Microstructural Study on Nb₃Al Superconducting Wires Prepared by Clad-Chip Extrusion Method

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A microstructural study on Nb₃Al superconducting wires prepared by the Clad-Chip Extrusion (CCE) method was carried out to understand the dependence of critical current density (J_c) on the reduction ratio of Nb/Al composite wire, the additive elements and the heat treatment conditions. The result reveals that the dominant factors which affect the J_c -property are the grain size and volume fraction of Nb₃Al (A15), Al concentration in the A15-phase, and the interface density between the superconducting Nb₃Al and normal Nb₂Al (σ) layers. It is also suggested that the uniformly distributed σ layer with an optimum thickness is needed for high J_c -performance in a high applied magnetic field. In order to obtain a desirable structure for high J_c -performance, the CCE-processed Nb/Al composite wire is required to be drawn to high reduction in area to have fine layered structure and to be subjected to the two-stage heat treatment.

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I. Introduction

High temperature superconductors have been extensively studied since its discovery⁽¹⁾ in 1986. At the present time, however, they have many problems to be overcome for practical wire applications to high-field superconducting magnets. Under such circumstances, there is still the need to develop the A15 type superconducting wires which are characterized by high critical current density, J_c , and high critical field, H_{c2} . Although a large number of A15 intermetallic compounds are superconducting, a few ones are of practical use because of their processing difficulty. So far only two compounds, Nb₃Sn and V₃Ga, have been produced on a commercial scale. In the case of them, the manufacturing difficulty has been largely overcome by utilizing the solid-state reaction between Nb(or V) and Sn(or Ga) dissolved in Cu, of which method is called "the bronze process"⁽²⁾⁻⁽⁴⁾. Furthermore, their variants⁽⁵⁾⁻⁽¹²⁾ have been also developed.

The Nb₃Al has been considered as an alternative to Nb₃Sn for high-magnetic-field applications because of its better inherent superconducting properties and strain tolerance. However, the bronze process is inapplicable for thermodynamic reasons to the manufacture of Nb₃Al wire. Alternative techniques have, therefore, been attempted to fabricate the Nb₃Al wire. In principle, two different processes have been used to form the A15-phase. One is the direct precipitation process⁽¹³⁾⁽¹⁴⁾, in which a supersaturated solid solution of Al in Nb is made by rapid quenching and then the A15 compound is formed by a precipitation reaction at an elevated tempera-

ture. The other is the direct reaction process⁽¹⁵⁾⁻⁽¹⁹⁾, in which a fine admixture of Nb and Al is made by plastic working and then it is converted into the A15 compound by a diffusion reaction. Fabrication of rapidly quenched superconducting wires is difficult for commercial use although a continuous liquid quenching apparatus has been reported⁽²⁰⁾. So, manufacturing research on the A15 wire has concentrated on the production of a fine admixture of Nb and Al, and the subsequent formation of the A15-phase through some direct reaction processes after the wire drawing. At least five distinct manufacturing processes have been explored so far; (1) the powder process⁽¹⁵⁾, in which a mixture of powders of the two primary constituents is extruded and drawn into a wire before reaction, (2) the "jelly-roll" process⁽¹⁶⁾, in which thin foils of the two constituents are rolled into a cylindrical compact and worked into a wire before reaction, (3) the liquid infiltration process⁽¹⁷⁾, in which a porous compact of Nb powder is infiltrated by liquid Al and the mixture is subsequently drawn into a wire before reaction, (4) the "Nb-tube" process⁽¹⁸⁾, in which a composite billet of a Nb-tube containing aluminum core inside is extruded and the restacked assembly of the single-core Nb/Al composites is re-extruded and drawn into a wire before reaction, (5) the "Clad-Chip Extrusion" method⁽¹⁹⁾, in which chips of laminated Nb and Al foil are extruded and drawn into a wire before reaction.

