CORRELATION OF MICROSTRUCTURE, CHEMICAL COMPOSITION AND RRR-VALUE IN HIGH PURITY NIOBIUM (NB-RRR)

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Abstract

Specification and working point of linear accelerators reaches the limit for the niobium cavities from a physical and metallurgical point of view. From literature it is known, that increased level of interstitial impurities and the presence of residual stresses after the final heat treatment can cause a severe degradation of the RRR value.

The possible influence of different impurity levels on the RRR value were calculated and discussed with regard to the current material specification for the XFEL project. For verification the results were compared with measured values from a melted niobium ingot. Sheet sections from one production lot, with RRR-values in the range of 360 to 430, have been analysed in the scanning electron microscope (SEM) utilizing EBSD (Electron backscattered diffraction) to study the scattering of the crystallographic texture.

The scatter of grain size, hardness and texture are in a typical range and in agreement with results from literature. Measured gas contents and RRR values on bulk niobium are in good agreement with the material specification. An influence of the observed texture variation on the RRR-value wasn't observable.

INTRODUCTION

High-purity niobium with a high residual resistivity ratio (Nb-RRR) is the key issue for the fabrication of superconducting accelerating cavities for future particle accelerators (XFEL, ILC). Starting material for fabrication of cavities are rolled polycrystalline Nb-RRR sheets with uniform grain sizes, which are subsequently processed by deep drawing, e-beam welding and surface treatment. To obtain high accelerating gradients and quality factors constant material properties in terms of thermal conductivity and RRR-values surface quality are necessary. [1,2]

In the course of cavity testing a high scatter of RRR-values has been observed throughout different investigation programs. The reason for these fluctuations could not be revealed by standard examination methods. Beside parameters for chemical and thermal treatment and surface condition of the inner surface of the cavity, material properties play an important role. Thermal conductivity and RRR values are strongly influenced by the content of interstitials (O,C,H and N), amount and distribution of impurities, grain size, texture, residual stresses and density of dislocations. [3]

In the context of our research we applied further investigations to get a comprehensive understanding about the influence of micro structural properties and impurity concentrations on the RRR value.

The influence of different impurity levels on the RRR value were estimated by calculation and discussed with regard to the current material specification for the XFEL project. For verification the results were compared with measured values from a melted niobium ingot used for production. On different sheet sections from the same production lot the homogeneity of microstructure and material properties were investigated in the annealed condition.

INFLUENCE OF IMPURITIES AND MICROSTRUCTURE ON RRR VALUE

To determine the quality of the niobium material, simple methods have been implemented for quality assurance. A common method to determine the purity and homogeneity of niobium is to measure the RRR-value. In the specification for XFEL the RRR value is determined with 300 or higher. The electrical resistivity is measured by using four point technique, with an applied magnetic field, to suppress the superconducting state. The RRR-value is defined as follows:

$$RRR = \frac{\rho(295K)}{\rho(4{,}2K)} \tag{1}$$

where ρ is the electrical resistivity at given temperature.

It is well known that the electrical resistivity of metals at temperatures close to T=0 K is mainly caused by impurities ρ_{fa}, defects ρ_d and for thin specimens by electron-surface-scattering ρ_s. At this temperature the intrinsic resistivity from electron-phonon scattering $\rho_{i(T)}$ is negligible, but it becomes dominant at room temperature. Hence,

$$\rho = \rho_i(T) + \rho_{fa} + \rho_d + \rho_s \tag{2}$$

The proportional constants for several impurities and micro structural defects (like e.g. vacancies, dislocations and grain boundaries) in niobium are shown in Figure 1. [4].

In order to achieve RRR values of 300 and higher the concentration of impurities must be kept as low as possible (see valid material specification for XFEL in Table 1). Zirconium is not included in the XFEL specification, the maximum value was taken from ASTM B 393-05, Type 5 for the sake of completeness. The

influence of dissolved impurities on the RRR value is proportional to their concentration. The constants are also given in Table 1. For Fe, Ni and Si the proportionality constants couldn't be found in literature. Therefore, the influence of these elements wasn't considered for the calculations.

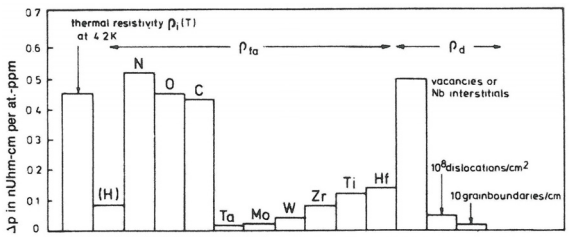

Figure 1: Influence of impurities and defects on the residual resistivity of Niobium [4].

