Quality Control of Nb for TESLA Superconducting Cavities

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Abstract

The interstitial impurities O, N, C, and H have major influence on the thermal conductivity of Nb. By rising of the thermal conductivity the thermal breakdown happens at higher field level. The thermal conductivity of Nb samples is measured at DESY. The dc RRR (residual resistance ratio) measurement, which gives information about the total impurity content and allows a rough estimation of the thermal conductivity, is applied to serial production. It is important to control the Nb quality during every stage of cavity fabrication and treatment "in situ". In particular the cavity is subjected to post purification (solid state gettering) in a DESY furnace. For estimation of gettering results a new non-destructive method of cavity ac RRR measurement was developed.
Another problem of material quality is the non homogeneous distribution of impurities in Nb. A foreign material enclosure was detected in one of the TTF cavity by means of X-ray micro radiography. Identification of the enclosure, which is Ta, was done at DESY HASYLAB by means of synchrotron radiation. We analyzed the advantages and disadvantages of different methods of non-destructive inspection (X-ray, neutron radiography, eddy current, ultrasonic) for identification of non homogeneities in Nb.

Introduction

The efficiency of an electromagnetic cavity depends on various parameters. Except for the basic microwave technology the type and the structure of the material play a decisive role. The application of unalloyed Nb in industrial scale for construction increased in importance with the building of the TESLA test facility (TTF) from the TESLA collaboration.
Niobium possesses a rather high temperature of superconductive transition Tc=9,2K, and high ductility of body centered metals, which allowed the half product fabrication at room temperature by deep drawing, spinning or hydroforming.

Properties of Nb for TTF superconducting cavities

The superconducting properties are influenced considerably by the purity of the material and the production technique. The interstitial impurity C, O, N, H damages most of the cavity performances. The total impurity content can be determined by measuring the specific Residual Resistivity Ratio RRR. The commercial Nb for cavities is produced by several melting cycles in the electron beam EB furnace. Over the last 10 years the RRR of Nb ingots, which were produced in a weight up to one ton, are improved to 300 from 30 by better melting practices. Cavities which were made from these sheets normally achieve a range of accelerating field Eacc=13-17 MV/m.
Table 1 corresponds a content of main impurities and some metallurgical parameters of the Nb sheets applied to fabrication of first 19 cavities for TTF.
The material for this production was delivered by two vendors: W.C. HERAEUS GmbH (Germany) and TELEDYNE WAH CHANG ALBANY (USA).
Increasing of RRR is desirable for improving the cavities performance. Currently the way of further increasing of RRR is the solid state gettering. These efforts included high temperature treatment (1400°C, 2-4 h) in vacuum (about 10^{-7} mbar) in presence of a Ti foil inside and

outside of a prepared cavity. The oxygen, most part of nitrogen and carbon leave the bulk Nb during the gettering and move towards the surface, where they build compounds with Ti. After this post purification treatment both cavity surfaces are etched to remove the damaged layer. The improvement of RRR in UHV DESY oven is roughly by a factor two now.
The quality control of Nb for superconducting cavities production points out three aspects:
a) purity, b) workability, c) surface quality.

Table 1 Properties of Nb sheets for TTF cavities

	HERAEUS	HERAEUS	HERAEUS	TEL.WAH CH.
Properties	Cav. -2,-1	Cav. D1...D6	Cav. S7...S12	Cav. C21
RRR	407-433	300 -380	278-350	312-529
Impurities content, %				
Ta	0,037	0,036	0,012	0,02
W	<0,005	<0,005	<0,005	<0,003
Ti	<0,001		<0,002	<0,004
Fe	<0,002	0,002	<0,002	<0,003
Si	<0,002	<0,002	<0,002	<0,002
Mo	<0,002	<0,002	<0,002	<0,003
Ni		<0,003	<0,002	
Zr		<0,003	<0,002	
H	<0,0005	<0,0005	<0,0005	<0,0003
N	<0,001	<0,001	<0,001	<0,002
O	<0,001-0,03	<0,001	<0,001	<0,004
C		<0,001	<0,001	
Mechanical properties				
Tensile strength, Rm, (N/mm2)	175	150 -180	152 - 160	157,6 - 161
Yield strength, Rp 0,2 (N/mm2)	53	60 -97	79 - 81	90,8 - 94,9
Elongation,%	54	38 -70	48 - 68	51 - 52
Hardness, HV10		38 -45	40 - 46	49
Grain size, ASTM	6,5-8,5	6 - 8.	5 -8,5	7
Recristal. heating.				
Temperature, °C	770	770	770 -800	
Time, h	1	1	1 -1,25	
Thickness, mm		2,69.....2,88	2,45.....2,85	2,67.... 2,90
Number of the sheet	40	150	275	120
Delivery data		Feb 94	Jul 94	Jan 95

