



# Relationship between Strain Effect and Martensitic Transformation in Multifilamentary Nb3Sn Wires

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# Relationship between strain effect and martensitic transformation in multifilamentary Nb<sub>3</sub>Sn wires

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For bronze-processed multifilamentary pure Nb<sub>3</sub>Sn and 2.3 at. % Ti added (Nb,Ti)<sub>3</sub>Sn wires, which were prepared under the condition of the same wire parameters such as the filament size, filament number, and bronze ratio, the strain effects on the critical current density were measured. The large difference of the residual strain between Nb<sub>3</sub>Sn and (Nb,Ti)<sub>3</sub>Sn wires was obtained. It was found that the martensitic transformation for Nb<sub>3</sub>Sn compound largely contributes to the residual strain through the variation of the elastic modulus in bronze-processed multifilamentary Nb<sub>3</sub>Sn wires. It was verified that the ternary element addition of Ti surely suppresses the martensitic transformation in the bronze processed multifilamentary Nb<sub>3</sub>Sn wire.

## I. INTRODUCTION

In multifilamentary Nb<sub>3</sub>Sn superconducting wires, many efforts for improvement of the critical current density  $J_c$  in high magnetic fields up to 20 T have been made. The flux pinning mechanism which is responsible for  $J_c$  is well known to be due to grain boundaries in Nb<sub>3</sub>Sn.<sup>1</sup> Since the  $J_c$ value in fields largely depends on the characteristics of pinning centers, it is of importance to control the microstructure such as stoichiometric composition or fine grain boundaries. In addition, the upper critical field  $B_{c2}$  principally affects the performance of  $J_c$  in high fields. Therefore, the effects of ternary element addition such as Ti or Ta in the bronzeprocessed Nb<sub>3</sub>Sn wires have been investigated, in order to improve pinning centers and increase  $B_{c2}^{2-4}$  Up to now, Ti-added Nb<sub>3</sub>Sn superconducting wires successfully contribute to realization of high-field superconducting magnets over 20 T.<sup>5,6</sup>

On the other hand, the martensitic transformation from a cubic to a tetragonal phase for the A15-Nb<sub>3</sub>Sn compound has been widely identified at low temperatures.<sup>7-10</sup> When the martensitic transformation occurs at low temperature, the  $B_{c2}$  value at 4.2 K for tetragonal Nb<sub>3</sub>Sn is by about 5 T lower than that for cubic one.<sup>11</sup> This lower  $B_{c2}$  value is the inferior point for the improvement of the high-field  $J_c$  characteristics. The transition temperature of the martensitic transformation sensitively depends on the specimen quality. The transformation can be suppressed by deviation from the stoichiometry<sup>9</sup> or by the ternary element addition<sup>12</sup> such as Ti or Ta. From the standpoint mentioned above, a detailed investigation on the martensitic transformation in Nb<sub>3</sub>Sn wires using an internal friction technique was reported by Kumakura et al.<sup>13</sup> The point of interest in their report is that the suppression of the martensitic transformation by the ternary element additions is not a dominant factor in the improvement of  $B_{c2}$ . Their results suggest that the improvement of  $B_{c2}$  is mainly attributed to the increase of the resistivity  $\rho_n$  which is related to the temperature slope of  $B_{c2}$ . In the practical multifilamentary Nb<sub>3</sub>Sn wires, it is very difficult to directly measure the resistivity of Nb<sub>3</sub>Sn and the martensitic transformation temperature of Nb<sub>3</sub>Sn by a resistive method because of a Cu stabilizer and a bronze matrix. Therefore, the subject on the effect of ternary element additions in Nb<sub>3</sub>Sn still remains unsettled for the martensitic transformation.