The control of the A15-phase formation is most important for Nb₃Al wire fabrication in the direct reaction process. The Nb-Al binary phase diagram⁽²¹⁾ indicates that the reacted A15-phase has a closer composition to stoichiometry at a higher reaction temperature. However, the grain growth becomes predominant at high temperatures, which lowers J_c . The heat treatment temperature range between 1173 and 1373 K is commonly used to compromise between these two effects. The lower reac-

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tion temperature is also favorable for the practical fabrication of Nb_3Al wires. The studies on the reactions between niobium and aluminum layers using a model system of Nb/Al multilayer samples revealed that the A15-phase forms only in the vicinity of the Nb/Al interface and ultrafine (submicron) layers are needed for the reaction to proceed at the low reaction temperature^{(22)–(24)}. Therefore Nb–Al composite must be deformed to extremely high reduction in area during wire drawing in order to increase the extent of the Nb/Al interface and thus the amount of the A15 phase.

The Clad-Chip Extrusion (CCE) method has the advantage of obtaining finely and uniformly distributed Nb/Al layers in the composite wire up to the high reduction in area⁽¹⁹⁾. It has been found that the J_c -property of the CCE-processed Nb_3Al wire is enhanced with increasing the reduction of the Nb/Al composite wire⁽²⁵⁾. The effect of additive elements on the J_c -property has been also reported on the CCE-processed Nb_3Al wires⁽²⁶⁾. However, the microstructural characterization has not been carried out though a fundamental understanding of the microstructure of phases produced by the reaction is essential for a further improvement of J_c . This paper describes the microstructural study on the A15-phase formation in the CCE-processed Nb_3Al wires to understand the effects of reduction ratio of Nb/Al composite wire, namely diffusion spacing, additive elements and heat treatments on the J_c -property.

II. Experimental Procedure

The CCE method for the Nb_3Al wire fabrication has

Fig. 1 Schematically drawn TEM-sample preparation method.

been reported in detail elsewhere⁽¹⁹⁾⁽²⁷⁾. Triple layered Al/Nb/Al clad foil with thickness of $200\text{ }\mu\text{m}$ which had the fraction of Nb and Al corresponding to the intended chemical composition of 77 mol%Nb and 23 mol%Al was prepared by cold rolling. Aluminum alloys were used when the effect of additive elements was studied. The clad-foil was cut into square pieces with a size of roughly $5\text{ mm} \times 5\text{ mm}$, and then they were randomly filled up into a copper sheath. The billet was extruded with a reduction ratio of 5 after evacuation and followed by mechanical reduction such as grooved-rolling and wire drawing to give the Nb/Al(Al-alloys) composite wire. An extruded Nb/Al(Al-alloys) composite bar showed good workabil-

Fig. 2 TEM micrographs of longitudinal section of unreacted wires after drawing to (a) $R = 2.3 \times 10^5$ and (b) $R = 4 \times 10^6$, where R is the cross sectional ratio of an initial billet to a final wire.

ity in wire drawing up to relatively high reduction ratio, R of 4×10^6 , where R is the cross-sectional ratio of an initial billet to a final wire. After heat treatment, critical temperature T_c and critical current I_c were measured by a standard four probe method. T_c was defined as the mid-point of the electrical resistivity transition and I_c was defined by the criterion of $100 \mu\text{V/m}$. The J_c was calculated by dividing I_c by the cross-sectional area of the wire without copper.

Figure 1 shows the method for transmission electron microscopy (TEM) sample preparation. The Nb₃Al wires were electroplated with nickel and mechanically polished both sides to the thickness of about $30 \mu\text{m}$. TEM samples were then prepared by Ar ion thinning. The TEM observation was carried out by JEM-2000EX and JEM-2000FX with an energy dispersive spectroscopy (EDS). The average grain size and the areal fraction of each phase and the interface density between the superconducting and normal phases, which was defined as the reciprocal of the sum of average spacing of each layer, were obtained by graphic treatment of the TEM micrographs. The observed phases were identified by TEM-EDX. The Al concentration in A15 was also measured with TEM-EDX after making a calibration curve.

