Transactions of the Materials Research Society of Japan 29 [1] 35-40 (2004)

Discovery and Development of Superconducting Materials for Engineering Applications

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Since discovery of high-T_c superconductors in 1986, the superconductivity is revived as one of environmentally oriented technologies, which shall be actively developed in the 21st century. In order to advance the superconductivity technology, we need further development in the comprehensive science and technology areas. They include the exploration of higher T_c materials, the stabilization of high pressure phase, the development of new synthesis technique, the improvement of manufacturing process for reducing cost/performance, the design of superconducting composite for application, the development of composite superconductors with superior performance, i.e., high critical current density and low ac loss. Once a new superconducting material is discovered, we need to integrate the above mentioned technologies to succeed industrial application. Here the superconducitng cable is a good example to discuss a rational route from the material synthesis to the engineering product. It is concluded how important the integration of physics, chemistry, material science and electrical engineering is for developing an ideal SC device with high total performance in the future.

Keywords: superconductivity, critical temperature, critical field, ac loss, power transmission cable

1.INTRODUCTION

There are two words representing the present title, which are "superconductivity" and "material". The word "superconductivity" is expressed by two Japanese words. One is preferably used by people who study more basic science. Another is used by people of more engineering side. Also the word "material" corresponds alternatively to two Japanese words. One gives a general concept including the nature. Another is used as a more limited purpose, which indicates the material applied for practical use. Two words are not the extremes presenting from the one side to another completely different side. The areas covered by two words overlap each other. The integration in the whole area gives comprehensive concept to the combined words "superconducting material".

Table 1 Translation of two words to Japanese characters.

Superconductivity	超伝導	超電導
Material	物質	材料

Here the present status on the industrialization of superconductivity (SC) technology is first reviewed and the future problems which should be solved are pointed out. Secondly the history of discovering SC materials is mentioned and the possibility of getting new SC materials is predicted. Thirdly the optimal fabrication technique is overviewed and the future trend is discussed. Fourthly the improvement of SC and other properties are emphasized to be important for the further practical applications.

2. INDUSTRIALIZATION OF SC TECHNOLOGY

SC technology is now widely recognized to be applicable in the advanced industry areas as listed in Table 2. SC materials developed for application are divided into two categolies depending on their critical temperature (T_c) [1]. Typical LT (Low T_c) - SC is Nb, Nb-Ti, Nb_3Sn, Nb_3Al and so on. Their T_c is less than 25 K. On the other hand, HT (High T_c) - SC is represented by oxide superconductors like (Bi, $Pb)_2Ba_2Ca_2Cu_3O_x$ (Bi2223), $Bi_2Ba_2CaCu_2O_x$ (Bi2212), $YBa_2Cu_3O_{6+x}$ (Y123). Some of SC equipments like MRI and SQUID are already industrialized. And some of them like MAGLEV and fusion reactor have been constructed as demonstrator towards the near future. At present, most of SC materials close to 95% used for application is LT-SCs[2].

Table 2 Available technology of superconductivity
SMES = Superconducting Magnetic Energy Storage,
MAGLEV = Magnetic Levitation Railway
SFQ = Single Flux Quantum
MRI = Magnetic Resonance Imaging
MEG = Magnetoencephalography

Field	Devices
Energy	Fusion reactor, Power generator, SMES, Flywheel, Power cable, Fault current limiter, Transformer, Current lead
Transportation	MAGLEV, Motor SC electromagnetic thrust ship, Electromagnetic brake
Environment	Magnetic separator, Purification apparatus of waste water
Manufacturing Process	Continuous iron casting, Single crystal growth
Information Technology	SQUID, SFQ circuit, Analog mixer, Microwave filter
Life Science	MRI, MEG
Basic Science	Accelerator, NMR, High field magnet

One of important applications is the coils generating magnetic field in the fusion reactor, which consists of three type of SC coils; central coil, vertical coil and troidal coil. Here the high energy plasma is enclosed by the toroidal coil. In ITER reactor[3], which is the most advanced project, the high magnetic field of 5.3 T is requested as the on-axis troidal field. The requirement for the SC wire is the critical current density higher than 550 A/mm^2 at 12T. Only the A15 compound SC wire is applicable for this purpose at present. During the development of coils, a great effort has been paid to construct such a high performance magnet coil, which has sufficiently high mechanical strength and stability together with high critical current density.

