NUCLEAR MICROPROBE STUDIES OF IMPURITIES SEGREGATION IN NIOBIUM USED FOR RADIOFREQUENCY CAVITIES

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SUMMARY
Grain boundaries of different niobium samples, including cavities samples were studied systematically by the mean of a nuclear microprobe in order to detect eventual segregation of tantalum or titanium, but also of light impurities like carbon and oxygen. This instrument allows to explore small areas (~ 1 μm^2) with a proton or a deuteron beam. Ion Induced X-Ray Emission allows to detect heavy impurities like Ti or Ta with a good sensitivity, while Nuclear Reactions can give the signature of oxygen or carbon. The presence at the surface of a natural oxide layer and a contamination layer gives us access only to qualitative analysis for these lighter elements. It was although possible to evidence differences of behaviour between sample originated from different suppliers, and to show some effects of annealings.

INTRODUCTION
Global niobium cavities' performances have shown to be improved by the use of purification annealing with of Titanium gettering. Nevertheless, slightly different annealing condition can give rise to very different value of RRR [1]. Moreover, if RRR gives us an estimation of the global (bulk) purity, we have no information about the local composition in the dissipative area (50-100 nm under the surface of the material). We shall show hereafter that samples with close values of RRR exhibit a different behavior, depending on annealing condition.

Indeed, in metals, interfaces like grain boundaries or metal-oxide interface act like a trapping defect and/or a short-circuit diffusing path. When we reach high purity material, it is even the only remaining defects. Paradoxically, the more pure the more likely we are to get some segregation phenomena.

As the surface also plays a key role in RF superconductivity, we have tried to explore more in detail the very narrow volume of the material located just under its surface.

Interfacial segregation can be as thin as some atomic monolayers. To evidence such local concentration, we need to get very high sensitivity and/or good lateral resolution. The nuclear microprobe facility, which performances have been described in details in [1], can be a useful tool to explore the surface vicinity.

EXPERIMENTAL CONDITIONS
Samples from different suppliers were studied, with or without heat treatments. All the samples were chemically etched (~2-6 μm) before analysis with the usual 1-1-2 acid mixture, in order to get rid of the titanium layer and/or surface contamination. In the case of samples cut from cavities, the internal surface was analyzed. For more details see : [1]

TITANIUM AT GRAIN BOUNDARIES
Titanium originated from purification annealing can be readily detected in grain boundaries as described in [2] and shown in fig 1 and 2
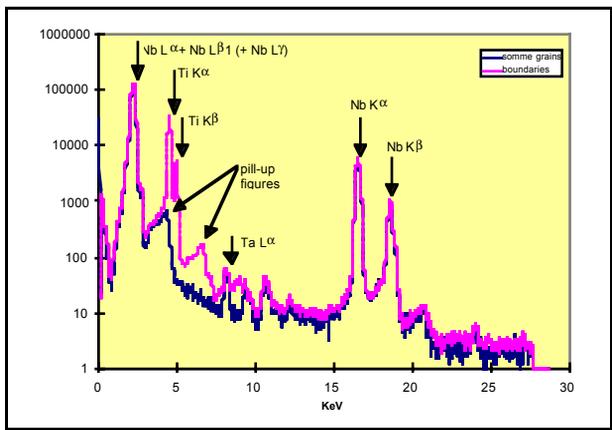
Figure 1: PIXE spectra showing the global contamination of titanium at grain boundaries for annealed samples (sum of several spectra)
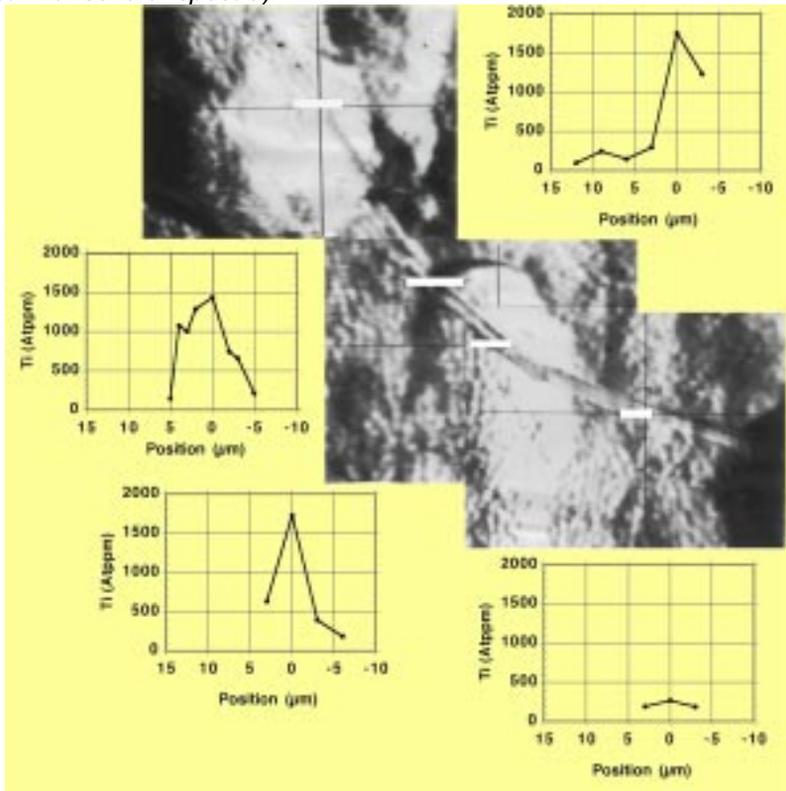