Moreover, there exists a strain effect on the superconducting properties such as  $T_c$ ,  $B_{c2}$ , and  $J_c$  in A15 compound. Especially, the large strain effect in Nb<sub>3</sub>Sn wires<sup>14</sup> attracts special attention as a crucial issue for practical use. The martensitic transformation is also sensitive to such strain, and the uniaxial stress for multifilamentary Nb<sub>3</sub>Sn wires induces a cubic-to-tetragonal phase transition.<sup>15</sup> Thereby, in the case of the bronze-processed multifilamentary Nb<sub>3</sub>Sn wires accompanying a large residual strain, the influence due to the martensitic transformation for the strain effect on  $J_c$  must be made clear. This is because the effect of the ternary element addition for the  $B_{c2}$  enhancement is complicatedly changed by both phenomena of the martensitic transformation and the strain effect.

The aim of the present work is to clarify the relationship between the martensitic transformation and the strain effect in bronze-processed multifilamentary Nb<sub>3</sub>Sn superconducting wires. The strain effects on  $J_c$  for pure Nb<sub>3</sub>Sn and Tiadded (Nb,Ti)<sub>3</sub>Sn wires were studied in detail. The residual strains obtained for Nb<sub>3</sub>Sn and (Nb,Ti)<sub>3</sub>Sn wires are elucidated, and the relationship between the martensitic transformation and the strain effect is discussed.

#### **II. EXPERIMENT**

Two kinds of typical bronze-processed multifilamentary  $Nb_3Sn$  superconducting wires were prepared for comparison. Table I lists the characteristics of the multifilamentary wires fabricated by a 13 wt. % Sn bronze route. Pure  $Nb_3Sn$  and Ti-added (Nb,Ti)<sub>3</sub>Sn wires consist of the same structural configuration such as the filament size, filament number, Ta barrier, and Cu ratio with each other, except for a ternary ele-

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TABLE I. Characteristics of bronze-processed multifilamentary  $Nb_3Sn$  and  $(Nb,Ti)_3Sn$  superconducting wires.

	Nb <sub>3</sub> Sn	(Nb,Ti) <sub>3</sub> Sn
Wire diameter (mm)	0.8	4
Bronze	Cu-13 wt % Sn	<del></del>
Core	Nb	Nb-1.2 wt % T
Filament diameter ( $\mu$ m)	3.4	←
Number of filaments	5587	<del>~~~</del>
Bronze/core ratio	4.1 -	· • • • • • • • • • • • • • • • • • • •
Cu/non-Cu ratio	0.78	←
Barrier	Ta	<del>~~~</del>

14 A.

ment addition of Ti in the  $(Nb,Ti)_3Sn$  wire. The quantity of Ti addition into a Nb core is 1.2 wt. % Ti, which corresponds to 2.3 at. % Ti. The heat treatments were carried out at 750 °C for 192 h in the Nb<sub>3</sub>Sn wire and at 670 °C for 192 h in the  $(Nb,Ti)_3Sn$  wire, respectively.

Figure 1 shows a cross-sectional view of the multifilamentary wires with the same wire structure, and Fig. 2(a) exhibits its magnification. There is no problem to form Nb<sub>3</sub>Sn compound with the Ta barrier. One notes that Nb cores fully reacted and entirely changed into Nb<sub>3</sub>Sn or (Nb,Ti)<sub>3</sub>Sn compound. There remains no unreacted Nb core in the A15 compound. For comparison, a (Nb,Ti)<sub>3</sub>Sn wire with unreacted Nb cores which was heat treated at 670 °C for 120 h is presented in Fig. 2(b).

In order to evaluate the stress-strain effect on  $J_c$ , a measuring apparatus equipped with a 15 T superconducting magnet was used.<sup>16</sup> Magnetic fields were applied perpendicular to the transport current. Short straight samples about 40 mm in length and with a gauge length of 17.5 mm were measured. Both ends of the wire sample were soldered to a Cu grip of a current terminal. The axial load of less than 50 kg and the transport current of less than 200 A were applicable. The strain measurement was detected by use of an extensometer, and the accuracy of the strain measurement was within

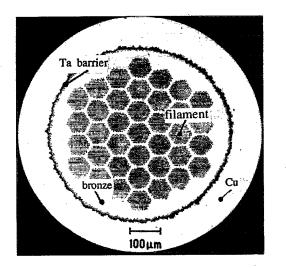
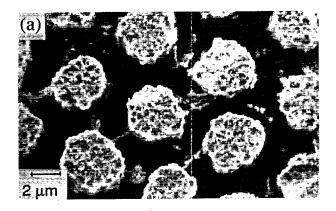