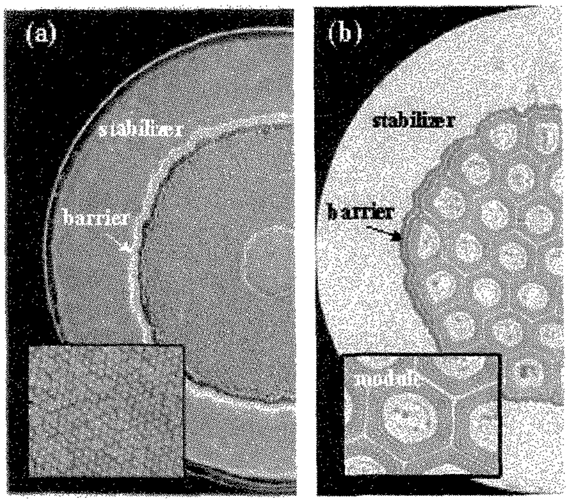

Fig.1 Cross-sectional view of two different types of Nb_3Sn multifilamentary SC wire. (a) Bronze processed wire (Furukawa Elect.) and Internal tin processed wire (Mitsubishi Elect.)

Figure 1(a) shows a typical Bronze processed wire with diameter of 0.8 mm. Around the central Bronze core with diameter of 0.12 mm, 8,058 Nb_3Sn filaments are embedded in the Bronze matrix. The filament diameter is 3.0 μm. Those filaments are closed by the Ta barrier and surrounded by Cu stabilizer. This wire has a performance of 667 A/mm^2 at 12T.

Figure 1(b) shows a typical microstructure of internal Sn processed A15 compound SC wire. The central part is separated into 37 modules. The center of each module is occupied by Sn. Sn diffuses towards Nb filaments, which locate outer part in the module. During heat treatment, Sn reacts with Nb to form Nb_3Sn. In order to get high critical current, fine SC filaments are embedded densely in the Cu-Sn matrix. Outside Ta barrier, Cu layer is surrounded, which is used as an electromagnetic stabilizer. The fabrication processes of Nb_3Sn composite wire have been essentially completed as a mature technique. Important point is to be able to fabricate such uniform wires longer than 10 km with large number of filaments between 1,000 and 100,000.

In the viewpoint of energy saving, some power electric devices are planned to be replaced by the equipments using superconductivity. One of them is the power transmission cable. When it is commercialized , the energy dissipation due to Joule heat will be tremendously suppressed. A typical power cable consists of 3 phase conductors. The current carrying and shielding parts are made from HT-SC Bi2223 tapes. Figure 2 shows the cross section of their Bi2223 multifilamentary tape[4]. SC filaments embedded in the pure silver and surrounded by the Ag alloy. The silver alloy is necessary to make the tape strong. It is seen that the morphology of the cross section is still primitive and irregular comparing with the industrialized Nb_3Sn wire mentioned above.

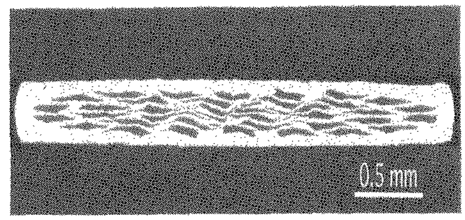

Fig. 2 Cross-sectional view of Bi2223 oxide multifilamentary tape (VAM1).

The performance requested for the SC wire of power cable is the critical current higher than 200 A and AC loss is less than 0.25 mW/Am, while the continuous wire longer than few km is absolutely desired. The present tape indicated in Fig. 2 does not satisfy the real demand. In order to realize this target performance, many efforts have been paid to get high critical current, low AC loss and high tensile strength. The total performance together with SC properties is indispensable to satisfy their requirement for industrialization. Therefore the first suggestion for industrialization of SC technology is to establish a perfect fabrication process for getting the high performance product.

