

MAGNETIC PROPERTY IMPROVEMENT OF NIOBIUM DOPED WITH RARE EARTH ELEMENTS*

F.S. He, T. Jiang, X.Y. Lu, F. Jiao, F. He and K. Zhao[†]

Institute of Heavy Ion Physics & State Key Laboratory of Nuclear Physics and Technology,
Peking University, Beijing 100871, China

H.Y. Zhao, Y.S. You, L. Chen

Ningxia Orient Tantalum Industry Co., Ltd., Shizuishan 753000, China

Abstract

In this article a new idea is proposed by PKU group to improve the magnetic property of Type-II superconductor niobium. Rare earth elements like scandium and yttrium are doped into ingot niobium during the smelting processes. A series of experiments have been done since 2010, and the preliminary testing results show that the magnetic property of niobium materials has been changed with different doping elements and proportions while the superconductive transition temperature almost does not change. This method may increase the superheating magnetic field of niobium so as to improve the performance of niobium cavity which is a key component of SRF accelerators. A large-size ingot has been made. A Tesla-type single-cell cavity made of Sc-doped niobium is being tested.

INTRODUCTION

Type-II superconductor niobium has important applications in the field of accelerators. However, the performance of niobium device is limited by the property of niobium material itself. For example, the superheating magnetic field of niobium is one of the limiting factors[1].

A new idea[2] is proposed by the group of Peking University (PKU) in this article that the property of the niobium material can be improved by introducing impurity into ingot niobium during the smelting process. Rare earth elements like scandium and yttrium are chosen as impurities. Since the end of 2010, a lot of research has been done by people of PKU and Ningxia Orient Tantalum Industry Co., Ltd. (OTIC). A series of smelting processes were conducted to produce niobium with different proportions of scandium and yttrium. The R-T, M-T and M-H curves of the new materials were measured. The results indicate that the superconductive transition temperature (T_c) almost does not change, while the magnetization curve of the impurity-doped niobium is significantly different from that of pure niobium. The lower and upper critical magnetic fields (H_{c1} , H_{c2}) of new materials change with different doping elements and proportions. The new method is promising to raise the superheating magnetic field in order to improve the performance of niobium cavity.

*Work supported by National Natural Science Foundation of China (Grant No 11175008).

[†]kzhao@pku.edu.cn

EFFECT OF IMPURITY ON SUPERCONDUCTOR

The transition temperature, critical magnetic field and surface resistance (R_{bc}) of a superconductor are correlated to each other, and they are of most concern for the superconductive radio frequency (SRF) applications. In this section, we will discuss how the impurities affect these properties.

Effect on T_c

It has been well-known that a small amount of non-magnetic impurity does not reduce the transition temperature of superconductivity. According to Anderson's theorem[3], as non-magnetic impurity in superconductor increases, the transition temperature will drop a little and then stop. If the impurity is magnetic, however, the transition temperature will continue to drop, and superconductivity will quickly be destroyed.

Effect on H_{c1} and H_{c2}

Impurity decreases the electron mean free path (l) by introducing more scatterings. According to the Pippard's theory[4], the effective coherence length (ξ_p) is thus reduced:

$$\frac{1}{\xi_p} = \frac{1}{\xi_0} + \frac{1}{\alpha l}, \quad (1)$$

where ξ_0 is the coherence length of pure superconductor, and $\alpha \sim 1$ is a constant. In a strong external magnetic field, we have

$$H_{c2}(T) = \frac{\phi_0}{\pi \mu_0 \xi^2(T)}, \quad (2)$$

where $H_{c2}(T)$ is the upper critical magnetic field, ϕ_0 is the magnetic flux quantum, μ_0 is the permeability of vacuum, $\xi(T)$ is the coherence length. Therefore H_{c2} increases as more impurity is introduced into a Type-II superconductor.

