Development of Coated Conductors by PLD Process for HTS Power Applications

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R&D efforts have been made for various applications of high temperature superconducting (HTS) conductors such as power cables, high field magnets and transformers. In Japan, a national project to develop materials and power applications using coated conductors was started in 2008. Since then, we have been fabricating coated conductors by pulsed laser deposition (PLD) for the development of a 5 kA, 66 kV class "3-in-One" HTS model cable system as a part of this project. In order to construct the HTS cable, stable production of coated conductors with high critical current density (Ic) is required. For this purpose, the deposition process of buffer and superconducting layers on the clad-type substrate are key technologies. We installed a 300 W high power excimer laser to our PLD equipment to obtain a thick superconducting layer. In addition, we improved the buffer layers to enhance the Ic property. Moreover, we used a wide tape of 30 mm to obtain large production throughput, and successfully obtained uniform superconducting characteristics across the tape width. As the Ic property of over 300 A/cm was confirmed for 100 m length, coated conductors have become promising for AC applications, especially for HTS cables aimed at lowering AC loss. In this study, we investigated the Ic values and stable manufacturing process of coated conductors by PLD process. Differences in characteristics were also discussed according to the length of the tape.

Keywords: high-temperature superconductors, coated conductors, power cable, AC loss

1. Introduction

It is highly expected that the use of high temperature superconducting (HTS) conductors will reduce the size of power transmission and other industrial equipment and increase the transmission capabilities. As the AC loss of HTS conductors is lower than that of the conventional power cable and electric equipment, world-wide R&D efforts have been made for HTS equipment in order to promote energy saving and prevent global warming. In Sumitomo Electric Industries, Ltd., an R&D project of 2nd generation HTS coated conductors and large current HTS cable system have been conducted since 2008 under a national project to develop materials & power applications of coated conductors⁽¹⁾. Recently, coated conductors show excellent performances of high current capacity and long length production as well as the potential of high critical current density (Jc) and low AC loss. These features of the coated conductors enable the HTS power cable to increase its transmission capacity with compact size as compared with that by using 1st generation HTS conductors such as bismuth strontium calcium copper oxide (BSCCO).

In this paper, we investigate the state-of-the-art coated conductors that use pulsed laser deposition (PLD) process on textured metal substrates in order to apply them to the HTS high power cable system.

2. R&D Scope

2-1 Coated Conductor program

In the national project, we have been fabricating coated conductors for the development of the 66 kV/5 kA

class "3-in-One" HTS model cable system. Under the R&D program of coated conductors, we are studying how to increase the Jc and developing a stable production process as important fabrication techniques. At the same time, long length coated conductors have been produced in order to demonstrate a 15 m long HTS cable system. Under the R&D program of the large current cable system, a 15m long-66kV/5kA class "3-in-One" HTS model cable system is being constructed. Table 1 shows the targets of the conductor and cable development project at Sumitomo Electric. The production of coated conductors of 10 mm in width and 10 km in total length is required, and a stable production process for such conductors needs to be established within four years. The required critical current (Ic) and piece length of the coated conductor are 300 A/cm and 20 m, respectively. In the HTS cable system, the total AC loss should be less than 2.1 W/m/phase at a 5 kA transport current. The outer diameter of the cable should be less than 150 mm in order to be installed in the conventional existing duct. A 31.5 kA overcurrent is applied to the cable for 2 seconds to confirm that no damage will be caused in case of any faults in the direct connection to real transmission lines.

2-2 Architecture of coated conductor and cable

Figure 1 shows the architecture of the coated conductor and HTS large current cable. The coated conductor is composed of a textured metal substrate, buffer layer, superconducting layer, Ag protection layer, and Cu stabilizing layer. We developed the clad-type textured metal substrate (clad substrate), which consists of a thin bi-axially textured Ni layer on a non-crystalline stainless tape, showing lower magnetism and higher mechanical strength than typical Ni-alloy textured substrates. We also developed a multi-buffer layer of CeO₂/YSZ/CeO₂ deposited by RF sputtering or electron beam (EB) evaporation process on the 30 mm wide clad substrates in 120 micron thickness. On the buffer layer, the Gd1Ba₂Cu₃O_x (GdBCO) superconducting layer was deposited by PLD process and the Ag protection layer was deposited by DC sputtering method. After the Ag deposition, oxygen annealing was performed, 30 mm wide conductor was cut into 6 tapes in 4 mm width or 12 tapes in 2 mm width and Cu-stabilizer was electrically plated around the wire⁽²⁾.