The second suggestion for its industrialization is to develop new superconductors with extremely high performance beyond the present superconductors. They may have one of extreme values with respect to T_c, B_{c2} and J_c.

3.DISCOVERY AND INVENTION of SC MATERIALS

Superconductive property has been reported in many kinds of materials. They are metal, oxide, organic substance and so on. This situation indicates that superconductivity is universal physical property and independent on specific group of elements. When a mass of electrons take place Bose condensation and form Cooper pair, they reveal superconductivity. Two different mechanisms on the Cooper pair formation operate alternatively on materials. One relates with metals (BCS materials), and another to Mott - Hubbard insulators (MH materials)[5]. According to BCS theory, critical temperature is given as a function of attractive interaction parameter V, density of state at Fermi level $N(E_f)$ as given by the equation,

$$T_c = \frac{3.57\hbar\theta_D}{\pi k_B}\exp\left[-\frac{1}{VN(E_F)}\right] \qquad (1)$$

where $k_B, \hbar, \theta_D$ are Boltzmann and Planck constants and Debye temperature. The equation tells us the increasing state density results in increasing critical temperature. The state density is proportional to the second derivative of energy with momentum at Fermi Energy, which is given as a function of effective mass. In the two dimensional materials, for instance, the effective mass diverges towards infinite in one direction, because the curvature of $E(k)$ becomes zero. So the lower dimensionality tends to produce higher critical temperature.

A typical example of BCS materials is a family of A15 compounds. Their crystal structure is isotropic as typically Nb_3Sn structure is shown in Fig.3. Two Nb atoms locate so closely that the one dimensional charge transfer takes place towards the closely linked Nb atom chain. Due to the quasi one dimensional conduction, it has been recognized that the high T_c is observed for A15 compounds[6].

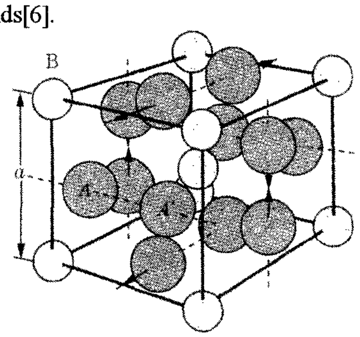

Fig. 3 Crystal structure of A15 compound, A_3B. Here Nb and Sn locate at A and B, respectively.

The second example of BCS materials is Fullerene. The molecules consisting of 60 carbon atoms occupy fcc - lattice site and alkaline or alkaline earth atoms locates in two types of interstitial site. In this family of materials, the critical temperature increases with increasing lattice constant as shown in Fig. 4. This relationship is also explained by the increase of state density at Fermi energy[7]. Carbon nanotube is also suggested to provide superconductivity, because one dimensional conduction is expected through linearly aligned metallic atoms in the tube. Till now, however, it has been not yet reported.

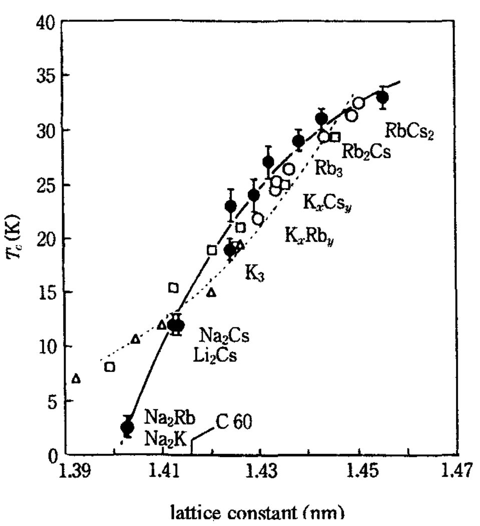

Fig. 4 Change of critical temperature as a function of lattice constant of fullerenes[8].

Another mechanism to reveal superconductivity operates in Mott- Hubbard insulators. By carrier doping, the conductivity appears in MH materials[9]. The critical temperature becomes maximum at an optimum carrier concentration as shown in Fig.5. Either under- or over-doping results in the lower critical temperature. As the mechanism forming Cooper pair is still unclear, it is not possible to predict theoretically the critical temperature.

