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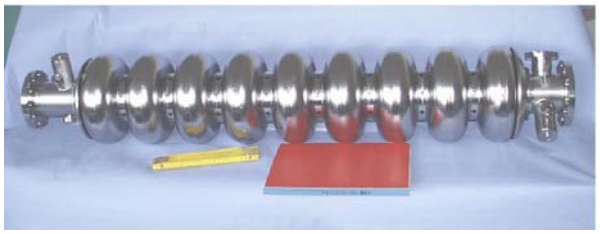

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"Report on Deposition of HTc Material by UHV Cathodic Arc"

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Abstract

The Cathodic Arc technique in high vacuum is a well known, mainly used to produce hard nitrides coatings on cutting tools having complex shapes. The very high energy of ions arriving on the substrate (up to several hundreds volts) is believed to be the origin of the excellent adhesion and the good quality of the treated materials.

On the other hand, to our knowledge, there was no literature on the production with the arc technique of nitrides for superconducting applications. One of the main reasons for that, we thought, was that, in high vacuum, contamination of the cathode originating from residual gases would deteriorate the purity and the transport properties of superconducting materials. On the contrary, the arc working in UHV we did develop would preserve the purity of the cathode material.

Therefore we started to investigate the production of nitrides for superconducting application using the UHV arc technique at low temperatures since we also believed that the thermal energy needed to grow good nitride films could be replaced by the kinetic and potential energy of ions arriving on the substrate.

Acknowledgements

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Report on Deposition HT_c Material by UHV Cathodic Arc

In principle, thin film deposition techniques for manufacturing a RF cavity open the way to the use of other superconducting materials which, unlike Nb, are not usable in bulk form for the purpose. The materials that first come into consideration are compounds with a higher critical temperature and a higher thermodynamic critical field than Nb.

This because a higher critical temperature, T_C , should correspond to a lower BCS resistance, R_{BCS}, and therefore improve the cavity quality factor at 4.2 K; in addition, a higher critical field would allow for a theoretically higher maximum accelerating field, once all other limitations of technological nature overcome.

When the cavity working temperature and its frequency have been fixed, e.g. at $T = 4.2K$ and $f = 500$ MHz respectively, R_{BCS} depends only on the material energy gap and on the material normal state resistivity.

All proposed materials are alloys (NbN, NbTiN, Nb_3Sn, V_3Si, …) with a relatively high electrical DC resistivity, $\rho_n = 1/\sigma_N$, even at low temperature, so that for them the so-called "dirty limit" condition

$$\xi_0 / l \gg 1 \qquad 1)$$

can be applied, where ξ_0 is the material coherence length and l its mean free path.
In the above limit, the theoretical formula given by the BCS theory for the surface resistance can be approximated by an expression of the form:

$$R_{BCS}(T) = A\omega^2 \sqrt{\rho_n} \frac{e^{-\alpha \frac{T_c}{T}}}{T} \qquad 2)$$

A being a constant weakly dependent on the material, ω the operating angular frequency, and $\alpha = \Delta / T_C$ is the strong coupling factor taken intio account simply by allowing its value to depart from the standard BCS one $\alpha = 1.76$.

Niobium based nitrides are, in particular, very promising materials for the realisation of superconducting thin film coated copper RF cavities for particle accelerators. According to the BCS theory, at an operation temperature of 4.2 K, their relatively high critical temperature should in fact allow for a higher quality factor than that of bulk Nb cavities or thin Nb film coated ones, at present in use.

In Fig. 1 Lines of equal R_{BCS}, computed in the strong coupling approximation at 4.2 K and 500 MHz, are plotted in bi-dimensional space (ρ_n, T_c),.

Measured R_{BCS} data are also plotted of sputtered films of (NbTi)N at 200°C (full square), (NbTi)N ones at 600°C (empty square) and NbN ones at 200°C. (empty circles). For comparison, under similar conditions, pure Nb sputtered Cu surfaces show $R_{BCS} \simeq 55 n\Omega$.