FIG. 1. Cross-sectional view in the bronze-route multifilamentary superconducting  $Nb_3Sn$  or  $(Nb_7Ti)_3Sn$  wire.



to 2 µm

FIG. 2. Scanning electron microscope (SEM) photographs in the bronzeroute multifilamentary (Nb,Ti)<sub>3</sub>Sn superconducting wires heat treated at 670 °C (a) for 192 h and (b) for 120 h.

0.05%. The critical current  $I_c$  was determined by a 1  $\mu$ V/cm criterion between voltage taps soldered at a distance of about 5 mm.

# III. RESULTS AND DISCUSSION

The  $J_c$  properties in fields up to 23 T for Nb<sub>3</sub>Sn and (Nb,Ti)<sub>3</sub>Sn wires are shown in Fig. 3. The  $J_c$  values of about 200 A/mm<sup>2</sup> in a cross-sectional area excloding the Cu stabilizer is obtained at 14 T for the Nb<sub>3</sub>Sn wire and at 17 T for the (Nb,Ti)<sub>3</sub>Sn wire, respectively.  $J_c$  for the Nb<sub>3</sub>Sn wire is slightly lower than that for ordinary bronze-processed multifilamentary Nb<sub>3</sub>Sn wires, while  $J_c$  for the (Nb,Ti)<sub>3</sub>Sn wire is comparable with the value reported so far.<sup>17</sup> The irreversibility field  $B^*$  at which  $J_c$  goes to zero<sup>18</sup> is measured to be about 21.8 T at 4.2 K for the Nb<sub>3</sub>Sn wire and also is lower in comparison with ~23 T for the typical Nb<sub>3</sub>Sn compound. This degradation of the superconducting properties for the Nb<sub>3</sub>Sn wire comes from a large strain effect, which is discussed below.

Figures 4(a) and 4(b) show the strain dependence of  $I_c$  for Nb<sub>3</sub>Sn and (Nb,Ti)<sub>3</sub>Sn wires, respectively. The measurements were performed at 14 T and 4.2 K.  $I_c$  measured without applied axial strain corresponds to that shown in Fig. 3. The (Nb,Ti)<sub>3</sub>Sn wire exhibits the weaker strain dependence

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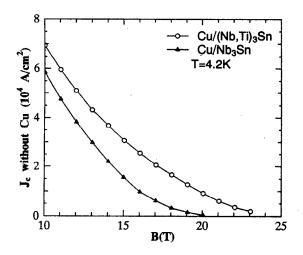


FIG. 3. Critical current density as a function of magnetic field in the bronzeroute multifilamentary Nb<sub>3</sub>Sn and (Nb,Ti)<sub>3</sub>Sn wires.

of  $J_c$  than the Nb<sub>3</sub>Sn wire, owing to the higher  $B_{c2}$  value in the (Nb,Ti)<sub>3</sub>Sn wire. The peak of  $I_c$  as a function of axial strain represents a strain-free state in bronze-processed multifilamentary Nb<sub>3</sub>Sn wires. The value of the residual strain was obtained to be 0.44% for the Nb<sub>3</sub>Sn wire and 0.35% for the (Nb,Ti)<sub>3</sub>Sn wire. Note that the residual strain for the

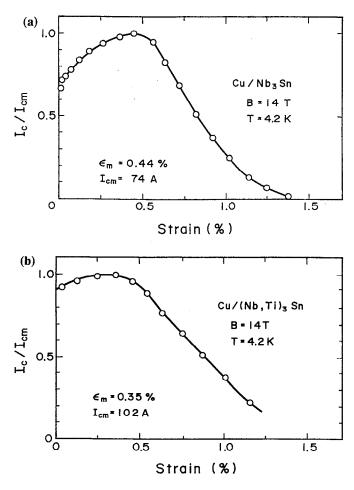


FIG. 4. Strain effect on the critical current in the bronze-route multifilamentary wires of (a) Nb<sub>3</sub>Sn and (b) (Nb,Ti)<sub>3</sub>Sn.

