Tensile Strength of Bronze-processed Nb₃Sn Compound with Titanium Addition*

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Synopsis

The microstructure and tensile behaviour at room temperature of bronze-processed multi-filamentary Nb₃Sn superconducting composite wire with titanium addition in bronze matrix were investigated after isothermal annealing treatment at 973 and 1 073 K up to 1 720 ks. The strength of Nb₃Sn compound was evaluated from the tensile behaviour of the wire, volume fraction of each component and stresses carried by ductile components (bronze, niobium and copper) at fracture of Nb₃Sn. It was found that the strength of Nb₃Sn compound decreased with increasing annealing temperature and time due to an increase in grain size and it was proportional to the inverse root of grain size in both cases of titanium addition and non-addition, which could be expressed by the Hall-Petch type equation empirically. The strength was reduced by titanium addition.

Key words: tensile strength; niobium-tin compound; superconductor; titanium addition.

I. Introduction

There are many requirements for commercial use of A15 type superconducting materials. One of them is, of course, excellent superconducting property with high critical temperature, high upper critical magnetic field and high critical current up to high magnetic field. Excellent mechanical property is also required. As the A15 type compounds are, in general, brittle, there arises serious limitation in handling. Furthermore, the brittleness gives a limit of strain tolerance in superconducting properties.¹⁻⁴⁾

It is well known that the superconducting property can be improved by alloying additions such as Ti,⁵⁻⁹⁾ Zr,¹⁰⁾ Hf,¹¹⁾ Ta,¹²⁾ Ga¹³⁾ and Mg¹⁴⁾ to the Nb core or to the bronze matrix. However, the mechanical property of Nb₃Sn compounds with these elements has not been studied in detail. The aim of the present work is to evaluate the strength of the Nb₃Sn compound with titanium addition and to compare it with the strength without titanium addition.

II. Experimental Procedure

The specimens employed in the present study were multi-filamentary composite wires supplied as the Japanese reference sample for Japan-US exchange for energy research of the Ministry of Education, Science and Culture of Japan. The specification is summarized in Table 1.

The specimens were annealed isothermally at 973 and 1 073 K up to 1 728 ks. After annealing, all specimens were embedded in resin and the cross sec-

tions were polished. Scanning electron microscopy and electron microprobe analysis were made on the polished sections to measure the volume fraction of Nb₃Sn compound: $V_{\text{Nb}_3\text{Sn}}$ that is the sum of the volume fractions of the Nb₃Sn compound formed on the niobium filaments and at the niobium barrier, the volume fraction of niobium: V_{Nb} that is the sum of the volume fractions of niobium filaments and the niobium barrier retained after reaction, and the tin concentration in the bronze matrix, X_{Sn} , with the correction for atomic number, absorption and fluorescence (ZAF) effects. The volume fraction of copper as the stabilizer was 0.462 for all heat treatments. The volume fraction of the bronze, V_{Bronze} , was calculated as $1 - V_{\text{Nb}} - V_{\text{Nb}_3\text{Sn}} - V_{\text{Cu}}$.

Tensile tests were carried out with an Instron-type tensile machine at room temperature at a strain rate of 3.33×10^{-3} /s. For each annealing treatment, two specimens were tested to be averaged. From the fracture surface observed with scanning electron microscopy, the average grain size of Nb₃Sn compounds was measured with the linear-line-intercept method.

III. Results and Discussion

1. Variation of Microstructure with Annealing Treatment

Figure 1 shows the variation of $V_{\text{Nb}_3\text{Sn}}$ and V_{Nb} as a function of annealing time t at the annealing temperatures of 973 and 1 073 K. The $V_{\text{Nb}_3\text{Sn}}$ increased and correspondingly the V_{Nb} decreased with increasing t . For further annealing, both $V_{\text{Nb}_3\text{Sn}}$ and V_{Nb} at 1 073 K became nearly constant. These variations correspond to the variation of tin concentration in bronze. Figure 2 shows the variation of X_{Sn} as a function of t . The X_{Sn} decreased with increasing t to approach zero. At 1 073 K, almost all of tin element was consumed when t exceeded about 10 ks and correspondingly the $V_{\text{Nb}_3\text{Sn}}$

Table 1. Specification of the present specimens.

