Magnetic property improvement of niobium doped with rare earth elements*

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A new idea is proposed by the PKU group to improve the magnetic properties of the 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. The preliminary testing results show that the magnetic properties of niobium materials have changed with different doping elements and proportions while the superconductive transition temperature does not change very much. This method may increase the superheating magnetic field of niobium so as to improve the performance of the niobium cavity, which is a key component of SRF accelerators. A Tesla-type single-cell cavity made of scandium-doped niobium is being fabricated.

Keywords: niobium, rare earth element, impurity, magnetization curve

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1. Introduction

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

A new idea[2] is proposed in this article by the group of Peking University (PKU) is 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 the people of PKU and Ningxia Orient Tantalum Industry Co., Ltd. (OTIC). A series of smelting processes were conducted to produce niobium with differing proportions to those 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) does not change very much, while the magnetization curve of the impurity-doped niobium is significantly different to 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.

2. Effect of impurity on superconductor

The transition temperature, critical magnetic field and BCS surface resistance (R_{BCS}) 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.

2.1. Effect on T_c

It is 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 superconductors increases, the transition temperature will drop a little and then stop. If, however, the impurity is magnetic, the transition temperature will continue to drop, and superconductivity will quickly be destroyed.

2.2. Effect on H_{c1} and H_{c2}

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

$$\frac{1}{\xi_p} = \frac{1}{\xi_0} + \frac{1}{\alpha l}, \tag{1}$$

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

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

where $H_{c2}(T)$ is the upper critical magnetic field, ϕ_0 is the magnetic flux quantum and μ_0 is the permeability of the vacuum. Therefore H_{c2} increases as more impurity is introduced

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into a Type-II superconductor. A two-band layered superconductor also has a similar effect.[6]

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.

The superheating magnetic field (H_{sh}) is proportional to the thermodynamic critical magnetic field (H_c)[1]

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

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

2.3. Effect on R_{BCS}

The BCS surface resistance (R_{BCS}) of niobium is at a minimum when the electron mean free path is about 20 nm 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[6] shows that non-magnetic impurity can possibly help keep the surface resistance low at the high magnetic field.

3. Simulation

In order to understand the dependence of H_{c1} on the electron mean free path (l), we tried to find out the relationship between H_{c1} and l by using the result of the Ginzburg–Landau theory in a "dirty" limit.

From Ginzburg–Landau theory, when the Ginzburg–Landau parameter is $\kappa \gg 1$ we can have[8]

$$H_{c1}(T) = \frac{1}{\sqrt{2}} H_c(T) \frac{1}{\kappa} \ln \kappa, \tag{4}$$

$$H_c(T) = \frac{\phi_0}{\sqrt{2}\pi\mu_0 \xi(T) \lambda(T)}, \tag{5}$$

where $\lambda(T)$ is the penetration depth. At the "dirty" limit ($l < \xi_0$), Gor'kov gave[9]

$$\xi(T) = 0.855(\xi_0 l)^{1/2} \left[\frac{T_c}{T_c - T}\right]^{1/2}, \tag{6}$$

$$\lambda(T) = 0.64\lambda_L(0) \left[\frac{\xi_0}{l} \frac{T_c}{T_c - T}\right]^{1/2}, \tag{7}$$

$$\kappa = 0.75 \frac{\lambda_L(0)}{l}, \tag{8}$$

where $\lambda_L(0)$ is the penetration depth at 0 K. At 0 K in the "dirty" limit ($l < \xi_0$), there is[10]

$$\lambda_L(0) = \lambda_L \sqrt{1 + \frac{\xi_0}{l}}, \tag{9}$$

where λ_L is the penetration depth of a pure superconductor at 0 K, a constant related to the material property. Substituting Eqs. (5)–(9) into Eq. (4), we can get

