Nb PURIFICATION by Ti GETTERING

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Abstract :

High purity niobium is required for SRF cavities in order to achieve high accelerating fields. Ti gettering at high temperature in a vacuum furnace appears to be a nice way to get rid of light elements (O, C & N). Using this technique, RRR as high as 2000 can be obtained from standard 160 RRR niobium samples. Results of heat treatment applied to low RRR samples are shown. The influence of metallic impurities is also discussed. Another important feature to point out for that kind of purification is the sample thickness dependence. An experimental profile of the local RRR as a function of depth is drawn. Finally, the improvement of the accelerating field obtained on heat treated cavities is clearly demonstrated.

Introduction

One of the requirements to achieve high gradients in bulk niobium superconducting cavities is to have a good thermal conductivity [1–8]. The value at low temperatures of this thermal conductivity κ is strongly dependent on the residual impurities in the metal which limit the mean-free path of normal electrons. The residual resistivity ratio (RRR) defined in the normal state as

$$RRR = \frac{\rho_{295K}}{\rho_{4.2K}}$$

is also relevant from the same limiting mechanism. In fact, if one neglects the phonon contribution to the thermal conductivity, one may easily show that κ is proportionnal to the RRR for T<20K. This still holds for superconductors in the superconducting state (the only difference is that normal electron contribution is so low for T<2.5K that phonon contribution may begin to contribute at low temperatures). Thus, improving the RRR will mean improving κ. As the RRR is much easier to measure, we shall focus on this quantity for the rest of this paper. The residual resistivity in the normal state is mainly due to light impurities in niobium and can be expressed for low concentrations as

$$\rho_{0K} = \sum_i c_i \left(\frac{\partial \rho}{\partial c}\right)_i$$

where c_i is the concentration of impurity i and $\left(\frac{\partial \rho}{\partial c}\right)_i$ the corresponding resistivity coefficient [2]. Light elements (C, O & N) have the most important contribution to ρ_{0K}. So, one way to increase the RRR is to purify the niobium from these impurities using a solid state getter as titanium, zirconium or hafnium [3]. Purification has to take place at high temperatures (above 1000°C) in order to allow for diffusion in the bulk.

RRR function of Time and Temperature

It has been well established that the gettering of light impurities is effective using titanium as a solid-state getter [4]. Samples of niobium 100mm long and a section of approximately 2x3 mm^2 having a starting RRR of 165 have been annealed in a furnace at different temperatures and for different times inside a titanium cylinder [5]. Experimental curves plotting the RRR after heat treatment as a function of time for the different temperatures are shown in figure 1. A theoretical model based on diffusion of impurities has been done showing that, for each temperature, there is a maximum value for the RRR [5]. This is due to Ti diffusion in the Nb which, although much slower than light impurities diffusion, may start degrading the resistivity. The experimental time to achieve RRR_{max} is longer than what can be estimated from the model, using official diffusion coefficients [All details are given in reference 5]. That might be understood by the fact that

i) Purification might be slowered by the kinetics of titanium sublimation

ii) In the simplified 2D model, higher orders of time diffusion are neglected (only one mean time diffusion of zero order is taken in account).

