Development of New Types of DI-BSCCO Wire

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Performances of Bi2223 high-temperature superconducting wires developed by Sumitomo Electric have been dramatically innovated since the introduction of the CT-OP (controlled over-pressure) sintering process in 2004. The critical current (Ic) of a short-length Bi2223 tape with a cross section of 1 mm^2 has reached 218 A. This Ic value is sufficient for use in various equipment that use superconductivity technologies such as high-field magnets, motors and cables. In commercial long tape with kilo-meter over length, the highest end-to-end Ic has exceeded 180A. These wires are named "DI-BSCCO" (dramatically innovative BSCCO) wires and are now manufactured commercially. The standard bare tape with high Ic is named Type H. Sumitomo Electric also produces the Type S that is lower in price and suitable for use in equipment for low current operation. Sumitomo Electric has also developed new types of DI-BSCCO wire, Type HT and Type ST. Each of Type HT and Type ST has a stainless steel tape or a brass tape soldered to it in order to provide strength, and its critical tensile stress and critical bending diameter have been improved by 80% and 30% at room temperature, respectively, from its predecessor type, while its Je is the same as that of Type H. Another indispensable characteristic that cannot be ignored when using superconductors in the alternating current (AC) application is lower AC loss. Sumitomo Electric has commercialized Type AC that has twisted filaments of an optimized size. As a solution to this, Sumitomo Electric is working to introduce a matrix that has much higher resistance and more optimized filament twist pitch.

1. Introduction

Since its discovery in 1986, many companies and laboratories have made efforts to commercialize Cu-oxide superconductors. This was because many Cu-oxide superconductors had higher critical temperatures than the liquid nitrogen boiling temperature (77.3 K). Therefore, the cost for cooling Cu-oxide superconducting systems is much lower than that for the systems using metallic superconductors such as NbTi. As a result of the introduction of the CT-OP (Controlled Over Pressure) sintering furnace in 2004, Sumitomo Electric succeeded in improving various characteristics such as critical current (I_c) and mechanical properties of Bi2223 wire. By optimizing all manufacturing conditions including powder preparation, deformation and sintering processes, this new Bi2223 wire has attained I_c = 218 A, which is the world record[1]. Sumitomo Electric has also established the technique for manufacturing the long-length and homogeneous-performance wire of up to 2 km each. This remarkably innovated Bi2223 wire is marketed under the brand name DI-BSCCO.

However, the specifications for all kinds of superconducting applications cannot be satisfied by high critical current only. In satisfying other types of specifications, higher mechanical strength and lower AC loss are also important properties for superconducting wires. For this reason, Sumitomo Electric is manufacturing DI-BSCCO with various features , Type H (High critical current), Type S (Slim), Type HT (High critical current and Tough), Type ST (Slim and Tough) and Type AC (AC use). Type H has the same structure as the conventional high I_c wire with a cross-sectional area of around 1 mm^2, but features dramatically higher I_c. Type S is manufactured at half the raw material cost because its cross-sectional area is a half that of Type H. Type HT and Type ST are the high strength wires made by reinforcing Type H and Type S with metallic tapes such as stainless tapes. They have the same I_c values as Type H and Type S and show remarkably high mechanical strengths. Type AC has the lowest AC loss among all types of DI-BSCCO and is the most suitable for an AC use. The feature of each type of DI-BSCCO is summarized in **Table 1**.

Table 1. Various features of different types of DI-BSCCO

Type of DI-BSCCO	I_c	Permissible tensile stress	Permissible bending diameter	AC loss	Price
Type H	◎	○	△	△	○
Type S	○	△	○	○	◎
Type HT	◎	◎	◎	△	○
Type ST	○	◎	◎	○	◎
Type AC	△	△	○	◎	○

2. Manufacturing process of DI-BSCCO wire

Figure 1 shows the manufacturing process of DI-BSCCO wires. Silver tubes containing precursor powder are drawn, assembled together, and then inserted into another silver-alloy tube. This is deformed into a tape after the drawing and rolling steps, and then repeatedly sintered and rolled. Because manufacturing conditions at each step can be easily controlled, this process is suitable for producing wires that are long and homogeneous in performance. Sumitomo Electric introduced the CT-OP sintering process at the second sintering step in order to accurately control the temperature and oxygen partial pressure while applying a gas pressure up to 30 MPa to the tape. As a result, various characteristics were dramatically improved as was mentioned previously. Because of its structure, the Bi2223 material is suitable for the powder-in-tube (PIT) method. A unit cell of Bi2223 has a lamination structure that contains a superconducting Cu-O layer and two insulating layers above and below the Cu-O layer. Moreover, Bi2223 easily cleaves because of the relatively small bonding force between the double Bi-O layers within each insulating layer. That is, in spite of their poor ductility, the filaments including Bi-based superconductors can be drawn along with silver or silver alloy during the drawing step, and orient in the *c*-axis direction during the rolling step. Therefore, the PIT method could be used in manufacturing Bi2223 wires.