When the external magnetic field increases above H_{c1} , magnetic flux begins to penetrate into the superconductor. Because the magnetic flux at the impurity has lower Gibbs energy, the flux will be trapped by the impurity and harder to penetrate. Therefore both the upper and lower critical magnetic fields increase.



Figure 1: Nb samples from OTIC. Sample A was pure Nb. Sample B failed to melt. Samples C to F were doped with different proportions of Sc.

The superheating magnetic field (H_{sh}) is proportional to thermal critical magnetic field[1]:

$$H_{sh}(T) = (1.044 \pm 0.001)H_c \left[1 - \left(\frac{T}{T_c}\right)^2\right]. \quad (3)$$

The rise of upper and lower critical magnetic fields can increase the superheating magnetic field.

Effect on R_{bcs}

The BCS surface resistance (R_{bcs}) of niobium has a minimum when the electron mean free path is about $40nm$ and the residual resistivity ratio (RRR) is close to 10[5]. However, the RRR of pure niobium used for cavity is typically above 250. As mentioned above, impurity introduced into niobium can shorten the electron mean free path and hence reduce the surface resistance. Meanwhile, a recent numerical simulation shows that non-magnetic impurity can possibly help keep the surface resistance low at high magnetic field[6].

EXPERIMENT

Impurity Choice

Rare earth elements scandium and yttrium are chosen as impurities. They have strong electronegativity and big ion volume, easy to introduce large scattering cross section to shorten the mean free path of electrons. They are also chemically stable in the air to simplify the melting process. And as mentioned above, they are non-magnetic. As a comparison, we also study niobium doped with lanthanum, a magnetic element.

Sample Preparation

A series of smelting processes were performed to produce niobium with different impurity elements and proportions. The processes are listed as follows:

- pure niobium was arc melted to clean the furnace;
- niobium with different amount of scandium, yttrium or lanthanum was arc melted;
- the samples were annealed at $900 \sim 1000^\circ C$;
- small samples were cut down by cold machining;
- the samples were then baked at $1200^\circ C$ for post purification;
- finally they were etched in buffered chemical polish to remove the surface layer.

Pure niobium was also prepared by the same processes as a comparison.

PKU group prepared two samples doped with scandium, three with yttrium and three with lanthanum. Ningxia OTIC provided seven samples doped with scandium. There were three different scandium proportions (referred to as low, medium and high in the rest of this article). In addition, the samples doped with yttrium and lanthanum were of the same proportion respectively. Each sample weighed about 30 to 50 grams before cold machining. Figure 1 shows a photo of some samples doped with scandium. Sample A was pure niobium, and Sample B was failed because the melting points of niobium and scandium are so different that they are hard to be melted together homogeneously.

Sample Test

The compositions of samples were analyzed by mass spectrometer (Agilent ICP-MS 7500cs).

The magnetization of the samples at different temperatures and external fields were tested by the Magnetic Property Measurement System (MPMS-XL, Quantum Design). The external magnetic field is $50Oe$ ($1Oe = 79.5775A/m$) for M-T measurement, and the testing temperature is about $4.0 \sim 4.2K$ for M-H measurement.

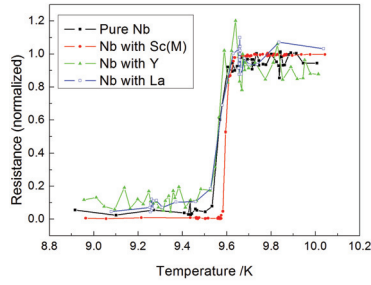
R-T curves were also tested. Samples were about $17mm$ by $0.5mm$ by $0.5mm$.

RESULTS & DISCUSSION

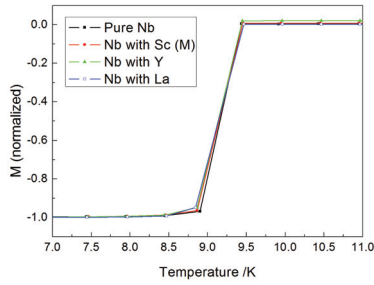
The measured proportions of impurities in the samples agreed well with the quantity of elements put into the furnace, which showed that the doping composition could be controlled in the melting process.