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TABLE II. Volume fractions (in %) for each component in  $Nb_3Sn$  composites.

	Nb <sub>3</sub> Sn	(Nb,Ti) <sub>3</sub> Sn
V <sub>Cu</sub>	43.8	<i>←</i>
V <sub>Cu</sub> V <sub>BZ</sub>	41.3	<b>(</b>
V <sub>Nb</sub>	0	←
V <sub>Nb3</sub> Sn V <sub>Ta</sub>	10.1	←
V <sub>Ta</sub>	4.84	<del>(</del>

Nb<sub>3</sub>Sn wire is larger than that for the (Nb,Ti)<sub>3</sub>Sn wire. The large residual strain for the Nb<sub>3</sub>Sn wire is consistent with slightly lower  $J_c$  and  $B^*$  values.

Now a great interest was focused on the difference between the residual strains obtained for Nb<sub>3</sub>Sn and (Nb,Ti)<sub>3</sub>Sn wires. In order to calculate the residual strain in bronzeprocessed multifilamentary Nb<sub>3</sub>Sn superconducting wires, we follow a simple analytical method presented by Easton et al.<sup>19</sup> The model is based on the volume fraction of each component treated individually in multifilamentary composites. It is considered that the Cu stabilizer and bronze matrix have much larger thermal contraction than the Nb<sub>3</sub>Sn compound, Nb core, and Ta barrier from reaction temperature to 4.2 K. Since the thermal-expansion coefficients of Nb<sub>3</sub>Sn, Nb, and Ta are nearly equal, the filament system combined with the Nb<sub>3</sub>Sn compound, Nb core, and Ta barrier can be regarded as undergoing the compressive stress. Therefore, the force balance in the absence of external applied stress is described as follows:

$$-\sigma_f = (V_{\rm Cu}\sigma_{\rm Cu} + V_{\rm BZ}\sigma_{\rm BZ})/V_f, \qquad (1)$$

where  $V_f$ ,  $V_{Cu}$ , and  $V_{BZ}$  and  $\sigma_f$ ,  $\sigma_{Cu}$ , and  $\sigma_{BZ}$  are the volume fraction and the residual stress of the filament system, Cu stabilizer, and bronze matrix, respectively. In addition, the combined modulus  $E_f$  in the filament system with the similar values of the thermal-expansion coefficient is given by

$$E_f = (V_{\rm Nb}E_{\rm Nb} + V_{\rm Nb_3Sn}E_{\rm Nb_3Sn} + V_{\rm Ta}E_{\rm Ta})/V_f, \qquad (2)$$

where  $V_{\rm Nb}$ ,  $V_{\rm Nb_3Sn}$ , and  $V_{\rm Ta}$  and  $E_{\rm Nb}$ ,  $E_{\rm Nb_3Sn}$ , and  $E_{\rm Ta}$  are the volume fraction and the elastic modulus of the Nb core, Nb<sub>3</sub>Sn compound, and Ta barrier, respectively. Then the residual strain  $\epsilon_r$  in the filament system of Nb, Nb<sub>3</sub>Sn, and Ta is derived from Hooke's law,

$$\varepsilon_r = \sigma_f / E_f. \tag{3}$$

To perform the analytical method for the prediction of the residual strain in bronze processed multifilamentary Nb<sub>3</sub>Sn wires, the volume fractions of each component were obtained from the conductor structure shown in Table I and Fig. 1. Table II lists the volume percentages of each component in Nb<sub>3</sub>Sn and (Nb,Ti)<sub>3</sub>Sn wires. Since there is no unreacted Nb core in both wire samples as already mentioned, the volume faction of Nb is  $V_{\rm Nb}=0$ . Therefore, the volume fraction of the filament system ( $V_{\rm Nb_3Sn} + V_{\rm Ta}$ ) is  $V_f = 14.9\%$  in both wires.

