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Technical Review

Functional Materials (Physics Edition)

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1. Introduction

In the course of the last hundred years of technological development at Nippon steel Corporation, especially in the last thirty years, various activities to develop new advanced materials have been conducted in diverse new fields with the aid of materials science and technology based on steelmaking technology. In this technical review, we describe the company's R&D on functional materials conducted in response to the changing markets and depict especially representative examples of the company's functional materials that have been developed to meet the needs of newly emerging markets and that have grown together with those markets.

2. Changing Markets and R&D on Materials that Meet New Market Needs

Over the past thirty years, as shown in **Fig. 1**, our lifestyles have dramatically changed as a result of technological innovations, perhaps most obviously due to semiconductors. The degree to which semiconductors, which began with LSI, have become integrated has risen exponentially,[1] while the volume of information that can be handled with semiconductors has increased phenomenally. In connection with the Internet, which has brought about the greatest revolution in information communication since Alexander Graham Bell invented the telephone, semiconductor use has grown very rapidly. It led to the development of the personal computer, cell phone and smartphone, which have each become a part of our everyday lives. Today it is possible to exchange information instantly on a global basis. Thus, thanks to the fusion of semiconductor technology and information technology (IT), we benefit from "enjoyable" and "convenient" IT. On the other hand, our society consumes massive—and ever increasing—amounts of energy. As a result, "being friendly to the environment" has become critical. In the case of automobiles, for example, the enforcement of regulations governing exhaust fumes and fuel efficiency prompted the development and/or improvement

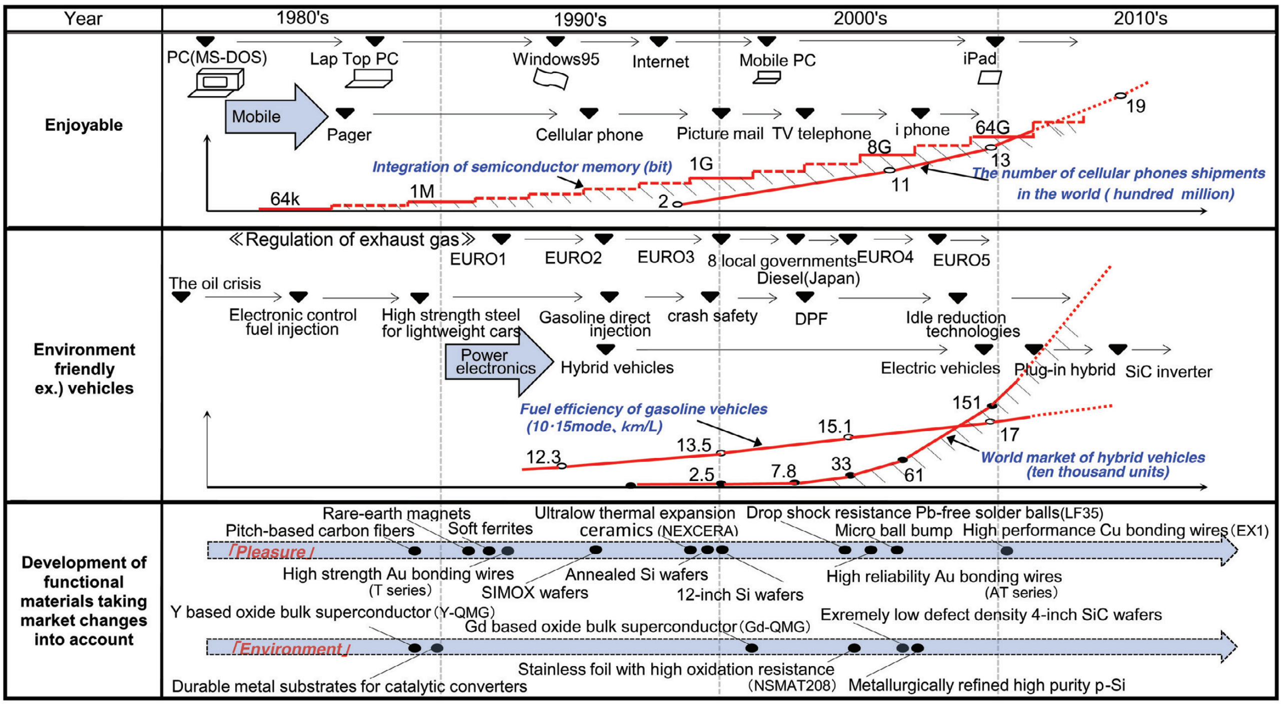

Fig. 1 Market changes in the last 30 years and functional materials developed at Nippon Steel Corp.