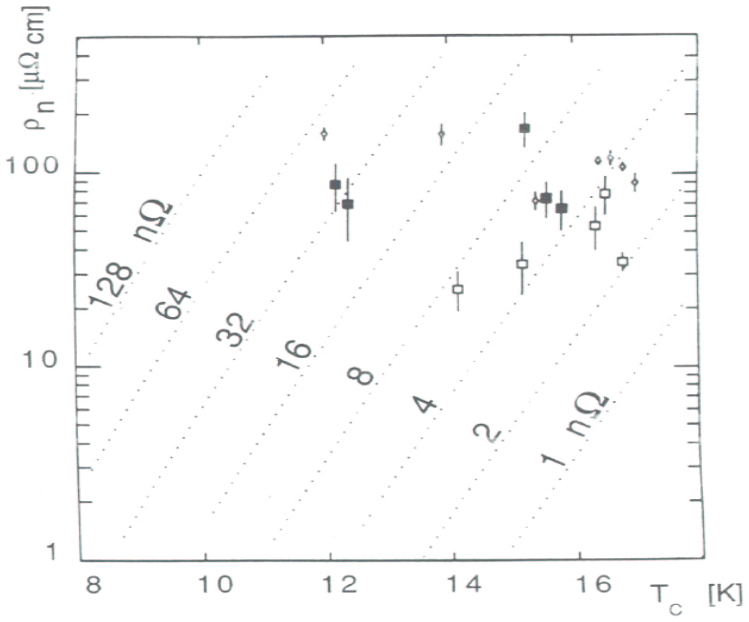

Fig. 1 - Lines of equal R_{BCS} at 4.2 K and 500 MHz in the bi-dimensional space (ρ_n,T_C), at T= 4.2 K, f = 500 MHz and in the strong coupling approximation. (NbTi)N at 200°C (full square); (NbTi)N at 600°C(empty square); NbN at 200°C. (empty circles).

The state of the art using Magnetron Sputtering

Deposition of NbN and (NbTi)N thin films by reactive sputtering (mainly planar magnetron sputtering) has been investigated by several authors.

Much work has been done in the planar configuration and excellent results were obtained. It has been shown that it is possible to epitaxially grow a NbN film on a MgO substrate even at room temperature and that the superconducting properties are very high quality. Unfortunately the deposition conditions (nitrogen flow rate, nitrogen/argon ratio, discharge power, substrate temperature…) are extremely critical and, in particular, the distance between cathode and substrate, which affects the energy of the ions reaching the substrate, plays a crucial role.

Two studies made at CERN have focussed on a cylindrical magnetron configuration designed to coat 500MHz RF copper cavities for LEP (*Sergio Calatroni's thesis*) and 1.5GHz ones (*Massimo Marino's PHD thesis*). Unfortunately the phase diagram of niobium and Nb-Ti nitride turns out to be quite complicated: the superconducting cubic (delta) phase, unstable at room temperature, in the case of niobium nitride is only stable at temperatures higher than 1300C and can be formed, in an equilibrium process, only at temperatures higher than 1380C. However, Magnetron Sputtering and arc deposition are not equilibrium processes and the cubic phase is expected to grow also at temperatures lower than 1300C. The best superconducting properties were in fact obtained by heating the substrate to at least 600C but heating substrates to ~200C

resulted in films with good superconducting properties and only a slightly lowered T_C (from about 17K at 600C to about 15K).

The above results can be (partially) understood considering that nitrides are obtained evaporating a metallic cathode (Nb, NbTi) in presence of Nitrogen or of an Argon/Nitrogen mixture. The reaction between nitrogen and the metal usually takes place on the surface of the growing film and the temperature of the substrate is important to provide the additional thermal energy needed to obtain the good cubic nitride phase (delta). If the nitrogen pressure is too high, the cathode surface itself becomes a nitride causing the deposited films to have poor structural and electronic qualities.