$$\begin{aligned} &\frac{H_{c1}}{\dfrac{\phi_0}{0.82\pi\mu_0\lambda_L^2}\dfrac{T_c - T}{T_c}} \\ &= \frac{l/\xi_0}{1 + \xi_0/l} \ln\left[\frac{0.75}{l}\lambda_L\sqrt{1 + \xi_0/l}\right] \\ &= \frac{l/\xi_0}{1 + \xi_0/l} \ln\left[0.75\frac{\lambda_L}{\xi_0}\frac{\xi_0}{l}\sqrt{1 + \xi_0/l}\right] \\ &= \frac{l/\xi_0}{1 + \xi_0/l} \ln\left[0.75\kappa_0\frac{\xi_0}{l}\sqrt{1 + \xi_0/l}\right], \end{aligned} \tag{10}$$

where $\kappa_0 = \lambda_L/\xi_0$ is the Ginzburg–Landau parameter of pure superconductor. The value of κ_0 does not affect the tendency of H_{c1} over l. Here $\kappa_0 = 5$ is adopted. Figure 1 shows the dependence of H_{c1} on the ratio of l and constant ξ_0. When the superconductor is pure, l is much longer than ξ_0, corresponding to the right end of the curve. As the impurity in the superconductor increases, l is shortened, and H_{c1} will raise up to the maximum. If the impurity continues to increase, with l shorten, H_{c1} will drop down again. This tendency means that certain proportions of impurity will raise the H_{c1} of the superconductor.

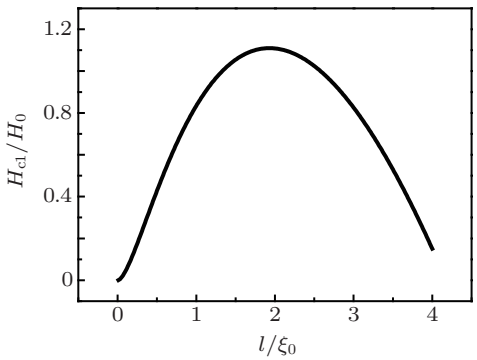


Fig. 1. The dependence of H_{c1} on l, where $H_0 = \frac{\phi_0}{0.82\pi\mu_0\lambda_L^2}\frac{T_c - T}{T_c}$.

4. Experiment

4.1. Impurity choice

Rare earth elements scandium and yttrium are chosen as impurities. They have strong electronegativity, big ion volumes and are easy to introduce large-scattering cross sections 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. For comparison, we also study niobium doped with lanthanum, a magnetic element.

4.2. Sample preparation

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

(i) pure niobium was arc melted to clean the furnace;

(ii) niobium with different amounts of scandium, yttrium or lanthanum was arc melted;

(iii) the samples were annealed at 900–1000 °C;

(iv) small samples were cut down by cold machining;

(v) the samples were then baked at 1200 °C for post purification;

(vi) 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 2 shows a photo of some samples doped with scandium. Sample A was pure niobium, and Sample B failed because the melting points of niobium and scandium are so different that they are hard to be melted together homogeneously.



Fig. 2. Niobium samples from OTIC. Sample A was pure niobium. Sample B failed to melt. Samples C to F were doped with different proportions of scandium.

4.3. 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). A slowly varying magnetic field was applied to the samples, which were all about 1 mm^3 in size. Since the superconductor excluded all the magnetic flux, the total magnetic moment of the sample would change the current in the detection coil, which was converted to voltage by a superconducting quantum interference device (SQUID) and then measured. The external magnetic field is 50 Oe (1 Oe = 79.5775 A/m) for *M*–*T* measurement, and the testing temperature is about 4.0–4.2 K for *M*–*H* measurement.

R–*T* curves were also tested. Samples were about 17 mm by 0.5 mm by 0.5 mm.

5. Results and discussion

The measured proportions of the 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 3 shows the *R*–*T* curves of pure niobium and niobium doped with different elements, and figure 4 shows the

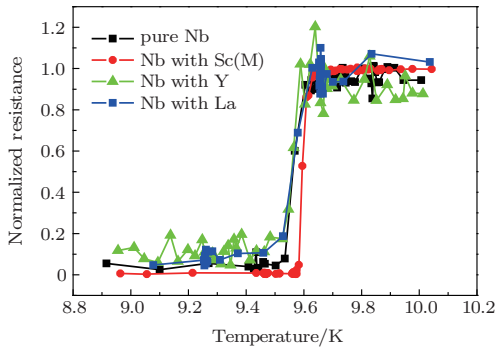


Fig. 3. *R*–*T* curves of pure niobium and niobium doped with scandium (medium proportion), yttrium, and lanthanum.