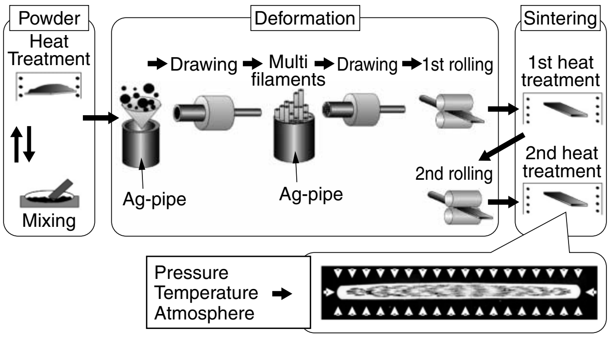

Fig. 1. Manufacturing process of DI-BSCCO (PIT method)

3. The characteristics of each DI-BSCCO

3-1 Type H (High I_c with cross-sectional area around 1 mm^2)

Type H has a feature of high critical current. **Figure 2** shows the I_c distribution in the longitudinal direction of a standard Type H. I_c was measured for every 4 m section from end to end by using the four probe method. A homogeneous high critical current was obtained from end to end as a result of the Bi2223 grain connectivity improved by the CT-OP process and the wholly optimized manufacturing conditions [1].

3-2 Type S (Small cross-sectional area)

Type S has a very small cross-sectional area, which is a half that of Type H. Because Type S is produced using the same process as that of producing Type H, Type S and Type H has the same over-all engineering critical current density (J_e) and the same architecture except for the size. This means that I_c of Type S is about a half that of Type H. The most important feature of Type S is that its price per unit length is considerably low. This is because the amount of raw materials needed for manufacturing Type S is a half that needed for Type H. Moreover, because of its thinner thickness, Type S also has a feature of bending with a very small diameter. Putting all features together, what it comes down to is that Type S, which is a compact superconducting wire, is suitable for the low operating current applications. The I_c distribution of a standard Type S is shown in **Fig. 2** along with that of Type H. It is observed that the average I_c of 90 A is obtained homogeneously from end to end over 560 m.

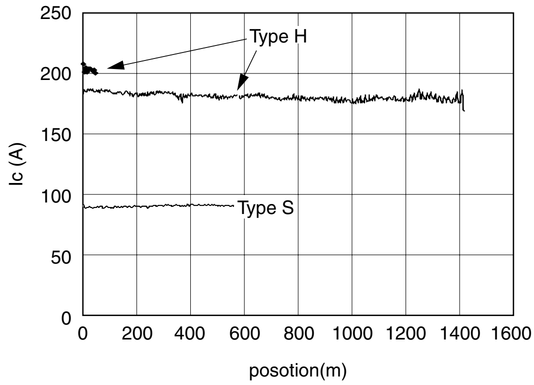

Fig. 2. I_c distributions of two Type H wires and one Type S wire (high I_c from end to end)

3-3 Type HT, Type ST (Type H and Type S reinforced with metallic tapes)

Type HT and Type ST are respectively Type H and Type S reinforced by metallic tapes. A superconducting tape and metallic tapes are put gathered in a solder solution container and then integrated on a die. The metallic tapes can be changed in accordance with various requirements, such as joint resistance, minimum permissible bend diameter and maximum permissible tensile stress. Both Bi2223 wire and two metallic tapes are soldered in a vessel. **Photo 1** shows a transverse cross-sectional image of Type HT with 20-μm-thick stainless tapes.