Fig. 1. Architecture of coated conductor and HTS cable

Fable	1.	Targets of	coated	conductor	and	cable	project
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Conductor	Characteristics	Ic > 300 A/cm, Piece length: 20 m	
Conductor	Production	Total >10 km @ 1 cm width	
	Capacity	5 kA-66 kV, 3 phase	
Cable	AC loss	2.1 W/m/phase @ 5 kA	
	Size	Length: 15 m Diameter < 150 mm duct	

A conventional multi-stranded Cu round cable was used as a former of the HTS cable. This former would act as both reinforced material of the cable and current shearing pass when large overcurrent generated in the grid. Several GdBCO conductors were used and assembled spirally on this former to form the HTS conductor of the cable. Moreover, electrical insulation sheets were formed on the HTS conductor, and several GdBCO conductors and Cu tapes were surrounded to form a shield on the insulation layer. As a result, single HTS cable core was completed. A stranded 3-single core was inserted into the double corrugated vacuum stainless pipe, and "3-in-One" structure was completed. Finally, liquid nitrogen was flown and circulated around the HTS cable inside of the double corrugated vacuum pipe.

3. Elementary Studies

3-1 Coated conductor program

In the national project, we aimed to construct the stable production technologies of GdBCO conductors by using PLD process on clad substrates (Clad-PLD conductor) in order to apply them to the large current HTS cable system as shown in **Table 2**. In this R&D project, we first developed high Ic technologies in order to reach the targets described above. Second, we established a mass production process of long length GdBCO conductors by using 30 mm width clad substrates to obtain the large production throughput. This process enabled stable production of the conductor to be applied to the HTS large current cable. In this project, we installed a new high power excimer laser in the PLD equipment to increase both yield and production capacities. The R&D approaches are summarized below:

- 1) Development of high Ic conductors by PLD process on the clad substrates
- 2) Establishment of stable production process, and increase of throughput and width of clad substrates
- 3) Improvement of Ic property and yield by installing a high power laser

Architecture	Materials	Process	Width, Thickness	
Textured Substrate	Clad-type	Clad and heat treatment	30 mm width 120 micron	
	CeO ₂	RF sputtering	100 nm	
Buffer layer	YSZ	or EB	200 nm	
	CeO ₂		70 nm	
SC layer	GdBCO	PLD	2 ~ 3 micron	
Protection layer	Ag	DC sputtering	2 ~ 8 micron	
Wire size	_	Mechanical slitting	30 mm width $\rightarrow 2 \text{ mm}/4 \text{ mm}$	
Stabilized layer	Cu	Electro plating	20 micron	
Critical current ((77K, self field)	Ic)	Ic ₂ (2 mm width) = $60 \sim 80$ A Ic ₄ (4 mm width) = $120 \sim 160$ A		

Table 2. Characteristics of Clad-PLD conductor

3-2 Buffer layer

In order to realize the homogeneous Clad-PLD conductor, surface flatness, homogeneous cube textured characteristics and stable deposition condition are necessary for the buffer layers. The multi-buffer layers of CeO₂/YSZ/CeO₂ were deposited on the 30 mm wide clad substrate by the reel-to-reel RF sputtering method. The first CeO₂ layer deposited on the substrate plays the role of a seed layer. The second YSZ layer prevents Ni inter-diffusion and reaction to the GdBCO layer. The third CeO₂ layer acts as the relaxation of lattice-mismatch between the YSZ and the GdBCO layers. Several R&D efforts were made to optimize the deposition condition, including the atmosphere and temperature, and to control the long time production process.

