

# Ni Alloy Laminated High Strength Bi-2223 Wire

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Sumitomo Electric Industries, Ltd. has developed and commercialized a high-strength DI-BSCCO Type HT-NX wire. This wire is reinforced with Ni alloy tapes and undergoes residual axial compression after lamination. The wire has a critical tensile stress of 400 MPa at 77K. The new wire structure successfully reduced the splice resistance without sacrificing the mechanical properties. This wire is highly useful for nuclear magnetic resonance and other high field magnetic applications.

Keywords: Bismuth-based superconductor, mechanical strength, lamination reinforcement, splice, and superconducting magnet

## 1. Introduction

Since the discovery of bismuth-based superconducting wires, Sumitomo Electric Industries, Ltd. has promoted the development of the wires to increase the critical current density,<sup>\*1</sup> transmission distance, and durability. The Company has commercialized a Bi-2223 superconducting wire, Dynamically-Innovative BSCCO (DI-BSCCO),<sup>(1)</sup> and now has been making efforts in terms of cost reduction and quality improvement to make the wire a marketable and profitable product.

For superconducting wires, it is important that critical current  $I_c$  is high. In addition, such wires need to have high mechanical strength when used for super conductive application devices. So far, various development activities have been conducted to improve the mechanical properties of Bi-2223 wires. Figure 1 shows traverse cross-sectional images of a Bi-2223 wire. The Bi-2223 wire is composed of the Ag and Ag alloy matrix containing a large number of Bi-2223 thin wire filaments. The controlled over-pressure (CT-OP) sintering process<sup>(2)</sup> developed in 2004 can reduce porosity and cracks from the Bi-2223 filaments, producing high density in ceramics. As a result, the strength of the filaments was drastically improved. In addition, to improve the strength of the Ag sheath, Ag alloys were actively adopted, which improved the mechanical properties of the Bi-2223 wires. Furthermore, property improvement was conducted with the optimization of the silver ratio<sup>\*2</sup> and the number of filament cores. The mechanical strength of compound wires such as Bi-2223 is considered based on the rule of mixtures; therefore, the volume fraction of the wire components greatly influences the mechanical strength and electrical properties of Bi-2223 wire. Increasing the silver ratio reduces the  $I_c$  of the wire. However, as for the mechanical properties of the wire, reducing the ratio of fragile ceramics parts enhances the properties of the metal, improving the mechanical properties of the wire. In addition, using multi-filamentary structure thins down the Bi-2223 made of ceramics. This improves the flexibility and mechanical properties of the wire. As for the  $I_c$  of the wire, it is thought that supercurrent flows only through the interface between the filament and the silver. Increasing the number of filament cores increases the number of effective interfaces, benefitting  $I_c$  improvement. However, excessively increasing the number

of filament cores impairs their uniformity during wire drawing. This causes filaments to connect to each other, which leads to bridging and decreases the  $I_c$ .

As described above, in many cases mechanical properties improvement is incompatible with  $I_c$  properties improvement in terms of wire design. Among several methods investigated, strength of the Bi-2223 wires is improved by laminating wires with high-strength reinforcement materials such as stainless steel and copper alloy as reported later.

So far, various tests and projects related to Bi-2223 wires have actively been conducted and have produced good results.<sup>(3)-(5)</sup> These include cable demonstration tests in which Bi-2223 wires are used, and the development of motors for which coils are used. However, applications such as nuclear magnetic resonance (NMR) apparatus, fusion reactors, and accelerators require a magnet with a high magnetic field. In this case, however, a considerably strong tensile stress (hoop stress) is applied to the Bi-2223 wire because the Lorentz force is generated by the high magnetic field and operating current. If a Bi-2223 wire is used for a part such as a magnet in an internal layer of NMR, it is thought that the tensile strength of the wire must be 400 MPa. Thus, the task is to further improve the strength of the DI-BSCCO wire.

Against this background, Sumitomo Electric promoted the development of a wire with drastically improved strength. Finally, it achieved the goal: A critical tensile stress of 400 MPa at 77 K. As a result of this, in April 2015, the Company started selling the Type HT-NX, which is a DI-BSCCO wire that uses Ni alloy for reinforcement. Since then, projects which use Bi-2223 for applications such as magnets in high magnetic fields have gradually been reported.<sup>(6),(7)</sup> The presence of Bi-2223 wires is greatly increasing. On the other hand, there was a problem that although high strength was achieved, the high resistivity of Ni alloy increases splice resistance when a superconducting wire is spliced.