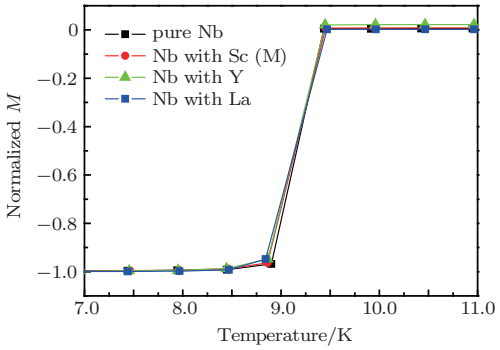


Fig. 4. *M*–*T* curves of pure niobium and niobium doped with scandium (medium proportion), yttrium, and lanthanum. External magnetic field is 50 Oe.

M–T curves of the same samples. The transition temperatures of samples doped with impurity are nearly the same as the temperature of the pure niobium sample used 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 5 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 minimum is fitted with a five-order polynomial. The value of H_{c1} can be obtained by comparing the two fitting curves (Fig. 6). The H_{c1} of niobium with different impurities is presented in Table 1. Compared to pure niobium, the H_{c1} of niobium doped with non-magnetic impurities (scandium and yttrium) raised by 100 Oe and 200 Oe respectively, while that of niobium doped with magnetic impurity (lanthanum) is reduced by nearly 100 Oe.

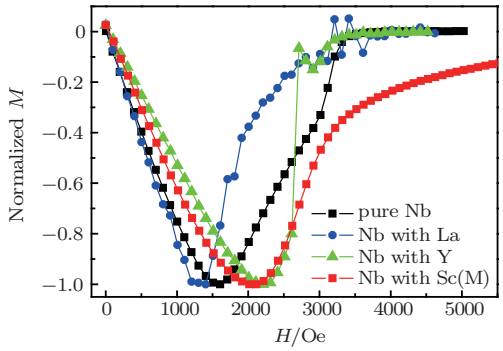


Fig. 5. M–H curves of pure niobium and niobium doped with different elements at $T = 4.0$ K.

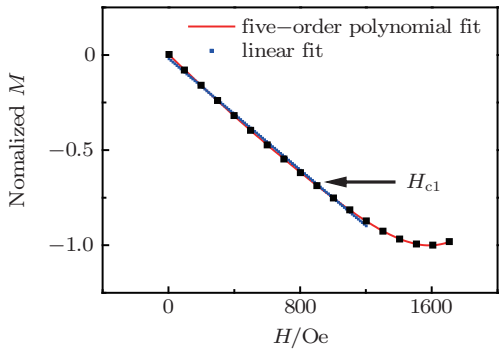


Fig. 6. Fitting and deviating point of H_{c1} on the M–H curve of pure niobium. The linear part of the M–H curve is fitted with a one-order polynomial, and the part from beginning to the minimum is fitted with a five-order polynomial. The abscissa of the deviating point is the value of H_{c1}.

Table 1. H_{c1} of pure niobium and niobium doped with different elements.

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

Figure 7 shows the M–H curves of pure niobium and niobium doped with different proportions of scandium. The sample with a low proportion of scandium was tested at 4.22 K, while other samples were tested at 4.0 K. The H_{c1} of niobium with a different composition of scandium is 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 1304 Oe to 1506 Oe. Also in this figure, the H_{c2} of niobium doped with scandium improves appreciably from 3518 Oe to 7431 Oe.

Figure 8 shows R–T curves of another niobium sample doped with high proportions of scandium in different external magnetic fields. It is revealed that the H_{c2} of niobium with high proportions of scandium is up to 1.1×10^4 Oe.