Concerning the first issue the interstitial impurities O, N, C, and H have major influence on the thermal conductivity of Nb. By rising of the thermal conductivity the thermal breakdown of the cavity takes place at a higher field level.
The thermal conductivity of Nb specimens as delivered and after refining are controlled at DESY. An example can be seen in Fig 1.

The phonon peak absence is significant for this material. The relationship between RRR and thermal conductivity can also be observed at Fig.1. The simplified relationship between RRR and thermal conductivity, $RRR=4 \bullet \lambda(4,2K)$ allows the employment of RRR control for estimation of the thermal conductivity.
The accuracy of the well known dc 4-point method is high enough, but it can be applied only as destructive method. On the other hand it is important to control the Nb quality "in situ" during every stage of cavity fabrication and treatment.

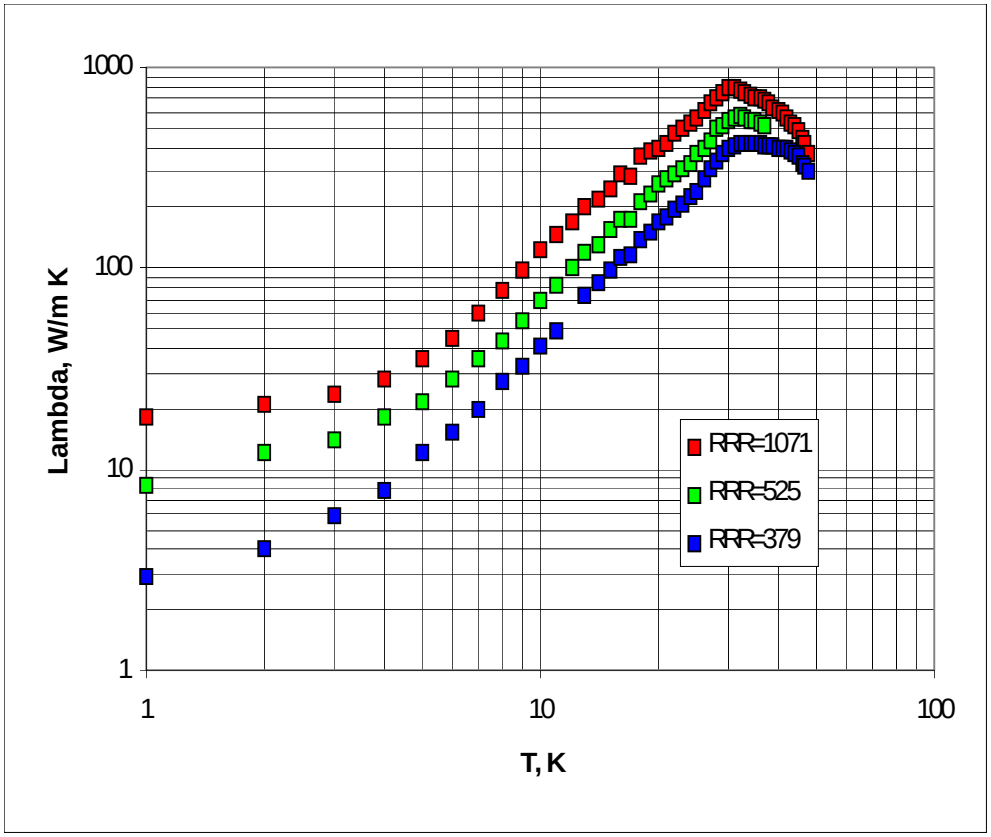


Fig. 1. Thermal conductivity of Nb as delivered (RRR=379) and after solid state gettering (RRR=525, RRR=1071).