This paper introduces the development of the extra high strength Type HT-NX wire and methods for low-resistance connection between wires.

## 2. Improving the Mechanical Properties of Bi-2223 Wires

### 2-1 Using a lamination reinforcement for making high-strength Bi-2223 wires

The mechanical properties of Bi-2223 wires were improved by the development of high-strength technologies that are CT-OP sintering and alloyed Ag sheath. As a result of compatibility with the design of  $I_c$ , the critical tensile stress could be increased to 130 MPa in liquid nitrogen boiling temperature (77.3 K).

However, since the mechanical strength of silver is limited, lamination reinforcement technology was developed. Lamination reinforcement is a wire reinforcing and processing technology in which three sheets, a Bi-2223 wire, and two reinforcing materials, are sandwiched together, integrated, and produced as one product in a molten solder bath (Fig. 1). Stainless steel (SUS: SS) and bronze-based copper compound metal (Cu-alloy: CA) are adopted as strengthening materials. When the two strengthening materials, SS and CA, are compared with each other, SS is superior in strength. However, the resistivity of CA is smaller than that of SS. Therefore, when wires are spliced for use, CA has the merit of reducing the splice resistance. Accordingly, SS or CA is selected depending on the application of the wire.

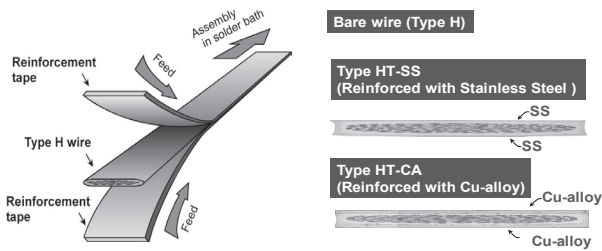


Fig. 1. Image of a lamination reinforcement and traverse cross-sectional images of wires

Table 1 shows the types of strengthening wires used for the commercialized DI-BSCCO wires. The wire made with the CT-OP sintering method is Type H (bare wire). The lamination reinforcement comprised of Type H and the SS reinforcing materials whose thickness is 20  $\mu\text{m}$  is called

Table 1. Specifications of the DI-BSCCO Type HT wires

Type	Ag sheath Bi-2223 DI-BSCCO			
	H	HT-SS	HT-CA	HT-NX
Lamination				
Material	–	Stainless steel	Cu alloy	Ni alloy
Thickness ( $\mu\text{m}$ )	–	20	50	30
Critical Current				
$I_c$ @sf (A)	180-200	180-200	180-200	180-200
Size				
Width (mm)	$4.3 \pm 0.2$	$4.5 \pm 0.1$	$4.5 \pm 0.1$	$4.5 \pm 0.2$
Thickness (mm)	$0.23 \pm 0.01$	$0.29 \pm 0.02$	$0.34 \pm 0.02$	$0.31 \pm 0.03$
Mechanical Properties				
Critical Wire Tension@RT (N) *	80	230	280	410
Critical Tensile Strength@77K (MPa) *	130	270	250	400
Critical Tensile Strain@77K (%) *	0.2	0.4	0.3	0.5
Critical Double Bending Diameter@RT (mm) *	80	60	60	40

\* 95%  $I_c$  retention, typical value

Type HT-SS. The lamination reinforcement comprised of Type H and the CA reinforcing materials whose thickness is 50  $\mu\text{m}$  is called Type HT-CA. At 77 K, the critical tensile stress of Type HT-SS wires is 270 MPa. On the other hand, Type HT-CA is designed so that its critical tensile stress is 250 MPa at 77 K. These indicate that the critical tensile stress of Type HT-SS and Type HT-CA is nearly twice as high as that of Type H.