It is estimated that the bronze matrix of Cu-13 wt % Sn before reaction changes into the bronze of Cu-4.3 wt % Sn

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TABLE III. Elastic modulus for various Nb<sub>3</sub>Sn.

Elastic modulus $E$ (GPa)	Ref.	
165	19, 20	
51	21	
109	21	
	165 51	

after reaction assuming Nb entirely converted to  $Nb_3Sn$  in the wires with the bronze ratio of 4.1. According to the useful relationship<sup>19</sup> in the form of

$$\sigma_{\rm BZ} = 18.37 \times (\text{wt \% Sn in bronze}) + 82.7 \text{ MPa},$$
 (4)

the yield stress of the bronze matrix in both Nb<sub>3</sub>Sn and (Nb,Ti)<sub>3</sub>Sn wires is calculated to be  $\sigma_{BZ}=159$  MPa. Further, assuming the typical value of  $\sigma_{Cu}=20.7$  MPa in the plastic behavior,  $\sigma_f=501$  MPa is obtained by use of Eq. (1).

Here we focus on the value of the elastic modulus for Nb<sub>3</sub>Sn compound. Various values of  $E_{Nb_3Sn}$  have been reported in single crystals<sup>19,20</sup> and bronze route wires.<sup>21</sup> The important point is that the modulus E in bronze-processed Nb<sub>3</sub>Sn wires, which was reported by Bussiere et al.,<sup>21</sup> is extremely low due to the martensitic transformation. It is noteworthy that there exists a large difference of E between Nb<sub>3</sub>Sn and (Nb,Ti)<sub>3</sub>Sn wires. Comparisons of the values of Eare made among the Nb<sub>3</sub>Sn single crystal, Nb<sub>3</sub>Sn wire, and (Nb,Ti)<sub>3</sub>Sn wire as indicated in Table III. Using the value of  $E_{\text{Ta}} = 186 \text{ GPa}$ ,<sup>21</sup>  $E_f = 172$ , 94.6, and 134 GPa are obtained for  $E_{\text{Nb},\text{Sn}} = 165$ , 51, and 109 GPa from Eq. (2). Then the prediction of the residual strain in bronze-processed multifilamentary Nb<sub>3</sub>Sn wires is exhibited using Hooke's law of Eq. (3). As a result,  $\epsilon_r = 0.29\%$ , 0.53%, and 0.37% are estimated for  $E_{\text{Nb}_3\text{Sn}} = 165$ , 51, and 109 GPa.

Utilizing analytically derived residual strains, one can compare these values with experimentally measured residual strains for bronze-processed multifilamentary Nb<sub>3</sub>Sn and (Nb,Ti)<sub>3</sub>Sn wires. It is found that the value of  $\epsilon_r = 0.35\%$ measured for the Ti-added (Nb,Ti)<sub>3</sub>Sn wire is in good agreement with the prediction of  $\epsilon_r = 0.37\%$  in the case of the elastic modulus with no martensitic transformation. On the other hand, the experimental result of  $\epsilon_r = 0.44\%$  for the pure Nb<sub>3</sub>Sn wire is clearly different from  $\epsilon_r = 0.29\%$  for Nb<sub>3</sub>Sn with E = 165 GPa, and is reasonably close to the calculated residual strain of  $\epsilon_r = 0.53\%$  for the Nb<sub>3</sub>Sn wire with the low E value due to the martensitic transformation. Therefore, in the compressive residual strain state the bronze-processed Nb<sub>3</sub>Sn wire surely exhibits the martensitic transformation. It is found that the martensitic tetragonal phase transformation is effectively suppressed in the bronzeprocessed Ti-added (Nb,Ti)<sub>3</sub>Sn wire.<sup>12</sup> The point is that the martensitic transformation is detectable by the comparison

between the analytical result and the direct measurement of the strain effect on  $J_c$  for the bronze-processed Nb<sub>3</sub>Sn wires with the strain-sensitive character.

