Development of high purity niobium used in SRF accelerating cavity*

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Abstract Niobium is widely used in SRF (Superconducting Radio Frequency) cavities due to its excellent superconductivity and workability. With the continuous development of technology, higher demands of material are raised. One of the key issues is that RRR (Residual Resistance Ratio) of the Nb material should be more than 300, which requires that the Nb ingot have even higher RRR. This article introduces the development and the experimental results of high purity niobium in OTIC in Ningxia (Ningxia Orient Tantalum Industry Co. Ltd.), and the test results of the single cell TESLA (Tera Electron volt energy Superconducting Linear Accelerator) shaped cavity manufactured by Peking University using Nb material from OTIC.

Key words high purity niobium, superconducting cavity, electron beam furnace, *RRR* value

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1 Introduction

Niobium is the most suitable material for superconducting cavity at radio frequency with its high melting point, good plasticity, low evaporation, stable chemistry, strong corrosion resistance, and good heat exchange, and it has been thoroughly studied because of its wide use in metallurgy, chemistry, aerospace, atomic energy, electronics, superconducting and so on[1—4]. In microwave applications, the limit to superconducting is set by thermodynamic critical magnetic field, which is below 1 T for all known superconductors; to lower the losses caused by flux pinning, type II superconductor should be used. Nb is a type II superconductor with good mechanical properties; its critical temperature T_c is 9.17 K, which is the highest among all metals; its thermodynamic critical field is about 200 mT. Other superconductors, such as Nb_3Sn (T_c=18 K), NbN (T_c=16.2 K for the δ phase), or $YBa_2Cu_3O_7$ (T_c=92 K), are more attractive at the first sight, but it is hard for them to form various shapes and to achieve uniform good material properties over a large surface area. The most successful candidate other than Nb is Nb_3Sn coated Nb, but the gradients achieved in such cavities are always below 15 MV/m. On the contrary, the 9 cell cavities using solid Nb have reached an average gradient of 33 MV/m since 2000; the highest gradient of single cell Nb cavity has even reached is 59 MV/m, so Nb is desirable for SRF cavities, and it has been chosen for the next-generation accelerator ILC (International Linear Collider)[5—8].

The research on SRF cavities has made rapid progress since 1970s in America, Europe, and Japan, and the art of Nb smelting has been managed by some companies. The suppliers of Nb applied in SRF cavities are Tokyo Denki in Japan , Wah Chang in USA, W.C. Heraeus in Germany, and CBMM (Companhia Brasileira de Metalurgia e Mineracão) in Brazil. Compared with overseas, the research on Nb material started late in 2001 in China, by Ningxia OTIC and Northwest Institute for Nonferrous Metal Research. And the Nb produced by OTIC has reached the TESLA technical requirements.

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2 Correlation between *RRR* and impurities

SRF cavities require material low impurities and high *RRR* value. Inclusions on the RF surface play the role of normal conducting nucleation sites for thermal breakdown; the dissolved impurities serve as scattering sites for the electrons not condensed into Cooper pairs. These impurities lower the thermal conductivity, thereby the cryomodule system can not cool down the cavities effectively, which will limit the maximum tolerable surface magnetic field. The thermal conductivity λ can be estimated by *RRR*, and it can be calculated by the impurity content as follows[9]:

$$\lambda(4.2\ \text{K}) \approx 0.25 \cdot RRR[\text{W/(m}\cdot\text{K)}], \tag{1}$$

$$RRR = \left(\sum f_{\text{i}}/r_{\text{i}}\right)^{-1}. \tag{2}$$

f_{i} means the content of impurity i (determined by the mass fraction in 10^{-6}); r_{i} is the relevant resistivity, which is listed in Table 1. To obtain a high thermal conductivity, the impurity content must be very low, especially for the interstitial elements (C, N, O, H) and Ta.

Table 1. The weight factor r_{i} of some impurities.

impurity atom i	r_{i} in 10^4 wt. 10^{-6}
N	0.44
O	0.58
C	0.47
H	0.36
Ta	111

3 Experiment process

3.1 Raw materials

The impurities in niobium can be divided into 4 types by characters: (1) O, N, H , C and other nonmetals; (2) Bi, As, Sb and other elements; (3) Metals with high vapor tension, such as Al, Mg, Fe, Co, Ni and Mn; (4) Metals with high vapor tension and high melting point, such as Ta, W, and Mo. Impurities of (1) to (3) could be removed by vacuum EB (Electron Beam) furnace melting and physical refining, for instance, C, N, O, and H will escape in the form of gas; but the melting points of Ta (2986 ℃) and W (3407 ℃) are higher than Nb (2468 ℃) , and their vapor tensions are lower, so impurities of (4) can not be removed even in high vacuum; hence, they should be reduced through recrystallizing process and avoiding secondary contamination.

The raw material is low C content Nb, which is produced from recrystallized NbAl alloy by applying thermo-aluminum process to Nb_2O_5. The impurity contents are listed in Table 2.

