

INFLUENCE OF COATING TEMPERATURE ON NIOBIUM FILMS

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Abstract

The coating of niobium on copper is the technology successfully used for the production of LEP accelerating cavities. A good understanding of the influence of the different coating parameters on the film properties can contribute to improve the RF performance of such cavities.

Several copper samples were coated with a 1.5 μm thick niobium film in a cylindrical magnetron sputtering system, using argon as discharge gas. To study the mere effect of the coating temperature, a 500MHz cavity was equipped with three sample-holders on the equatorial region. The latter were kept at different temperatures during the baking and the simultaneous coating (150°C, 250°C and 350°C). The films were characterised by measuring the RRR, critical temperature, total Ar content, lattice parameter. Films deposited at higher temperatures show higher RRR and lower Ar content. The film lattice parameter and, consequently, the critical temperature change with the coating temperature. The results are interpreted in term of the film bombardment during the growth, of higher niobium surface mobility at higher temperature and of the different thermal expansion coefficients between the niobium film and the substrate.

1. Introduction

The superconducting cavity technology for particle accelerators is based essentially on forming and welding of bulk niobium sheets [1]. The experience gained at CERN for LEP cavities shows that a valid alternative consists in coating copper cavities with a thin Nb film [2]. This technology is also advantageous compared to niobium bulk since copper is cheaper than niobium.

Films show quite a different RF behaviour with respect to bulk. In particular, due to the lower RRR, the surface resistance of a niobium film at 4.2 K is lower than for bulk. Defects present in the film act as pinning centres for the magnetic field resulting in a dependence of the surface resistance on the trapped magnetic flux of $\sim 5\text{n}\Omega/\text{G}$ compared to $>100\text{n}\Omega/\text{G}$ for the bulk case [3]. Even if a residual resistance of a few $\text{n}\Omega$ is measured at zero accelerating field it often deteriorates with the increasing accelerating field. This deterioration is one of the limiting factors of the niobium film technology. A study of the influence of coating temperature on the film properties has been undertaken to have additional information on the film structure which can help understanding such a behaviour.

2. Experimental Procedure

Samples are produced in a cylindrical magnetron sputtering configuration inside a 500 MHz cavity (see fig. 1). Three sample holders are installed on the equator of a stainless steel cavity, each of them supporting four copper samples (10 mm x 35 mm). The temperature of the three sample holders can be independently controlled at 150 °C, 250 °C and 350 °C and kept constant during the baking and the coating. The system is pumped by a turbomolecular pump; after a 20 hours bake at 250 °C an ultimate pressure as low as 10^{-9} Torr is reached at room temperature. The coating parameters (400V, 7.5A, argon pressure 9×10^{-4} mbar, time 50 minutes) for the 1.5 μm niobium-coated samples are the ones typically used to coat 500 MHz cavities except for the different substrate temperatures. After the coating, the samples are exposed to air and analysed by Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD). The inductive measurement of critical temperature, resistive measurement of RRR and measurement of the total argon content are also performed.

