QUALITY CONTROL AND PURIFICATION HEAT TREATMENT OF NIOBIUM FOR TTF

A. Brinkmann, D. Hui, H. Kaiser, D. Proch, W. Singer, X. Singer
Deutsches Elektronen-Synchrotron DESY, Notkestrasse 85, 22607 Hamburg, Germany

Abstract

Eddy current scanning with improved apparatus mainly is applied for quality control of Nb sheets. About 500 sheets for third series of TTF cavities were tested. Some irregularities were detected. Supplementary nondestructive analysis was carried out by Neutron Activation, X-ray Fluorescence and Large Chamber Scanning Electron Microscope.

A SQUID Gradiometer system, developed at F.I.T. Messtechnik was applied for diagnostic in Nb sheets and a 9 cell cavity. Its extremely high sensitivity allows to find distributed in-homogeneity.

A series of purification heat treatments of Nb from different suppliers was done. The RRR measurement, traction test, hardness measurement and microstructure analysis have shown, that marked change of properties starts at temperatures above 1000°C.

The penetration of Ti into Nb during purification heat treatment is discussed. The thickness of the Ti layer is about 10 µm and its penetration depth by boundary diffusion is about 100µm.

The routine-RRR control of all cavities was made non-destructively. The collected data show that accelerating voltage tends to increase with RRR.

QUALITY CONTROL OF NB SHEETS FOR TTF

The eddy current scanning system is applied as a main method of the quality control of Nb sheets for TTF. The system was developed at BAM (Berlin) [1]. The update of the system consist of two new aspects (Fig. 1).

Firstly the scanning system is set up as a rotating system. This construction allow to reduce the mechanical vibration, appeared during start and stop of the scanning head in the old system. New system rotates the Nb sheet continuously, the scanning head is placed like the tangential arm of a record player. These improvement permitted to reach higher sensitivity and to reduce the measuring time (10 min instead 25 min per sheet).

The sensitivity improvement can be conclude from comparison of the Fig. 2 and Fig. 3, where the same grinding pit was scanned with the old and a new system.

Secondly a two frequency principle was applied. It is well known [2], that the penetration depth of eddy current signal δ for the same material depends only on the frequency f.

Where ρ is the resistivity and µ the magnetic permeability of the material.

A two frequency apparatus give the possibility to separate the surface and bulk defects. Scanning with high frequency (about 1 MHz) allow to detect the surface irregularities and the low frequency test (about 150 kHz) can find the bulk inclusions. The apparatus picks up both (high frequency and low frequency) signals, which can be subtracted from each other.

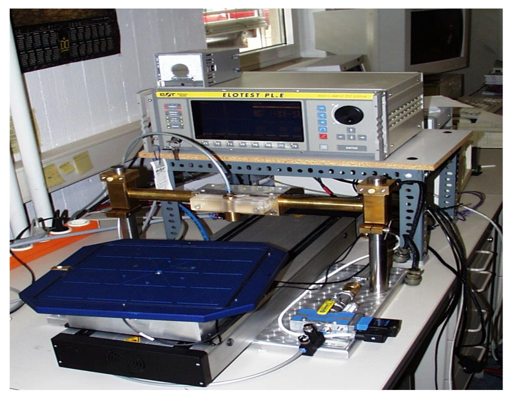

Fig.1 The eddy current scanning system

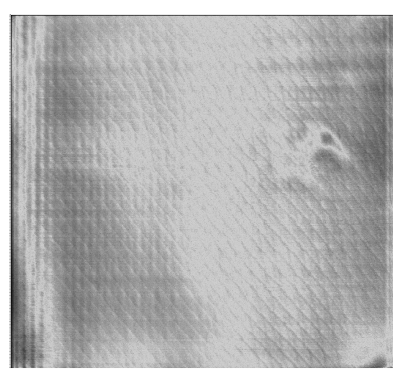

Fig. 2 Example of the scanning of the Nb sheet H28 with old scanning system

About 500 sheets for third fabrication series of TTF cavity were tested. In less then 7% of sheets some irregularities have been detected. A nondestructive identification of defects can be done by neutron activation analysis NAA, X-ray Fluorescence Analysis SURFA [1]. The first method is more efficient for analysis of layers close to the surface (with a penetration depth between few µm and few hundred µm), NAA delivers the information about bulk Nb and demonstrates very high sensitivity to Ta enclosures in Nb. A possibility of nondestructive Energy Dispersive X-Ray Analysis on the surface of the Nb sheets appeared with the creation of a Large Chamber Scanning Electron Microscope by the Firma VISITEC (Grevesmuehlen, Germany) [3]. This permits to separate the rest of foreign material inclusions on the surface from the grinding pits.