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of technologies to control fuel injection systems, reduce car body weight, purify waste gases, and so on. It is fair to say that the introduction of a hybrid car by Toyota in 1997 brought about a major change in the development of automotive engines that use fossil fuels.

In view of the dramatic changes in the markets mentioned above, Nippon Steel started developing new functional materials in the mid-1980s. Since then, the new materials business (present-day Nippon Steel Materials Co., Ltd.) has offered the most advanced and functional materials to the market.2) They include: metallic materials (packaging materials, stainless steel foils), ceramic materials (fine ceramics), and crystalline materials (silicon, silicon carbide (SiC), and superconductors), etc.

In the development of those new materials, the company has always attached primary importance to going back to fundamental principles and the essence of technology to solve any problems along the way. That has been made possible by the component technologies of materials science that have been accumulated in the process of developing various new materials. Representative examples of these component technologies include: control of metallic structures (thin wires, foils, crystalline textures), control of powder forming (fine ceramics), and control of crystal defects (single-crystal orientation, point defects, dislocations).

3. Packaging Materials Adapted to Changes in the Field of IT

Of the semiconductor-related technologies, the advent of microprocessors with highly integrated semiconductor circuits to perform arithmetic operations may be said to have led to the subsequent dramatic advances in semiconductor technology. Today, at a two-dimensional level, the degree of integration has breeched Moore’s law to reach an atomic-level circuit. At the same time, packaging technology for stacking, protecting, and connecting the elements together has made remarkable progress to allow for high-density, high-performance packaging.3) Conventional linear packaging has evolved to planar packaging. In the late 1990s, the ball grid array (BGA) came to be used. Today BGA is mainstream in terms of high-density packaging for PCs and cell phones (**Fig. 2**). With the ever-increasing demand for smaller, thinner, three-dimensional packages, the materials for those high-density, high-performance packages (PKG) are required to be even more reliable under severe operational environments.4) Nippon Steel’s packaging materials have been commercialized by Nippon Micrometal Corporation, which now holds a 15% share of the world market for micro-balls (MB) for BGA and a 25% share for bonding wires (BW). We describe below the two packaging materials that have contributed to the above achievements.

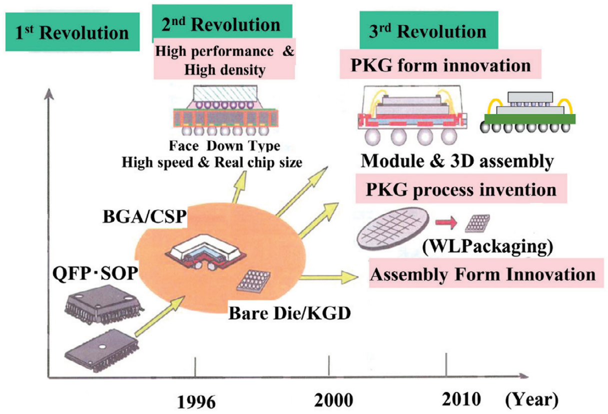


Fig. 2 Historical changes of high-density semiconductor PKG

One is MB “LF35” 5), a solder offering good drop-shock reliability, developed in response to the need for lead-free solders and the spread of cell phones. Under the EU-RoHS Directive, the use of lead-containing solders in household appliances was banned in 2006. As a result, it became necessary to switch from conventional tin-lead eutectic solder to a lead-free solder. The standard formula for lead-free solder (Sn-3.0Ag-0.5Cu) that had previously been used was hard and brittle compared to the conventional tin-lead eutectic solder. Since that posed a serious problem for cell phones in terms of impact resistance if dropped, the PKG had to be reinforced with an expensive under-filling resin. In order to resolve this problem, Nippon Steel—with its eye on creating a soft, low-Ag, lead-free solder—developed a new lead-free solder, LF35, with good drop-shock reliability by using a material doped with an extremely small amount of Ni to control the structure of the intermetallic compound (IMC) formed at the soldered joint (**Fig. 3**). Since LF35 was specified by one of the world’s leading cell phone manufacturers, it has become the de facto lead-free solder.