Figure 6 shows a homologous series of crystal structure, which consist of charge reserved layer and Cu-oxide layers. The superconductivity changes depending on the number of Cu-oxide layers. The relationship between the critical temperature and the layer number is shown in Fig. 6 for various homologous series compounds. It is seen that the critical temperature reaches maximum at the layer number of 3 or 4, then tends to decrease. This tendency relates to the optimum hole concentration. Further the highest temperature discovered till now is 164 K for mercury Hg1223 oxide under high pressure[11].

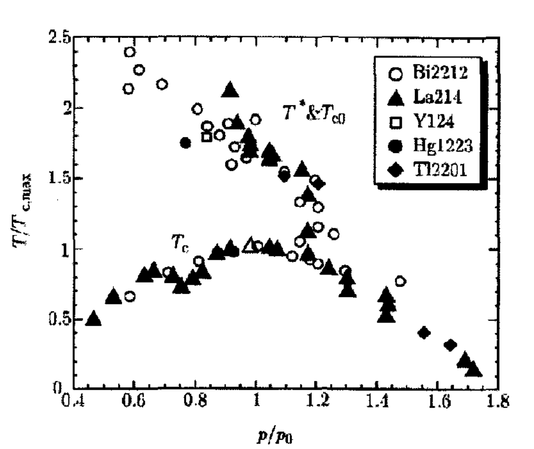

Fig. 5 Carrier concentration dependence of characteristic temperatures, T_c and T_g for various HT-SCs[10].

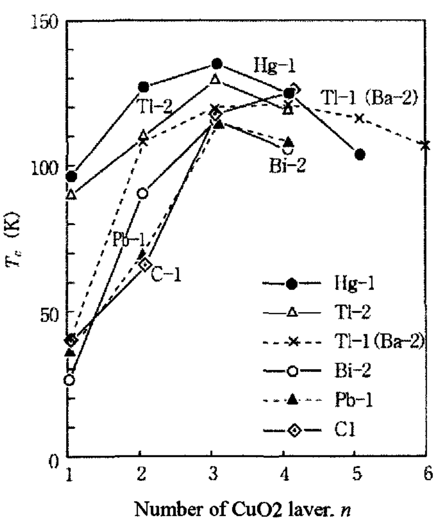

Fig.6 Change of critical temperature as a function of CuO_2 layer number in the M-$m2(n$-$1)n$ type compounds.

Since discovery of superconductivity in 1911, the highest critical temperature has renewed time to time.

Firstly 4.15 K was recorded for mercury, the highest one in the family of A15 compounds is 23.2 K for Nb_3Ge. The highest one for fullerene was 33 K for $RbCs_2C_{60}$. As shown in Fig.6, the highest one of oxide SCs is 135 K for Hg1223 at atmospheric pressure. Some guidelines are proposed to discover and invent new material with higher T_c. One of them is to explore materials under high pressure, where we can change easily the state density, the intensity of transfer integration and the interaction parameter. Here $CuBa_2Ca_3Cu_4O_x$ oxide is reported to show superconductivity below 117 K under high pressure[13]. This compound is interesting for application, because it does not include poison element. The second is to explore low-dimensional materials systematically. One example is to discover new homologous series of oxide SCs. One of other possibilities is to investigate the mechanism of one dimensional conductivity in the carbon nanotube. The third is to create a two dimensional array of specific atoms on the surface of semi-insulating substrate by atom manipulation. A localized electronic state is isolated in the area surrounded by those two dimensional array and there a Bose condensation of localized electrons might be expected. The fourth is to investigate non-equilibrium state when the carrier is injected to the system [14]. Just above T_c, there exists a mixed state including superconducting fluctuation [15]. When temperature decreases close to the crossover temperature to the superconducting phase, the degree of coherency (Maki-Thompson term) and/or the size (Aslamazov-Larkin term) of superconducting part increases. By using one of supercondcuting transistor, it is essentially proposed to inject Cooper pairs through Josephson junction and make them remain in the system as non-equilibrium state within a finite time.