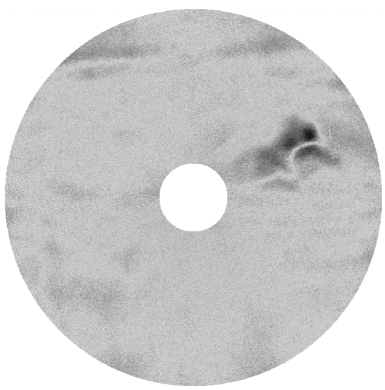

Fig. 3 Example of the scanning of the Nb sheet H28 with a updated scanning system

The application of high-temperature superconducting sensors SQUID (Superconducting Quantum Interference Device) gives a new perspective for the diagnostic in Nb. For example a SQUID Gradiometer system, developed at F.I.T. Messtechnik [4] has an extremely high magnetic field resolution. Magnetic fields of 1pT value can be registered without any problems. The device does not need any magnetic shielding and is therefore suitable for testing of rather large components.

Two methods of nondestructive testing are applied. The first method is based on the registration of remanent magnetic fields of inclusions. The second one is based on a thermoelectric effect and is efficient even for nonmagnetic inclusions. The artificially generated temperature gradient causes the thermal voltage and connected with it magnetic field on the boundary between main material and inclusion. The latter one can be measured with SQUID Gradiometer system.

Some Nb sheets of TESLA dimensions with material inclusions, found by eddy current scanning test, were successfully tested with SQUID Gradiometer system. For example an inclusion detected by eddy current in Nb sheet and identified by Large chamber SEM as a sand paper particle (because of enhanced concentration of Si) was clearly seen on SQUID Gradiometer test too. The Ta inclusions can also be observed with rather high resolution in Nb sheets.

Furthermore the SQUID method is more sensitive than eddy current method. For example a with eddy current method not detectable iron particle of size less then 50µm was found inside of one of the Nb sheets. The decreasing of the magnetic field signal is proportional to $1/R^5$ (R-distance to the inclusion). This makes possible the detection of rather deep inclusions in the material or investigation of the inside surface of closed parts like cavities. The measurement confirm this. The signal from the 50µm big particle was clearly observed during measurement at both sides of the sheet.

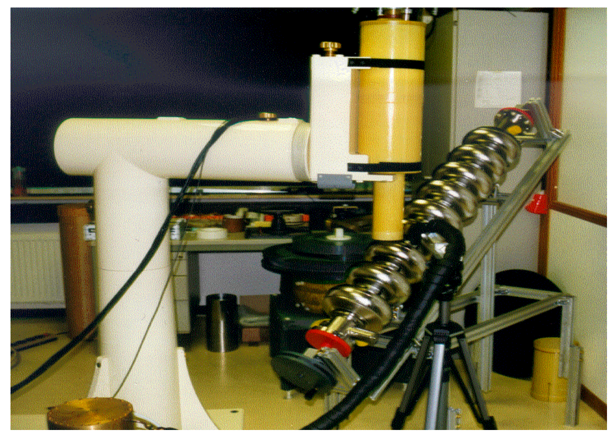

Fig. 4 The SQUID Gradiometer

The SQUID Gradiometer of F.I.T. allow to test rather large parts non destructively, for example 9 cell TESLA cavities. The cavity S35, that reaches above 20 MV/m accelerating field, was examined with the SQUID Gradiometer (Fig. 4). Some irregularities were detected in the cell 3 and 7 by application of a thermoelectric method, which roughly correlates with results of temperature mapping of this cavity [5]. It makes sense to mention, that similarly distributed inhomogeneity was detected earlier in the Nb sheets too.