The other packaging material is “ EX1,” a copper BW developed in response to the hikes in gold price and the changes triggered by the Lehman shock.6) Over the past fifty years, many attempts have been made to utilize copper BW. However, copper BW has inferior oxidation resistance compared to gold BW. Besides, it is so hard that it tends to damage the chips easily. Therefore, copper BW had only been used in certain power devices with low pin counts. In the wake of the Lehman shock in 2009, the price of gold began to rise sharply. In order to cut down on gold use, it became common practice to reduce the diameter of gold BW for the semiconductor PKG assembly (from 22.5 μm to 18 μm). However, that was insufficient to absorb the surge in the gold price. From the standpoint of improving the oxidation resistance of copper BW and the long-term reliability at the bond of the copper BW, Nippon Steel developed EX1—the first Pd-coated copper BW applicable in the packaging of LSIs (**Fig. 4**). The copper BW with a simple Pd coating posed a number of problems, such as abnormal ball formation and surface layer separation. Therefore, on the basis of clarifying the defect mechanisms, the company developed multilayer wire technology that allows for an original design of the structure thickness of the Pd surface layer and the interface between Pd and Cu. EX1 has solved the problems involved in using conventional bare copper BWs, such as the decline in BW life due to oxidation (EX1 has prolonged BW life from one week to three months; **Fig. 5** (a)) and the need to supply hydrogen during bonding (EX1 does not require a hydrogen supply).

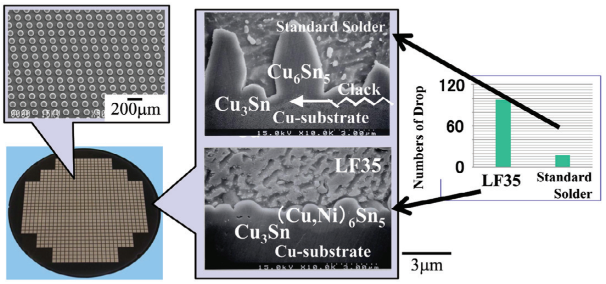
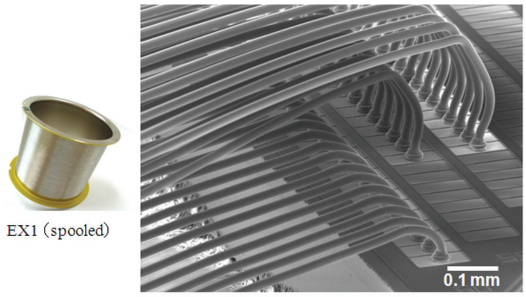


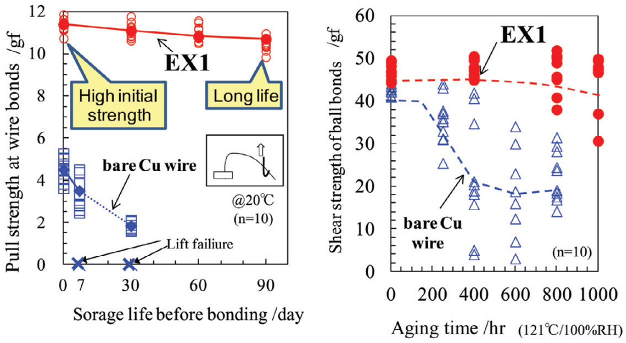
Fig. 3 Drop shock properties for LF35 solder and standard solder The bumped wafers processed by micro-ball bumping method (ball size: 80 μm in diameter, pad pitch: 150 μm).



EX1 (spooled)

Bond appearance of EX1
(diameter: 18 μm, bond pitch: 50 μm, three layer bonding)

Fig. 4 EX1 wire and its high density bonding



(a)Wire bond strength after storage in air before bonding

(b)Ball bond reliability after high humidity aging test

Fig. 5 Wire bond strength and ball bond reliability of EX1

According to a customer who evaluated the long-term reliability of conventional bare copper BW, the decline in bond strength caused by a crack in the bond between the copper BW and Al electrode after heating at high humidity could prevent the practical application of copper BW (Fig. 5 (b)). The above decline in strength was found ascribable to corrosion of the IMC formed in the joint interface. That problem could be solved by causing a Pd-enriched layer to be formed in the bond interface and thereby controlling the growth of IMC. By suppressing the growth of corrosive IMC, EX1 ensures long-term reliability that permits using automotive LSIs even under high temperatures. EX1, with its superior oxidation resistance, became very popular around the world for its bonding performance and long-term reliability soon after it was put on sale. Having become the de facto standard in the field of copper BWs in a short time, EX1 maintains a predominant share of the market.