### 2-2 Lamination reinforcement technology

For further mechanical properties improvement of Type HT wires, the important factors are to apply high residual compressive stress to the Type H wires during the production of lamination reinforcement and to select the type of reinforcing materials to be used.<sup>(8)</sup> The processes for applying residual compressive stress to the Type H wires are as follows: The reinforcing materials are distorted (pre-tension) more than the superconducting wire, lamination reinforcement is conducted, and then, when residual stress is redistributed to each element by relaxing to equilibrium after removing pre-tension, the residual compressive stress is applied as compressive stress (left of Fig. 2). In addition, the residual compressive stress is also applied by the difference in the coefficient of thermal expansion (CTE) between the Type H wire and the reinforcing materials (right of Fig. 2). When the CTE of the reinforcing materials is higher than that of the Type H wire, compressive stress is applied to the Type H wire by the temperature change from the temperature at which the lamination reinforcement is produced to the temperature at which it is cooled. Therefore, the selection of the reinforcing material is particularly important. Since the important factor is how the residual compressive stress is applied to the Type H wire, the reinforcing material is required to have the following properties: high yield strength, high Young's modulus, and high CTE. Furthermore, for applied devices, the reinforcing material must be non-magnetic and have low resistivity. In addition, when considered for industrial products, the reinforcing materials must be low cost and commercially viable.

Considering the above factors, Sumitomo Electric has selected Ni alloy, whose yield strength (1,800 MPa) and Young's modulus (200 GPa) are higher than those of stainless steel tape and whose CTE is higher than that of Type H, for the reinforcing materials. Incidentally, a recent study showed that there is a limit for the compressive stress that can be applied to Type H wires. Studies evaluating the properties of the compressive side are still in progress.

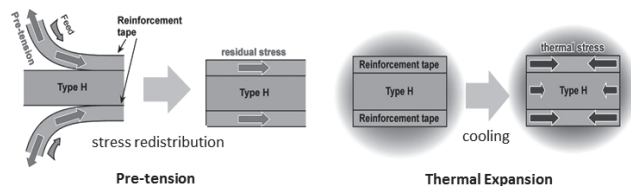


Fig.2. Residual compressive stress applied to the Type H wire

### 3. Mechanical Properties of Type HT-NX Wires

As the reinforcement tapes get thicker, the strength of the Type HT wire is also improved. However, the thickened wire increases the coil diameter when the wire is wound into a coil. Therefore, it is important that the wire is as thin as possible, and that the value of the supercurrent flowing per unit area in section is larger. Accordingly, the Company adopted a Ni alloy whose thickness was 30  $\mu\text{m}$  and made a prototype of a Type H wire whose thickness was designed to be 0.20 mm. Figure 3 shows the stress-strain curves, which were recorded at 77 K, of the prototype of the Type HT-NX wire and of other types of HT wires. For the tensile strain dependency of the critical current, two indexes that show the start of the macroscopic yielding due to the fracture of B1-2223 filaments are defined: Critical tensile stress that is the stress with which the critical current value after a tensile test retains at 95% of the critical current value before the test, and critical tensile strain that is the strain with which the above condition is achieved. Generally, these values are thought to correspond to reversible stress limit  $R_y$  and reversible strain limit  $A_y$  in the stress-strain curve. Figure 3 shows that the reversible stress limit  $R_y$  and reversible strain limit  $A_y$  of the wire produced by reinforcing Ni alloy tape (NX) reach 460 MPa and 0.55%, respectively. The characteristics of the reinforced NX wire are by far better than those of wire, which is made of reinforced SUS tape and the thickness of which is 20  $\mu\text{m}$ , and those of the wire, which is made of reinforced copper alloy tape and the thickness of which is 50  $\mu\text{m}$ . In addition, it is characteristic that at 77 K, the breaking stress and breaking strain of the NX wire reach around 700 MPa and 1.6%, respectively.

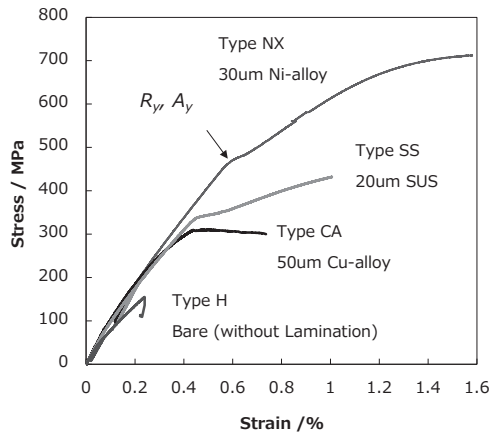


Fig. 3. Stress-strain curve of the DI-BSCCO wire

Figure 4 shows the stress dependence of normalized critical current for each type of the DI-BSCCO wires at 77 K. The critical tensile stress of the wire (Type HT-NX) reinforced with Ni alloy tape reached 443 MPa, and the critical tensile strain of the wire reached 0.53%. Thus, the properties of the reinforced wire were drastically improved. As the stress-strain curves show, the values of the revers-

ible stress limit and reversible strain limit of the reinforced wire were close to the results of the tensile test. The critical current decreased gradually in the reversible region and abruptly decreased beyond critical stress due to the macroscopic fracture of the filaments.