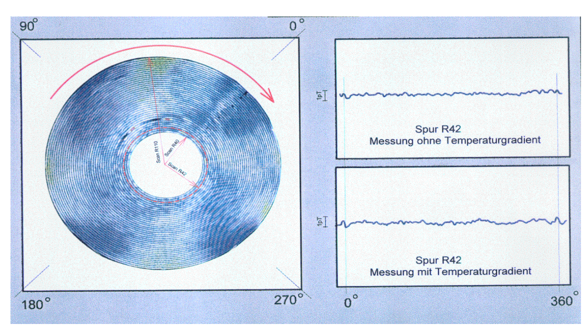

Fig.5 Example of the homogeneous sheet, detected by the SQUID Gradiometer

Few sheets from each Nb supplier were tested. The example of the homogeneous and not inhomogeneous sheets can be seen on the Fig.5 and Fig.6.

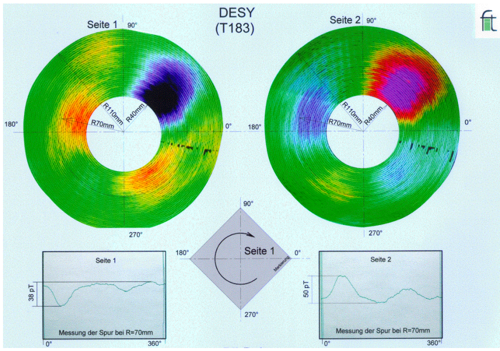

Fig.6 Example of the inhomogeneous sheet, detected by the SQUID Gradiometer

PURIFICATION HEAT TREATMENT OF NIOBIUM

The purity of the niobium can be additionally improved by the purification heat treatment, (called often solid state gettering too). The foreign metal Me (for example Ti, or Y) is vapor deposited on the surface of niobium at high temperature. The bonding enthalpy of this metal to the interstitial impurities such as oxygen, nitrogen or carbon should be higher than of Nb. The creation of the Me_xO, Me_xN and Me_xC compounds reduce the concentration of interstitial impurities in the surface of Nb. Moreover the Me protect the absorption of the rest gas from the furnace environment. On the other hand the high temperature intensifies the diffusion of the interstitial impurities from inside to surface and as result allow to purify the balk Nb too. This procedure has an another positive effects for cavity performance. The annealing itself at high temperature homogenizes the niobium additionally (dissolves small segregations of different nature, for example rests of oxides, clusters of foreign materials and so on).

The temperature and duration of the purification annealing depend on the evaporation rate of the getter material and diffusion rate of the impurities. Pure titanium is applied for solid state gettering of TTF cavities with annealing parameters 1400°C, 4 hours (or a combination 1400°C, 1h plus 1350°C, 3h).

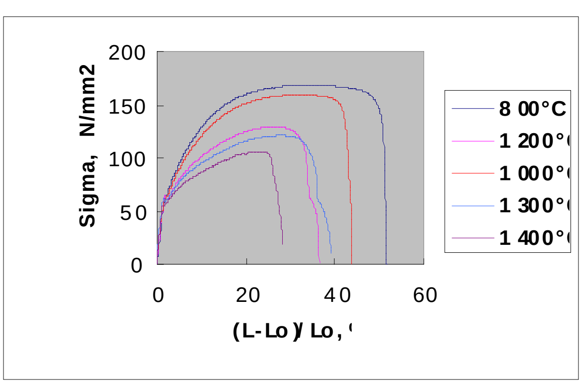

Fig.7 Strain-stress curves of HERAEUS Nb after

In order to learn more about properties of Nb after purification heat treatment a series of annealings at different temperatures (800°C, 1000°C, 1200°C, 1400°C) for 4hours with Ti and without Ti were done. Niobium of three companies, that supplied material for TTF (HERAEUS, Oremet Wah Chang and Tokyo Denkai) were tested. The mechanical properties, microstructure and RRR are analyzed. Some results can be seen in Fig.7-12.