A standard Bi2223 superconducting wire has several dozen superconducting filaments covered by silver or silver alloy. In other words, it is a composite material

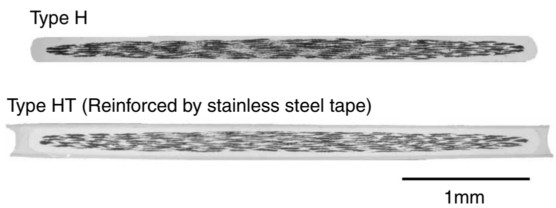

Photo 1. Cross-sectional image of Type HT (Type H with two stainless tapes soldered to it)

that consists of a ductile metal and non-ductile ceramic. So when an excess tensile or bending load is applied to a Bi2223 tape, the filaments where superconducting current passes are broken. When an external force exceeding a certain level is applied, grain connectivity weakens and critical current is decreased. Such stress is applied to the tape while producing a multi-strand conductor or feeding electricity to a superconducting coil, as well as while going through a normal manufacturing line. The case where electricity is fed to a superconducting coil at a low temperature in a high magnetic field is given as an example. The DI-BSCCO wire is expected to be used in high magnetic field applications such as nuclear magnetic resonance (NMR) equipment because DI-BSCCO exhibits excellent critical current properties in magnetic fields higher than 10 T [(2)]. But in this case, a considerable hoop stress is applied to the Bi2223 wire because the Lorentz force is generated by high magnetic field and operating current. When such a stress is added to a superconducting tape wound around the coil, I_c needs to be kept at its initial value.

A mechanical test on a superconducting wire is usually executed through the following method. The method of tensile stress tolerance test at room temperature is given as an example. After a certain load is applied to a sample, the critical current of the unloaded sample is measured in liquid nitrogen. Then a little higher load is applied to the same specimen at room temperature. During the course of this cycle, the deterioration of I_c occurs after a certain amount of load is applied. This phenomenon is caused by the fracture of filaments as mentioned above. The maximum tensile stress is defined as that when I_c comes to 95% of its initial value.

At the initial stage of the development of Bi2223 wires, the maximum permissible tensile stress in liquid nitrogen was less than 100 MPa because pure silver was used as the material for outer sheath. By modifying the sheath material from pure silver to silver alloy and improving the Young's modulus of Bi2223 filaments by densifying the filaments using the CT-OP sintering process, the maximum permissible tensile stress could be increased to more than 150 MPa [(3)]. Furthermore, Sumitomo Electric has developed Type HT and Type ST having the dramatically improved mechanical properties, and has commercialized these wires. The relationship between I_c and tensile stress of each type of the DI-BSCCO wires at room temperature is shown in **Fig. 3**. The I_c values of the two Type HT wires, each reinforced with two 20-µm-thick stainless steel tapes and two 50-µm-thick stainless steel tapes, proved that no degradations occurred after the wires were respectively loaded with tensile stresses about 300 MPa and 400 MPa. Therefore it has been proven that the maximum permissible tensile stress of Type HT is increased to twice that of Type H owing to the reinforcement by stainless steel tapes. The maximum permissible tensile stress in liquid nitrogen is also improved as shown in **Fig. 4**. The company other than Sumitomo Electric who supplies Bi2223 wires is American Superconductor Corporation (AMSC). The maximum permissible tensile stress of Type H made by

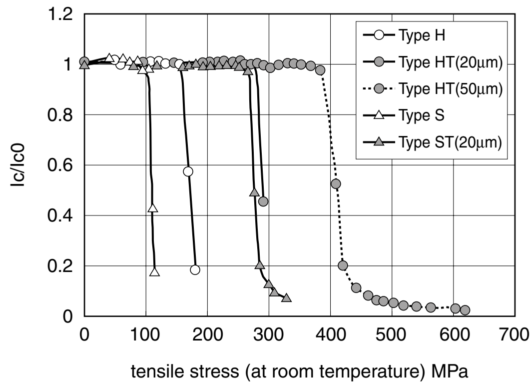

Fig. 3. Tensile stress dependence of normalized I_c at room temperature

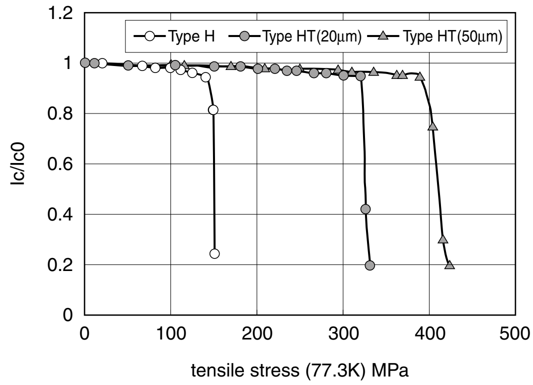

Fig. 4. Tensile stress dependence of normalized I_c at 77.3 K.