#### **IV. CONCLUSION**

The clearly different residual strains were obtained from the strain effect on the critical current density  $J_c$  for bronzeprocessed multifilamentary pure Nb<sub>3</sub>Sn and 2.3 at. % Tiadded (Nb,Ti)<sub>3</sub>Sn wires, which were prepared under the condition of the same wire parameters such as the filament size, filament number, and bronze ratio. It was found that the martensitic transformation for the Nb<sub>3</sub>Sn compound largely contributes to the residual strain through the variation of the elastic modulus in bronze processed multifilamentary Nb<sub>3</sub>Sn wires. The martensitic transformation is detectable by the strain effect on  $J_c$  for the strain-sensitive bronze-route Nb<sub>3</sub>Sn composites.

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- <sup>1</sup>R. E. Enstrom and J. R. Appert, J. Appl. Phys. 43, 1915 (1972).
- <sup>2</sup>J. D. Livingston, IEEE Trans. Magn. MAG-14, 611 (1978).
- <sup>3</sup>K. Tachikawa, T. Asano, and T. Takeuchi, Appl. Phys. Lett. **39**, 766 (1981).
- <sup>4</sup>M. Suenaga, S. Okuda, R. Sabatini, K. Itoh, and T. S. Luhman, Adv. Cryo. Eng. **28**, 379 (1982).
- <sup>5</sup>P. Turowski and Th. Schneider, Physica B 155, 87 (1989).
- <sup>6</sup>T. Kiyoshi, K. Inoue, K. Itoh, T. Takeuchi, H. Wada, H. Maeda, K. Kuroishi, F. Suzuki, T. Takizawa, N. Tada, and H. Mori, IEEE Trans. Appl. Supercond. 3, 78 (1993).
- <sup>7</sup>R. Mailfert, B. W. Batterman, and J. J. Hanak, Phys. Lett. A 24, 315 (1967).
- <sup>8</sup>L. J. Vieland, R. W. Cohen, and W. Rehwald, Phys. Rev. Lett. 26, 373 (1971).
- <sup>9</sup>H. Devantary, J. L. Jorda, M. Decroux, J. Muller, and R. Flükiger, J. Mater. Sci. 16, 2145 (1981).
- <sup>10</sup>N. Toyota, T. Kobayashi, M. Kataoka, H. F. J. Watanabe, T. Fukase, Y. Muto, and F. Takei, J. Phys. Soc. Jpn. 57, 3089 (1988).
- <sup>11</sup>S. Foner and E. J. McNiff, Jr., Solid State Commun. 39, 959 (1981).
- <sup>12</sup>D. O. Welch, Adv. Cryo. Eng. 30, 671 (1984).
- <sup>13</sup>H. Kumakura, K. Tachikawa, C. L. Snead, Jr., and M. Suenaga, J. Jpn. Inst. Met. 49, 792 (1985) (in Japanese).
- <sup>14</sup>J. W. Ekin, Cryogenics 20, 611 (1980).
- <sup>15</sup> R. Flükiger, W. Schauer, W. Specking, L. Oddi, L. Pintschovius, W. Müllner, and B. Lachal, Adv. Cryo. Eng. 28, 361 (1982).
- <sup>16</sup>K. Katagiri, T. Okada, K. Noto, A. Nagata, and K. Watanabe, Sci. Rep. RITU A 37, 92 (1992).
- <sup>17</sup> K. Watanabe, K. Noto, and Y. Muto, IEEE Trans. Magn. 27, 1759 (1991).
- <sup>18</sup> K. Watanabe, Jpn. J. Appl. Phys. **31**, L1586 (1992),
- <sup>19</sup>D. S. Easton, D. M. Kroeger, W. Specking, and C. C. Koch, J. Appl. Phys. 51, 2748 (1980).
- <sup>20</sup> W. Rehwald, M. Rayl, R. W. Cohen, and G. D. Cody, Phys. Rev. B 6, 363 (1972).
- <sup>21</sup>J. F. Bussiere, B. Faucher, C. L. Snead, Jr., and M. Suenaga, Adv. Cryo. Eng. 28, 453 (1982).

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