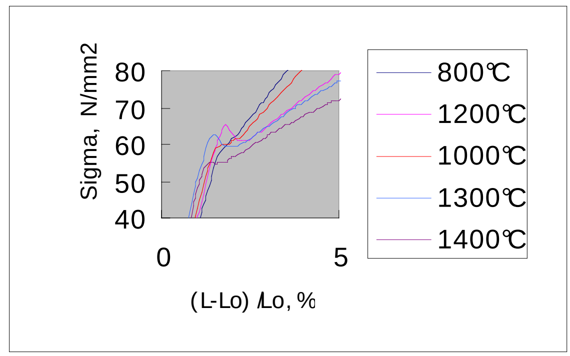

Fig. 8. Strain-stress curves of HERAEUS Nb, annealed at different temperatures 4h with Ti

The typical result of tensile test represents Fig 7. The stress-strain curves show, that raising the annealing temperature from 800°C to 1400°C reduces the breaking elongation and the tensile strength almost by a factor two. A big difference between annealing with Ti and without Ti was observed in the region of transition from elastic to plastic behavior (Fig. 8-9).

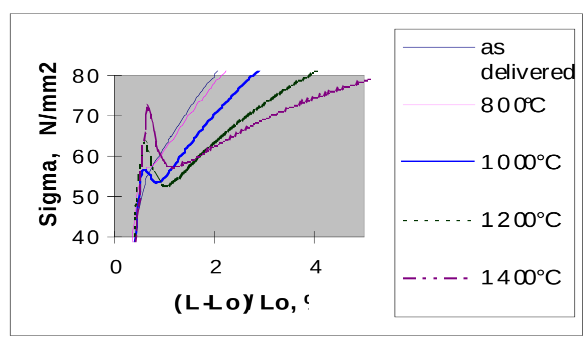

Fig. 9. Strain-stress curves of HERAEUS Nb, annealed at different temperatures 4h without Ti

The upper and lower yield point can be clearly seen in both cases. Such strain-stress curves are typical for body centered cubic metals like Nb, if it contains traces of interstitial impurity atoms. This fact suggests that the dislocations are strongly pinned by impurity atoms [6]. Impurity atoms, which differ in size from the host atoms of a lattice are diffused to a dislocation line and create close to it a so called impurity cloud. The impurity cloud pins the dislocation and makes its motion difficult. The upper yield point can be explained as a stress needed for breaking the

cloud the dislocation can move at a lower stress level, which presents the lower yield point.
The annealing with Ti reduces the concentration of interstitial impurities and, in a good accordance with pinning mechanism, reduces the difference between upper and lower yield points by increasing of annealing temperature. On the contrary the annealing without Ti increases the content of interstitial impurities and the ratio of the upper to the lower yield point. These results shows, that a qualitative conclusion about grade of Nb purity can be drown from the behavior of it stress-strain characteristic.

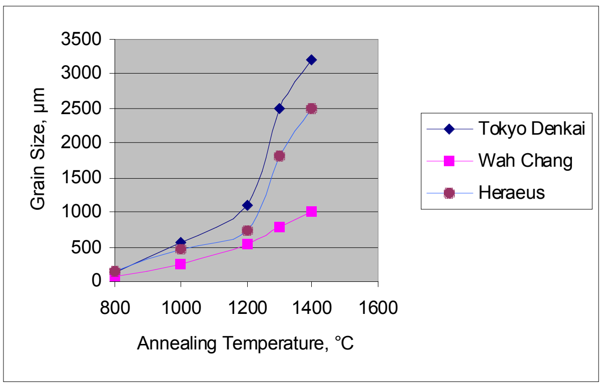

Fig. 10 Grain size versus the annealing temperature for Nb of different suppliers

The grain growth during annealing of the Nb of different suppliers can be seen in Fig. 10. The essential growth of the grain starts at 1000°C. It is interesting to notice a correlation between the diameter of the Nb ingot and the grain size in the sheet (the grain size is proportional to 1/D, where D is the ingot diameter).
The behavior of the hardness HV10 during annealing with Ti and without Ti is represented by Fig.11. The hardness almost does not change with grain growth. Only at high annealing temperatures, when the difference in purity becomes significant, the hardness weakly decreases or increases for samples annealed with Ti or without Ti, respectively.