Table 2. The impurity content of raw material.

elements	content/10^{-6}
C	$\leqslant$15
N	$\leqslant$300
O	$\leqslant$500
W	$\leqslant$30
Mo	$\leqslant$30
Fe	$\leqslant$50
Si	$\leqslant$200
Ti	$\leqslant$20
Ni	$\leqslant$20
Ta	$\leqslant$200

3.2 Equipment

The equipment for R&D is a 600 kw EB furnace from ALD Vacuum Technologies GmbH in Germany. The furnace has two pumps with a speed of 50000 L/s, one melting chamber with vacuum 5×10^{-4} Pa , two melting stations, and a rotary device in the ingot-drawing system. One time melting by EB furnace could use the horizontal material feeding, during the process of feeding, the melting quality could be improved by rotating the ingot-drawing mode, which could remove the melting pool shadow phenomenon effectively.

3.3 Experimental process

The experiments were carried out on the horizontal EB furnace. The contamination control has been improved by changing the melting time, melting speed and the crucible size, to optimize the melting process for higher *RRR* and lower costs. At last, 4 sample ingots were mode for the tests.

4 Results and discussion

4.1 The impact of parameter changes

The interstitial elements can be reduced by the melting and refining process, so by reasonably increasing melting times. We find that the interstitial element contents are reduced to less than 10×10^{-6} after 4 or 5 melting times, and the *RRR* of Nb ingots is above 300 after 4 melting times, which is shown in Fig. 1.

RRR is also related to the size of crucible. We measured the *RRR* at different positions of the ingots, and the results show that under the same melting conditions, the *RRR* gets higher with increasing of the crucible diameter, which is shown in Table 3. This may be due to the increase of volatilization area.

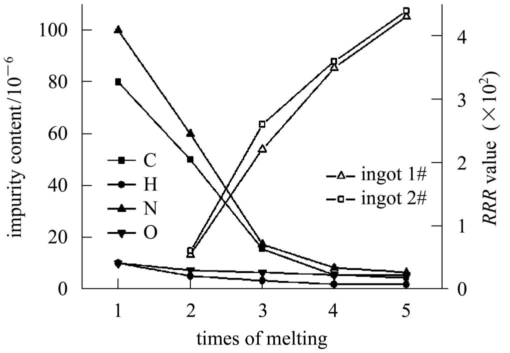

Fig. 1. The solid dots indicate the correlation between melting times and impurity contents; the open dots indicate the correlation between melting times and RRR value.

Table 3. Correlation between crucible size and RRR.

crucible diameter/mm	RRR			
160	108	107	109	105
200	163	189	159	177
220	200	250	260	195
250	379	363	370	334

4.2 Test results of Nb ingot

Some of the sample ingots were sent to DESY (Deutsches Elektronen-Synchrotron) to measure their mechanical and SRF properties. The mechanical property results are shown in Fig. 2; the yield strength of Nb ingot is higher than 40 MPa, which indicates good workability.

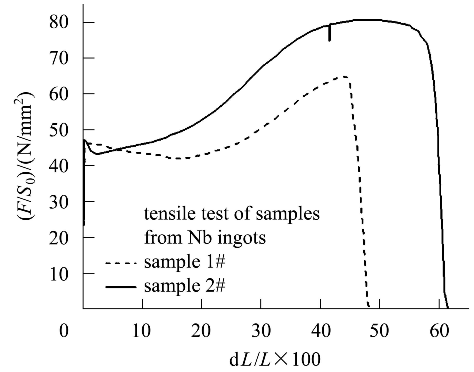

Fig. 2. Tensile test of samples 1# and 2# from Nb Ingot.

The main impurity contents of our 4 sample ingots are measured by gas analysis, and we have estimated the RRR values using Eq. (2). The results are higher than the actual values due to the reference sample problem, and they are listed in Table 4. More detailed results for high purity Nb ingot after 4 melting times, using GDMS (Glow Discharge mass spectrometry) analysis, are listed in Table 6.

Table 4. Impurity contents (in 10^{-6}) and estimated RRR of Nb Ingots.

	TESLA requirements	1#	2#	3#	4#
C	$\leqslant 10$	5	7	7	5
N	$\leqslant 10$	9	5	5	9
O	$\leqslant 10$	5	5	5	5
H	$\leqslant 2$	2	2	2	1
W	$\leqslant 70$	17	16	16	12
Mo	$\leqslant 50$	10	10	10	10
Ti	$\leqslant 50$	<5	<5	<5	<5
Fe	$\leqslant 30$	<5	5	5	5
Si	$\leqslant 30$	<10	<10	<10	<10
Ni	$\leqslant 30$	<5	<5	<5	<5
Ta	$\leqslant 500$	100	<100	<100	<100
RRR	$\geqslant 300$	333	419	414	359

The RRR of Nb ingot is also measured both by the IEE.AC (Institute of Electrical Engineering, Chinese Academy of Sciences) and DESY at 6 different positions (top, middle, and bottom), and the results are listed in Table 5; as there is 10% error in results, the IEE.AC has chosen the minimum, while DESY has chosen the maximum.