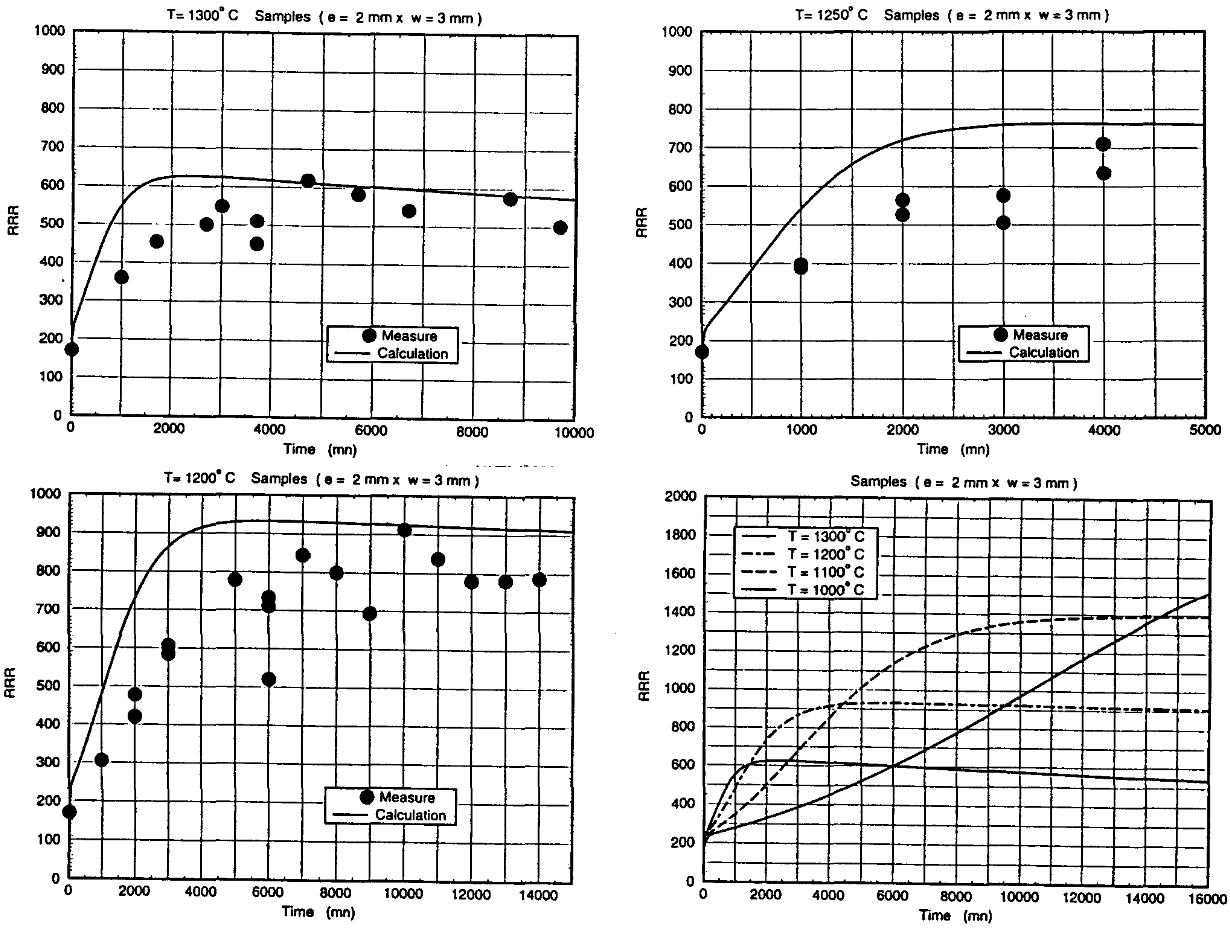

Figure 1 – RRR as a function of time of heat treatment for different temperatures

But the most suprising fact is that the value of RRR_{max} is temperature dependent : the lower the temperature, the higher the value! Of course, the drawback is that the time then to reach this maximum is longer. For example, at 1200°C, maximum RRR obtained is 900 (in 10000 minutes) whereas at 1300°C, it does not exceed 600 (time= 5000 min.). This phenomenon is still unexplained. One of the hypothesis could be that the thermodynamic equilibrium between the concentration of one given impurity in the metal and its partial pressure in the residual vacuum is modified following an exponential increase with temperature. Anyhow, the conclusion is that one has to anneal at low temperatures (but still high enough to allow diffusion) in order to achieve higher values of RRR.

An optimized heat treatment

Considering what have been found above, an optimized heat treatment has been elaborated minimizing the time needed to reach some given RRR. The idea is to separate the Ti deposition process from the effective gettering one. Ti sublimation is done by heating at relatively high temperature (1300°C here) for a few hours giving enough titanium for purification while reaching a RRR of about 350. Then, the temperature is slowly lowered to 1000°C achieving the best purification (fig. 2).

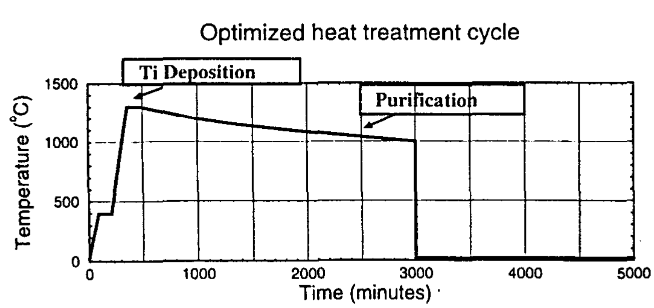

Figure 2 – The optimized heat treatment temperature cycle in the furnace.