Table 1: XFEL Material specification for Nb-RRR 300, chemical analysis of Nb ingot "Lot 3212" and proportional constants for dissolved impurities [4,5,6]

Element	Max. [µg/g]	Ingot Lot 3212 [µg/g]	proportional constant [Ω*cm/at%]
Hydrogen	2	1	$8{,}2 * 10^{-11}$
Nitrogen	10	3	$5{,}2 * 10^{-10}$
Oxygen	10	2	$4{,}5 * 10^{-10}$
Carbon	10	1	$4{,}3 * 10^{-10}$
Tantalum	500	106	$2{,}5 * 10^{-11}$
Tungsten	70	5	$4{,}2 * 10^{-11}$
Titanium	50	5	$1{,}2 * 10^{-10}$
Iron	30	3	-
Molybdenum	50	4	$2{,}8 * 10^{-11}$
Nickel	30	3	-
Silicon	30	7	-
Zirconium [6]	100	2	$8{,}2 * 10^{-11}$
Ref.		measured	

On the basis of equations (1) and (2) RRR-values can be predicted theoretically. Considering only the electron photon scattering from equation (2) for an ideal, defect and impurities free niobium bulk material, the maximum theoretical RRR value can be calculated. Using ρ_i (295 K) = $14.58 \cdot 10^{-6}$ and ρ_i (4,2 K) = $4.5 \cdot 10^{-10}$ [Ω * cm / at%] the RRR value yields at 32400.

The effect of common interstitial impurities like H, N, O, and C on the RRR-value is shown in Figure 2. Starting point for each curve is the RRR-value at a value of RRR=492, where the maximum concentration for other impurities (Ta, Ti, W, Mo and Zr) were used according XFEL specification. It can be clearly seen that the highest negative input comes from H. Independently from the other interstitials; concentrations of 2 µg/g lower the RRR-value near to the minimum allowed value of 300. Considering the maximum content of interstitials according XFEL specification, the RRR value drops down to 134 (without consideration of the other impurities). In Table 1 exemplarily the chemical analysis and the measured RRR value for a melted niobium ingot (lot 3212) are given. Calculation of the RRR value based on the given contents of impurities and interstitials leads to a value of RRR=490. The measured value for the ingot is at RRR=364.

Under consideration, that strains caused by the large temperature gradients during ingot solidification are not regarded, the calculated and measured RRR-values are in good correlation.

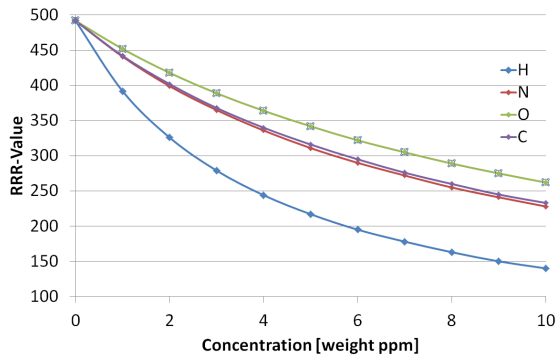

Figure 2: RRR-value of Niobium as a function of interstitial impurities.

CHARACTERISATION OF CRYSTALLOGRAPHIC TEXTURE

Starting from the melted niobium ingot sheet production is done by forging to break down the initially large grains and to bring the material in a desired shape for subsequent rolling to final dimension. Heat treatment at the final stage causes changes in the microstructure by recovery, recrystallization and grain growth. It is well known, that rolling and annealing of metal sheets leads to distinct crystallographic textures. Work of Bieler et.al. shows already the appearance of pronounced textures in recrystallized niobium sheets with strong variation within the sheet thickness and different samples. [3]

From the melted niobium ingot (lot 3212, chemical composition as cast is given in Table 1, sheets were produced according the established production route for Nb-RRR at Plansee. [7] After final heat treatment three different sheet sections from the same production and annealing lot with a nominal thickness of 2,8 mm were taken for characterization (specimens 35, 37 and 40). Task of the investigation was to study the scattering of crystallographic texture within one production lot in

comparison to the measured RRR-values and micro-hardness measurement (Table 2).

The samples taken from the sheet sections have been analysed in the scanning electron microscope (SEM) utilizing EBSD (Electron backscattered diffraction). The specimen geometry and dominant textures in the related areas are schematically illustrated in Figure 3a. The colour code for crystallographic orientations in the IPF-figures (inverse pole figure) is shown in Figure 3 b.