Table 5. RRR test results of ingot sample 2#.

crucible diameter/mm	possition					
	1	2	3	4	5	6
IEE.AC	412	426	419	419	417	420
DESY	460	466	437	485	467	526

Table 6. GDMS results of impurity contents (in 10^{-6}) in Nb ingot.

atom	content	atom	content	atom	content	atom	content	atom	content
Li	<0.005	V	<0.001	Y	<0.001	Ce	<0.001	W	1.2
Be	<0.005	Cr	<0.005	Zr	<0.02	Pr	<0.005	Re	<0.007
B	<0.009	Mn	<0.005	Mo	0.37	Ta	<100	Os	<0.005
F	<0.008	Fe	<0.005	Ru	<0.005	Nd	<0.01	Ir	<0.005
Na	<0.06	Co	<0.001	Rh	<0.001	Sm	<0.007	Pt	<0.005
Mg	0.07	Ni	<0.005	Pd	<0.006	Eu	<0.005	Hg	<0.02
Al	<0.005	Cu	<0.007	Cd	0.77	Gd	<0.005	Tl	<0.001
Si	0.25	Zn	<0.005	Sn	<0.03	Tb	<0.001	Pb	<0.005
P	0.08	Ga	<0.007	Sb	<0.008	Dy	<0.005	Bi	<0.008
S	<0.005	Ge	<0.04	In	0.02	Ho	<0.001	Th	<0.001
Cl	0.09	As	<0.005	I	<0.001	Er	<0.005	U	<0.001
K	<0.01	Br	<0.01	Te	<0.01	Tm	<0.005		
Ca	<0.009	Se	<0.009	Cs	<0.2	Yb	<0.006		
Sc	<0.001	Rb	<0.001	Ba	<0.005	Lu	<0.001		
Ti	0.002	Sr	<0.001	La	<0.001	Hf	<0.005		

4.3 Test results of SRF cavity

Using high purity Nb material, Peking University has manufactured some TESLA shaped single cell cavities, and the multi-cell cavities are being manufactured. One of the single cell cavity was surface treated and tested at JLab (Jefferson Lab) in USA1). The test result is shown in Fig. 3, where Q_0 is the intrinsic quality factor of the cavity; the magnetic quench field is 185 mT, which is close to the theoretical limit of niobium, which corresponds to an accelerating gradient of 43.5 MV/m, one of the highest fields obtained in a single cell cavity of this shape.

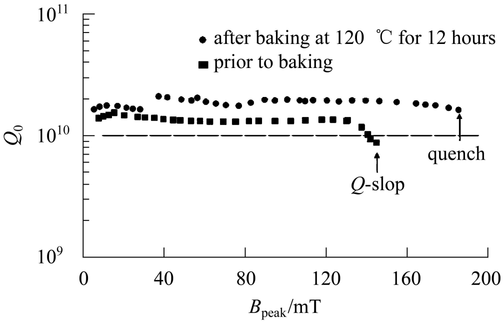

Fig. 3. Performance of the first PKU produced single cell cavity, made from OTIC large grain Nb1).

JLab has also manufactured some single cell TESLA shaped cavities using Nb material from different suppliers. The cavities were applied post-purification with Ti at 1200 ℃ for 3 hours, 50 μm BCP (Buffered Chemical Polish), and "in situ" baking at 120 ℃ for 12 hours. Then the performance of cavities were tested, and the results were listed in Table 7[10]. We can see that the Nb material from OTIC has reached the world advanced level.

Table 7. Performance of cavities using Nb from different suppliers.

supplier	Ta content/10^{-6}	RRR	$H_{\max}$/mT	Q_0
CBMM	800—1500	280	131	1.04×10^{10}
W.C.Heraeus	<500	500	146	1.05×10^{10}
Ningxia OTIC	<150	330	142	1.14×10^{10}
Wah Chang	<500	>300		

5 Conclusion

The Ningxia OTIC has made high purity Nb ingots with RRR higher than 300 from the melted niobium with low C content, which is produced from NbAl alloy by applying thermo aluminum process to Nb_2O_5, by recrystallization 4 times in an EB furnace. We find that reasonable increasing of melting times could decrease the content of interstitial elements and improve the RRR; under the same melting conditions, enlarging the crucible size could increase RRR.

A single cell, TESLA shaped cavity using high purity Nb material from OTIC was manufactured by Peking University, and it was surface-treated and tested at JLab. The results show that it has reached an accelerating gradient of 43.5 MV/m, and a quality factor of more than 1×10^{10}.

We would like to thank all the people in IEE.AC, DESY, and JLab who helped us test the performance of the Nb ingots and cavities. We are especially grateful to Peter. Kneisel at JLab for his great efforts of cavity surface treatment and Dieter. Proch in DESY for his consistent support to our research.

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