III. Results and Discussion

1. Microstructure of unreacted Nb/Al composite wires

Figure 2 shows TEM micrographs of the longitudinal section of unreacted wires after drawing to (a) $R=2.3 \times 10^5$ and (b) $R=4 \times 10^6$. The wires consist of the Nb and Al layers aligned in the drawing direction. The layers are more finely and uniformly deformed in the high reduction wire ($R=4 \times 10^6$) than in the low reduction wire ($R=2.3 \times 10^5$). The thickness of Nb-layer in the high reduction wire is about 80 nm, which is almost the same as calculated one from the reduction ratio. The diffraction pattern shows that the fiber texture parallel to [011] for the Nb-layer and [111] for the Al layer develops more significantly in the high reduction wire than in the low reduction wire.

2. J_c -property and microstructure of reacted binary wires with high reduction

Figure 3 shows TEM micrographs of the longitudinal section of the reacted wires with high reduction ($R=4 \times 10^6$), which were subjected to the single-stage heat treatment of (a) 1023 K–345.6 ks, (b) 1023 K–1036 ks and (c) 1273 K–120 s, respectively. Three phases of Nb₃Al (A15), Nb₂Al (σ) and unreacted Nb are observed layer by layer in Fig. 3(a) and (c). In Fig. 3(b), however, unreacted Nb is not identified but only A15 and σ phases are observed. Figure 4 shows TEM micrographs of the longitudinal section of the reacted wires ($R=4 \times 10^6$), which were subjected to the two-stage heat treatment of (a) 1273 K–120 s followed by 1023 K–84.6 ks, (b) 1273 K–

Fig. 3 TEM micrographs of longitudinal section of reacted wires ($R=4 \times 10^6$), which were subjected to the single-stage heat treatment of (a) 1023 K–345.6 ks, (b) 1023 K–1036 ks and (c) 1273 K–120 s, respectively.

120 s followed by 1023 K–345.6 ks and (c) 1273 K–120 s followed by 1023 K–604.8 ks, respectively. All of them show the A15 and σ phases layer by layer without the unreacted Nb phase. Figure 5 shows J_c - B curves for the same wires as shown in Figs. 3 and 4, indicating that the two-stage heat treatment results in enhancement of the J_c -property. Among them, the heat treatment condition of 1273 K–120 s followed by 1023 K–345.6 s yields the highest J_c property, which is the optimum condition in

Fig. 4 TEM micrographs of longitudinal section of reacted wires ($R=4 \times 10^6$), which are subjected to the two-stage heat treatment of (a) 1273 K-120 s followed by 1023 K-84.6 ks, (b) 1273 K-120 s followed by 1023 K-345.6 ks and (c) 1273 K-120 s followed by 1023 K-604.8 ks, respectively.

this experiment. The relation between the J_c -property and heat treatment conditions shown in Fig. 5 will be discussed below focusing on the observed microstructures such as the grain size and the volume fraction of the A15 phase, the Al concentration in the A15 phase, and the interface density between the superconducting and normal phases.

Figure 6 shows the relation between measured grain size of the A15 phase and heat treatment time. The grain size increases with heat treatment time and the samples with coarse grains show a low J_c -property in the magnetic fields, as denoted by $\blacktriangle$, ∇ , $\diamond$ in Fig. 5. However, J_c does

Fig. 5 J_c - B curves for the same wires shown in Figs. 3 and 4.

Fig. 6 Relation between measured grain size of A15-phase and heat treatment time for the binary wire ($R=4 \times 10^6$).

not depend only on the grain size because the sample heat-treated for a short time ($\bullet$ in Fig. 5) possesses a smaller grain size than the heat treated one in the optimized condition ($\blacksquare$ in Fig. 5), but the former shows lower J_c values than the latter.

Figure 7 shows the relation between the measured areal

Fig. 7 Relation between measured areal fraction of respective phases and heat treatment conditions for the binary wire ($R=4 \times 10^6$).