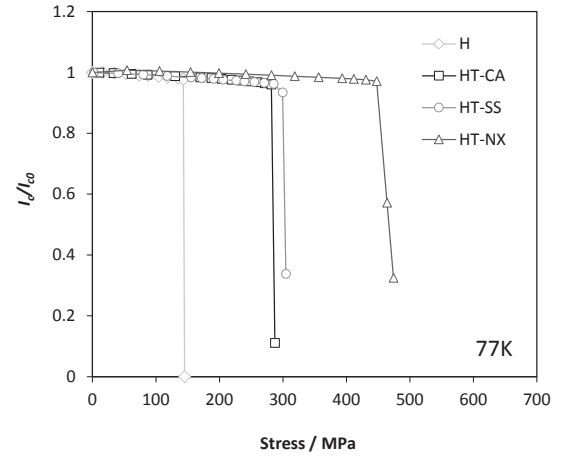


Fig. 4. Applied stress dependence of the normalized critical currents for Bi-2223 wires laminated with and without reinforcing tapes

Figure 5 shows the results of a double bending test at room temperature. When the wire applied to a bending jig is bent at a predetermined bending diameter, tensile strain and compressive strain are respectively applied to the outside and inside of the neutral surface of the wire. The double bending test is an evaluation method in which the wire, which was bent once, is reversed and bent at a predetermined bending diameter to apply compressive strain to the side to which tensile strain was applied. This is a tough test for wires. The minimum critical double bending diameter is defined as the diameter which maintains 95% of the initial critical current value. The critical double bending diameter of the Type HT-NX wire is 35 mm, which demonstrates that the double bending properties are improved.

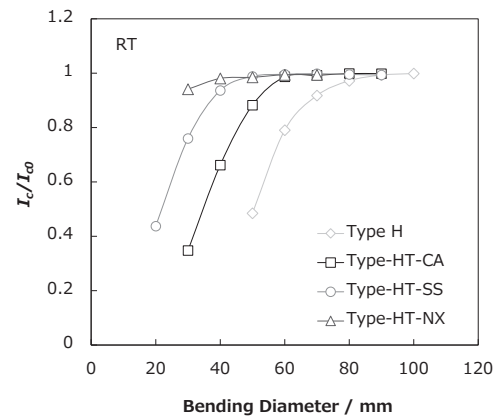


Fig. 5. Double bending diameters dependence of the normalized critical currents at room temperature for Bi-2223 wires laminated with and without reinforcing tapes

Due to the mass-production technology, Sumitomo Electric is commercializing the Type HT-NX wire that uses Type H with a thickness of 0.23 mm. The critical tensile stress at 77 K is designed to be 400 MPa.

Figure 6 shows the results of a fatigue test of the Type HT-NX wire, whose thickness is designed to be 0.23 mm, at 77 K. In the test, stress loads were repeatedly applied to the wire. While a load was applied to the wire,  $I_c$  was measured, and the measured  $I_c$  was compared with the  $I_c$  value before the test to measure the retention of the critical current value. In comparison with the specification value of the Type HT-NX, 400 MPa, at least 95% of the  $I_c$  retention was kept in  $10^5$  cyclic load tests (100,000 times) in which loads of up to 370 MPa (93% of the specified load) were applied.