When we assume 50% increase of critical temperature, which is the highest value reported till now, it is about 246 K. This indicates the real temperature in the home refrigerator. This expectation of new HT-SC would be not far from reality. Figure 5 shows the change of characteristic temperatures as a function of hole concentration. Also the temperature for pseudo-gap is shown. It is higher than T_c by 50% just on the maximum critical temperature. At present, the physical meaning of pseudo-gap is unclear, but the onset of pseudo-gap has been recognized to relate closely to superconductivity.

4.OPTIMAL FABRICATION PROCESS OF SC DEVICES

Since 1986, many Cu-oxide superconductors have been investigated to develop SC devices for application. As mentioned in Sec.2, necessary requirements on the structure and subsidiary properties have to be satisfied. Only a few number of oxides are survived as candidates for industrialization. They are Bi2223, Bi2212, Y123 and RE123, where RE means rare earth elements. Here it is discussed about the present status and the future demand for these materials.

Physical properties of materials are in general divided into two categories of intrinsic and extrinsic one. Intrinsic properties are critical temperature, critical field, Young modulus, thermal expansion coefficient, and so on. Their quantity depends on each material and is very hard to be changed by microstructure control. A new high HT-SC with innovative intrinsic property can be explored according to several proposed principles mentioned above in Sec. 3. On the other hand, extrinsic properties are critical current, irreversible field, strain effect of I_c, ac loss, mechanical strength and so on. Their quantity acn be improved by structure control.

Table 3 Performance of Bi2223 multifilamentary tapes

Manufacture	I_c (A)	J_c (A/mm^2)	L (m)
A(USA)	150	400	150
B(Japan)	110	350	550
C(Germany)	100	320	550
D(Grmany)	78	(310)	
E(China)	65	(250)	
G(Korea)	40	(250)	300

The fabrication process of Bi2223 multifilamentary tape is briefly introduced. The precursor powder is filled in the silver tube. The composite is hot-extruded to get the wire with small diameter. Short pieces are filled again in the large silver tube. Then it is reduced in diameter by extrusion. In order to control the microstructure, the thermomechanical treatment is applied. Several industries develop this PIT -processed Bi2223 tapes in the world as listed in Table 3. The long tapes with several 100 m are now obtainable where the number of filaments in the range between 19 and 121 as a typical cross section is shown in Fig. 2. The maximum critical current density J_c for the long tapes is reported to be 400 A/mm^2 at 77 K and the yield strength is 120 MPa at R.T.

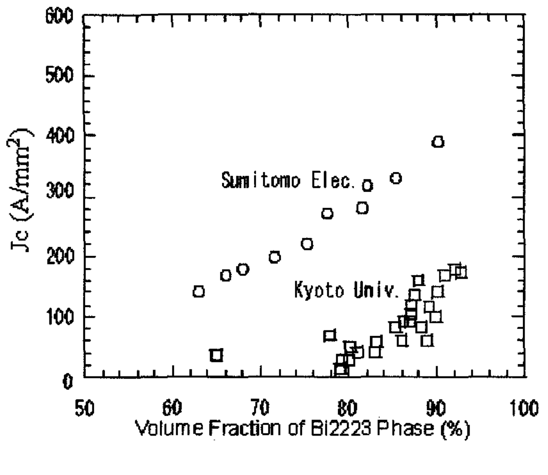

Fig. 7 Change of critical current density as a function of volume fraction of Bi2223 phase in the tape [16, 17]

A common feature of microstructure for those tapes is summarized in the following. Figure 7 shows the volume fraction dependence of critical current density for Bi2223 tapes. The J_c starts to increase beyond a threshold of volume fraction and increases with increasing volume fraction. Also the J_c depends on the misalignment between neighboring grains as shown in Fig. 8. They indicate that the J_c is limited by G.B. weak link. When the tape was carefully prepared, the smallest angle was reported to become about 9 degree. The open space remains still in the oxide layer, of which the least volume was estimated about 15%. The residual carbon was reported to remain in the oxide layer by 200 ppm or more. The inverse correlation has been recognized between J_c and carbon content. Their imperfections limit greatly the critical current density. Therefore in order to develop higher performance tape, the imperfections mentioned above shall be perfectly eliminated. When eliminating G.B. weak link, the critical current is limited by the flux pinning sites in the grains. At present, the defects produced by radiation damage is known to act as pinning center. Their size is in order of nm scale. When introducing nm-scale defects in the matrix, an ideally high value of J_c will be realized, which is expected to exceed 2 kA/mm^2.