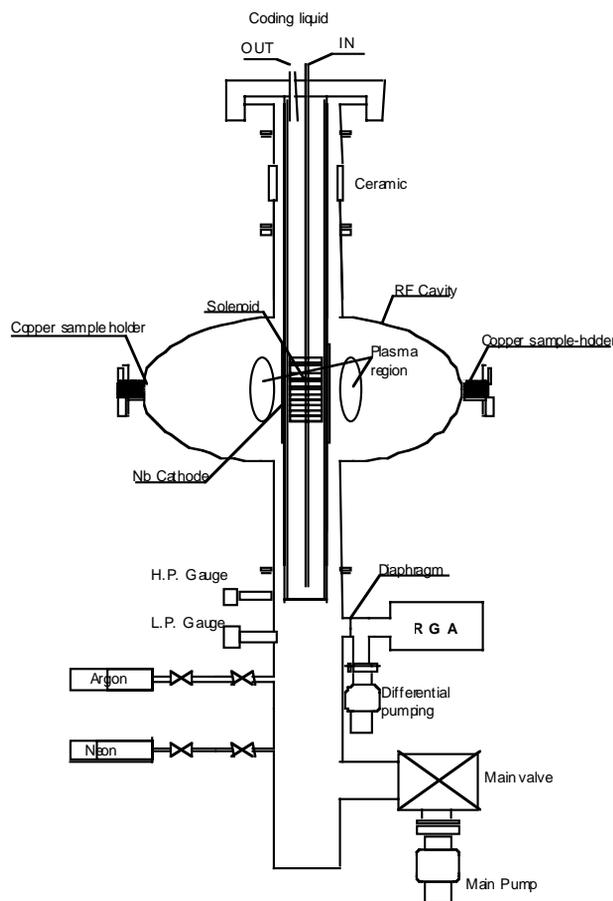


Fig. 1. Schematic view of the sputtering system

2a. Measurement of the Ar content

The copper substrate is removed from the coated samples by immersion in a nitric acid solution. To measure the Ar content of the niobium film the extractions of Ar by heating the film in a HV furnace was firstly tried. Detectable outgassing of argon started at 1300°C and monotonically increased up to 1500°C (maximum furnace temperature). Argon was not completely removed at this temperature.

The technique actually used to fully extract all the argon consists in melting the niobium film. To do so we put the niobium film in contact with a nickel foil and we heat them together. Nickel and niobium form an eutectic ($\text{Nb}_{0.40}\text{Ni}_{0.60}$) which melts at 1175°C . All the gases extracted from the melted film are cumulated in the furnace. When the film is completely melted we open a by-pass that connects the furnace to an UHV system, where a calibrated Residual Gas Analyser (RGA) allows a quantitative measurement of argon. The three samples were measured in sequence, and the argon calibration was performed before and after the measurement. The experimental results for the 3 samples are illustrated in Fig. 2 together with two background measurements. The current corresponding to the mass 40 is plotted versus the time: the total amount of argon can be calculated from the area of the signal subtracting the background once the sensitivity for the gas, the conductance and the pumping speed are known.

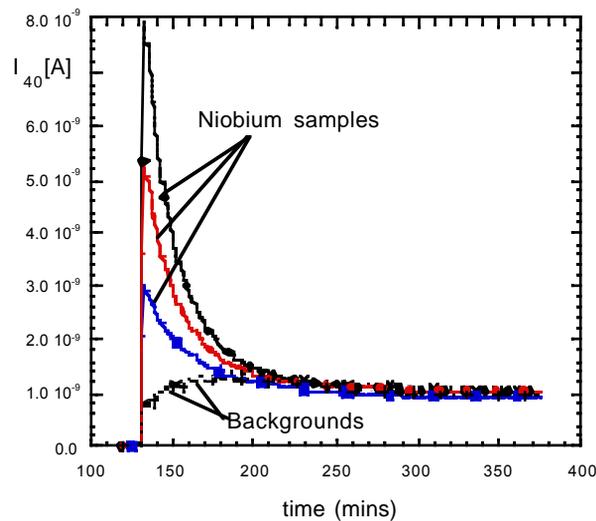


Fig 2. Current of mass 40 for the 3 samples. The total Ar content is obtained from the area below the curve after the subtraction of the background.

2b. Measurement of RRR

The measurement of RRR gives important information on the quality of the produced film. The residual resistivity is a measure of impurity and lattice defects content. In case of niobium films deposited on insulator substrates like quartz, RRR is measured by a standard four-lead technique. On the other hand if the substrate has a much lower resistance than the film (like in the case of niobium on a copper substrate) the measure requires the removal of the substrate. For a better handling of the film we glued a kapton adhesive tape on its free surface before dissolving the copper substrate in a nitric acid bath. The copper on the two extremities of the sample is protected with a resistant varnish to keep a good welding area. We checked that the nitric acid does not deteriorate the RRR values of our films in two ways: by dissolving the copper of two identical films with two different chemicals and by leaving a niobium film on a quartz substrate in the dissolving solution for 48 hours: In both cases, we observed no change in RRR.