A new non-destructive method of ac RRR measurement was developed at DESY for this aim /1/. The technique involves two concentric coils situated close to the object. A current with definite frequency is established in the primary coil, the magnetic field of this coil induces eddy current in the metal. The resulting magnetic field induces a signal in the pick up coil. This signal is a function of the material resistivity. For elimination of the inductive voltage, which the primary coil creates in the pick up coil without object, two identical contrary directed pick up coils are used. The superconductive jump of the signal is measured for RRR identification. In practice it is reasonable to obtain the required RRR value from the previously created calibration curve. Using of standard samples with known RRR allows to achieve an accuracy within 5-10%.
A summary of TTF cavities RRR measurement is presented in the Table 2. Actually the RRR values for post purified material obtained by means of ac measurement are higher than dc RRR

values. After refining the impurities are located more distant from the cavity surface and this courses higher RRR in areas close to the surface. In contrast to the dc method, which gives the average RRR value, the ac RRR corresponds the information close to the Nb surface. The penetration depth of the signal in our case is about 0,5-1 mm and can be established due set up of the frequency.

Table 2. Results of ac and dc RRR control of TTF cavities

Cavity	RRR dc	RRR ac	Note
	sample	cavity	
P2	386		1400°C, 4h, Ti, 30h
D2	348		1400°C,4h,Ti, 82h
D2		312	1400°C,4h,Ti 82h, welding position
D4	525		1400°C,4h, Ti, Cycle
D6	528		1400°C,4h, Ti, Cycle
D3	525		1400°C,4h, Ti, Cycle
D1	528	575	1400°C,4h, Ti, Cycle
D5		200	before processing
D5	496		1400°C, 1h; 1250°C, 3h, Ti
S7	575	550	1400°C, 1h; 1250°C, 3h, Ti
S8	463		1400°C,1h;1350°C,3h, Ti
S9	464		1400°C, 1h;1350°C,3h, Ti
S10	518	635	1400°C, 1h;1350°C,3h, Ti
S11	421	612	1400°C, 1h;1350°C,3h, Ti
S12		220	before processing
S12		234	welding position, before processing
C21		341	2nd cell, before processing
C21		361	3rd cell, before processing
C21		302	2nd cell, before process. (welding position)
C21		336	4th cell, before processing
C21		354	7th cell, 800°C, 2 h
C21		371	7th cell, 800°C, 2 h
C21		293	4th cell, before process. (welding position)

The half cells of the cavities are made at the rule by deep drawing from sheet. There are some efforts for fabrication of seamless cavities by hydroforming from tube. Both procedures require small grain size (ASTM grain size 5 to 6), recristallisation of nearly 100% and absence of

anisotropy. For test of workability a two dimensional stretching device is applied, so that revealing of anisotropy in the sheets becomes easier.