Energy-resolved ion mass spectroscopy has been recently applied to obtain information on the reactive sputtering process and to measure the particle bombardment on the growing film (*Massimo Marino' Thesis*). It was found that the transition from the metal to nitride sputtering regime, which takes place when the reactive gas injection rate exceeds a threshold dependent on the discharge power, involves a considerable decrease in the mean energy of the incoming ions. This was considered to be at the origin of the poor superconducting properties of films deposited in the nitride-sputtering regime.

A series of 1.5 GHz (NbTi)N/Cu cavities has been coated at CERN, varying the cathode composition, the film thickness and the deposition temperature. The RF tests show in several cases the presence of an additional low energy-gap contribution to the BCS surface resistance [ref]. A serious drawback in the performance of these cavities is represented by the relatively high value of the residual resistance, and its strong increase with increasing accelerating field. As a result, a residual resistance value of 1000nΩ is reached for accelerating field (E_{acc}) about 2 - 2.5 MV/m (**Fig.** 2)

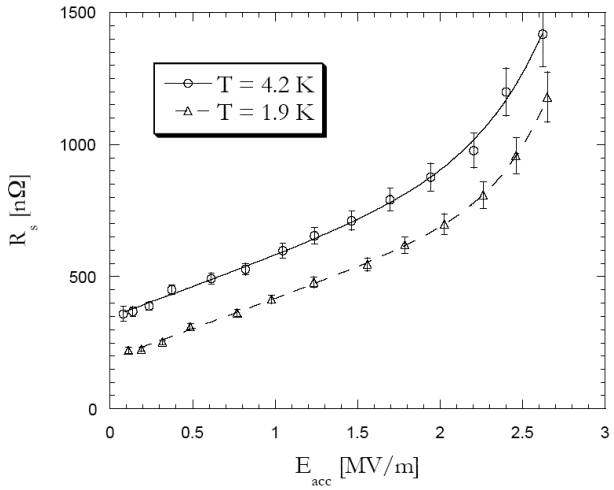

Fig. 2: Measured surface resistance vs. accelerating field of a typical 1.5GHz, magnetron sputtered cavity coated with (NbTi)N at CERN. The deviation from the linear behaviour, observed for E_{acc} > 2 MV/m, is related to the onset of field emission (*M. Marino PhD thesis*).

As a consequence, in the best cases, the quality factor at 4.2 K is higher than for Nb/Cu cavities only for accelerating fields much lower than those required by particle accelerators. The reason for such behaviour is not completely understood, however it is our opinion that the low energy-gap contribution is due to the magnetron sputtering technique failure to produce the proper deposition conditions over the whole cell surface. Field dependent degradation of the surface resistance could also be due, as proposed by Attanasio, Maritato and Vaglio [Vaglio91], to the presence of a granular structure with different phases along grain boundaries producing a weak coupling between superconducting grains.

Status of nitrides deposition by UHV cathodic arc

The Cathodic Arc technique in high vacuum is a well known, mainly used to produce hard nitrides coatings on cutting tools having complex shapes. The very high energy of ions arriving on the substrate (up to several hundreds volts) is believed to be the origin of the excellent adhesion and the good quality of the treated materials.

On the other hand, to our knowledge, there was no literature on the production with the arc technique of nitrides for superconducting applications. One of the main reasons for that, we thought, was that, in high vacuum, contamination of the cathode originating from residual gases would deteriorate the purity and the transport properties of superconducting materials. On the contrary, the arc working in UHV we did develop would preserve the purity of the cathode material.

We did therefore proposed to investigate the production of nitrides for superconducting application using the UHV arc technique at low temperatures since we also believed that the thermal energy needed to grow good nitride films could be replaced by the kinetic and potential energy of ions arriving on the substrate.

In fact, while the kinetic energy of arc produced Nb ions is on average ~100eV, the presence of a gas such as Argon or Nitrogen in the vacuum chamber, can reduce it to few tenth of eV. On the other hand, Nb ions have a potential energy of about 45 eV due to their +3 average ionization, which is reduced, by charge transfer between niobium ions and the nitrogen gas, to ~7eV of single ionized Nb.