Figure 2: this figure shows a photographic montage of one grain boundary that was explored in detail. Note the change in concentration that occurs when the orientation of the barrier changes.

These results show that titanium can diffuse deeply into niobium, but only if it finds an easy pathway. As the results in terms of concentration are diluted by the probed volume, one can expect that the segregation at the grain boundaries is locally quite large and, therefore, have a significant influence on the conducting and super-conducting properties of niobium.

It can also explain why purification annealings are not effective unless sufficient chemical etching. Safa et al have shown [2] on sample that specific temperature conditions can decrease the Titanium diffusion inside the material, while improving the RRR in a great extent. In the next §, we shall see that prolonged heat treatments might irreversibly degrade cavities performances

CAVITIES CONTAMINATED WITH TITANIUM

Two 1.5-GHz niobium cavities (3.2 mm thick) were tested with a diagnostic thermometry system at Cornell [3]. Their behavior was characterized by unusual losses that were negligible at low fields, but increased *exponentially* with the peak surface electric field (E_{pk}), resulting in a rapidly declining Q_0 (Figure 3). These losses were prevalent throughout the high magnetic field region (Figure 4).

Previously, these two cavities had been the subject of an investigation of high-temperature heat treatment, to evaluate the benefit on emission reduction.[4] Both cavities had been heat treated numerous times at very high temperatures. They were vacuum-baked for a total of 16 hours at $T <$ 1450ºC using titanium **on the outside only** for solid state gettering.[4] In addition, the cavities were also treated at temperatures as high as 1600 - 1700ºC for eight hours. Above 1450ºC the vapor pressure of pure titanium is too high for conventional cavity purification, so NbTi was used instead. *Again, getter material was only applied to the outside of the cavity*. Tests following the heat treatments in 1989 demonstrated that, at that time, the cavities had a field independent Q up to high fields (see Figure 3).
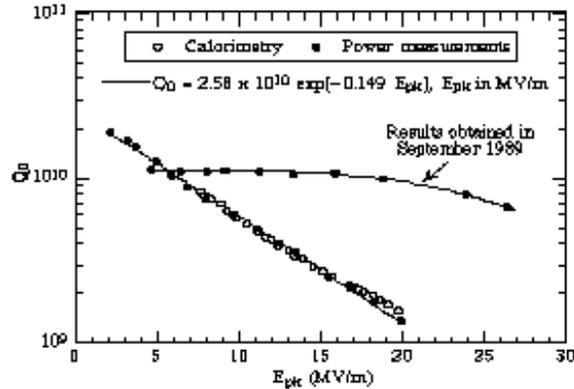

Figure 3: Q_0 versus E_{pk} of a cavity heat treated at very high temperatures. Both (conventional) rf power measurements and results from the thermometry system are included. For comparison, results from 1989, where no Q-degradation was observed, are also depicted.
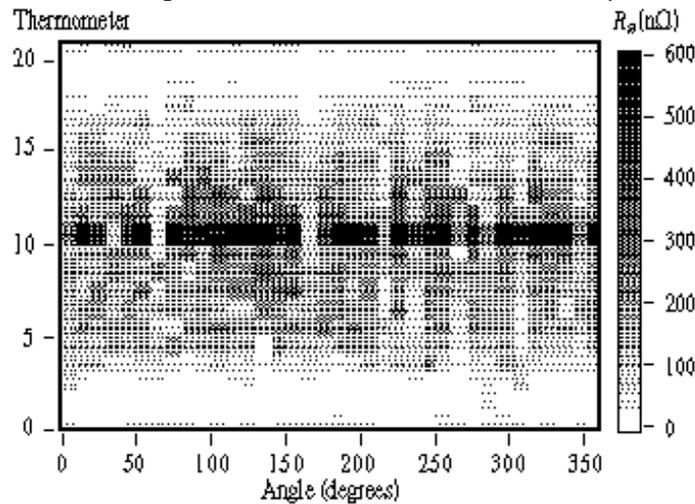