Non Homogeneities in Niobium

Another problem of material quality is the non homogeneous distribution of components in Nb. For example a foreign material inclusion was discovered in cavity D6 even after solid state gettering.
The cold test in the vertical cryostat of cavity D6 has shown the poor performance in cell 5. The application of a rotating T-R mapping system, which is applied at DESY for diagnostic of the hot spots in TTF 9-cell cavities, detected the sharp temperature increasing in the definite area of the 5th cell /2/. The eddy current inspection of this cavity from outside with an extremely sensitive probe was done at the BAM (Bundesanstalt fuer Materialforschung und -pruefung, Berlin). A remarkable signal deviation at the same area was found. At the same time careful inspection of the inner surface by means of an endoscope system did not demonstrate any kind of disturbance.
The dumb-bell was cut out from cavity D6 for further non-destructive investigations. The X-ray micro radiography with area detector and high spatial resolution (about 10 µm), that was done at BAM, allows to discover a black spot on the photograph of analyzed Nb area. The cross section of it was about 0,2-0,3 mm and the shadow indicates a foreign material inclusion with higher density and atom number in comparison with Nb.
The next step was the non-destructive identification of the inclusion. First of all the thermal neutron radiography facility Gentra-3 of the GKSS (Forschungszentrum Geesthacht) was used, which is designed for the examination of large objects. The attenuation of the beam is due to the interaction of neutrons with nuclei. The efficiency of the method depends on the absorption coefficient of the object and it differs from X-ray method. In any case some elements can be strong absorber for X-ray but transparent for neutrons and vice versa. Unfortunately the absorption coefficient of the inclusion material is very close to Nb (what turns out later) and therefore this irradiation test was without success.
Identification of the inclusion was done at DESY in Hamburger Synchrotronstrahlungslabor HASYLAB. The synchrotron radiation produced at Hamburger storage ring DORIS thanks to high intensity can be used for identification of very small inclusions of different chemical elements. The most important method for this is the fluorescence analysis. Fluorescence appeared during spontaneous returns of exited atoms or molecules to the basic status. Owing to the fact that the synchrotron radiation has a high spread of energy (from visible light till the hard X-ray) the tunability of synchrotron radiation allows the selective excitations of elements.
There are two variations of fluorescence method.
In synchrotron radiation fluorescence analysis SYRFA the excitation is done with the white beam and a semiconductor detector analyses the energy of the fluorescence.
In the XAFS topography method the energy selection occurs in the primary beam. One observes the absorption edge of definite elements.
The advantage of the fluorescence method is high surface resolution (few micrometers) and a very high sensitivity (sometimes few particle per billion). The disadvantage is the small penetration depth (between few tenth and a couple of hundreds micrometers). This allows the detection of element traces close to the surface only.
Both versions of the fluorescence method were applied in our case. The XAFS method has shown, that the fluorescence takes place in the area that is interesting for us at energies close to L_3 =9,881 KeV, L_2=11,136 KeV, L_1= 11,682 KeV, which corresponds the L lines of tantalum. Certainly the Nb reflexes are also presented.

The SURFA method has allowed more detailed investigation of the Ta enclosure. The fluorescence experiment was carried out in a wide energy range from 0 to 60 KeV. At first a spectrum far away from the spot was got, the second one in the middle of the spot. Both spectrums display the Nb lines and in addition Ta lines according to the vendor specification. The content of dissolved Ta in Nb is roughly 200 ppm. This Ta is responsible for the reflex obtained away from the spot (Ta background). But in the middle of the spot the Ta signal increases by a factor of 10. This means that Ta is not completely dissolved and this area represents a cluster of Nb-Ta alloy with Ta content about 2000 ppm, which is uncommonly high.
The spot area was scanned in two perpendicular directions (Fig. 2).
It turns out, that the spot has an oval shape with a size of about 0,5 mm in one- and 1 mm in another direction.
A model of inclusion can be imagined under consideration of X-ray experiments. It consists of a nuclei inside the Nb with a rather high concentration of Ta, that can be registrated by means of X-ray. There is a halo around the nuclei with less Ta concentration. The halo is spread rather widely and has achieved the surface. This can be indicated thanks to the synchrotron fluorescence.