At present, the buffer layer shows around 6 degrees of

in-plain alignment for CeO2 (111) pole across the 30 mm tape width. The crystallinity of the third CeO2 layer, cube textured ratio defined by I(200)/[I(200)+I(111)], was analyzed by XRD. The value showed highly uniform crystallinity over 95% for 80 m length as shown in Fig. $2^{(3)}$. In addition, we found that the surface morphology of the buffer layer strongly affected the superconducting properties by using EB evaporation method. Figure 3 (a) shows scanning electron microscope (SEM) images of surface morphology of seed and cap layers deposited by the RF sputtering method. A number of small cracks in the submicron scale were observed on the seed layer. This surface condition degrades the flatness of the cap layer and crystal orientation. To make a crack-free seed layer, we used the EB evaporation method. Figure 3 (b) shows SEM surface images of the seed layer deposited by the EB method. After optimizing the deposition parameters, the surface became significantly flat. Moreover, numerous precipitates or grain boundaries on the cap layer were disappeared. The progress in the buffer layer deposition process contributed to the increase of the Ic value.



Fig. 2. Longitudinal cube-textured characteristics of CeO₂/YSZ/CeO₂ long buffer layer





(b) Seed layer (left) and cap layer (right) by EB

Fig. 3. Improvement of surface morphology of buffer layers by using EB evaporation method

3-3 Enhancement of Ic properties of SC layers

The GdBCO superconducting layer was fabricated on the $CeO_2/YSZ/CeO_2$ buffer layers by a reel-to-reel PLD system with a 300 W Kr-F excimer laser. The deposition was

repeated for several times at a tape moving speed of 24 m/h under 10 Pa of the O2 partial pressure. In this study, we compared the Ic properties of the GdBCO layers deposited by the 300 W laser and by a previous 200 W laser. We first observed the effect of laser power on Ic properties of GdBCO layers. Figure 4 shows the plasma plume distributions across the 30 mm wide tape, which were deposited by the previous 200 W laser and the new 300 W laser. The Ic value of the GdBCO layer grown by the new 300 W laser was about 1.5 times larger than that of the layer deposited by the previous 200 W laser. This was simply caused by the effect of a thick GdBCO with 2.8 microns, which was 1.3 times thicker than the previous GdBCO layer with 2.1 microns. In Fig. 4, the 300 W laser obviously enlarged the plasma plume on the GdBCO target. In our PLD equipment, the plasma plume is optimized to cover the 30 mm wide substrates completely in combination with the line beam technique. Thus, by using the new 300 W laser, Ic property was enhanced and production and the yield of the GdBCO layer was significantly improved.

Figure 5 shows the increase in Ic values of 30 mm-width Clad-PLD conductors. The Ic property of 2.1 micron GdBCO conductors (TC330 ~ TC332) tends to be saturated by 250 A/cm. However, the Ic values of 2.8 micron GdBCO conductors (TC335, KS001) were improved to 350 ~ 400 A/cm after the installation of the 300 W laser. **Figure 5** also indicates that the Ic value of the 2.8 micron GdBCO conductor (KS010) goes up to the 500 A/cm level when it is fabricated on the buffer layer by EB evaporation. Thus, Ic property has been greatly improved by applying thick GdBCO layers on the crack free buffer layer. The liner re-



(a) 200 W laser

(b) 300 W laser

Fig. 4. Comparison of plasma plum between 200 W laser and 300 W laser



Fig. 5. Increase in Ic values of 30 mm-width Clad-PLD conductors

lationship between Ic values and GdBCO thickness up to 1.5 microns was also observed for this conductor (KS010), and high Jc of 3 MA/cm² was confirmed. Above 1.5 microns, Jc was degraded to the 2 MA/cm² level and Ic value became close to 500 A/cm at 3 microns.

3-4 Long length performance of conductors

By using the improved manufacturing process of the buffer layer and superconducting layer, we manufactured high Ic GdBCO tapes exceeding 400 A/cm, 30 mm wide, and 100 m long. A 30 mm wide tape deposited on the Ag protection layer was cut into 6 tapes of 4 mm width by a continuous slitter machine. Each 4 mm tape was plated electrically with a 20 micron Cu stabilizer, and the Ic value was measured for every 1.5 m by adopting a continuous four-probe technique.

Figure 6 shows a typical longitudinal Ic distribution of a 4 mm wide GdBCO conductor. The minimum and maximum Ic values were 178 A (445 A/cm) and 190 A (475 A/cm), respectively. The Ic property consistently increases from start to end. We found that this Ic distribution was strongly influenced by the cube textured ratio of the buffer layer. **Figure 7** shows a typical longitudinal Ic distribution of a 2 mm wide GdBCO conductor. Although the mechanical slitting degrades Ic values about 8 % in the case of the 2 mm width conductor, Ic values were nearly 60 A. Based on these results, we demonstrated the long length GdBCO conductor production process for a 66 kV-5 kA class, 3-in-One HTS model cable with high Ic over 300 A/cm.