Figure 4: "Flattened" surface resistance map of one of the heat-treated cavities, as deduced by thermometry. The equator is at thermometer #10, and is characterized by a dark band because the cavity is thinner along the weld. The irises are at thermometers #1 and #19. For reference: A cavity with $Q_0 = 10^{10}$ should have a surface resistance of about 27 nΩ .

It was also demonstrated that hydride precipitation cannot be responsible for the anomalous losses [3]. On the other hand, Titanium was detected at the grain boundaries on the internal surface, as shown on figure 5.
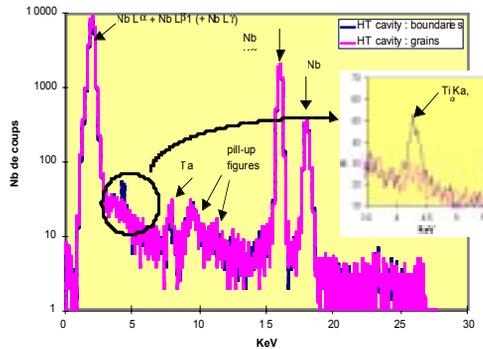
Figure 5 : PIXE spectra for cavities samples.

It appears that the **titanium diffused almost all the way from the outside cavity surface to the rf surface**, only to be uncovered by repeated etches.

Note that samples taken from another cavity heat treated *below* 1450ºC were also analyzed, but no titanium was detected. Correspondingly, no Q degradation had been observed. This was despite the fact that the cavity had been thinned to 1.2 mm by repeated etching.

Intergranular losses : The exponential drop of Q_0 in Figure 3 is reminiscent of the losses observed in sputtered niobium-on-copper and NbTiN-coated cavities. It is believed that the granularity of the superconducting film is responsible for the losses.[6-8] The grain boundaries form weak Josephson junctions through which the superconducting currents have to tunnel. If the critical current density of the junctions is exceeded, the individual grains "decouple", resulting in excessive power dissipation.

However, diffusion along grain boundaries can occur at much greater rates than volume diffusion. Measurements show that the diffusion constant in the grain boundaries of many materials is enhanced by factors as high as 10^5 to 10^6.[9] Thus, diffusion distances up to 3 mm - 10 mm may be possible in 8 hours at 1700ºC. (See [1, 3] and references therein for more details).

We suspect that rapid diffusion along the grain boundaries had allowed titanium to move through most of the cavity wall and to segregate between the grains. The fact that the equator, which is only half the thickness of the rest of the cavity, was very lossy (see the dark band in Figure 4) lends its support to this theory.

TANTALUM

The Tantalum content is usually linked to the Ta content of the original ore and thus can vary from one batch to another for the same supplier. Local inclusions of Ta are always possible in the initial ore, but are far less probable after the whole fabrication process which involves several crushing and melting, The big differences observed in table 1 can be more accurately explained by the fact that the different Nb suppliers use different ores sources for the fabrication of niobium.

Supplier	Tantalum bulk content
Teledyne	640 Wppm
Goodfellow	470 Wppm
Cabott	910 Wppm
Heraeus	40 Wppm

Table 1: Tantalum content from different Nb batches (Flame spectroscopy, blind test performed by Heraeus)