Sumitomo Electric is superior to that of HTS High Strength Plus made by AMSC, whose structure is almost the same as Type H but has a maximum permissible tensile stress of 200 MPa at room temperature (this value is found in the AMSC catalog [(4)]). AMSC also produces YBCO thin film using a textured Ni substrate produced by the rolling-assisted biaxially textured substrates (RABiTS) method. The maximum permissible tensile stress of Type HT is also superior to that of Type H, the catalog value at room temperature is 250 MPa [(5)]. This means that Type HT shows reliable tensile stress properties.

When a tape is bent, tensile strain and compressive strain are respectively applied to the outside and inside of the neutral surface. Hence, I_c decreases as bending diameter becomes smaller, because higher strains cause fracture of the filament. However, for use in compact superconducting equipment, critical current is required not to degrade during bending at small diameter. Type HT and Type ST developed by Sumitomo Electric are dramatically improved in terms of not only maximum permissible tensile stress but also minimum permissible bending diameter. **Figure 5** shows the bending diameter dependence of I_c in each type of DI-BSCCO. It is revealed that the minimum permissible bending diameter of Type HT, produced by soldering two pieces of stainless tapes each 20 µm in thickness to Type H, is improved to 30 mm, which is about a half that of Type H, which is 58 mm. It was also proven that Type HT is extremely flexible, as the minimum permissible bending diameter of Type HT bent in only one direction is 29 mm, which is almost the same as that when bent in both directions. The same tendency is seen in the cases of Type ST and Type S, whose minimum permissible bending diameters are 25 mm and 38 mm, respectively. Accordingly, Type HT and Type ST are thought to be sufficiently applicable for solenoid coils and extremely compact race track coils.

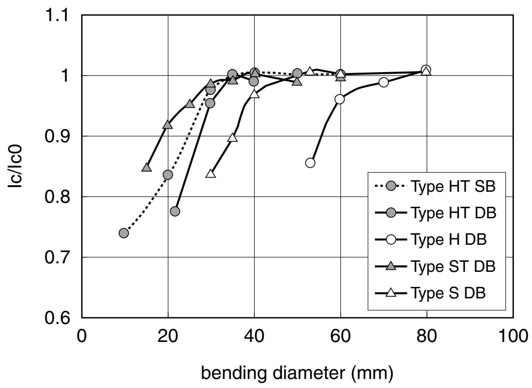

Fig. 5. Bending diameter dependence of normalized I_c

3-4 Type AC (Low AC loss)

Although superconductor is free from energy dissipation under a direct current, a magnetic hysteresis loss occurs in a superconductor carrying an alternative current, which is called AC loss. For reducing AC loss, it is effective to make hysteresis loop smaller by subdividing superconducting filaments. A practical superconducting wire is formed as a multi-filamentary wire that consists of fine superconducting filaments embedded in a metal matrix. As was mentioned previously, silver-sheathed Bi2223 wire employed a multi-filament structure for the purpose of enhancing flexibility, and the same structure can be used for AC applications. But in an AC use, only subdividing the superconducting filaments is not enough. An induced current called the coupling current flows between the outer filaments through the matrix. When the coupling current is not attenuated immediately, the hysteresis loss should increase even though the superconducting filaments are subdivided, because several filaments come to electrically link together and become equivalent to one thick bulk of filaments. Therefore, the coupling time constant must be smaller. Also, a Joule loss generated in a matrix by coupling current, called the coupling loss, must also decrease. At certain frequencies, the coupling loss may be so large that it becomes problematic. One of the methods for reducing these losses is to twist the filaments. This is because it is well known that a coupling loss is proportional to the square of the twisting pitch. Theoretically, a coupling loss must decrease to one fourth when the twisting pitch is shortened by a half [6].

Sumitomo Electric has succeeded in subdividing the filaments and shortening the twisting pitch by optimizing the whole manufacturing conditions, especially the deforming conditions. There had been various problems such as the snapping of wires and fracturing of filaments due to work-hardening, but Sumitomo Electric has applied the above mentioned optimization approaches to successfully prepare the low AC loss type slim wire with a twisting pitch of 3 mm. In the evaluation of AC losses, the AC loss per unit length normalized by I_c is ordinarily used so that the evaluation can be done equally on various samples with different I_c. The critical current density (J_c) differs for each sample if all the samples have the same silver ratio. When J_c becomes higher, it will be relatively hard to pass the corresponding coupling current through the metal, because a higher resistance is produced and the coupling loss is decreased. This is the reason why the samples with different I_c have different AC losses although they have the same construction.