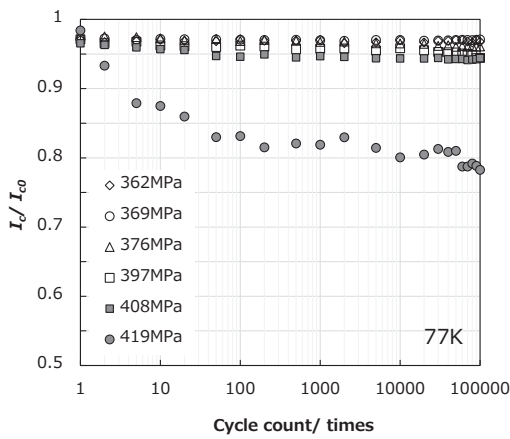


Fig. 6. Results of a fatigue test of the Type HT-NX wire at 77 K

#### 4. Splice of Bi-2223 Wires

For superconductor application, the splice of wires may be required. Generally, for such splice, two superconducting wires are overlapped with one another, and the overlapping part is connected with solder. In the splicing part, since current flows through two layers of reinforcing materials and through the normal conductor part of the solder, Joule heat is generated due to resistance. In applications for superconducting cables, the Type HT-CA wires, which use copper alloy as reinforcing materials, are used. Since the resistivity of the copper alloy is small, the splice resistance is not a problem. On the other hand, as for the Type HT-NX wire, which was developed to be used for magnets in high magnetic fields, the resistivity of the Ni alloy is high, resulting in large resistance in the splicing part. In proportion to the large resistance, the Joule heat generated in the splicing part increases. Therefore, reducing the amount of heat generated is a problem.

Figure 7 shows the correlation between the splice resistance of each spliced wire and its overlapping length. The splice resistance is influenced by the resistivity and thickness of each component. The splice resistance is lowest when Type H is spliced to Type H. The splice resistance increases in the order of Type HT-CA, HT-SS, and

HT-NX. In addition, the splice resistance is inversely proportional to the overlapping length. If the overlapping length of Type HT-NX wires gets longer, the problem of high splice resistance seems to be settled. However, in reality, as in the case shown in Fig. 8, if an overlapping length is increased, a difference in the rigidity of the splicing part decreases the curvature at the edge of the splicing part. This is thought to be the cause of the degradation of the double bending properties of the wire. Therefore, what was required was the development of a splice method that maintains the mechanical properties of spliced wires while reducing connection splice resistance.

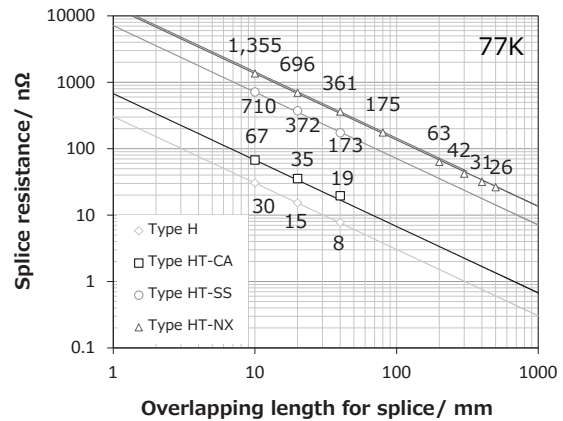


Fig. 7. Dependence of the splice resistance of various wires on overlapping lengths

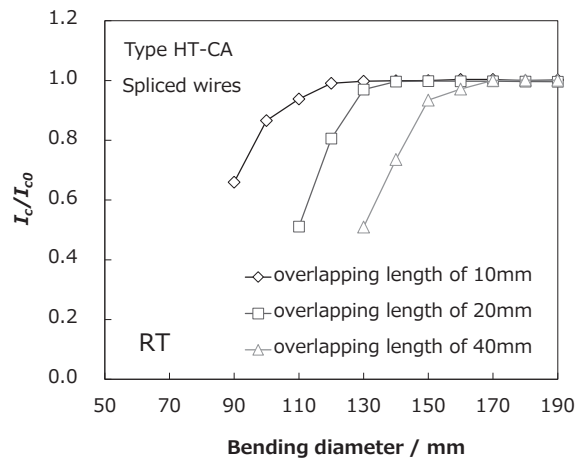


Fig. 8. Double bending properties (RT) of spliced wires with different overlapping lengths

#### 4-1 Development of a low-resistance splice method

Figure 9A shows the longitudinal cross-sectional images of the spliced wires produced by normal overlapping superconducting wires. Since current must pass through the two Ni alloy wires and solder, the splice resistance increases. Therefore, as Fig. 9B shows, if reinforcing materials, which are part of the lamination reinforcement, are removed and the two wires are spliced, the splice resis-



tance is expected to be reduced. However, this structure greatly deteriorates the mechanical properties of the splicing part. Therefore, as Fig. 9C shows, the naked edge of one core wire is placed on one reinforcing material of the other wire, and the copper tape that is nearly as thick as the reinforcing material is placed in the created gap. In this structure, the Ni alloy is removed from the current-carrying part, which is expected to provide low splice resistance. Since the upper and lower reinforcing materials to which pre-tension is applied remain in the longitudinal direction, the mechanical strength of the splicing part is maintained. We tried to produce a spliced wire (low-resistance spliced wire) whose structure is as shown in Fig. 9C.