The most important thing to develop next is packaging technology that allows for operation of the elements under high temperatures to improve the efficiency of electrical energy use by SiC power devices. Specifically, future development of packaging technology for heat-resistant die attaches, device electrodes, wiring, connectors, sealers and radiators is awaited.

4. SiC Wafers Adapted to Changes in the Field of Power Electronics

Electricity is believed to be an extremely important form of energy from its excellent properties of usability. On the other hand, the double oil crisis of the 1970s cast fresh light on the need for diverse energy resources for electricity as well as improved energy efficiency: i.e., the saving of energy. In addition, as we entered the 1990s, global environmental destruction ascribable to mass consumption of fossil fuels emerged as an important key issue. At the "Earth Summit" held in 1992, attempts were made to obligate participating countries to reduce their emissions of CO_2 and other greenhouse gases. Under these circumstances, it is important to press ahead with the efficient use of electrical energy. To that end, technology to efficiently convert and control the form of electrical power in accordance with its specific usage is called for. Power electronics forms the basis for that technology.

Since the early 1990s, from the standpoint of further enhancing the efficiency of electrical energy utilization to cope with the ever-increasing demand for electricity, Nippon Steel, with its eye on the superior properties realizable by SiC over Si, has been developing large, high-quality, single SiC crystals as a new high-performance power device material in order to replace Si, because Si-based devices were fast reaching the operating property limit determined by the intrinsic material properties of Si. Since SiC is manufactured using the vapor-phase deposition process at very high temperatures exceeding 2,000℃,[7] high-quality single crystals of SiC are extremely difficult to grow. Therefore, during the 1990s, the company had to pursue its basic studies using single crystals not more than about an inch in diameter, such as analyses of dislocations in the SiC crystals (**Fig. 6**). During that period, the company successfully established various bases for important technologies necessary to control the growth of high-quality single SiC crystals, including the establishment of a crystal dislocation evaluation method by means of etching in molten KOH, the a-face growth technique that can completely suppress dislocation generation,[8] and establishment of databases such as the hot-zone structure for crystal growth, and the fundamentals of phenomenon in single crystal growth, etc.

In and after 2000, on the basis of the accumulated technological assets mentioned above, Nippon Steel has continued to develop its technologies to increase the size of SiC single crystals. In the meantime, the company established various techniques to stabilize the 4H-type SiC crystal that is suitable for power device applications. As a result, for the first time in Japan, the company succeeded in realizing a four-inch diameter 4H-SiC single crystal wafer with an extremely low defect density.[9] In addition, as shown in **Fig. 7**, the company has further developed its technology to control the stacking structure of crystals at an atomic level, thereby establishing accurate control of SiC growth with a highly homogeneous structure throughout the crystal. In addition, concerning dislocations in single SiC crystals, the company has expanded a technology which permits controlling

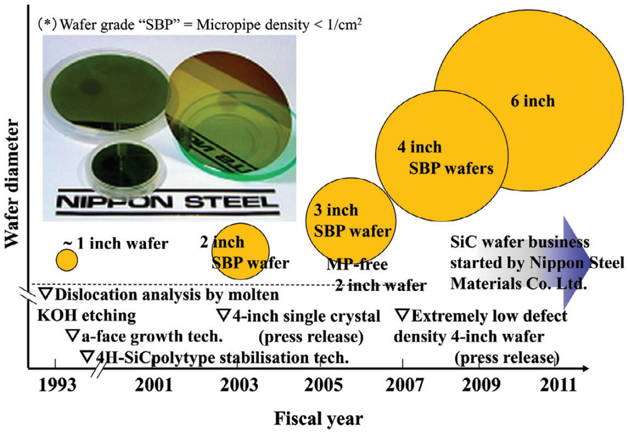


Fig. 6 R&D history of SiC single crystal wafers in Nippon Steel Corp.