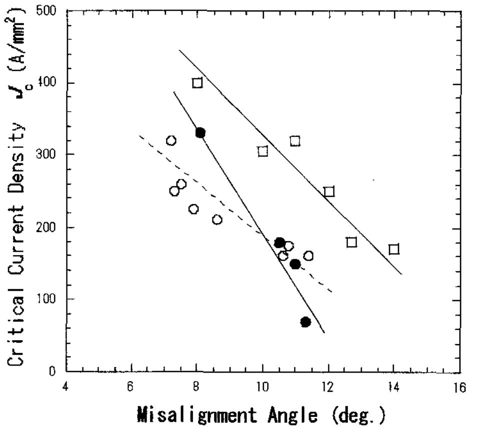

Fig. 8 Change of Jc as a function of misalignment angle for Bi2223 multifilamentary tapes[18].

As mentioned in Sec. 2, the SC composite wire (tape) is used as a component of the electric magnet. In practice, the wire is exerted by complicated stresses during fabrication and under operation. The Hoop stress is estimated to reach 800 MPa when the magnetic field of 20 T is generated by using the magnet with coil radius of 0.2 m and current density of 400 A/mm^2. At present, no Bi2223 composite tape can hold this large Hoop stress. In order to strength the composite, there are essentially two

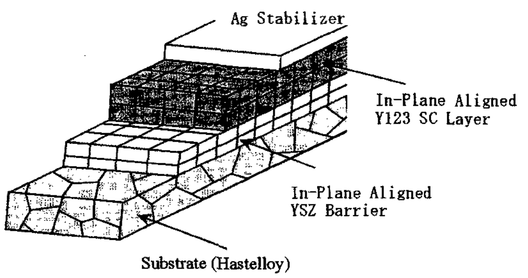

Fig. 9 Structure of coated conductor fabricated by IBAD technique.

technologies. One is to support the tape by pasting the supplementary member like stainless steel. Second is to improve the mechanical property of each component by dispersion hardening of Ag alloy and eliminating the porosity in the oxide layer as shown in Fig. 2.

In order to use SC wire(tape) for ac devices, much effort should be paid to reduce ac loss[19], which is originated from the coupling, the hysteresis and eddy current losses. Hysteresis loss can be reduced by designing the filament arrangement topologically. Eddy current loss is reduced by increasing the resistivity of Ag alloy matrix. Coupling loss is reduced by twisting of filaments and by inserting barrier layer between two filaments. All attempts till now succeeded to reduce the ac loss, but still the ac loss should be reduced to the level of 0.1 mW/Am. For realizing this final target, a new creative technology is expected.

Y123 is expected to be developed as a next generation superconductor. As the irreversibility field is higher than that of Bi2223, it can be used under high magnetic fields at 77 K. This is great advantageous for application and remarkably reduces cost/ performance overall the SC technology. The transport property of Y123 is seriously limited by GB weak link. Small misalignment angle less than a few degree is indispensable for Y123 good conductor.

Table 3 Architecture of Y123 coated conductor and its fabrication technique and materials used there.
GZO: $Gd_2Zr_2O_7$, LZO: $LaZrO_3$, EBS: Electron Beam Sputtering, PLD: Pulse Laser Deposition, TFA-MOD: Metal Organic Deposition, IBAD: Ion Beam Assisted Deposition, TMT: Thermomechanical Treatment.