Fig. 6. Longitudinal Ic distribution of 4 mm-width Clad-PLD conductor

4. Conductor Production

4-1 Production of Clad-PLD conductors

At the GdBCO deposition, we newly installed a 300 W high power laser, developed a precise temperature control technique and reduced the excess heat effect on the substrates by increasing the tape moving speed. As shown in Fig. 5, Ic exceeded 400 A/cm at the center and left side of the 30 mm width substrate. As a result of R&D efforts for high Ic performance of a thick GdBCO layer and good Ic distribution across the width of 30 mm, the total amount of 10 mm width GdBCO conductors produced every month has reached 1 km. In the development of homogeneous Clad-PLD conductors, we observed the crystalline characteristics by using XRD and the surface morphology of each layer by SEM or AFM. The obtained data was analyzed and fed backed to the relationship between characteristics and deposition process conditions for buffer and superconducting layers to accelerate our R&D efforts.

Based on these production technologies, 3 km Clad-PLD conductors with 10 mm width were fabricated on the 30 mm substrates. The GdBCO layer was 2.1 microns and the target Ic value was 200 A/cm. **Figure 8** shows the relationship between Ic performance and piece length of 4 mm width conductors. When the Ic value is over 200 A/cm, the yield becomes 34%. This data confirms that the stable production process has been achieved for GdBCO conductors with a satisfactory Ic value and piece length for HTS model cable.



Fig. 8. Ic distributions of 4 mm-width Clad-PLD conductors



Fig. 7. Longitudinal Ic distribution of 2 mm-width Clad-PLD conductor

4-2 Characteristics of long time durations

The production conditions and various operational circumstances of 66 kV class HTS large current cable were evaluated in order to study the Ic characteristics of the Clad-PLD coated conductor after the long-time durations. **Table 3** shows typical production conditions of the 66 kV class HTS large current cable.

Based on this study, fundamental criteria for evaluating the long term durations of superconducting characteristics of the Clad-PLD conductor are summarized as follows.

- 1) Superconducting characteristics (Tc, Jc, Ic, etc.) vs. humidity, temperature and vacuum
- 2) Heat cycle characteristics of Ic property between LN_2 temperature and 100 °C
- Mechanical properties (0.15% compression, 0.3% tensile, spiral characteristics)
- 4) Over current characteristics

Long term duration tests corresponding to the aforementioned four criteria were performed and main contributors affecting Ic characteristics were evaluated. Figure 9 and 10 show the dependence of humidity, temperature and vacuum circumstances on Ic characteristics. In Fig. 9, the Ic value showed no degradation under the three kinds of vacuum heat conditions, such as 100°C, 150°C and 100°C, with 30 mm diameter bending. In Fig. 10, the Ic value also showed no degradation at the 67 mbar H₂O hu-

Table 3.	Production	conditions of HTS	S large current cable
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Parameter		Conditions		
	Temperature	Room temperature		
	Humidity	40% ~ 100%		
Conductor	Duration time	1 year		
	Ic measurement	Heat cycle (room temp. ~ 77K)		
	Handle of conductor	Bending diameter: 100 mm		
	Temperature	-10°C to 50°C		
	Humidity	40% ~ 100%		
Production	Bending	45 mm ~ 50 mm in diameter		
of HTS	Bending	45 mm in diameter (1 kgf tension)		
cable	Corrugated vacuum stainless pipe	Vacuum, 100°C with 10 days (maximum)		
	Side pressure	15 kg/m (maximum)		
Installation	Humidity	Room temperature ~ 65K		
	Long term stress	0.3% tension (maximum)		
	Heat cycle	Room temperature ~ 77K		
Operation	Pressure	0.2 MPaG ~ 1 MPaG (77K)		
	Over current	31.5 kA at 2 sec		



Fig. 9. Time duration of Ic property under vacuum condition

midity heat conditions from room temperature to 80°C after 600 hours have passed. However, the Ic value decreased with increasing time and temperature when the test temperature was over 115°C. As the condition in which Ic degradation occurred is far from the real duration condition of the HTS cable, Ic degradation would not be occurred in the practical HTS cable productions⁽⁴⁾.