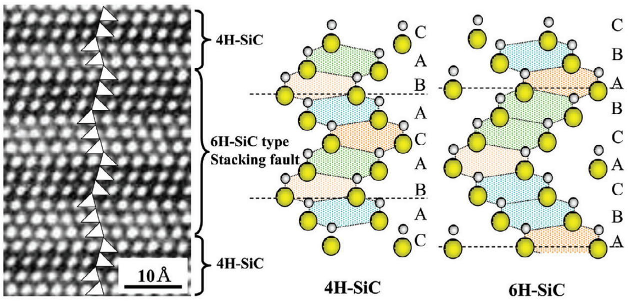


Fig. 7 Atomic configuration of 6H-SiC type stacking fault observed in 4H-SiC single crystal wafers using HRTEM

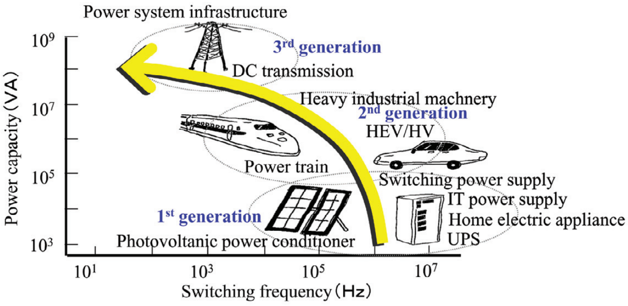


Fig. 9 Applications and generation development of SiC power devices

dislocation generation by using, for example, photoluminescence (PL), a tool for analyzing dislocation structures.[10)]

Using PL at a wavelength of 420 nm, the company observed the extending process of a basal plane dislocation (a form of edge dislocation on the (0001) plane) in a SiC epitaxial layer. **Fig. 8** shows the results of the observation. It can be seen that as a result of irradiation by an ultraviolet light with wavelengths of around 360 nm, the basal plane dislocation, which is a perfect dislocation, decomposes into two partial dislocations, forming a four-sided Shockley-type stacking fault region. It is expected that through the establishment of such technology enabling us to control the dynamic behavior of the dislocations, it will surely lead to the next generation of high-quality single SiC crystals with lower densities of dislocations such as basal plane dislocations and threading screw dislocations.

Employing the company's unique crystal growth processes comprising of the defect-control technologies described above, Nippon Steel Materials started a SiC wafer business in 2009. Much is expected of the high-performance SiC power devices fabricated on our SiC wafer products since they will help increase the efficiency of power consumption (power loss reduction expected by 70% to 90%), reduce the size of power systems down to between a tenth and a thirtieth of the volume, and improve the heat resistance properties of the power systems, giving rise to reducing the load due to cooling systems.[11)] As shown in **Fig. 9**, various types of SiC power devices with different power capacities and switching frequencies are being developed concurrently. In view of the promising future for HEV/EV, demand for a stable supply of six-inch SiC wafers which are necessary for cost-effective production of higher-power SiC devices becomes especially stronger. In order to meet the above demand, Nippon Steel, through participation in a national project led by the Ministry of Economy, Trade and Industry, contributes to the improvement of SiC materials by developing technology for mass production of such six-inch SiC wafers. The company expects that SiC power electronics will help realize an ideal society in which electric power is utilized much more efficiently.

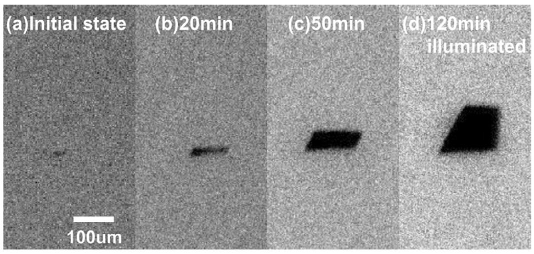


Fig. 8 Time-dependent evolution of stacking faults under UV illumination observed in a 4H-SiC epitaxial layer using 420 nm photoluminescence microscopy (black contrasted areas correspond to stacking faults)

5. Materials for the Ever-Growing Field of Energy Creation

In response to the mounting cry for "environmental friendliness," the whole world is rapidly shifting toward renewable energies. Among these, solar and wind power generation are each expected to account for a fourth of all energy production by 2040.[12)]

5.1 High-purity silicon feedstock for photovoltaic power generation

Mainstream photovoltaic power generation systems are based on silicon, which has been used for at least twenty years and is inexhaustible and nonpoisonous. The key point is technology to economically manufacture high-purity silicon feedstock.