Overall diameter	1.048 mm
Composition of bronze	Cu-13.2 wt%Sn-0.3 wt%Ti
Copper to non-copper ratio	0.86
Bronze ratio	2.5
Filament diameter	~4 μm
Number of filaments	361 × 31
Barrier	Niobium
Twist	None

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Fig. 1. Variations of V_{Nb_3Sn} and V_{Nb} as a function of t .

Fig. 2. Variation of X_{Sn} as a function of t .

and V_{Nb} remained constant for further annealing. On the contrary, at 973 K, long annealing time was necessary for the consumption of tin element, and the V_{Nb_3Sn} , V_{Nb} and X_{Sn} reached their final values when t exceeded about 1 000 ks.

Figure 3 shows the variation of grain size of the Nb_3Sn compound, d , as a function of t . The data were compared with the data of our previous work¹⁵⁾ without titanium addition in bronze. The d increased with increasing t for both cases of addition and non-addition of titanium. Within the range investigated, the grain size of Nb_3Sn compound with titanium addition was smaller than that without titanium addition.

2. Tensile Behaviour of Composite Wire

Figure 4 shows typical stress-strain curves of the composite specimens annealed at 973 K for various times. The specimens annealed for a short time showed large plastic deformation while those annealed for a long time fractured in a brittle manner without apparent plastic deformation. These two types of fracture mode have been observed also for the multifilamentary Nb_3Sn composite wire without titanium addition in our previous work.¹⁶⁾ As in our previous

Fig. 3. Variation of d as a function of t , in comparison with the data without titanium addition taken from Ref. 15). The T and S refer to with and without titanium addition, respectively.

Fig. 4. Typical stress-strain curves of the composites annealed at 973 K for various periods.

work, the fracture mode of the former specimens is named as type I and that of the latter ones as type II. The reason why the specimens annealed for a short time showed type I but those annealed for a long time type II could be accounted for on the basis of the theories on fiber-reinforcement¹⁶⁻¹⁸⁾ as follows. When the amount of Nb_3Sn is small, the drop of load bearing capacity due to breakage of Nb_3Sn compound can be compensated by the work hardening of the ductile constituents of copper, bronze and niobium and therefore the composite specimens can be elongated even after the breakage of Nb_3Sn compound. In this case, the breakage of Nb_3Sn compound does not lead to fracture of specimens as a whole. On the contrary, when the amount of Nb_3Sn compound is large, the load bearing capacity reaches the highest at the stress level where the Nb_3Sn compound shows the ultimate tensile strength. In this case, the composite specimens fracture when the Nb_3Sn compound is broken, leading to brittle fracture mode.

In the case of type II specimens, the strength of Nb_3Sn compound can be evaluated from the strength of specimens since the breakage of Nb_3Sn compound determines the strength of specimens.¹⁶⁾ In the case of type I specimens, the strength of the compound

should be evaluated from the stress level of composites at fracture of the compound. Then the fracture morphology of Nb₃Sn compound at various strains was examined by etching off the copper, niobium barrier and some portion of bronze, as in our previous work.^{15,16)} Figure 5 shows typical appearances of the Nb₃Sn compound of type I at the strains indicated on the stress-strain curve. It is apparent that the Nb₃Sn compound began fracturing when overall plastic deformation of the specimens took place. This feature is quite the same as that observed in the type I specimens without titanium addition.^{15,16)} At high strains, the Nb₃Sn compound showed multiple fracture. This multiple fracture phenomenon is caused by the stress transfer from bronze and niobium filaments to previously broken Nb₃Sn compound, which is again broken into shorter segments.¹⁵⁻¹⁸⁾