The microprobe shows that Tantalum seems to be evenly distributed, at least in the first few micron of the surface. Nevertheless, the result of the calculation, for Cabott material for instance, gives a concentration about 665 ± 30 Wppm, which is slightly lower than what is detected with flame spectroscopy. This comparison does not allows to put totally aside the hypothesis of some local segregation of tantalum.
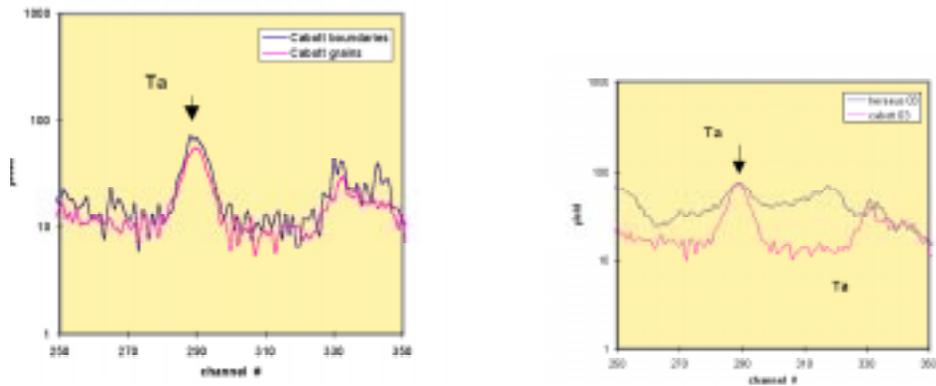
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Figure 6: Tantalum La peak for different suppliers

OXYGEN AND CARBON

RAW MATERIAL : As can be observed on figure 7, raw material exhibit an important Carbon contamination near the surface (very thin peak), and mostly found in grains. No difference can be observed between grain and boundaries for oxygen, but the contamination seems to extend deeper in the material (broader peaks). Unfortunately we haven't got enough statistical information do exploit these spectra further.
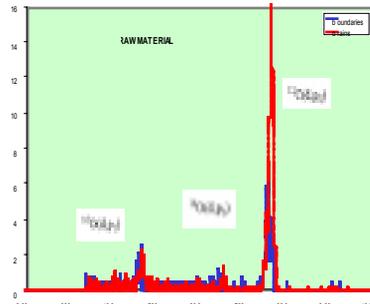

Figure 7 : comparison between grain and boundaries for unannealed material (mean values)

EFFECT OF ANNEALING

After purification, the global contamination is reduced mainly inside grains. Oxygen contamination did not change much in boundaries, but was a lot reduced in the bulk.
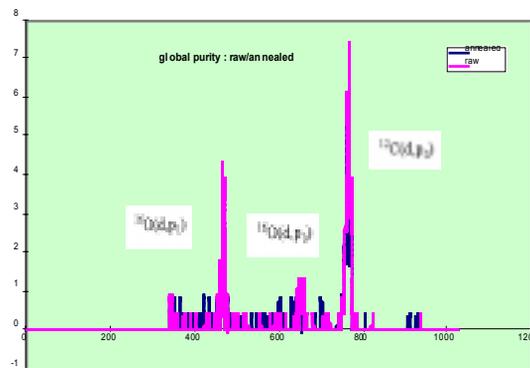

Figure 8: Comparison of O and C contamination between raw and annealed niobium (mean values)
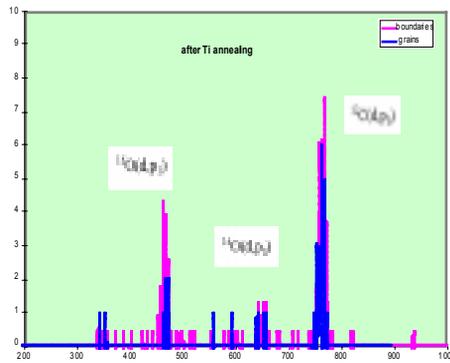
Figure 9: Comparison of O and C contamination between grain and boundaries for annealed niobium (mean values)

INFLUENCE OF ANNEALING CONDITIONS

To get an estimation of the profile and quantitative estimation of the concentration, one need to get more statistical counts. This was realized with the help of a "macroprobe" from IPN-Lyon, with a beam of higher energy. Figure 10 shows the profile of concentration obtained with this experimental conditions