2c. Superconducting critical temperature

The measurement of the critical temperature is done by a standard inductive method using the Meissner effect. The sample is placed between the primary and the secondary

coil and the induced voltage in the secondary is recorded using a lock-in amplifier as function of the temperature. Care is taken to work at low frequency (2 Hz), to avoid the screen effect of copper, and at low field (~1 G) to reduce the effect of the finite size of the sample. The samples are cooled by He gas circulation and their temperature is controlled by changing the temperature of the He gas. The measurements are always performed in both directions (decreasing and increasing the temperature) to ascertain that there are no gradients between the sample and the thermometer. A niobium bulk sample of RRR ~300 was measured to check the calibration of the thermometer and result was 9.24 ± 0.04 K

2d. X-ray diffraction

The films are analysed by XRD in the Bragg-Brentano ($\theta/2\theta$) and in detector-scan configuration using a Siemens D5000 diffractometre with a Cu source. The spectra are collected from for 2θ values going from 25 to 130 degrees.

To improve the least square regression which is used for the back extrapolation of the lattice parameter [4], spectra are collected without the nickel filter to obtain additional peaks due to the K_{β} radiation. The peak position and the FWHM are evaluated by a split function fitting the peaks.

3. Results and discussion

The results obtained are summarised in Table I and discussed in the next subsections.

Substrate	T_{coat} [°C]	Ar content [ppm]	RRR	T_c [K]	a_s [Å]
copper	150°C			9.46 ± 0.03	3.3264 ± 0.0012
copper	250°C			9.41 ± 0.03	3.3235 ± 0.0011
copper	350°C			9.32 ± 0.05	3.3198 ± 0.0011
dissolved	150°C	420 ± 50	13 ± 1	9.24 ± 0.05	3.3050 ± 0.0010
dissolved	250°C	240 ± 40	22 ± 4	9.27 ± 0.05	3.3024 ± 0.0010
dissolved	350°C	130 ± 30	40 ± 5	9.23 ± 0.05	3.3003 ± 0.0012

Table I. Results on niobium samples coated at different temperatures (T_{coat}). The critical temperature T_c was measured by inductive method and it is the temperature at 50% of the transition; a_s is the niobium lattice parameter measured in the $\theta/2\theta$ configuration.

3a Ar content and RRR

It is well known that during the coating the discharge gas can be reflected by the cathode as high energy neutral and can be implanted in the film [5]. The influence of the discharge voltage or the discharge bias on the noble gas concentration in the film is well studied [6] Argon content in the film is reported not depend on coating temperatures for temperature lower than 350°C [7]

The results on Argon content and RRR are shown in Fig. 3. The influence of coating temperature on the argon content seems to be important at temperature as low as 150°C.