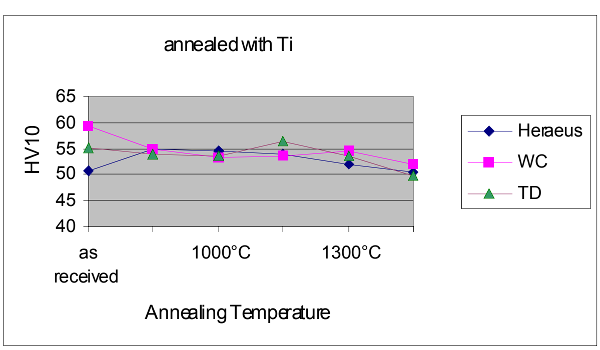

Fig. 11 Hardness HV10 versus the annealing temperature for Nb of different suppliers

The tendency of RRR behavior is similar for Nb of all the RRR (Fig. 12) and annealing without Ti reduces it. The significant changes of RRR starts from 1000-1200°C.
The RRR described above is the mean value. Interesting is, to understand how is the RRR distribution in a cross-section of the Nb sheet. In the work [7] the solid state gettering process was analyzed theoretically. A definite distribution of the interstitial impurities in the cross section of the sheet

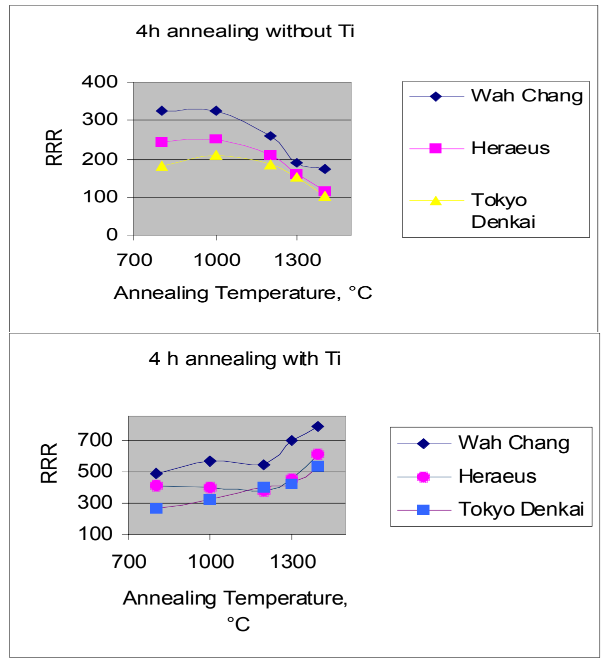

Fig.12 RRR versus the annealing temperature for Nb of different suppliers.

takes place after purification. The concentration of O, N, C decreases from the center to the edges so that the RRR should go up in the same direction. Unfortunately it is not possible to carry out a direct RRR measurement of the purified sample layer by layer. For this purpose, a rough method was proposed in the work [8]. A niobium sample after purification heat treatment was etched layer by layer, and the RRR was measured after each step. The RRR distribution of such sample is shown in Fig.13. It can be clearly seen, that the RRR near of the surface is much higher than that inside of the sample. This behavior is in a good agreement with the calculations of [7] and the results presented in Ref. [9].
No doubt the RRR is one of the important parameters of the cavity performances. A nondestructive eddy current method of the RRR measurement developed at DESY [10] allows to do the routines RRR control of the cavity during its cool down or heat up for HF test in the vertical cryostat. The collected data of RRR versus accelerating gradient for TTF cavities are shown in Fig. 14. The tendency of the increasing of accelerating gradient with the RRR rise is apparent. For the cavities with RRR higher then 500 the trend is not so clear. Probably another mechanisms plays a leading role here.

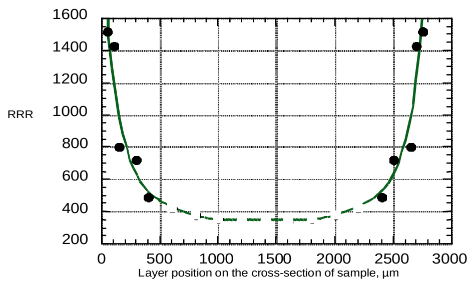

Fig.13 The RRR distribution in the 2,8 mm thick sample purified with Ti

In the purification heat treatment should be taken into consideration the interaction of Ti with Nb. There are two important aspects. On one side the titanium creates a layer on the Nb surface and on the other side it diffuses deeper inside of the Nb.