As stated above, it was confirmed that the breakage of Nb₃Sn compound occurred at the apparent initiation of overall plastic deformation of specimens in type I, while it occurred at the fracture of specimens in type II. The stresses of composite specimens, σ_c^A , at which the Nb₃Sn compound fractures, can be taken at the points shown by arrows in Fig. 4. Figure 6 shows the variation of σ_c^A as a function of t . The open and closed marks correspond to the types I and II, respectively. The σ_c^A did not vary much for short annealing time but decreased with increasing t for long annealing time.

3. Tensile Strength of Nb₃Sn Compound

The σ_c^A is approximately given by^{15-17,19)}

$$\sigma_c^A = \sigma_{Nb_3Sn} V_{Nb_3Sn} + \sigma_{Bronze}^* V_{Bronze} + \sigma_{Nb}^* V_{Nb} + \sigma_{Cu}^* V_{Cu}, \dots\dots\dots(1)$$

where, σ_{Nb_3Sn} : the tensile strength of Nb₃Sn compound
 σ^* : the stress carried by the component shown by the subscript at the fracture of Nb₃Sn compound.

In general, as the residual stresses are exerted in all constituents due to difference in thermal contraction among the constituents,^{20,21)} it is very difficult to estimate the value of σ^* exactly. However, to a first approximation, the value of σ^* could be given by the yield stress as shown in Ref. 16), since the bronze, copper and niobium strain-hardened not so much at the fracture strain of the Nb₃Sn compound and the fracture strain of the compound was small.

The value of σ_{Bronze}^* can be obtained by assuming that the influence of titanium-addition on yield stress of the bronze is small, since the amount of titanium in bronze is 0.3 wt% at most, which decreases with increasing annealing time. On this assumption, the yield stress of bronze is given by $70+22X_{Sn}$ (at %),¹⁵⁾ from which σ_{Bronze}^* and σ_{Cu}^* can be known by substituting the measured values of X_{Sn} and $X_{Sn}=0$, respectively. The yield stress of niobium is taken to be 233 MPa for annealing at 973 K and 210 MPa at 1 073 K as in our previous work.^{15,16)}

The σ_{Nb_3Sn} is evaluated to a first approximation by

Fig. 5. Appearance of the Nb₃Sn compound at the strains indicated on the stress-strain curve of the type I specimen annealed at 973 K for 43.2 ks.

Fig. 6. Variation of σ_c^A as a function of t . The open and closed marks refer to the types I and II, respectively.

substituting the measured and estimated values of σ_c^A , σ^* and V into Eq. (1). Figure 7 shows the variation of σ_{Nb_3Sn} as a function of t , in comparison with that without titanium addition taken from Ref. 15). Three distinct features are found.

- (a) Longer annealing time at a given annealing temperature lowers the σ_{Nb_3Sn} for both cases of addition and non-addition of titanium.
- (b) Higher annealing temperature at a given annealing time lowers the σ_{Nb_3Sn} for both cases of addition and non-addition.
- (c) There is a tendency that the σ_{Nb_3Sn} with titanium addition is lower than that without addition under the same annealing treatment.

In our previous work,¹⁵⁾ it has been shown that the

Fig. 7. Variation of $\sigma_{\text{Nb}_3\text{Sn}}$ as a function of t , in comparison with the data without titanium addition taken from Ref. 15).

tensile strength of Nb_3Sn compound without titanium addition has strong dependency on grain size d , and it could be described empirically in the form given by

$$\sigma_{\text{Nb}_3\text{Sn}} = \sigma_0 + kd^{-1/2}, \dots\dots\dots(2)$$

where, σ_0, k : constant.
Then it was examined if the strength of the Nb_3Sn compound with titanium addition could be expressed in the same manner. Figure 8 shows the measured values of $\sigma_{\text{Nb}_3\text{Sn}}$ plotted against $d^{-1/2}$ for both cases of addition and non-addition of titanium. The strength of the Nb_3Sn compound can be described by Eq. (2), which is the Hall-Petch^{22,23)} type equation when $\sigma_0 \neq 0$ and the Orowan type equation when $\sigma_0 = 0$.