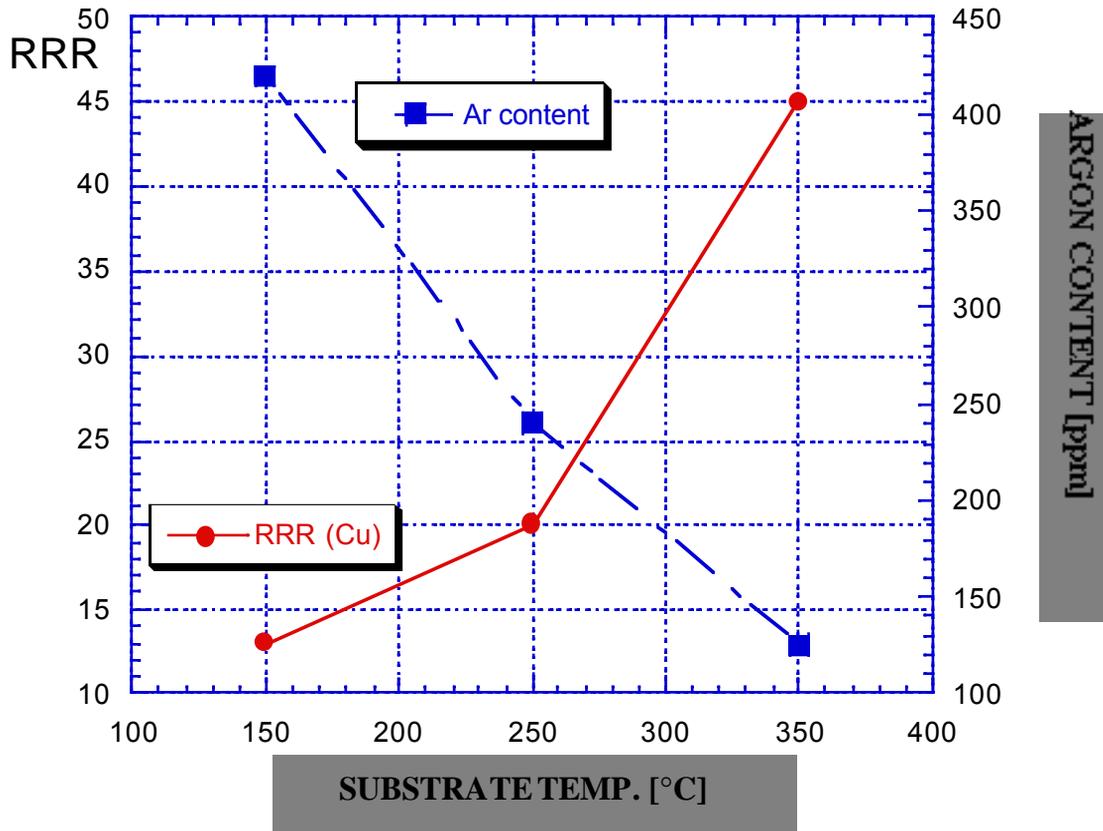


Fig. 3. RRR and Ar content of niobium films as function of the coating temperature. The measurements have been done on niobium films after dissolving the copper substrate. The point size is chosen to be equal to the error of the measurement.

As expected the RRR of niobium increases with the coating temperature since the higher surface mobility during the coating contributes to reduce lattice defects and impurities content like argon. The high RRR values obtained even at relatively low temperature (usually niobium is deposited on substrate at 600-800°C) are essentially due to the good vacuum in the deposition chamber and to the large area of coating that acts as a getter pump during and after the coating. The good vacuum conditions drastically reduce the reactive impurity content in the niobium film that results in an increase of RRR. Preliminary results indicate that reducing the sputtering rate and increasing the substrate temperature should result in a further RRR increase.

3b Structure

The x-ray spectra show that the niobium films grow preferentially in the $\langle 110 \rangle$ direction, independent of the coating temperature. The convolution of the peaks due to the $K_{\alpha 1}$ and $K_{\alpha 2}$ lines is due to small grain size and/or to the strain in the film. The dependence of the peak FWHM on $\tan\theta$ clearly indicates that microstrains are mainly responsible for peak broadening (see Fig. 4).

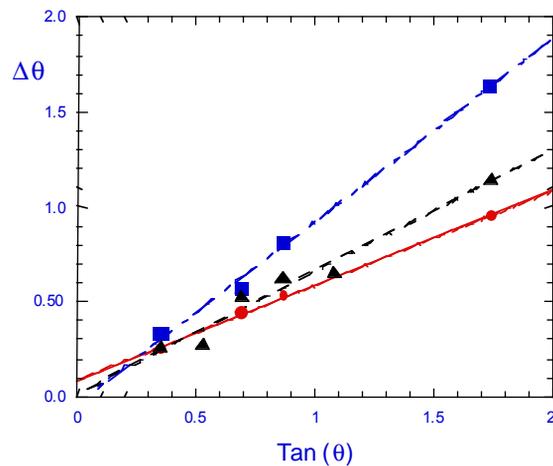


Fig. 4. The FWHM for the 3 films is proportional to $\tan\theta$ indicating that peak broadening is essentially due to strain in the film

The lattice parameter of niobium films deposited on copper is expanded in the z direction. X-ray spectra collected from niobium films after the dissolution of copper substrate show a lattice parameter that is very close to the niobium bulk value (3.303\AA) for all the coating temperatures. These results indicate that the lattice deformations in our niobium films are mostly due to the presence of the substrate (the film is free in z and the measured expansion in this direction can only be a consequence of the compression in the xy plane).