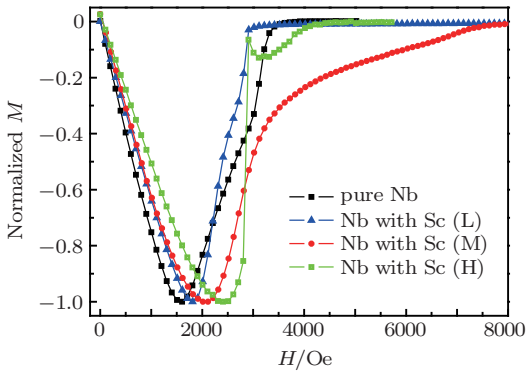


Fig. 7. M–H curves of pure niobium and niobium doped with different proportions of scandium.

Table 2. H_{c1} of pure niobium and niobium doped with different proportions of scandium.

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

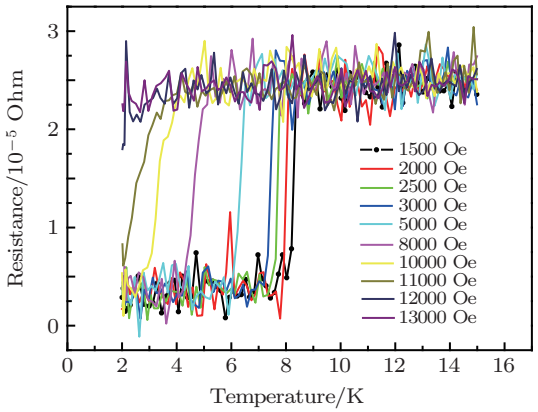


Fig. 8. R–T curves of niobium doped with high proportions of scandium in different external magnetic fields.

6. 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. 9) were sliced out. After annealing at 1100 °C for 90 min, RRR and some mechanical properties were measured (presented in Table 3).

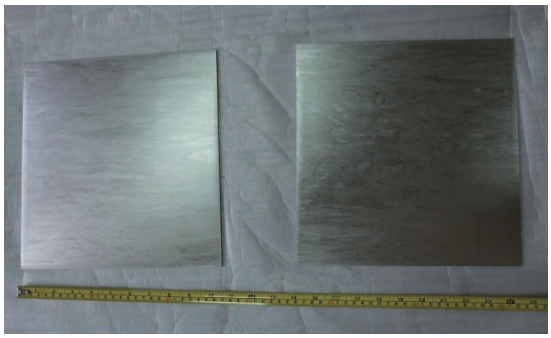


Fig. 9. Niobium sheet doped with scandium, 265 mm × 265 mm × 2.8 mm.

Table 3. RRR and some mechanical properties of niobium ingot doped with scandium.

RRR	Yield strength	Breaking strength	Elongation
127	210 MPa	312.2 MPa	38.7%

We have measured the M–H curves of two samples selected at random from the ingot, as shown in Fig. 10. From the curves the H_{c1} of the two samples are separately 1812 Oe and 1811 Oe, which are quite higher than that of pure niobium.

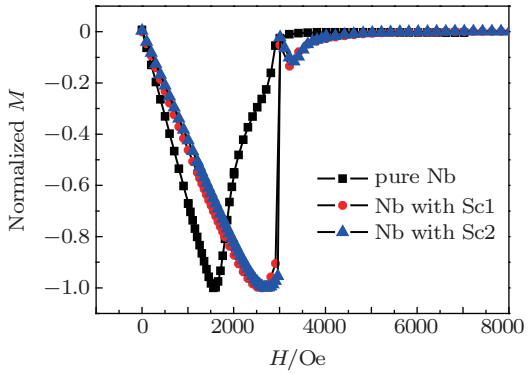


Fig. 10. M–H curves of pure niobium and niobium ingot doped with scandium at $T = 4.0$ K.

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

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 sample sizes and new melting methods and crafts. A 1.3-GHz Tesla-type single-cell cavity made of scandium-doped niobium is being fabricated in China. The cavity will be vertically tested to measure the accelerating gradient, quench field and surface resistance.

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