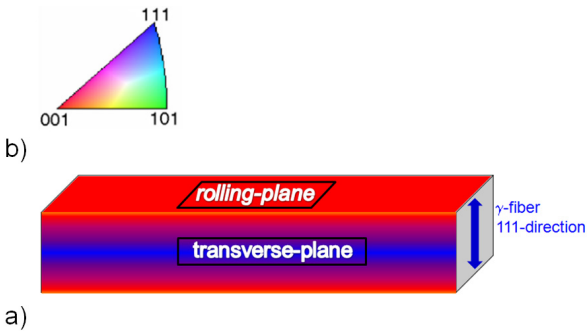

Figure 3: a) Specimen geometry and dominant textures. b) Color code for crystallographic orientations.

The measured textures (IPF's) are illustrated in Figure 4 for the rolling plane and Figure 5 for the transversal plane respectively. The black dots in Figure 5 are the marks from hardness measurement (see below). The shortcuts RD, TD and ND stand for rolling-direction, transverse-direction and normal-direction as defined in Figure 3b.

In the rolling plane all specimens possesses a very dominant cube texture (Figure 4). The average grain size in the rolling-plane varies between 50 µm (specimen 35) and 65 µm (specimen 40).

In the transversal plane the specimens are much more inhomogeneous and different among each other (Figure 5). The widths of the pictures represent nearly the sheet thickness. In the center of the sheet, a more or less dominant {111} texture is present. Near to the edge (rolling surface) a {001} texture becomes more and more dominant, but not exclusively. Also the grain size scatters in a wide range between 45 µm in the surface area and 150 µm in the center.

The pictures confirm the results from [3] where also remarkable inhomogeneity's in grain size and texture within the same batch was found. On the one hand the inhomogeneity can be explained by the structural condition of the melted block, where coarse grains with a variety of orientations are present, which can cause different textures in the final sheet. On the other hand it is well known that during rolling, caused by differently orientated strain paths, slip systems are activated which rotate crystals in the center of the sheet parallel to the normal direction {111}.

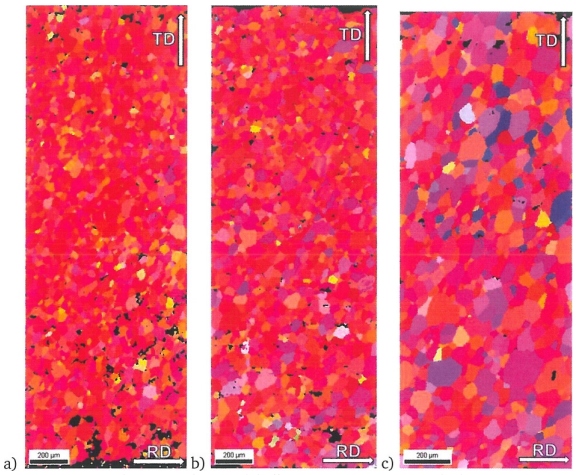

Figure 4: Texture analysis (IPF), rolling plane a) specimen 35, b) specimen 37, c) specimen 40.

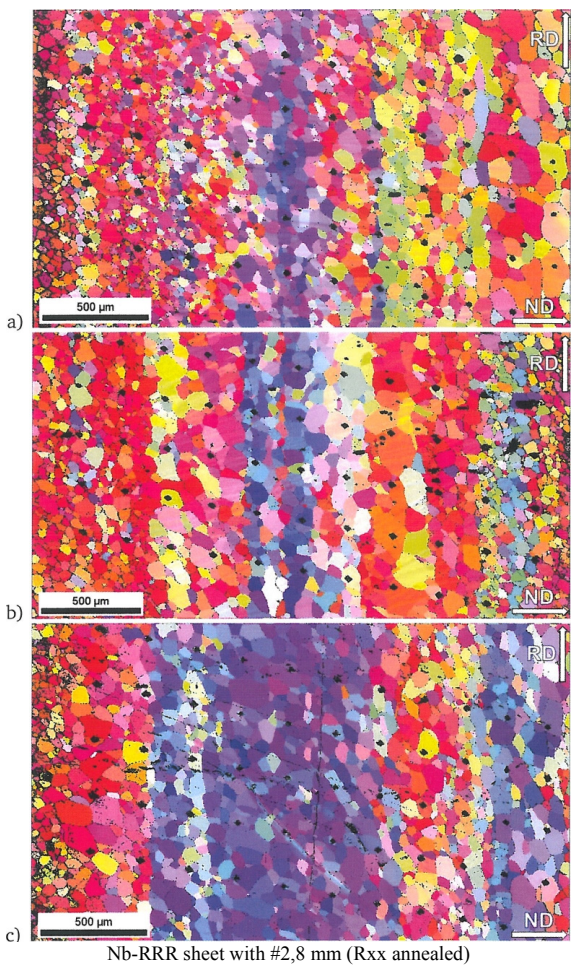

Figure 5: Texture analysis (IPF), transverse plane a) specimen 35, b) specimen 37, c) specimen 40.