Two main phenomena are responsible for the film compression:

- The thermal stress due to the different thermal expansion coefficient between niobium and substrate
- The bombardment of high energy neutrals [9] and the self-bombardment of the sputtering metal [10]

The expansion in z direction contributed by differential thermal expansion between Nb and Cu can be calculated under two hypotheses:

- 1) by supposing that the niobium layer can be considered as an isotropic elastic body (absence of preferential growth in z direction). In this case the expansion in z direction, due to the isotropic contraction of the niobium in the xy plane contributed by the differential thermal contraction of niobium and copper, can be calculated on the basis of the tabulated Poisson number (0.39 for niobium).
- 2) By supposing that the niobium layer is perfectly oriented with its $\langle 110 \rangle$ axis of growth parallel to the z direction. In this case the xy plane can be considered elastically isotropic and having an elastic module equal to 103 GPa. $E_{\langle 110 \rangle} = E_z = 92$ GPa has been calculated by the niobium elastic constant c_{11} , c_{12} , c_{44} . The expansion in z can be evaluated through finite element analysis (ansys).

Coating temperature	Calculated		experimental
	Isotropy	<110> oriented	
150°C	3.3066	3.3060	3.3264±0.0012
250°C	3.3116	3.3097	3.3235±0.0011
350°C	3.3170	3.3137	3.3198±0.0011

Table 2. Lattice parameter for niobium deposited on copper calculated from the different thermal expansion coefficients compared to the experimental value (values are quoted in Angstrom)

The experimental value of expansion in z at 150°C is much greater than the calculated thermal contribution as a simple thermoelastic effect.

To better separate the thermal contribution from the intrinsic contribution due to the bombardment during the growth we deposited a niobium film on a niobium substrate at 150°C and we measured a lattice parameter equal to 3.3190±0.001Å that is free of thermal contribution. The difference between the lattice parameter measured on Nb/Cu and the calculated thermal contribution is in good agreement with the value measured for niobium on niobium (see also Fig. 5).

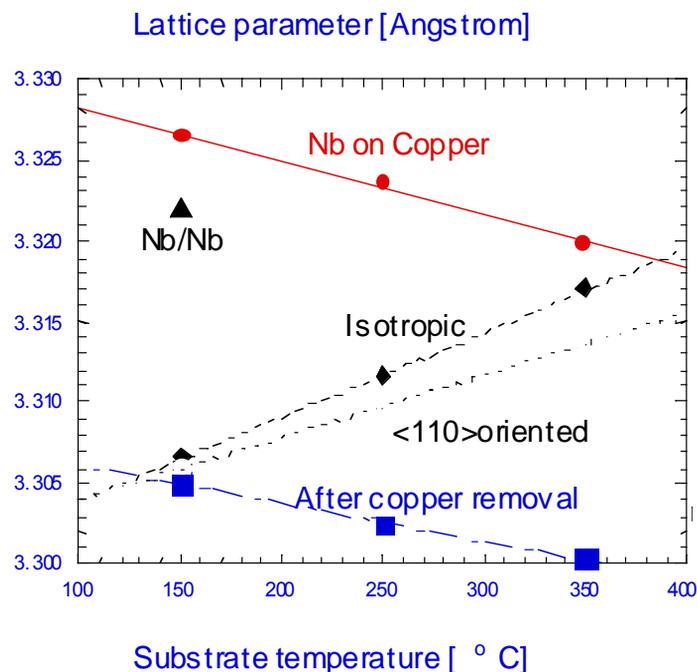


Fig. 5. Lattice parameter as function of the coating temperature for all the samples. Lines are intended to guide eyes along the same family of points.