Such a reduction in kinetic and potential energy due to the presence of nitrogen in the vacuum chamber can be compensated by applying a negative bias to the substrate to precisely adjust the energy of ions hitting the substrate, in a similar way as done by adjusting the cathode-substrate distance in the magnetron sputtering case, in order to obtain the desired structural and superconducting properties.

It was also thought that in such a way good superconducting films could be produced over a larger range of deposition parameters, which would allow to obtain a uniform coating over the whole surface of a cavity cell. *(and remove the origin of the low energy-gap contribution to the surface resistance.)*

This conjecture was supported by our first deposition on 13 November 2001 when, using a very simple and not optimized system, a few sapphire samples were UHV arc coated in nitrogen atmosphere, at different N partial pressures.

$R_{BCS}(T)$ of the best coated sample (see Fig.3) showing a ~5K wide transition to the SC state starting at about 15K, was a clear indication that the cubic δ phase was

formed. Despite the fact that the result was not excellent, since the wide transition indicated that the film was not uniform, with the presence of several phases, in particular beta and gamma ones with low nitrogen content, we were convinced that it would be possible to optimize the deposition parameters and the film superconducting properties.

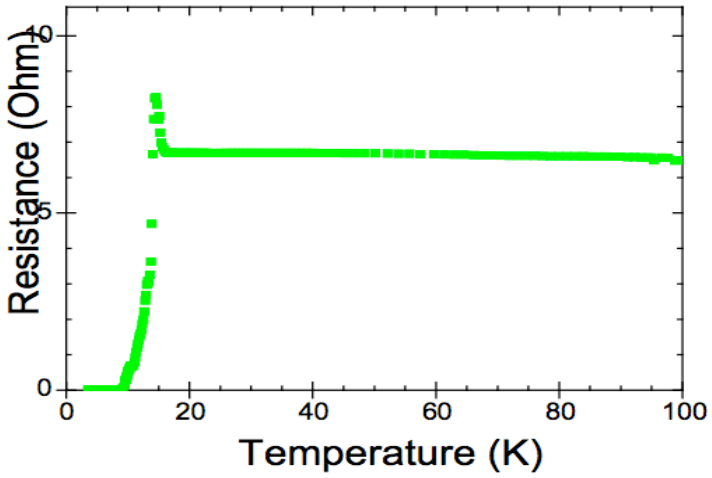

Figure 3 -Transition to the superconducting state of one of the first UHV arc deposited NbN samples.

We then optimised the deposition system in term of arc ignition, plasma transport, arc stability and thermal stability for the production of good superconducting Niobium films. A new vacuum system was built, on the basis of the experience acquired producing niobium films, to which a N injection line was added equipped with mass-flow meter in order to control the nitrogen flux. Extra coils were also added to control the magnetic configuration and the plasma transport in order to optimize the Nb ion flux reaching the substrate. A schematic drawing of the magnetic configuration of the nitride deposition system is shown in **Fig.** 4.