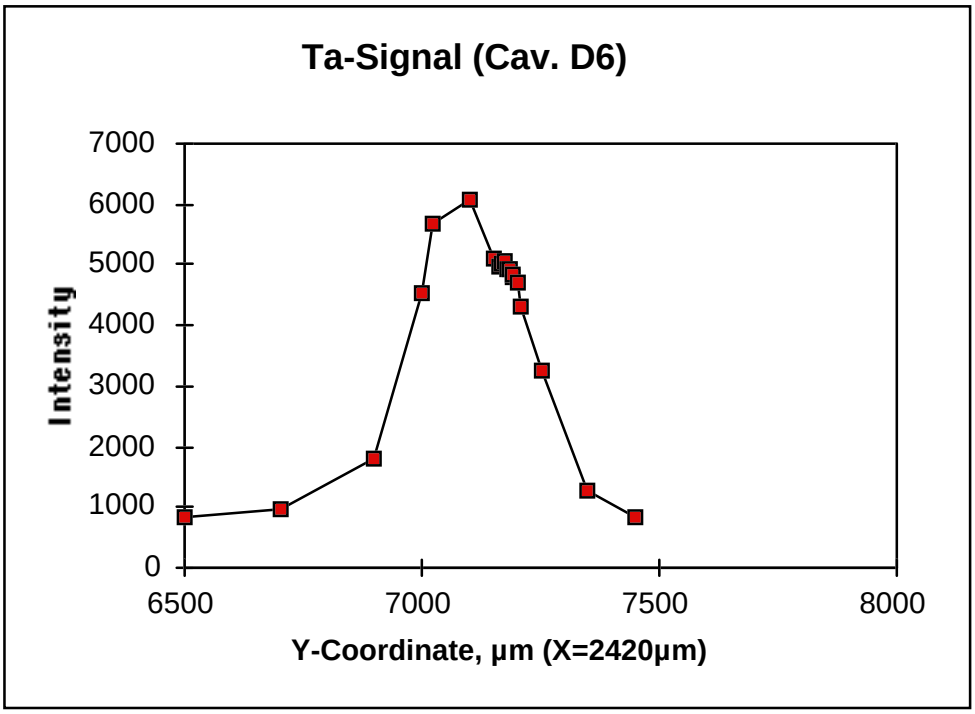
Fig. 3 represents schematically the described imagination. The impurity distribution in the spot area is typical for incomplete dissolution of the components during melting. This event is a bit surprising because the Nb ingot was melted few times in the EB furnace. The Nb-Ta alloys create a solid state solution in the whole concentration region within 0-100%, which is well known from it phase diagram. It should be expected the complete dissolution of the components. Nevertheless the melting point of Ta is roughly 500°C higher than that of Nb. If the temperature was not sufficiently high during the melting or the melting time was too short this phenomena can happen in principle.
Obtained content of Ta in the spot gives the opportunity to estimate the RRR with the aid of the empirical formula, which describes the influence of different impurity elements on RRR /3, 4/.

$$RRR = \frac{R(300\,K)}{R(10\,K) + \sum_{i=1}^{4} \frac{\partial R_i}{\partial C_i} C_i}$$

i= 1 (=oxygen), i= 2 (=nitrogen), i= 3 (=carbon),

i=4(=tantalum)

R(300K)=1,46·10^{-5}Ω cm, R(10K)=8,7·10^{-9} Ω cm



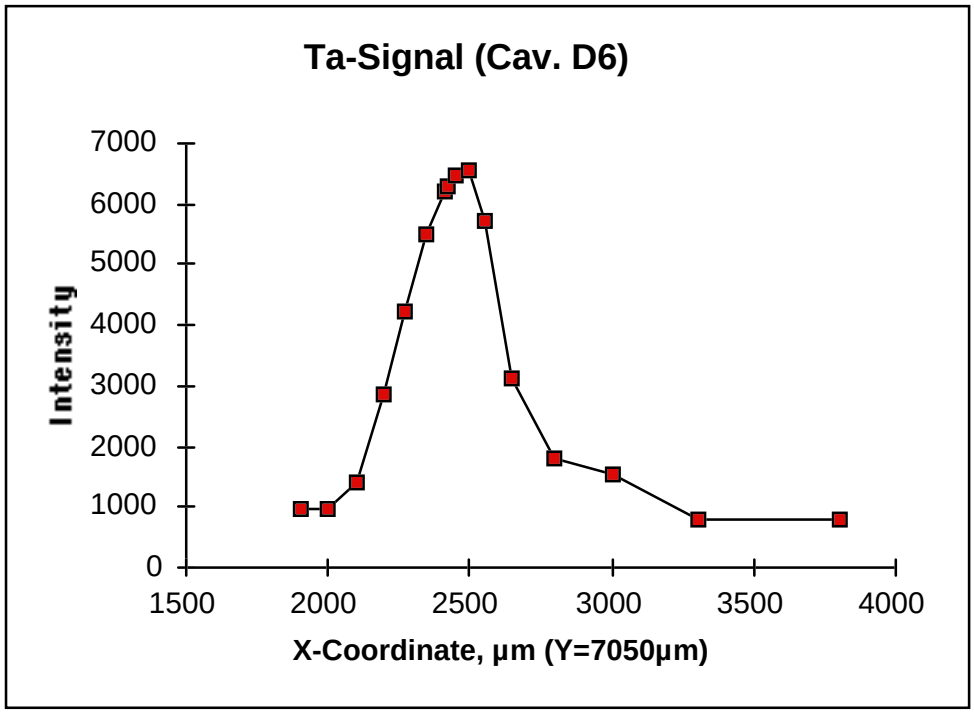


Fig. 2 . Sizes of Ta spot in cavity D6.