Figure 2 is the R-T and M-T curves of pure niobium and niobium doped with different elements. The transition temperatures of samples doped with impurity are nearly the same as the temperature of pure niobium sample separately in the R-T testing and M-T testing. These two figures show that the impurity does not change the superconductive transition temperature.

Figure 3 shows the M-H curves of pure niobium and niobium doped with different elements. The magnetic field at which the M-H curve becomes nonlinear is the H_{c1} of the material. The linear part of M-H curve is fitted with a one-order polynomial, and the part from beginning to the min-



(a) R-T curves



(b) M-T curves

Figure 2: R-T and M-T curves of pure Nb and Nb doped with Sc (medium proportion), Y and La.

imum is fitted with a five-order polynomial. The value of H_{c1} can be obtained by comparing the two fitting curves (Fig. 4). The H_{c1} of niobium with different impurities are presented in Table 1. Compared to pure niobium, the H_{c1} of niobium doped with non-magnetic impurities (scandium and yttrium) raise by $100Oe$ and $200Oe$ respectively, while that of niobium doped with magnetic impurity (lanthanum) is reduced by nearly $100Oe$.

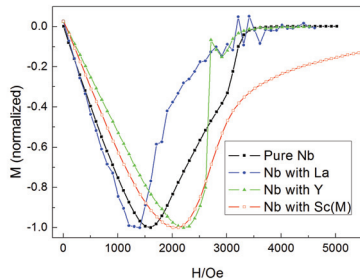


Figure 3: M-H curves of pure Nb and Nb doped with different elements at $T = 4.0K$.

Table 1: H_{c1} of pure Nb and Nb doped with different elements

Impurity	Pure	Sc(M)	Y	La
H_{c1}/Oe	1304	1408	1508	1205

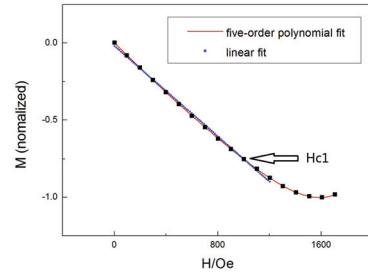


Figure 4: M-H curves of pure Nb and Nb doped with different elements at $T = 4.0K$.

Figure 5 shows the M-H curves of pure niobium and niobium doped with different proportions of scandium. The sample with low proportion of scandium was tested at $4.22K$, while other samples were tested at $4.0K$. The H_{c1} of niobium with different composition of scandium are also presented in Table 2. As the composition of scandium goes up, the M-H curve moves to the right, and H_{c1} gradually increases from $1304Oe$ to $1506Oe$. Also in this figure, the H_{c2} of niobium doped with scandium improves appreciably from $3518Oe$ to $7431Oe$.

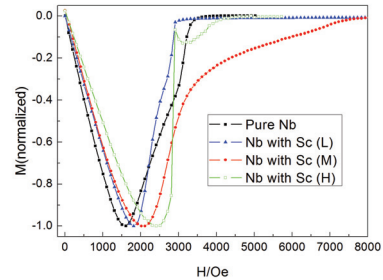


Figure 5: M-H curves of pure Nb and Nb doped with different proportions of Sc.

Table 2: H_{c1} of pure Nb and Nb doped with different proportions of Sc

Impurity	Pure	Sc(L)	Sc(M)	Sc(H)
H_{c1}/Oe	1304	1353	1408	1506

Figure 6 shows R-T curves of another niobium sample doped with low proportion of scandium in different external magnetic fields. It is revealed that H_{c2} of niobium with low proportion of scandium is up to $1.1 \times 10^4 Oe$.

