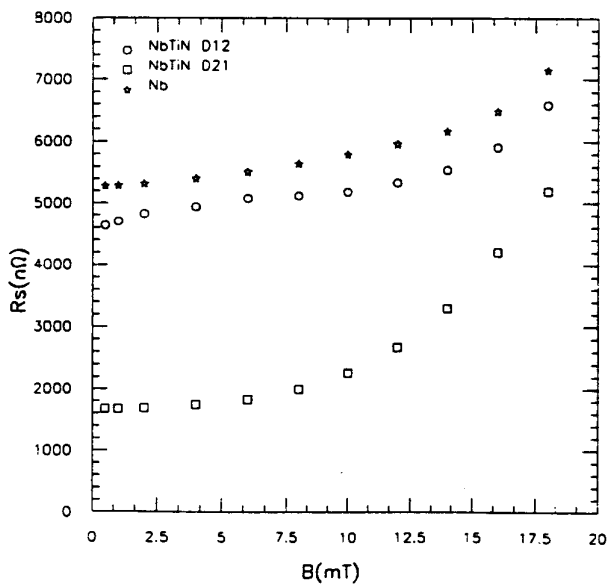


Fig.5 Surface resistance of the D12 ($Nb_{0.36}Ti_{0.64}N$)and D21 ($Nb_{0.70}Ti_{0.30}N$) coatings compared to the surface resistance of a massive Nb disc at f=4 GHz and T=4.2 K

- From all the results we have obtained with coatings prepared in different conditions, one can distinguish 2 sorts of R_s(B) curves:

a first one (D21 type, fig.4 and 5) with low R_s values at low field, but with a steep slope with B and a quench from B=11 to 22 mT.

a second one (D12 type, fig.4 and 5) with higher values of R_s at low field, but with a much lower increase with B and a quench from B=20 to 28 mT.

- The correlations between the sputtering parameters, the sample characterizations, and the R_s values are still not clear, but we have observed two general tendencies:

1. The BCS surface resistance is lower for high Nb content coatings. From the two first $Nb_{0.70}Ti_{0.30}N$ coatings recently tested the measured BCS resistance was 60% lower than for the preceding $Nb_{0.36}Ti_{0.64}N$ ones in relation with a corresponding increase of T_c from 13.4 to 15.4 K.

2. The R_s(B) slope decreases significantly and the maximum field increases when the coatings are prepared with a negative bias voltage applied to the substrate during sputtering (between -50 and -100 V).

- The maximum RF magnetic field limited by quench has been obtained with the D12 end plate of $Nb_{0.36}Ti_{0.64}$N composition and Tc=12.95 K. Its value of 28 mT corresponds to the critical field H_{c1} for $Nb_{0.36}Ti_{0.64}$N films reported in [1] . In all our tests of NbTiN coatings on copper discs no particular local heating has been detected by the thermometers just before quenching (measured ΔT not higher than 350 mK). Moreover, for the two films of lowest R_s: D1 and D21 for which no RF power limitation has occured at 4.2 K, the quench field level was the same at T=4.2 K and T=1.6 K. This seems to reveal a magnetic quench occuring at a field level more or less close to the critical field H_{c1}, but more investigation is needed to verify such an hypothesis.

Conclusion

A surface resistance lower by a factor of 3 than the surface resistance of niobium has been obtained at 4.2 K and 4 Ghz (about 1600 nΩ compared to 5200 nΩ for niobium). Significant improvement of the R_{BCS} value has been achieved after we have increased the niobium content of the coatings up to the $Nb_{0.70}Ti_{0.30}N$ composition. But the residual surface resistance is important : the lowest obtained i.e 400 nΩ at 1.6 K and 4 GHz is much higher than the 70 nΩ niobium one.

The maximum field level attained before quenching is 28 mT, value which corresponds to the critical field H_{c1} reported in [1]. We expect to determine soon whether the quenches in our deposits are of magnetic or thermal origin.

Our work will now consist in preparing NbTiN coatings with the new sputtering set up that we have developped in our laboratory, and in completing their optimization before depositing inside cylindrical 1.5 GHz cavities.

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