Fig. 10. Time duration of Ic property under humid conditions

Next, dependence of the conductor heat cycle on Ic characteristics was evaluated. Ic deviation was measured under many heat cycles between the room temperature and liquid N2 temperature, which simulated the practical HTS cable production conditions. Figure 11 shows the test results when 30 times heat cycles were adopted. The Ic value showed no significant degradation during the 30time heat cycle and showed no change in the Ic value with and without Cu stabilization. In the practical HTS cable system, the heat cycle between room temperature and liquid N2 temperature is corresponding to the heat increase in maintenance of the installed HTS cable system. In the actual operation of the HTS cable, the heat cycle for such maintenance work should be less than 30 times, and therefore fundamental performance of the Clad-PLD conductor for the duration of the heat cycle was confirmed.



Fig. 11. Dependence of heat cycle on Ic (room temperature to liquid N_2 temperature)

4-3 Mechanical properties

Several test methods were used to evaluate stress-strain effects on the Ic characteristics of the Clad-PLD conductor. First, loads of simple mechanical bending, tensile and spiral were adopted at the room temperature, and then the Ic value was measured at 77.3 K. In these tests, the stress was increased until Ic degradation occurred as shown in **Fig. 12 and 13**. In this study, we found that critical bending stress was 20 mm in diameter, and critical tensile stress was 300 MPa in tension. These values are much higher than those of the practical HTS cable production conditions. Therefore, it was demonstrated that the Clad-PLD conductor has enough margin.

For the spiral bending properties, minimum spiral pitch, when the Ic value began to degrade, was found to be 100 mm with a 16 mm diameter former for HTS large current cable design. As this parameters are lower than the critical value in the practical cable production, it was confirmed that the Ic property of the Clad-PLD conductor can be maintained for a long time.



Fig. 12. Bending stress effect on the Ic of Clad-PLD conductor



Fig. 13. Tensile stress effect on the Ic property of Clad-PLD conductor

4-4 Other properties

Over current characteristics of the Clad-PLD conductor was evaluated at the condition of 31.5 kA for 2 seconds. In this test, two kinds of conductors were used. One is with 10 micron Cu and the other is 20 micron Cu. In this conductor test, the current wave was calculated by analyzing the fault condition of HTS cable, and the degradation point of Ic property was evaluated by increasing the load peak alternating current. It was confirmed that the Ic value was not significantly changed during the tests repeated 30 times when the load current was less than the critical peak current (Ipeak), in which the Ic value begun to degrade. Other electro-magnetic characteristics, such as Jc vs. width of the conductors, were measured by using the knife-edge method and the low temperature hall-probe method. It was found from these evaluations that Ic distribution was influenced by the grain size of clad substrates, and the Ic value decreased around 150 ~ 200 micron area from the edge of the Clad-PLD conductor by a mechanical slitting method⁽⁵⁾⁻⁽⁸⁾.



Fig. 14. Evaluation of current distribution of Clad-PLD conductor by hall probe method



5. Conclusion

We have manufactured GdBCO coated conductors on low-magnetic clad-type textured metal substrates by using PLD for HTS power cables with large current and low AC loss. High Ic and homogeneous characteristics of GdBCO conductors are required for the fabrication of the 66 kV-5 kA class "3-in-One" HTS model cable system. For the HTS cable application, stable and high-throughput manufacturing process of the conductor was established. At the same time, several practical conductor technologies, such as narrow wire by mechanical slitting and electro-plating of Cu, were developed. The improvement of the stable manufacturing process for long length (100 ~ 200 m class) GdBCO conductors with high Ic property (over 400 A/cm) has been in progress based on the improvement of highlyoriented flatness technologies for the buffer layer and the precise composition control technique of the superconducting layer.

In the future, we are going to construct the stable manufacturing technologies of the Clad-PLD conductors with higher performance and long length at a lower cost. We also intend to supply the conductors to the HTS market, which is going to grow for the advancement of human life and prevention of global warming. We would like to open a new HTS market by applying the GdBCO coated conductors to various power applications and demonstration programs.

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