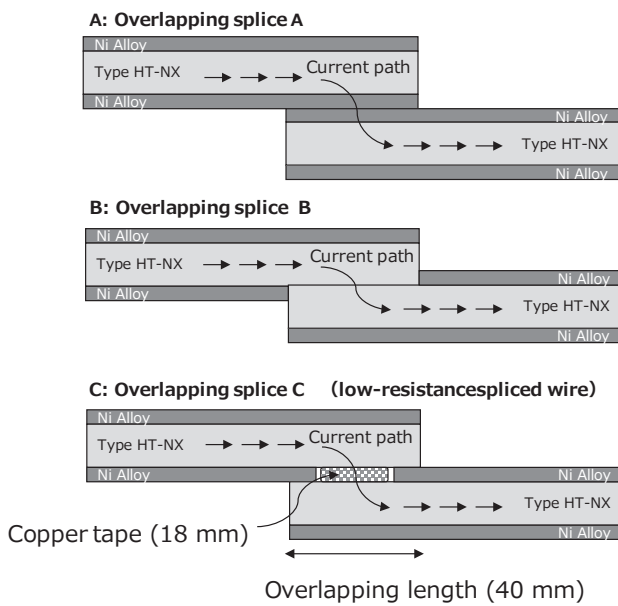


Fig. 9. Pattern diagrams of the longitudinal cross-sectional images of the spliced parts (overlap method)

#### 4-2 Peeling one reinforcing material

To splice two wires to achieve the structure shown in Fig. 9C while maintaining the mechanical strength of the splicing part, only one reinforcing material of two Type HT-NX wires needs to be peeled off (peeling). In addition, the pre-tension of the reinforcing material that is opposite to the reinforcing material that is peeled off must remain. To neatly peel the reinforcing material, the solder needs to be melted. If the solder on both sides completely melts, the pre-tension is released, weakening the mechanical strength of the splicing part. Therefore, it is necessary to skillfully melt only the solder on one side and peel only the reinforcing material from the wire. In addition, even if a part of the reinforcing material is skillfully peeled off, strong pre-tension is applied to the other reinforcing material. Because of this, if a large area of one reinforcing material is peeled off from the Type HT-NX wire, the wire flips over. Accordingly, only a certain length can be peeled from the reinforcing material.

To skillfully perform the peeling, (1) place the wire on

a hot plate, (2) warm the wire to a temperature that is slightly lower than the decomposition temperature of the solder used for the lamination reinforcement, and then (3) pull up the edge of the reinforcing material with cutting pliers while applying heat to the reinforcing material with a soldering iron (see the left photo of Photos 1). The right photo of Photos 1 shows the wire from which a part of one reinforcing material is peeled off. Since the reinforcing material was peeled while the pre-tension remained on the other side of the reinforcing material, the wire is flipping over. However, when up to 30 mm of the reinforcing material was peeled, the properties of the wire were not greatly affected after spliced. Considering the results of trial production, we adopted a design in which the overlapping length is 40 mm, the length of the peeled section is 30 mm, and the length of the gap (in which 18-mm copper tape is installed) between the two wires is 20 mm (Fig. 9C).



Photos 1. Peeling of the reinforcing material and the wire from which one reinforcing material is peeled off

The prototype of the low-resistance spliced wire is made of the Type HT-NX wire comprised of Ni alloy whose thickness is 25  $\mu\text{m}$  and wire whose width is 4.0 mm and whose thickness is 0.24 mm. The prototype underwent various tests. Figure 10 shows the current/voltage characteristics of the spliced wire made up of the peeled Type HT-NX wires that were spliced with the structure shown in Fig. 9C and of the spliced wire made up of the wires that were spliced with the structure (overlapping length of 40 mm) shown in Fig. 9A. The test temperature was 77 K. The