Fig. 8 Relation between measured Al content in A15 phase and heat treatment conditions for the binary wire ($R=4 \times 10^6$).

fraction of the respective phases and the heat treatment conditions. In general, it is believed that the increase in volume fraction of the A15 phase enhances the overall critical current density. However, the volume fraction of the A15 phase does not seem to influence the J_c -property by itself because the single-stage heat treatment yields a higher volume fraction of the A15 phase than the two-stage heat treatment, but the former shows lower J_c values than the latter (see Fig. 5).

The aluminum content in the A15-phase affects superconducting properties, especially $T_c^{(21)}$. Figure 8 shows the relation between measured Al content in the A15 phase and heat treatment conditions. The measured T_c values are also plotted in the figure. Both the single-stage heat treatment for a short time at high temperature (1273 K–120 s) and the one for a long time at low temperature (1023 K–345.6 ks) yield the A15 phase with low Al content as shown in Fig. 8. In the two-stage heat treatment, the Al content increases with the second-stage heat treatment time and shows a peak value at the condition of 1273 K–120 s followed by 1023 K–345.6 ks, where the highest J_c value was obtained in this work (see Fig. 5). This can be interpreted in terms of the enhancement of the ordering in the A15 phase, which is accompanied by the increase of Al content.

The interface between superconducting phase and normal phase has been suggested to be an effective pinning site⁽²⁸⁾. Figure 9 shows the relation between heat treatment condition and interface density between the superconducting phase (A15) and the normal phase (σ), where the interface density is defined as the dividing unit spacing ($1 \mu\text{m}$) of the layered structure by a sum of the average spacing of superconducting ($d_s, \mu\text{m}$) and normal ($d_n, \mu\text{m}$) layers as schematically shown in Fig. 10. The single-stage heat treatment yields a lower density than the

Fig. 9 Relation between heat treatment conditions and interface density between superconducting and normal phases for the CCE-processed Nb₃Al wires ($R=4 \times 10^6$).

two-stage heat treatment. The interface density decreases with heat treatment time in both of the single-stage and two-stage heat treatments. Such a decrease in the interface density can be related to the lower J_c -property. From this point of view, it is considered that the interface density between the superconducting and normal layers plays an important role in the enhancement of the J_c -

Fig. 10 Schematic drawing of typical microstructure on the CCE-processed Nb_3Al wire.

property.

From the above discussion, it is concluded that the CCE-processed Nb/Al composite wire with high reduction must be heat-treated so as to suppress the grain growth of the A15 phase, to increase the volume fraction of the A15 phase, to increase the Al content in the A15 phase, and to increase the interface density between normal and superconducting layers for enhancement of the J_c -property.

3. J_c -property and microstructure of reacted binary wires with low reduction

Figure 11 shows TEM micrographs of the longitudinal section of the reacted wires with low reduction ($R=2.3 \times 10^5$) which were subjected to the two-stage heat treatment of (a) 1173 K–300 s followed by 1023 K–345.6 ks, (b) 1273 K–300 s followed by 1023 K–345.6 ks and (c) 1373 K–120 s followed by 1023 K–345.6 ks, respectively. Three phases of Nb_3Al , Nb_2Al and unreacted Nb are observed in Fig. 11(a) and the average grain size of Nb_3Al is about 90 nm. The sample (b) heat-treated at a higher temperature than the sample (a) also shows three phases. The average grain size of Nb_3Al in the sample (b) increases to about 150 nm. The heat treatment condition (c), the highest first-stage treatment temperature in Fig. 9, yields the A15 and σ phases without unreacted Nb, and the average grain size of Nb_3Al is almost the same as the sample (b).

Figure 12 shows the dependence of Al content in A15-phase and the interface density between the superconducting and normal layers on the heat treatment conditions. Figure 13 shows J_c - B curves for the wires which were subjected to the same heat treatment as shown in Fig. 11. By comparing Fig. 12 with Fig. 13, it is revealed that both of the high Al content in the A15 phase and the high interface density increase the J_c value in a similar way to the wires with high reduction. But the J_c -property is much lower in the low reduction wire than in the high reduction one (see Figs. 5 and 13).