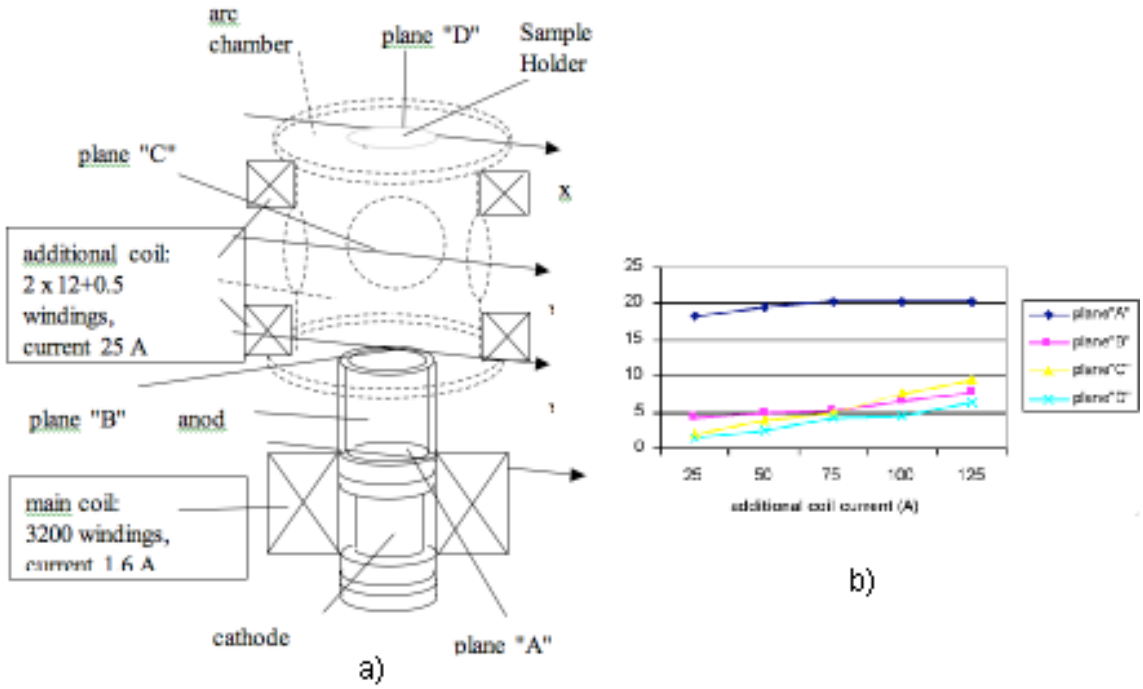

Figure 4 a) schematic drawing of the magnetic configuration of the nitride deposition system (low part) and vertical component of the magnetic field along different planes as function of the current in the coils. b) Vertical component of magnetic field vs additional coil current . Main coil current is 1.6A. *(Figura a) da aggiustare)*

Spectra of the residual gas composition are showm, after bake-out to a pressure of ~$2x10^{-10}$mbar (a) and after injection of small amount of nitrogen (b), showing that the only injected masses are 14 and 28, corresponding to atomic and molecular nitrogen respectively.

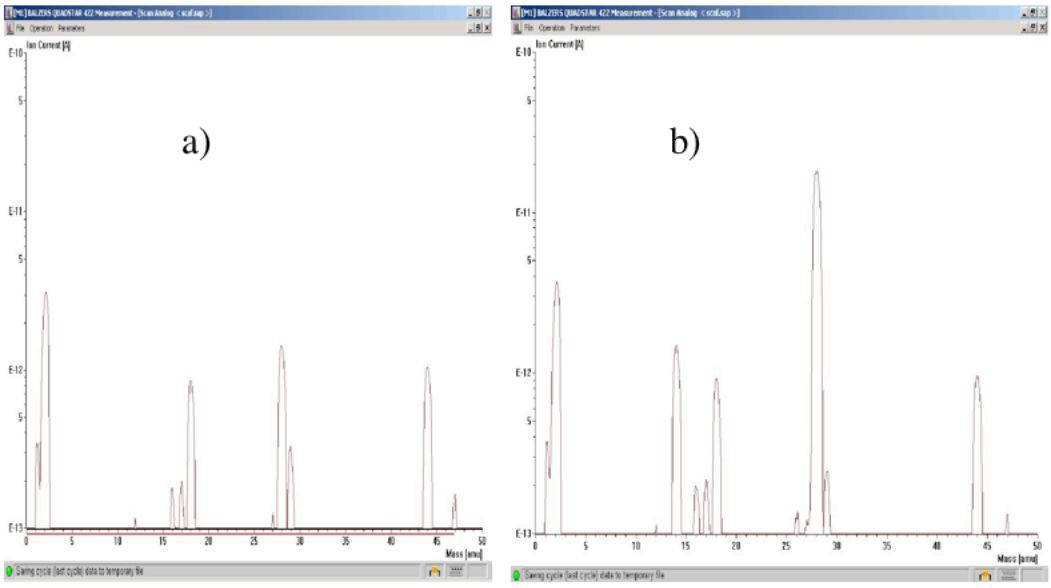

Fig. 5 - Residual gas spectra: a) after bake-out, b) after injection of a small amount of pure nitrogen.