The normalized magnetization loss of the developed slim wire with a 3 mm twist pitch measured while applying an alternating magnetic field having an amplitude of 0.2 T at a frequency of 50 Hz perpendicular to the tape surface was decreased to 11.9 W/kA/m, which is less than a half that of Type H. Moreover, the normalized magnetization loss measured while applying an alternating magnetic field having an amplitude of 0.07 T at a frequency of 50 Hz parallel to the tape surface was decreased to 0.12 W/kA/m, which is less than a third that of Type H. **Figures 6** and **7** show the frequency dependence of the normalized magnetization loss in a 0.07 T parallel magnetic field and a 0.1 T vertical magnetic field, respectively. Although it is likely that shortening the twisting pitch is profoundly effective in reducing the magnetization loss in the vertical magnetic fields, the amounts of loss reduction of Type AC and Type H are smaller at higher frequencies than at lower frequencies. It is appropriate to understand that shortening the twisting pitch is effective in reducing the magnetization loss only at lower frequencies and that the loss reductions at higher frequencies are mainly due to the fact that the wire slimmed to half the width of Type H. Therefore, it is necessary to take a measure for maintaining coupling between filaments even at higher frequencies. However, because AC motors are commonly used at relatively low frequencies of about 20 Hz, the development of this wire is an excellent result for application to superconducting AC motors. **Table 2** shows the AC loss of DI-BSCCO at the frequencies at which cables and motors operate. The development of Type ACT, a high-strength version of Type AC reinforced with steel tapes or other reinforcements, is underway to bring out a new low AC loss wire that is high in strength and easy to use. The mechanical properties have been dynamically improved as mentioned earlier, so Type ACT is expected to offer a great advantage when applied to compact superconducting systems.

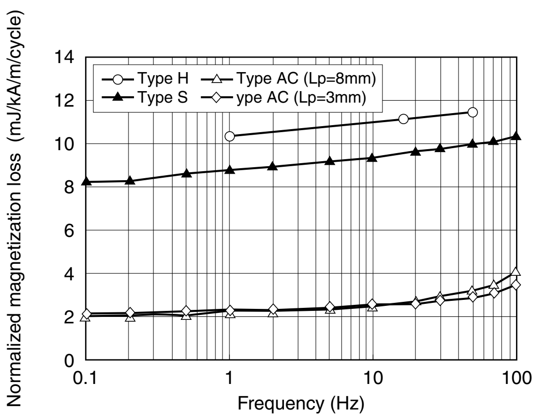

Fig. 6. Normalized AC magnetization losses in parallel AC magnetic fields

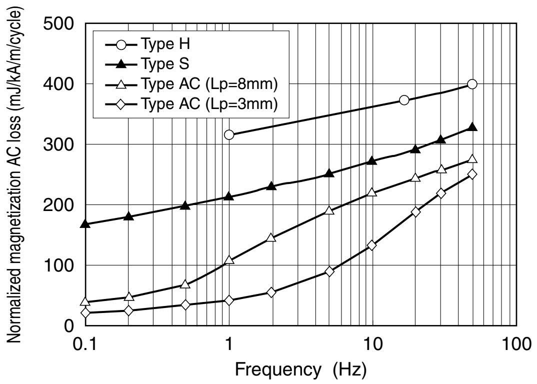

Fig. 7. Normalized AC magnetization losses in parallel AC magnetic fields

Table 2. Normalized AC losses of Type AC and Type H.

	Width	Thickness	L_p	I_c	AC loss[W/kA/m]	
	[mm]	[mm]	[mm]	[A]	B⊥ @0.2T, 50Hz, 77K	B// @0.07T, 50Hz, 77K
Type AC	2.0	0.17	3	32	21	0.16
	2.4	0.18	8	53	17	0.17
Type H	4.0	0.23	–	180	20	0.57

4. DI-BSCCO Type HT application example (Hoop stress test) (7)

DI-BSCCO shows an excellent critical current performance in all ultra-high magnetic fields (8), but because a very large tensile load is added to the tape wound to a superconducting coil used in a ultra-high-field magnet, the design limitation for applying DI-BSCCO to NMR systems is not critical current but maximum permissible tensile stress. DI-BSCCO Type HT is expected to be suitable for this application because its maximum permissible tensile stress is improved dynamically.