A few niobium samples cut from sheets supplied by Heraeus with a starting RRR of 155 were heat treated following that procedure. They reached a final RRR close to 2000 (fig. 3). This confirms the fact that the initial RRR was mainly limited by light impurities (C, O & N) and that almost all of those can be removed when applying the optimized heat treatment.

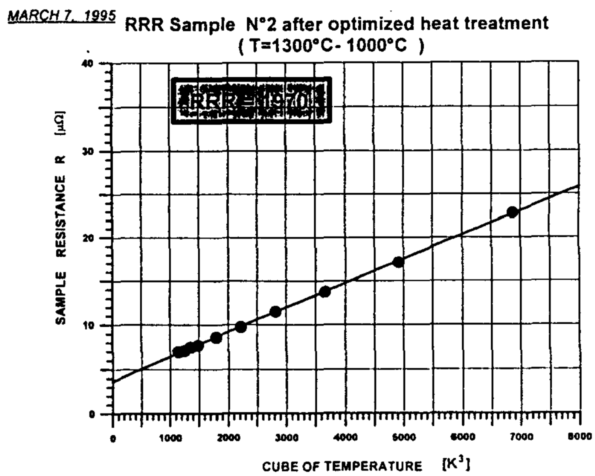

Figure 3 – A sample with an initial RRR of 155 showing a RRR of about 2000 after an optimized heat treatment.

Purification of low RRR niobium

Following the very good results obtained on RRR 155 samples, one may ask how far the standard reactor grade niobium (typically RRR 30) may be purified. Clear interest would be their cheaper price and better mechanical properties prior to annealing. Reactor grade niobium sheets have been purchased from different companies and the optimized purification process previously described applied on samples. Results giving the final RRR are summarized in the following table. The best RRR achieved is 566 which might be sufficient for most applications. This time, the RRR limit seems to be due to the amount of residual metallic impurities (for example Ta) even though these have a resistivity coefficient $\left(\frac{\partial \rho}{\partial c}\right)$ five times lower than the light impurities one [2].

Nb from	Initial RRR	Final RRR	Ta (ppm)
Wah Chang	34	566	< 1000
Cabot	34	427	650
Cabot	27	270	835
Plansee	24	300	< 1000

Depth profile

The basic mechanism of purification is based on the diffusion of light impurities in the bulk. Thus, it may be expected that this process will not be uniform in the sheet. Purification should be more efficient at the surface where gettering occurs as compared to the deep bulk. As a consequence, the RRR will not be uniform because the annealing time may not be long enough to reach equilibrium. One has to be aware that an experimental measure will give an *average* value for the RRR.
This has been confirmed on two samples (initial RRR 160) heat treated with the optimized cycle for only 1000 minutes. The average RRR has been measured to be 800. Then, chemically etching step by step the samples, a simple calculation can allow to deduce (from the measured RRR) the real local RRR of the etched part. RRR profile shown in figure 4 clearly demonstrate the non uniformity. The RRR of the surface is measured to be as high as 2650 whereas the bulk value has only increased to about 500.

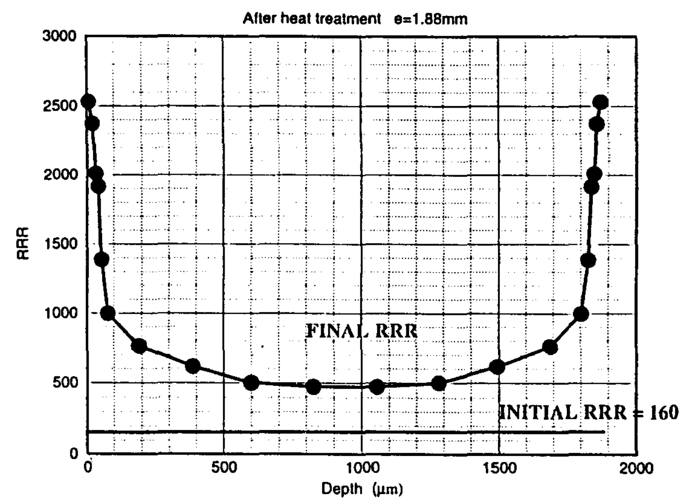

Figure 4 – Local RRR profile as a function of depth in the sample.

Heat treatment of cavities

Quenches in superconducting RF cavities made of standard RRR160 niobium appear to occur at accelerating fields E_{acc} between 15 and 23 MV/m. This level is much lower than what might be expected from calculations if no local defect is assumed [1, 7]. The thermal model also indicates that the quench field level will increase if the thermal conductivity is improved. Two results supporting the benefit of heat treatment applied on cavities are discussed here. The first is obtained on a 1.5GHz 3–cells cavity that previously quenched at a very low level (6.5 MV/m) due to an identified (by means of X-rays) defect at the equator weld. Improvment after heat treatment is obvious (fig. 5 where the field is limited at 22MV/m by available RF power).