Despite having coated a number of sapphire samples under different conditions, ranging from room temperature to 200C , from a 0V to -120V bias and with a nitrogen pressure from $1x10^{-4}$mbar to $1x10^{-1}$mbar, no results better than those of Fig. 3 were obtained.

On the other hand, adhesion problems were experienced inside the vacuum system, as evidenced in figure 6. Peeling was present on all parts of the vacuum system connected to ground while good adhesion was obtained on the only negative biased surface of the sample holder. Because for safety reasons the major part of the vacuum system was grounded peeling was a severe problem because peeled-off metallic fragments would fall into the cathode region causing short-circuiting the cathode to the anode.

Fig.6 – Peeling on the anode in the cathodic region

According to what reported in literature on nitrides deposition by sputtering, there are two fundamental regulating the growth of Nb nitride films:

a) the ratio between the Nb deposition rate and the flux of nitrogen atoms at the surface of the growing film must be kept at a given, constant value. A limit on the maximum discharge power is set by the nitrogen pressure becoming high enough for the cathode to turn into a nitride which reduces the energy of the evaporated ions;

b) the substrate temperature and/or the cathode-substrate distance

In the arc deposition case we expect the important parameters to be the same. Considering that in the sputtering case the typical nitrogen pressure in the vacuum chamber is the range of 10^{-3}mbar, in our tests the arc discharge current was kept constant, at the relatively low value of 100Amp, while the nitrogen pressure in the chamber was varied from 10^{-5} to 10^{-1}mbar in steps usually of a factor 2. Sample bias values were also varied from 0 up to -120V in 20V steps. No nitride cubic phases were obtained but only lower nitrogen content β and γ phases.

The results indicated that the nitrogen pressure should be further increased, but unfortunately the arc started becoming unstable as the pressure was increased above $\sim10^{-2}$mbar making it impossible to deposit film at pressures of $\sim10^{-1}$mbar or higher.

The instability was connected with an inversion in the sign of the current on the biased sample holder. Since the sample holder was negative biased (between -40 and -120V) we usually register a positive ion current, however, after injection of nitrogen the current reduces with increasing pressure and starts to become negative for pressure higher than 10-2mbar.

The arc current value and the magnetic coil configuration were then changed to reduce the niobium ion flux on the sample, and the measurements repeated but without success.
A much finer scan of the nitrogen pressure and possibly of the bias values would have probably been needed but it was concluded that it would be too time consuming in view of the other higher priority project tasks and, most of all, because it was felt that the extreme criticality of parameters would make it very difficult to obtain the desired phase everywhere on the cavity cell complex geometry surface.

Furthermore, SEM images showed the presence of aggregates on the film surface: on the nitride films, together with the usual macro–particle Nb spheres originating from the cathode, there were several particles with micrometer dimension and complex shapes, as shown in Fig.7. Such aggregates are believed to be formed in flight, from cathode to substrate, and to cannot be easily eliminated by the 90 degree macro-particle filters.