Then the following test was conducted in cooperation with Dr. Tsukasa Kiyoshi and Dr. Shinji Matsumoto of the National Institute for Materials Science (NIMS) who have been developing superconducting magnets. A ø280 mm one-turn coil made of Type HT was inserted in the inner layer of a large-scale magnet owned by NIMS. And then a hoop stress was applied to the coil by conducting electricity at liquid helium temperature in 14 T. The longitudinal strain was measured by using a strain gauge attached to the surface of the tape. Whether the composite tape is either elastic or plastic was thereby tested. The *I-V* characteristics of this tape before and after the hoop stress was applied were measured by the four probe method.

Figure 8 shows the stress dependence of the I_c retention ratio (I_c/I_{c0}) and the strain. The stress in the figure is hoop stress (*BJR*) that is equal to the magnetic flux density (*B*) times the current density (*J*) times the coil radius (*R*). As a result, no degradation of critical current was observed until conducting the electricity which caused a 330 MPa hoop stress. Type HT was thus proven to have high enough performance to be applied to the magnet coils for NMR systems. **Figure 8** also shows that there were residual strains after the hoop stress was applied, indicating that the stainless steel tapes show plastic behavior. By using other metal reinforcing tapes which have higher strength than stainless tapes, Type HT is expected to have a much smaller residual strain and a much higher maximum permissible hoop stress.

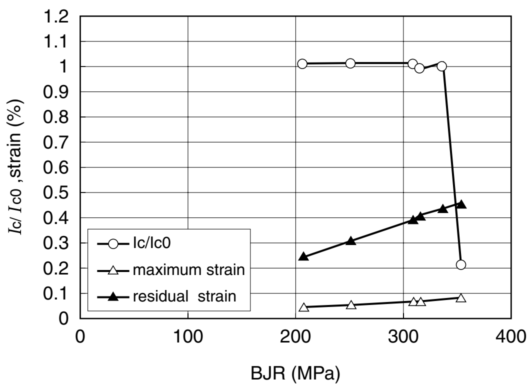

Fig. 8. Hoop stress test result (I_c: after hoop stress is applied in liquid nitrogen, maximum and residual strains: during hoop stress is applied in liquid helium)

5. DI-BSCCO catalog

Sumitomo Electric has already released the DI-BSCCO catalog and published it on its web site (9) to help customers choose the most suitable type of DI-BSCCO for various practical uses. In other words, DI-BSCCO is now being commercialized to help accelerate the spread of the superconducting technology. It is expected that various characteristics of DI-BSCCO will be improved more dramatically in the near future. The next chapter describes the current vision on performance improvement of DI-BSCCO.

6. Prospects for performance improvement and cost reduction

The economical efficacy of superconducting equipment may depend on the cost per performance of the superconducting wire used in it. For example, the rated current of conductor is proportional to I_c multiplied by the number of superconducting wires. Therefore, the cost for superconducting wire needs to be discussed not merely as per unit cost but in terms of cost per performance. The authors considered that the cost per performance of superconducting wire can be significantly reduced by enhancing I_c, and are now focusing on the improvement of I_c[10]. At present, non-superconducting particles such as (Ca-Sr)-Cu-O still exist in the filaments of DI-BSCCO after the CT-OP sintered process. These non-superconducting particles are one of the causes of the misalignment of Bi2223 grains and the main cause of the blockage of superconducting currents. **Figure 9** shows that an obvious negative exponential correlation exists between I_c and the misalignment angle from the tape surface. It is expected that I_c of the wire increases as the misalignment angle reduces as a result of reducing non-superconducting particles [1]. Moreover, although Bi2223 materials have several disadvantages such as anisotropic electric and magnetic properties and insufficient pinning strength, I_c in high magnetic fields can be increased by optimizing the amount of carriers and improving the construction of Bi2223 single crystals. For example, it was reported that T_c has risen to 117.8 K [11], which is a dynamic increase from the conventional well-known value, 110 K.