Hardness measurements in the transverse-plane were performed to clarify the distribution of impurities in the sheet material. In order to get a high lateral resolution the Vickers method (HV 0.05) were used. Thereby smaller agglomerations of impurities can be detected. Measurements were performed on micrographs over the sheet thickness. The positions of the hardness indentations are related to the positions of the hardness measurements in Figure 6. To get a representative amount of values the measurements were repeated five times. The standard deviation is given by the corresponding error bars. The black dots in Figure 5 stem from hardness indentations. Due to overlapping scatter bars of the measurements the hardness variations detected can be seen taken as a trend.

The average hardness for all sheets is between 55 and 70 HV0,05. As one can note from Figure 6, hardness is slightly increased in the surface areas as compared to the center of the sheets. Due to the low test load the absolute values are slightly higher compared to standard hardness measurement with HV5.

It is obvious, that different grain size and texture has no effect on the hardness. The hardness in fine-grained areas (e.g. specimen 35 at 220 µm depth, {001}) is in the same range as in coarse-grain areas (e.g. specimen 40 at 1100 µm depth, {111}). It can be assumed, that for the higher hardness in the surface area slightly increased contents of interstitially dissolved impurities are responsible. In Figure 6 also the measured RRR value is given for the investigated samples. The scattering of the values (RRR = 369 – 428) can be explained by the range of interstitials. Due to the same reason of overlapping scatter bars, a relation between texture, hardness and RRR-value couldn't be established.

In Table 2 the range of values from the microstructural characterization, hardness and RRR measurement for the investigated sheet sections are summarized. For completion also the values for interstitials (H, N, O and C) are given. If a higher content of interstitials would be responsible for the increased hardness values near the surface, it is obvious from Table 2 that the gas content and RRR value of the bulk material wouldn't be influenced directly. Both, the gas content and RRR values, are in good agreement with the material specification.

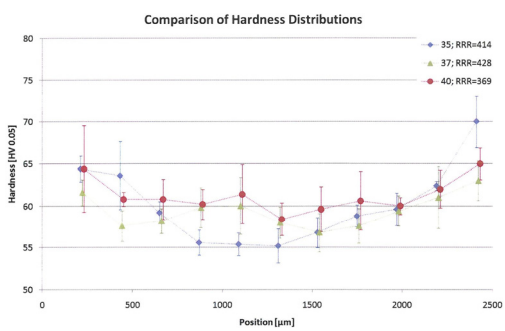

Figure 6: Comparison of hardness distributions (position "zero" indicates the sheet surface).

Table 2: Investigation results on Nb-RRR sheet sections made from Nb ingot "Lot 3212" billet with nominal thickness of 2,8 (annealed)

Specimen	Range of values (specimen 35, 37 and 40)
Grain size [µm] (rolling plane)	50 – 65
Grain size [µm] (transversal plane)	45 – 150
Hardness [HV 0,05] (transversal plane)	59 – 61
RRR value [measured]	369 – 428
Hydrogen [µm]	1
Nitrogen [µm]	4 – 5
Oxygen [µm]	2 – 5
Carbon [µm]	1 – 5
RRR value [measured]	369 – 428

SUMMARY

Specification and working point of linear accelerators reaches the limit for the niobium cavities from a physical and metallurgical point of view. From literature it is known, that increased level of interstitial impurities and the presence of residual stresses after the final heat treatment can cause a severe degradation of the RRR value.

The possible influence of different impurity levels on the RRR value were calculated and discussed with regard to the current material specification for the XFEL project. For verification the results were compared with measured values from a melted niobium ingot. The agreement between the theoretical calculations and the measurements gave evidence that the most adverse effect on the RRR-values is caused by interstitial impurities.

To clarify if microstructural distinctions could be the cause for scattering of material properties the crystallographic textures have been investigated on different sheet section from one production lot in the recrystallized condition. Comparing the specimens, remarkable inhomogeneity's in grain size and texture, especially in the transversal direction was found. A {111} y-fiber texture dominates in the center of the sheet and a {100} cubic-texture dominates on the surface.

Data comparison with literature showed that the scatter of grain size, hardness and texture are in a typical range. Measured gas contents and RRR values on bulk niobium are in good agreement with the material specification. An influence of the observed texture variation on the RRR-value wasn't observable.

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