LARGE INGOT

To test the mechanical properties of the doping niobium, we have made a large-size niobium ingot doped with scandium in OTIC, from which two sheets (Fig. 7) were sliced out. After annealing at $1100^\circ C$ for 90 min, RRR and

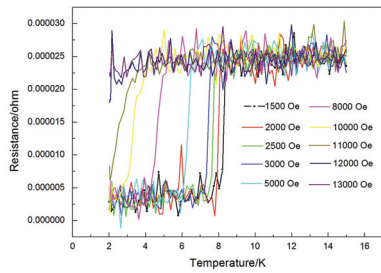


Figure 6: R-T curves of Nb doped with low proportion of Sc in different external magnetic fields.

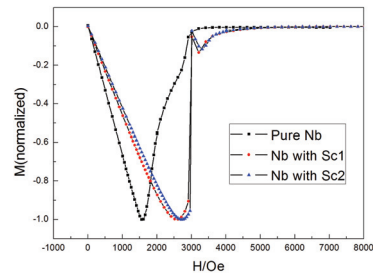


Figure 8: M-H curves of pure Nb and Nb ingot doped with Sc at $T = 4.0K$.



Figure 7: Nb sheets doped with Sc, $265mm \times 265mm \times 2.8mm$.



Figure 9: 1.3 GHz Tesla-type single-cell cavity. The equator welds was done in JLab.

Table 3: Some mechanical properties and RRR of Nb ingot doped with Sc

RRR	yield strength	breaking strength	elongation
127	210MPa	312.2MPa	38.7%

some mechanical properties were measured (presented in Table 3), which met the requirement of cavity fabrication.

We have measured the M-H curves of two samples selected at random from the ingot, as shown in Fig. 8. From the curves H_{c1} of the two samples are separately 1812Oe and 1811Oe, which are quite higher than the H_{c1} of pure niobium.

We have fabricated a 1.3 GHz Tesla-type single-cell cavity (Fig. 9), which is made of the niobium sheets doped with scandium. More tests will be carried out to understand the RF and thermal property of this new material.

CONCLUSION

A new method to improve the property of niobium is reported in this article. A series of experiments have shown that by doping rare earth elements into ingot, the lower critical magnetic field of the Type-II superconductor niobium is raised significantly by the non-magnetic impurity and reduced by magnetic impurity. At the same time, the superconductive transition temperature is not affected. It may be

06 Material studies

F. Basic R&D bulk Nb - High performances

a new way to improve the performance of niobium cavity for SRF accelerator.

More tests are required to deepen the understanding about the effect of impurity in niobium, especially the effect of yttrium. Further experiments are needed to test the RF, thermal and mechanical properties of the new material, which calls for larger size of samples and new melting method and crafts. A 1.3 GHz Tesla-type single-cell cavity made of Sc-doped niobium has been fabricated. The cavity will be vertically tested to measure the accelerating gradient, quench field and surface resistance.

ACKNOWLEDGMENT

We would like to express our gratitude to Prof. Z.Z. Gan in PKU for evaluating the feasibility of our idea, Dr. J.K. Hao, S.W. Quan and L. Lin in PKU for their support in preparation of the ingot and cavity. We also acknowledge Prof. G.F. Sun at University of Science and Technology Beijing for his support and advice.

REFERENCES

- [1] N. Valles and M. Liepe. The superheating field of niobium: theory and experiment. In Proceedings of the 15th International Conference on RF Superconductivity, 2011.
- [2] K. Zhao, Impurities of Rare Earth Element in Bulk Nb as a Potential Way to Improve the Cavity SRF Performance. In TESLA Technology Collaboration meeting, JLab, 2012.

ISBN 978-3-95450-143-4

- [3] P. W. Anderson, Phys. Chem. Solids 11, 26 (1959).
- [4] A. B. Pippard, Proc. Roy. Soc. Lond. A216 547 (1953).
- [5] H. Padamsee, RF Superconductivity: science, technology, and applications Wiley, page 44, 2009.
- [6] F. P.-J. Lin and A. Gurevich, Phys. Rev. B85, 054513 (2012).