Although the first heat treatment of 1273 K–120 s in the two-stage treatment is optimum for the high reduction wire, it is not applicable to the low reduction wire

Fig. 11 TEM micrographs of longitudinal section of reacted wires with low reduction ($R=2.3 \times 10^5$) subjected to the two-stage heat treatment of (a) 1173 K–300 s followed by 1023 K–345.6 ks, (b) 1273 K–300 s followed by 1023 K–345.6 ks and (c) 1373 K–120 s followed by 1023 K–345.6 ks, respectively.

but the longer holding time of 300 s is required for enhancement of the J_c -property. That is, the thick layers of Nb and Al in the low reduction wire require the longer holding time at high temperature in order to form the A15 compound. This heat treatment condition causes grain growth and reduces interface density. This is the reason why the low reduction wires show lower J_c -property than the high reduction ones. Thus, it is evident that Nb–Al composite wires with high reduction and optimization of heat treatment are demanded to enhance the J_c -property in the direct reaction process.

Fig. 12 Dependence of Al content in A15-phase and interface density between superconducting and normal phases on heat treatment conditions in the binary wire ($R=2.3 \times 10^5$).

Fig. 13 J_c - B curves for the same wires shown in Fig. 11.

4. Effect of additive elements

Figure 14 shows J_c - B curves of the wires with several additive elements, which were heat treated under the respective optimum conditions. Addition of Mg and Ti using Al alloys in the CCE method lowers the optimum heat treatment temperature compared with the binary wire⁽²⁶⁾. Both of Mg- and Ti-containing wires

Fig. 14 J_c - B curves for Ti-, Mg- and Sn-added wires, which were heat treated under each optimum condition.

Fig. 15 TEM micrograph of longitudinal section of 4 mol%Mg-added wire ($R=3 \times 10^6$) subjected to the two-stage heat treatment of 1173 K-960 s followed by 1023 K-345.6 ks.

($R=3 \times 10^6$) show almost the same J_c -property as the binary wire with high reduction which was subjected to the optimum heat treatment. In these respects, Mg and Ti are effective elements for the CCE-processed Nb₃Al wire. On the other hand, the Sn addition results in low J_c -property in spite of the same reduction ($R=2 \times 10^6$).

Figure 15 shows a TEM micrograph of the longitudinal section of the 4 mol%Mg-added wire ($R=3 \times 10^6$) which was subjected to the two-stage heat treatment of 1173 K-960 s followed by 1023 K-345.6 ks. Many isolated spherical Kirkendall voids are observed only in the Mg-added sample, which is one of the most distinctive features. It is considered that they affect the instability⁽²⁶⁾

of the I - V curves at the I_c measurement in magnetic fields. Another feature is that unreacted Nb is not identified but the A15 and σ phases are observed though the heat treatment temperature was lowered to 1173 K, of which condition yielded unreacted Nb in the binary sample. It is revealed that the Mg addition promotes the formation of the A15 and σ compounds in a low temperature reaction. The Mg addition decreases the average grain size and increased the interface density compared with the binary sample. Both of these factors may enhance the J_c -property. But the volume fraction of A15 is reduced by the Mg addition compared with the binary wire, which may reduce the J_c -property. Competition between these opposite factors decides the J_c -property which is almost the same as the binary one. In addition, the thickness of the σ phase seems to affect the J_c -property because it decreases notably compared with the binary one.

Figure 16 shows a TEM micrograph of the longitudinal section of the 1 mol%Ti-added wire ($R=3 \times 10^6$) which was subjected to the two-stage heat treatment of 1173 K-

600 s followed by 1023 K-345.6 ks. The microstructure is composed of the A15 and σ phases without unreacted Nb in a similar manner to the Mg-added sample. Ti is also an effective element enhancing the compounds formation in low temperature reaction. Compared with the Mg-added sample, the Ti-added one shows less Kirkendall voids, well-aligned structure of the A15 and σ phases, and more volume fraction and smaller grain size (70 nm) of the A15 phase. Those factors seem to enhance the J_c -property but there was not so notable enhancement of the J_c -property compared with the binary sample (see Fig. 14). Possible factors reducing the J_c -property in this sample are the lower values of T_c and thickness of the σ phase than those in the binary sample; T_c is 16.8 K and 17.0 K, and the average thickness of the σ phase is 150 and 260 nm for the Ti-added and binary samples, respectively.