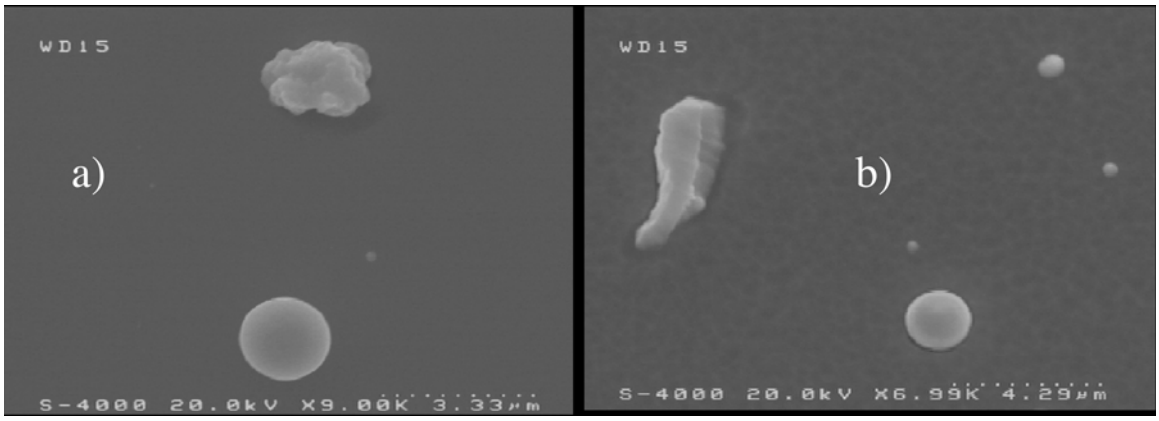

Figure 7 - SEM images of nitride film surfaces: spherical niobium macrodroplet are present together with aggregates of different shapes probably formed from the reaction of niobium and nitrogen in flight from the cathode and the substrate.

Conclusion

Several films have been deposited using a niobium cathode in a nitrogen atmosphere. The nitrogen pressure, arc current and voltage bias were varied in order to obtain nitride films with good superconducting properties. Despite the effort the maximum Tc obtained was ~15K with a large transition width. The films were not uniform and presented on the surface aggregates of irregular shape formed in flight. While further work would be needed to optimize the deposition parameters in a planar arc configuration, due to the extreme criticality of parameters it was concluded that it would be very difficult to obtain the desired nitride cubic phase everywhere on a cavity cell complex geometry surface.

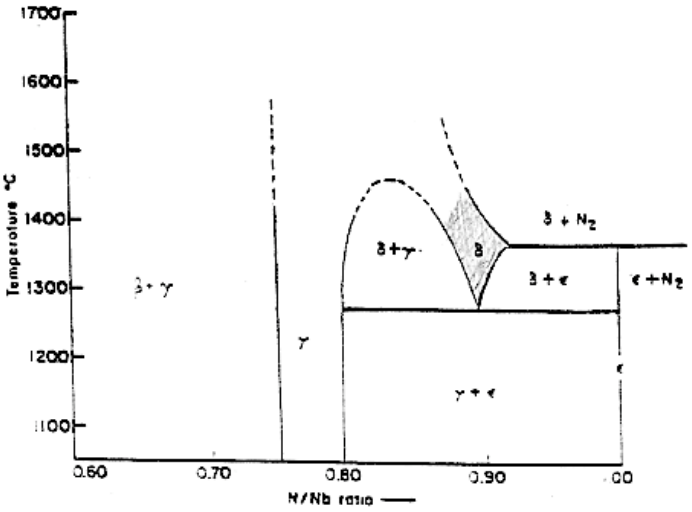

Fig. 8 - Phase diagram of NbN at nitrogen atmospheric pressure: the grey area indicates the narrow region where the superconducting delta phase can be obtained without the presence of other phases.

The delta-cubic phase is thermodynamically stable only at temperature higher than 1280C and in a narrow range of nitrogen concentration. The film deposition techniques are not at the thermo dynamical equilibrium and they should provide the energy necessary to form the cubic phase. Probably in the arc deposition the niobium ion energy distribution is too large to obtain a single-phase film (a large difference in ion energy is equivalent to a different temperature). To deposit single-phase films we should develop techniques that allow to uniform the ion energy distributions. However, even if theoretically achievable, they it was found that it cannot be easily applied to such a complex cavity shape.

References:

[Vaglio91] C. Attanasio, L. Maritato, R. Vaglio Phys Rev B 43 (1991) 6128