The Hall-Petch relation is derived from the concept that crack is nucleated by the dislocation pile-ups against grain boundaries.^{22,23,25)} Therefore, in order to apply the Hall-Petch relation, it should be confirmed that microscopic plastic flow occurs in the Nb_3Sn compound at room temperature. Experimentally this compound is brittle at room temperature, but a possibility that microscopic plastic deformation occurs in a limited scale can not be disputed since it is known that the plastic flow occurs under high hydrostatic pressure at room temperature and also under no and ambient pressure at high temperature.²⁶⁻²⁸⁾ At present it is not certain whether plastic flow occurs or not at room temperature. Therefore the applicability of the Hall-Petch relation can not be discussed further based on the physical model. However, it should be noted that the strength of some brittle ceramic materials which show nonyielding can be described empirically by the Hall-Petch type relation despite that there is no satisfactory physical model.²⁹⁾ Thus, even if no plastic deformation occurs in the Nb_3Sn compound, the relation between strength and grain size might be described empirically by the Hall-Petch type relation.

Within the data shown in Fig. 8, the σ_0 is relatively

Fig. 8. The $\sigma_{\text{Nb}_3\text{Sn}}$ plotted against $d^{-1/2}$, in comparison with the data without titanium addition taken from Ref. 15).

small ($\sigma_0 = 0.03$ and 0.06 GPa for the compounds with and without titanium addition, respectively). If σ_0 is regarded to be zero, the present result that the $\sigma_{\text{Nb}_3\text{Sn}}$ is proportional to $d^{-1/2}$ can be explained by applying the Griffith theory²⁹⁾ by considering that crack is nucleated by the grain boundary fracture and the grain size is equal to crack length. In this case, Eq. (2) can be written as

$$\sigma_{\text{Nb}_3\text{Sn}} = [4E_{\text{Nb}_3\text{Sn}}\gamma/(\pi d)]^{1/2}, \dots\dots\dots(3)$$

where, $E_{\text{Nb}_3\text{Sn}}$: the Young's modulus of the Nb_3Sn compound
 γ : the surface energy.

The slope in the $\sigma_{\text{Nb}_3\text{Sn}}-d^{-1/2}$ relation corresponds to $(4E_{\text{Nb}_3\text{Sn}}\gamma/\pi)^{1/2}$. Substituting the slopes shown in Fig. 8 and $E_{\text{Nb}_3\text{Sn}} = 165$ GPa,²¹⁾ we have $\gamma = 1.8$ and 1.2 J/m² for the compounds with and without titanium addition, respectively. As the fracture of the compound occurs mostly at the grain boundary, the difference in γ is considered to result from the difference in surface energy of the grain boundary. According to Suenaga*, titanium segregates to grain boundaries. If we assume that titanium reduces the surface energy, the present results can be understood in terms of titanium segregation. However, this assumption requires verification in further study.

Within the accuracy of the present work, it is difficult to determine which of the above mechanisms is responsible for the fracture of compounds. However, Eq. (2) can predict the strength of compounds with and without titanium addition as a function of grain size at least empirically. This finding is useful for the design of practical superconducting wires from mechanical view point.

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IV. Conclusions

(1) The strength of Nb₃Sn compound with and without titanium addition decreases with increasing annealing temperature and time due to increase in grain size.

(2) The strength of Nb₃Sn compound is proportional to the inverse root of grain size without regard to titanium addition. This is analogous to the Hall-Petch type relation.

(3) The strength of Nb₃Sn compound is reduced by titanium addition.

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