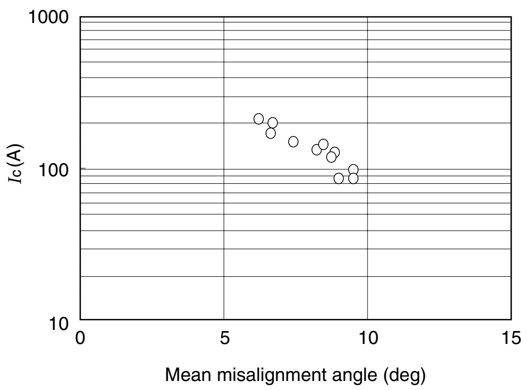

Fig. 9. Mean misalignment angle dependence of I_c

There are many cases in superconducting applications such as double pancake coil where joining of wires is required. Joint resistance is a very important issue in designing such products that use superconducting wires because the increase of joint resistance causes the increase of Joule heat, and causes such adverse effects as heat generation. Hence, Type HT must essentially have both high mechanical performance and low joint resistance. It is expected that the presently commonly used reinforcing tapes will be further improved in these properties. Although the longitudinal elastic modulus of stainless steel tape is about 1.5 times that of brass tape, the resistance of brass tape is about ten times lower than that of stainless steel. Both stainless steel and brass reinforcing tapes have their strong and weak points. This indicates that there is still room for improvement of the performances of reinforcing tapes. It is expected that use of drastically innovated reinforcing tapes will allow Type HT to find wider applications. On the other hand, the most bendable of superconducting wires that are currently available may be thin film superconductor tape manufactured by Superpower Inc. This tape wire is said to have a minimum bending diameter of 11 mm [12], but its bending tolerance was tested with the HASTELLOY substrate side outside [13], meaning that this wire cannot be applied easily to the cases where the joining of superconducting wires is required because of its high joint resistance. Presently Type ST can be bent to 25 mm. There is still room for further improvement such as the development of new reinforcing tape and wire joining method. It is expected that DI-BSCCO will be used in applications where wires are required to be bent at smaller diameters.

AC loss is reduced not only by the reduction in twist pitch but also by the introduction of electric insulation layer. One measure for decreasing coupling time constant is the development of higher-resistance matrix, so considerable research has been done on Bi2223 wires. The matrix material of the above-mentioned slim wire having a dynamically lowered AC loss is pure silver. Accordingly, it is expected that AC loss will be further reduced by the introduction of technical advances such as non-silver matrix materials and filament barriers. Moreover, as a matter of fact, AC loss is deeply linked with critical current mentioned previously. The hysteresis loss generated in a superconductor increases in proportion to I_c. However, whether in a cable or motor, the size of conductor is determined by rated current. Larger critical current means less number of wires is needed. This leads to the fact that the hysteresis loss of the conductor as a whole dose not increase even when the critical current increases. What needs to be considered carefully is coupling loss, but it can be easily suppressed in wires with high critical currents for the following two reasons. First, a large coupling current flowing through a superconductor with a high critical current density becomes suppressed relative to the high electric field in the metallic matrix of the wire. Second, shorter wire twist pitch is effective for electromagnetic decoupling, and a narrow wire is easier to twist than a thick wire. However, because the critical current decreases as the width of wire decreases, the use of narrow wire results into the increase of the total wire length used in a device. However, in the case of the DI-BSCCO wire that has a high critical current of 200 A, even if its cross-sectional area is reduced by 50%, the wire can still carry a critical current as high as 100 A. Because of these reasons, improving J_c of the wire is also indispensable in reducing AC loss.

7. Conclusions

Sumitomo Electric has developed and commercialized DI-BSCCO Type H having the same structure and a higher critical current compared with the conventional high I_c type BSCCO wire. Moreover, in order to widen the application range of Bi2223 wire in the field of superconductive products, Sumitomo Electric has also developed Type S for low operating currents that can be produced at about half the cost of Type H, Type HT and Type ST respectively having the same critical current and twice higher mechanical strength compared with Type H and Type S, and Type AC for AC use that shows a dynamically lowered AC loss. The characteristics achieved by these wires are so excellent that they can satisfy a very wide variety of requirements in superconducting applications. Sumitomo Electric will continue making efforts to enhance each performance characteristic of DI-BSCCO for the purpose of contributing to the commercialization of superconducting technologies.

8. Acknowledgement

The authors thank Dr. Koso Osamura of the Research Institute for Applied Science (RIAS) for his help in the measurement of mechanical properties. The authors also thank Dr. Tsukasa Kiyoshi and Dr. Shinji Matsumoto of National Institute for Materials Science (NIMS) for their great assistance in the experimental work of the hoop stress test.

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