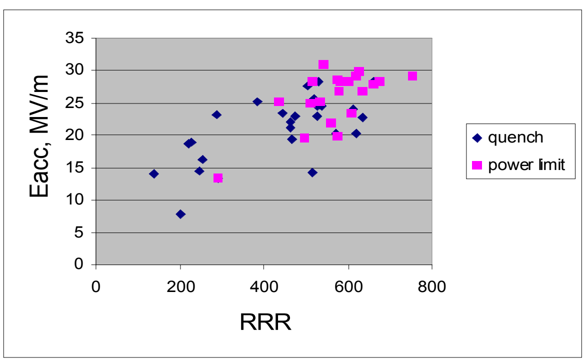

Fig. 14 Eacc(RRR) dependence for TTF cavities limited by quench and power

The EDX line scan from the surface to the inside direction of the sample purified in the furnace together with one of the TTF cavity S8 represents Fig. 15.

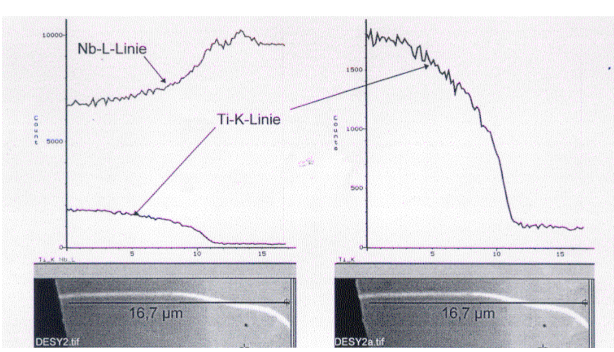

Fig. 15 The EDX scan of the sample purified with Ti

The Ti layer can be clearly seen in the back scattering contrast of SEM, the thickness of the Ti layer is about 10 µm. Results of a quantitative EDX point analysis shows (table 1) that Ti covered the Nb surface not completely

Table 1: Point analysis of the Ti layer on Nb after purification heat treatment

Analysis point	Element	At %	Wt %
Surface	Ti-K	42,03	27,21
	Nb-L	57,97	72,79
7 µm deep	Ti-K	16,02	8,95
	Nb-L	83,98	91,05

One can suppose a much higher penetration of Ti into Nb along the grain boundaries, than can be observed by SEM. This penetration depth is very difficult to measure correctly. For example the resolution limit of Ti signal of SEM is about 1%. Moreover the area of the beam impact on the sample is bigger than 1 µm. This means, if for example only one or two atom layers of the grain boundary are covered up with Ti, the Ti signal can not be registered. Some data about the diffusion of the Ti into Nb are collected in the table 2.

Table 2: Penetration depth of Ti during purification heat treatment

Depth, µm	Annealed	Method	Ref.
57	1400°C, 4h	AES	11
100	1400°C, 4h	SIMS	12
36	1400°C,1h+1250°C,3h	AES	11
50	1300°C, 6h	AES	13

There are some discrepancies, but it is clear, that anyway a layer with the thickness about 100µm should be removed after purification heat treatment of the cavity.

CONCLUSIONS

The upgraded eddy current scanning system is applied as a main instrument for quality control of Nb sheets. More than 500 sheets for third series of TTF cavity production were tested. Some irregularities were detected.

A nondestructive identification of defects can be done by neutron activation analysis NAA, X-ray Fluorescence Analysis SURFA, Large Chamber Scanning Electron Microscope.

The application of high-temperature superconducting magnet sensors SQUID for diagnostic of foreign material inclusions in Nb gives a new perspective for the diagnostic. A non destructive test of the inside surface of the TESLA cavity is possible with this technique.

A series of purification heat treatments of Nb from different suppliers (HERAEUS, Oremet Wah Chang and Tokyo Denkai) was done. The RRR measurement, traction test, hardness measurement and microstructure analysis have shown, that marked change of properties starts at temperatures above 1000°C.

The penetration of the Ti into Nb during purification heat treatment is discussed. The thickness of the Ti layer on Nb is about 10 µm and the penetration depth of the Ti by the boundary diffusion is about 100µm.

The routine RRR control of the TTF cavity during its cool down or heat up for HF test in the vertical cryostat was done non destructively. The collected data show that accelerating voltage tends to increase with RRR.

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