Layer	Material	Fab. Technique
Stabilizer	Cu, Ag	EBS
SC	Y123, RE123	PLD, TFA-MOD
Barrier III	CeO_2	IBAD
Barrier II	MgO, Y_2O_3, LZO	PLD
Barrier I	GZO, YSZ, NiO	EBS, MOD
Substrate	Ni, Ni-W, Ni-Cr	TMT

In order to realize an ideal Y123 conductor, the following architecture has been generally requested. As shown in Fig.9, the substrate should be composed by metallic material, because of fabrication of long length tape. Several candidates have been proposed till now; Ni and Ag and their alloy. There are two strategies for the substrate. One is to use the aligned substrate for inducing the preferred oriented crystal growth. In order to get well aligned microstructure of Ni or Ag, the re-crystallization is used to be applied after heavy deformation. This technology is called RABiTS method [20]. Another is to use the randomly oriented substrate. The latter case called IBAD method [21], the oriented barrier layer has to be grown. Barrier layer is necessary from the following reasons. (1) to prevent the reaction between the substrate and the SC layer, (2) to get subsidiary alignment. Two or three layers are necessary to satisfy their requirements. Several kinds of materials are used like NiO, GZO, LZO, MgO, Y_2O_3 and CeO_2. Barrier layer is grown by means of IBAD, PLD, MOCVD and so on.

Table 4 Performance of Y123 coated conductor

Manuf-acture	Barrier +Subst.	SC Layer	I_c / J_c (A)/(kA/mm^2)	L (m)
A(Jap.)	IBAD	PLD	38/7.6	100
B(Jap.)	ISD	PLD	15/1.5	50
C(EU)	IBAD	PLD	78/22	10
D(USA)	RABiTS	TFA-MOD	184/23	10
E(USA)	IBAD	MOCVD	111/-	18

Y123 thin film with thickness of 05 to 2 μm is deposited on the well aligned barrier layer. Superconducting Y123 layer is fabricated by means of PLD, TFA-MOD and other techniques. The PLD technique is expensive. On the other hand, TFA-MOD[22] is cheap process, but the chemical byproduct is no so easy to waste. Many efforts are paid to get high performance Y123 coated conductor. However, at present, no unique fabrication technique has been established for getting industrially available product.

Best results obtained till now are listed in Table 4. One of them is called IBAD technique, which was originally invented in Japan. The critical current is 38A and the length is 100 m[23]. Another is called RABITs invented originally in U.S.A. The critical current is 184 A and the length is 10 m[24]. The final target is I_c = 300 A and L = 1000m. Still many innovative progresses on the fabrication techniques are requested. To reduce the cost/performance is also very important issue.

5.SUMMARY

As listed in Table 1, many advanced technologies are waiting to use superconductivity. When electricity is generated by SC generator, brought by SC power cable, transformed to low voltage by SC transformer and stored by SMES, its efficiency very much improved. It becomes possible to bring electricity over the world by using SC power cable. MAGLEV trains will bring quickly people anywhere in the world. When a large scale computer is composed of SFQ circuits, the calculating speed will be increased by 1,000 times comparing with the present semiconductor device. In medical applications, high performance MRI, cardiograph and so on will be developed for human health. Such a situation might be called the superconductivity world.

As discussed above, the superconductivity technology has not yet completed for applying fully to the future advanced human society, where keeping the clean circumstance around human life and reducing energy consumption. Once a high performance superconductor with high T_c is synthesized, the design and control of microstructure might be soon carried out to realize high J_c, low ac loss and high strength. A quick progress is only achieved when the systematic and integrated R&D is indispensable from the broad area of physics, chemistry, material science and electrical engineering. Of course, it is impossible to predict it, but still a lot of new information and techniques are needed, which have been not yet investigated and developed till now.

In order to promote soundly the science and technology of superconductivity and succeed a great development in near future, the following two actions are absolutely requested: (1) Comprehensive education in the field of engineering chemistry, metal science and engineering, (2) Effective R&D in cooperation with experts in the field of material science, mechanical engineering, electrical engineering as well as chemistry and physics.

As a conclusion, a dream is that the human shall realize a superconducting material usable in home refrigerator, which is poison-less and recyclable.

Acknowledgements: The author expresses his hearty thank Dr. S. Endo, Furukawa Electric. Co and Dr Y. Kubo, Mitsubishi Electric. Co for photographs of Nb_3Sn wires.

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(Received October 9, 2003; Accepted December 1, 2003)