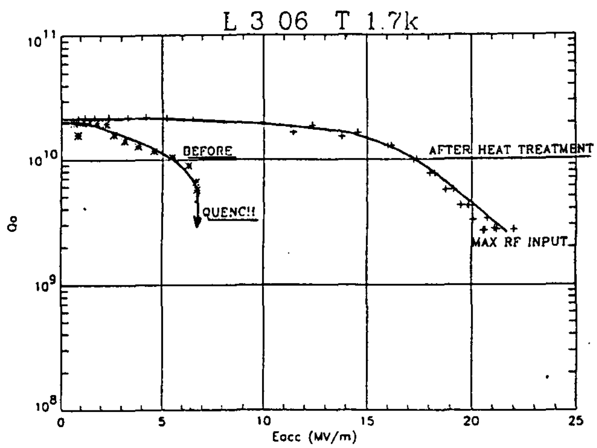

Figure 5 – A 3-cell 1.5GHz cavity having a quench at an accelerating field of 6.5MV/m due to an identified defect. After heat treatment, its quench level was pushed up higher than 22MV/m.

The second cavity shown is a "typical" single cell 1.3GHz exhibiting a quench at 17MV/m. Annealing has been applied at 1200°C for 5000min. (the final RRR is expected to be around 700). Here again, the improvement is impressive as the cavity went up to 32MV/m without any quench (fig. 6, RF power limitation). Another advantage of the optimized heat treatment is that Ti will not diffuse deep in the niobium [9]. Therefore, it will not be necessary to make a heavy chemical etching after it to recover good superconducting behaviour. For example, this cavity exhibited a high Q_0 after a chemical etching of only 14μm.

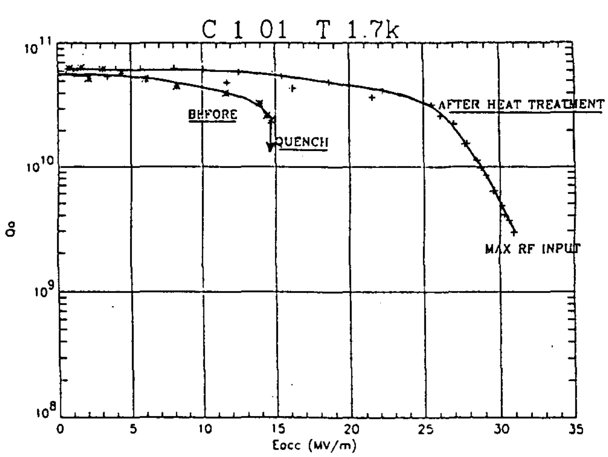

Figure 6 – A standard 1.3GHz single cell cavity quenching before heat treatment below 15MV/m. It achieved 32MV/m without quenching (field emission limited).

The question that immediately arises is why the heat treatment works so well (Accelerating gradient can be improved by 50% to 100%). Three answers can be considered :

i) RRR — Part of improvment is certainly due to the increase in RRR. But calculations [1,6] predict that this part accounts for only 25% increase.

ii) Homogeneization — It is known that the RRR is not uniform in the sheet. The rapid diffusion of light impurities during heat treatment could help making it much more homogeneous.

iii) Dilution of defect — It has been pointed out earlier that the quench is probably caused by a local lossy defect. This defect might progressively dissolve in the bulk during annealing ending up with less RF losses.

Further investigations are necessary to determine which of these three hypothesis is most likely to be predominant during the heat treatment process. Nevertheless, it is definitely demonstrated that a good heat treatment is efficient for increasing accelerating fields in superconducting niobium cavities.

Conclusion

To summarize, niobium can be purified by a proper heat treatment with titanium gettering from almost all its light impurities. Residual metallic impurities will limit the final RRR. RRR achieved are over 2000 for samples having an initial RRR of 160 and up to 560 for reactor grade niobium (RRR 30). The purification process is based on diffusion and starts at the surface. Heat treatment applied on RF cavities seems to be very efficient. The improvement in the accelerating field is even higher than what might be expected from the corresponding increasing in RRR. Thermal stability is presumably helped by homogeneization or dilution of defects during annealing.

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