Figure 17 shows a TEM micrograph of the longitudinal section of the 5 mol%Sn-added wire ($R=2 \times 10^6$) which was subjected to the optimized heat treatment of 1273 K-120 s followed by 1023 K-345.6 ks. The sample had T_c of 16.7 K which was almost the same as Mg- and Ti-added

Fig. 16 TEM micrograph of longitudinal section of 1 mol%Ti-added wire ($R=3 \times 10^6$) subjected to the two-stage heat treatment of 1173 K-600 s followed by 1023 K-345.6 ks.

Fig. 17 TEM micrograph of longitudinal section of 5 mol%Sn-added wire ($R=2 \times 10^6$) subjected to the two-stage heat treatment of 1273 K-120 s followed by 1023 K-345.6 ks.

Table 1 Results of TEM analysis and the superconducting properties.

Specimen	Phase	V_f (%)	Thickness (nm)	Grain size (nm)	Interface density	T_c (K)	J_c (Am^{-2}) 14T, 4.2 K
Nb/Al binary ($R=4 \times 10^6$)	Nb ₃ Al	62	450	120	1.4	17.0	5.3×10^8
	Nb ₂ Al	38	260	—			
	Nb	—	—	—			
Nb/Al binary ($R=2.3 \times 10^5$)	Nb ₃ Al	63	570	150	1.1	16.6	1.3×10^8
	Nb ₂ Al	28	260	—			
	Nb	9	80	—			
4%Mg-addition ($R=3 \times 10^6$)	Nb ₃ Al	53	190	100	2.8	16.7	3.6×10^8
	Nb ₂ Al	47	160	—			
	Nb	—	—	—			
1%Ti-addition ($R=3 \times 10^6$)	Nb ₃ Al	70	350	70	2.0	16.8	3.8×10^8
	Nb ₂ Al	30	160	—			
	Nb	—	—	—			
5%Sn-addition ($R=2 \times 10^6$)	Nb ₃ Al	85	900	130	0.9	16.7	1.9×10^8
	Nb ₂ Al	15	160	—			
	Nb	—	—	—			

ones. The most distinctive microstructural feature in this sample is the extreme increase in the volume fraction of the A15 phase with less σ phase and without unreacted Nb. However, the sample was low in the J_c -property as shown in Fig. 14. A possible explanation may be given by the less interface density between the superconducting and normal phases.

The above-mentioned data are summarized in Table 1. Again, the role of the σ layers is emphasized to be important for J_c -performance in high magnetic fields.

IV. Summary

The TEM observation on the CCE-processed Nb₃Al wires was carried out to study the relation between the J_c -property and the microstructure. The results are summarized as follows:

(1) The dominant factors which affect the J_c -property are the grain size and the volume fraction of the A15 phase, the Al content in the A15 phase, and the interface density between the superconducting and normal layers.

(2) The CCE-processed Nb/Al composite wire is required to be drawn to a high reduction to have the finely and uniformly distributed Nb/Al-layered structure, which can be converted into the favorable structure for the high J_c -property by heat treatment.

(3) The two-stage heat treatment is effective for the high J_c property. The first stage heat treatment at high temperatures for a short time yields fine grains of the A15 phase with low Al content and low ordering. The subsequent second one at low temperature for a long time leads to the enhancement of the ordering accompanied by the increase of Al content in the A15 phase without grain growth.

(4) Homogeneously distributed normal layers (σ phase) with an optimum thickness are necessary for high J_c -performance in the high applied magnetic fields.

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