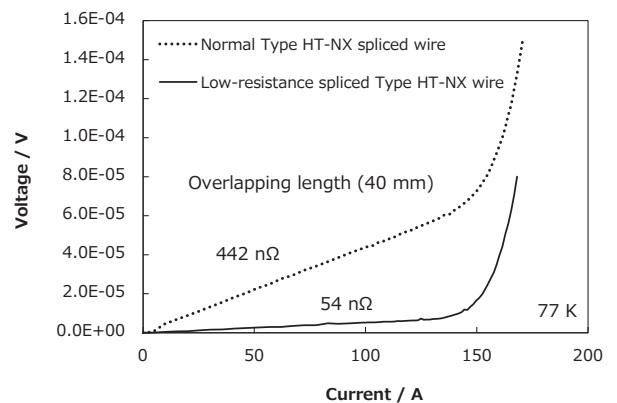


Fig. 10. Splice resistance of the low-resistance spliced Type HT-NX wire

splice resistance values were calculated by the slopes on the graphic chart. When the splice was made with the low-resistance splice method (Fig. 9C), the splice resistance was 54 nΩ. This value is 88% lower than 442 nΩ, which was the splice resistance of the wire spliced with the conventional splice method (Fig. 9A).

Figure 11 shows the results of the tensile test conducted at a temperature of 77 K. The critical tensile stress of the low-resistance spliced wire was 416 MPa, which is close to 423 MPa, the tensile stress of the Type HT-NX wire. This means that the tensile stress properties of the former wire are nearly equal to those of the latter wire. Figure 12 shows the results of a bending test. The critical double bending diameter of the Type HT-NX was 30 mm, but that of the low-resistance spliced wire was 70 mm since the thickness of the splicing part is about twice that of one wire. In Fig. 8, with an overlapping length of 40 mm, the smallest double bending properties of the Type HT-CA spliced wire were 160 mm. Compared with the double bending properties of the existing spliced wire, those of the low-resistance spliced wire are greatly improved.

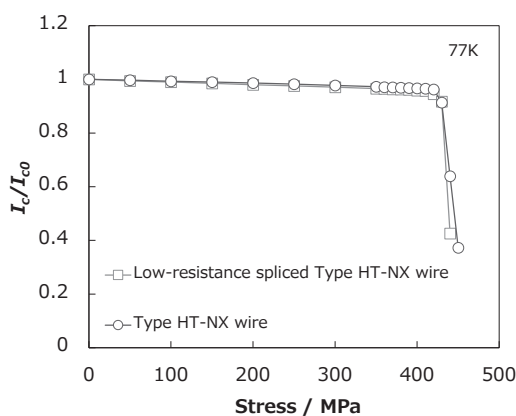


Fig. 11. Tensile properties of the low-resistance spliced Type HT-NX wire

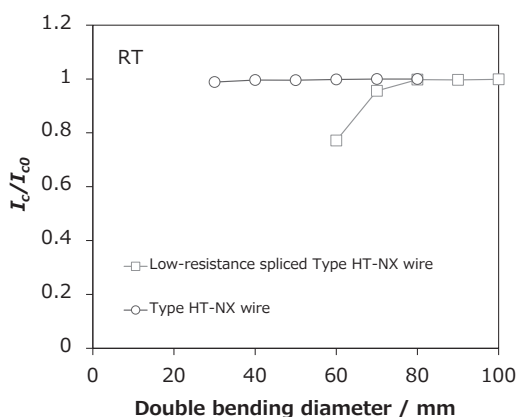


Fig. 12. Double bending properties of the low-resistance spliced Type HT-NX wire

## 5. Conclusion

Sumitomo Electric developed the extra high strength Type HT-NX wire, which achieves a critical tensile strength of 400 MPa at 77 K. Thanks to the new technique—peeling of reinforcing materials—and the new splicing structure, the splice resistance that had been a challenge to the splice of wires was successfully reduced by 88% without any reduction in the mechanical strength of the wires.

The above method has gradually been adopted for wires for the development of high magnetic field NMR. In the future, the Type HT-NX wire is expected to be used for high field magnet applications.

• DI-BSCCO and CT-OP are trademarks or registered trademarks of Sumitomo Electric Industries, Ltd..

### Technical Terms

- \*1 Critical current density: Maximum current density, with which current can flow, while maintaining a superconducting state. Generally, the current value at which a voltage of 1 μV/cm is generated is defined as critical current  $I_c$ . Critical current density is the value that is obtained by dividing  $I_c$  by the total area of the filament.
- \*2 Silver ratio: In the cross section of a wire, the silver ratio is defined by dividing the silver area by the total area of the Bi-2223 filament.

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