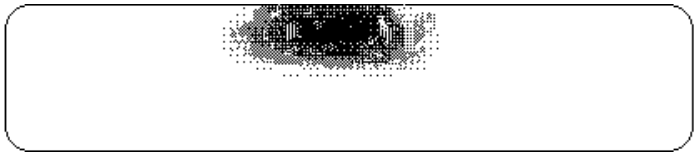


Fig. 3. Tantalum enclosure in the cavity wall .

The values $\partial R_i / \partial C_i$ have been found by using of pure and doped /4/ samples: for N: 3,49 x10^{-9} Ω cm/wt. ppm ; C: 3,33 x10^{-9} Ω cm/wt. ppm; O: 2,64 x10^{-9} Ω cm/wt. ppm; Ta: 0,12 x10^{-9} Ω cm/wt. ppm respectively. The results of calculation can be extracted from Table 3.

Table 3 Comparison of RRR values for Nb in the spot and outside

Nb 300				
Before Solid State Gettering				
O, µg/g	N, µg/g	C, µg/g	Ta, µg/g	RRR (calc.)
2	1,5	1,5	200	335
After Solid State Gettering				
O, µg/g	N, µg/g	C, µg/g	Ta, µg/g	RRR(calc.)
0,04	0,45	0,45	200	475
Ta- Spot				
Before Solid State Gettering				
O, µg/g	N, µg/g	C, µg/g	Ta, µg/g	RRR(calc.)
2	1,5	1,5	2000	56
After Solid State Gettering				
O, µg/g	N, µg/g	C, µg/g	Ta, µg/g	RRR(calc.)
0,04	0,45	0,45	2000	59

The Ta contribution in the spot determines the RRR value. It is about before post purification (much less than 300). Unfortunately the solid state gettering is not in a position to reduce the Ta concentration in Nb. Therefore even after post purification, when the content of oxygen, nitrogen and carbon is significantly reduced, the RRR value remains almost the same.
Embedded inclusions, voids, cracks and scratches deeper than 15 µm cannot be tolerated in the Nb sheet. Surface control of Nb is made by visual inspection, anodization and looking for

discoloration, water soaking and looking for rust traces. It should be taken into account, that removing 100-200 μm of material from the surface occurs during cavity preparation. Inner defects that locate close to the surface become free. This means the quality control should be done both at the surface and inside of the Nb in the closest to the surface area. After analysis of the advantages and disadvantages of different methods of non-destructive inspection (X-ray, neutron radiography, eddy current, ultrasonic and so on) for identification of non homogeneities in Nb it points out that the most suitable method for our aim is the eddy current control. It allows to control the surface and the area close to the surface. The penetration depth can be changed due to the frequency choice. On one hand the modern eddy current facilities can scan large areas with rather high speed. For instance a Nb sheet of 262x262 mm can be scanned with trace distance of 0,1 mm in half an hour. On the other hand the high resolution can be achieved due to improving of the probe. It is possible to detect defects of few hundred micrometers size in the depth of few hundred micrometers. A new eddy current system is being created now at DESY in the collaboration with BAM. It will be applied for non-destructive control of the Nb sheets for the next TTF cavities.

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References

[1] W. Singer, D. Proch, Proc. 7th Workshop on RF Superconductivity October 17-20, 1995, Paris, France, 547.

[2] Q.S. Shu, G. Deppe, W.-D. Moeller, M. Pekeler, D. Proch, Proc. 7th Workshop on RF Superconductivity October 17-20, 1995, Paris, France, 523.

[3] W. Singer, D. Proch, TESLA Report,1996.

[4] M. Hoermann, The production of high thermal conductivity niobium for high frequency superconductors on a technical scale, Hanau (1988).