The observed dependence of the lattice parameter of the niobium-film on temperature of coating cannot be explained on the base of the thermal contribution. The higher difference between measured strain and thermal strain at low temperature might be due to the decreased surface mobility of the niobium atoms with decreasing coating temperature. A second hypothesis would be that the annealed copper used as substrate could be plastically deformed near the interface by the niobium layer during the cool

down from the higher temperatures. We plan to produce Nb on Nb samples at different temperatures to evaluate the evolution of the intrinsic contribution with temperature and discriminate between these two possible explanations.

3c Superconducting critical temperature

The results are shown in Fig. 5 as function of the niobium lattice parameter. A niobium bulk sample of RRR=300 was measured to check the calibration of the thermometer. The reported critical temperatures are the temperatures at half transition. The results are in qualitative agreement with Heim and Kay [7] The higher critical temperature found in [7] could be due to the resistive method used to measure the T_c . As for the lattice parameter, after the copper dissolution, the T_c returns to the standard niobium value.

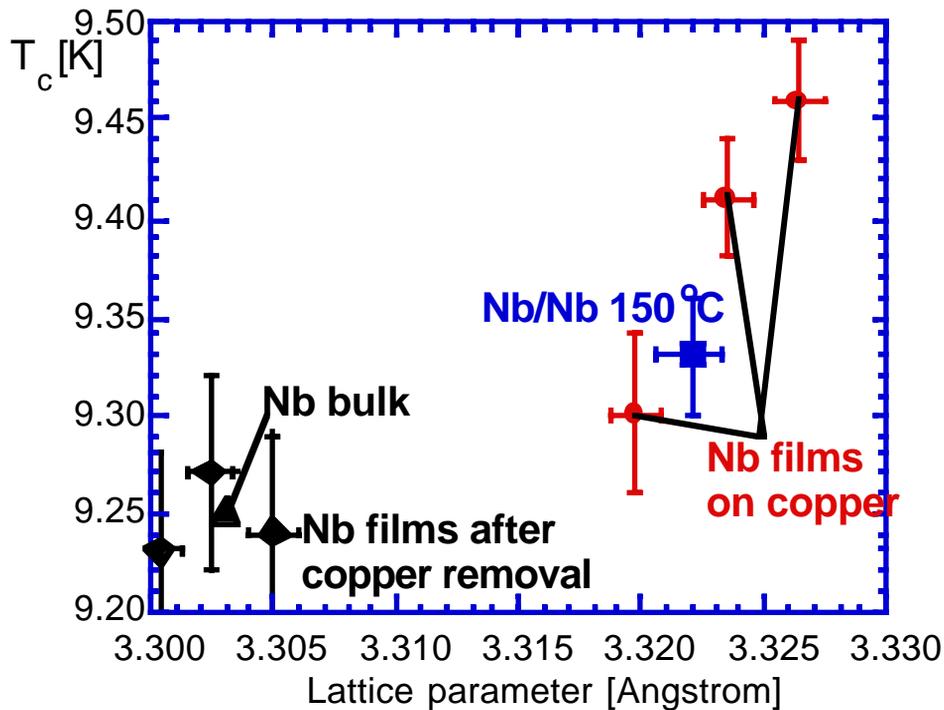


Fig. 6. Dependence of critical temperature on niobium lattice parameter. The bulk value is reported as reference. It is also show the reduction of critical temperature once the copper substrate is removed and the data obtained from a Nb/Nb film.

4. Conclusions

Substrate temperature during the coating influences the niobium film properties. In particular increasing the coating temperature the quality of niobium films improves as far as Ar content and RRR are concerned. The niobium films are in a compressive stress that is mainly due to the bombardment of high energy neutral (argon and/or niobium) and it is reduced when the substrate is coated at higher temperatures. Future studies are needed to understand if this reduction is related to the recovery or to the reduced mechanical properties of the copper substrate.

Due to the particular geometry where all the vacuum chamber is covered with the film the impurities present in the niobium layer are reduced respect to the standard planar magnetron sputtering: Therefore the coating system developed for cavity production is a powerful tool to obtain films of high quality.

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