As can be observed on figure 10a) and 10b), samples with high RRR value can exhibit fairly high concentration of impurities near the surface. Moreover, samples with close value of RRR like the ones in 10c) and 10d) can have a very different composition near the surface.
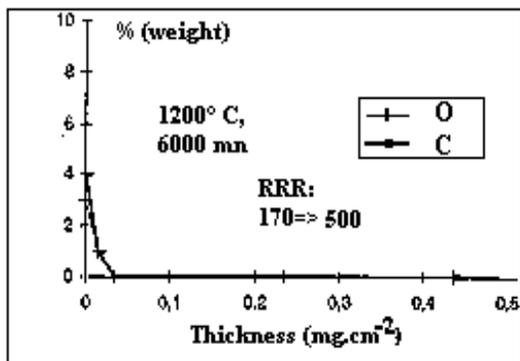
RRR measurements obviously don't give sufficient indications about the local purity near the surface. An increase in thermal conductivity can be counterbalanced by a local pollution that increases surface resistance.
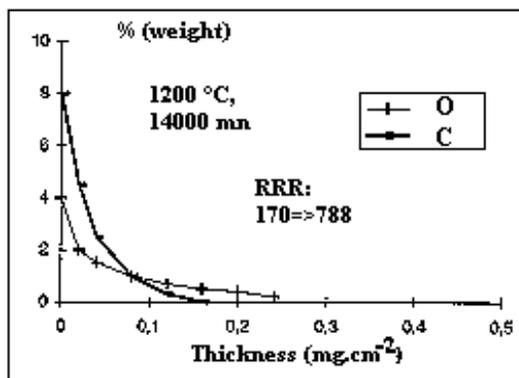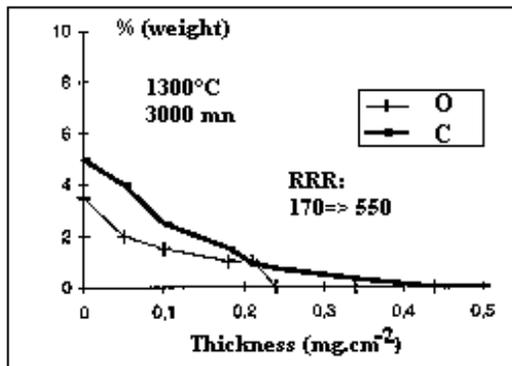

10a)
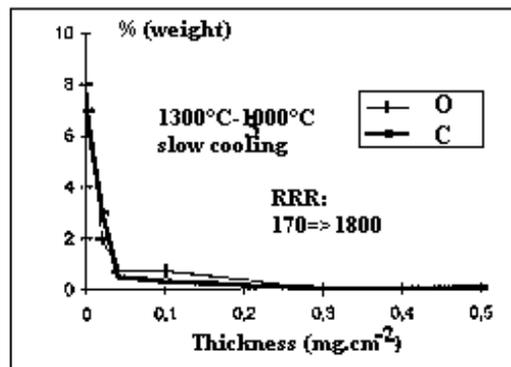
10b)

10c)

10)d

Figure 10 : profile concentration of oxygen and carbon for four different annealing conditions,along with RRR measurement.

CONCLUSION

With the use of systematic purification annealing, the niobium of the cavities has become very pure, and we have less trouble with thermal conductivity. In our quest for high gradients we need now to explore very tiny details of the matter. Nuclear microprobe has proven to be an helpful tool in this domain where few techniques are available and even fewer are easy to handle. Now that the existence of localized, micron-sized defect can be evidenced, we must find out which type of

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influence they have on the RF behavior of the cavities ; in particular, surface composition might play a key role in the Q_0 limitation that is sometimes observed at high accelerating fields.

REFERENCES

[1] ANTOINE C., BONIN B., SAFA H., BERTHIER B., TESSIER E., TROCELLIER P., CHEVARIER N., ROUX B., "Evidence of preferential diffusion and segregation of impurities at grain boundaries in very pure niobium used for radiofrequences cavities", .J. Applied Physics 81 (1997) 1677

[2] H. SAFA, D. MOFFATY, B. BONIN, F. KOECHLIN, "advances in purification of niobium by solid state gettering with niobium", J of Alloys & Compounds, <u>232</u>, 281-288, (1996)

[3] J. KNOBLOCH, PhD Thesis, Cornell, (1997), and References therein

[4] H. Padamsee et al. "New results on rf and dc field emission". In Y. Kojima, editor, Proceedings of the Fourth Workshop on RF Superconductivity, p. 207, Tsukuba, Japan, 1989

[5] J. Pelleg. Philosophical Magazine 21(172), 735 (1970).

[6] B. Bonin and H. Safa. Superconductor Science and Technology 4, 257 (1991).

[7] G. Müller. Microwave properties of high-Tc superconductors. In Y. Kojima, editor, Proceedings of the Fourth Workshop on RF Superconductivity, p. 267, Tsukuba, Japan, 1989.

[8] T. L. Hylton et al. Applied Physics Letters 53(14), 1343 (1988).

[9] I. Kaur, Y. Mishin, and W. Gust. "Fundamentals of Grain and Interphase Boundary Diffusion". Wiley & Sons, Chichester, 3rd edition, 1995.