At present, silicon is mostly manufactured using the Siemens method, which was actually developed to produce silicon for semiconductors (upper diagram in **Fig. 10**). In this process, low-purity metallic silicon is transformed into crude trichlorosilane ($SiHCl_3$), any impurities are removed from the crude trichlorosilane by distillation, and the high-purity trichlorosilane is then reduced into high-purity silicon. Although this process permits high-purity silicon of 9N level to be obtained, it has the following drawbacks. The process involves energy intensive chemical reactions; it generates highly poisonous $SiCl_4$ as a by-product; and it requires a huge chemical plant, that is, massive financial investment.

On the other hand, since silicon of 6N purity is considered sufficient for solar cells, the application of metallurgical techniques to its manufacture has been studied for several decades. Namely, that is the technique to remove such impurities as B, P and Fe thermodynamically without changing the chemical form of Si. However, it has not been put to practical use because of the difficulties involved in removing B and P, which are thermodynamically close to Si.

By evolving the application of its metallurgical technology fos-

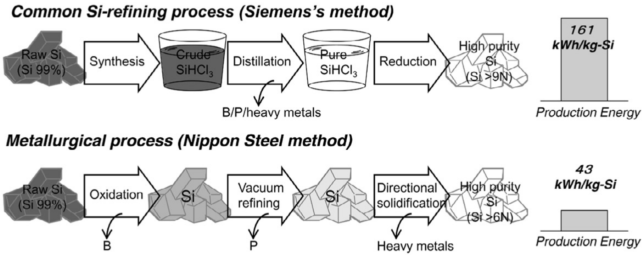


Fig.10 Unique metallurgical Si-refining process developed by Nippon Steel Corp.

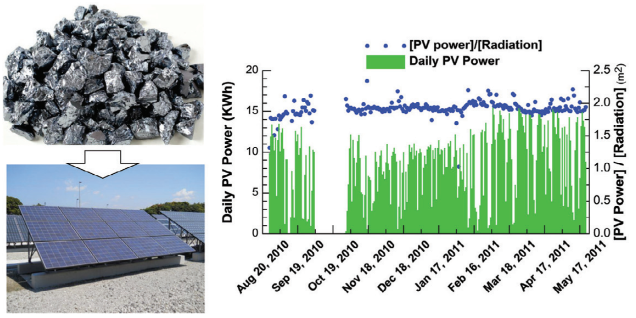


Fig.11 High purity poly Si made by NS Solar Material Co., Ltd and a long-term power generation test of solar panels made from NS's poly Si

tered in the steelmaking process, Nippon Steel has developed a new silicon refining process that consumes less energy and does not produce any poisonous by-products (lower diagram in Fig. 10).[13] The new process, which was industrialized by NS Solar Materials Co., Ltd. in 2008, produces high-purity silicon ingots at a rate of 500 tons/year (**Fig. 11**).

At present, the energy required to manufacture photovoltaic generation equipment is recovered in about two years from the time the equipment is put into operation (EPBT: energy payback time). Half of that energy is for silicon feedstock manufacturing by the Siemens method. With the new method, the energy required to manufacture silicon feedstock can be reduced to about a quarter. Therefore, it is possible to significantly shorten the EPBT.[14]

5.2 Superconducting bulk material for wind power generation

In the field of wind power generation, generator capacity has been continually expanding. Today, the 2-MW class is mainstream. Most recently, an experimental 5-MW-class generator has been made, and even a 10-MW-class generator is planned. However, as shown in **Fig. 12**,[15] a generator of 2 MW or more requires an extremely heavy nacelle. Besides, the step-up gear housed in the nacelle can cause problems. It is said, therefore, that with existing technology, the 5-MW class is the practical limit. A superconductor with a strong magnetic field that permits the generator to produce a large torque at low speed (this is difficult to achieve with any other material) is considered the key technologically to the realization of a 10-MW-class generator of the same weight and size as a 5-MW generator.[16]

There are two ways to produce a strong magnetic field with a superconductor. One is using a coil of superconducting wire, and the other is using a superconducting bulk material as a permanent magnet. The bulk material option is notable for its compact size and ability to produce a strong magnetic field. Nippon Steel has first developed the high Jc (critical current density) superconducting bulk material (QMG®) comprised of single crystalline RE-Ba-Cu-O-based superconducting phase (RE: rare earth element, typically Y). Much was expected of RE-based materials since they can be used with liquid nitrogen as the coolant. However, the conventional sintering process for those materials was impeded by a low J_c.[17] Nippon Steel solved the problem by developing a new manufacturing process that controls both the crystal growth and the microstructure.[18]

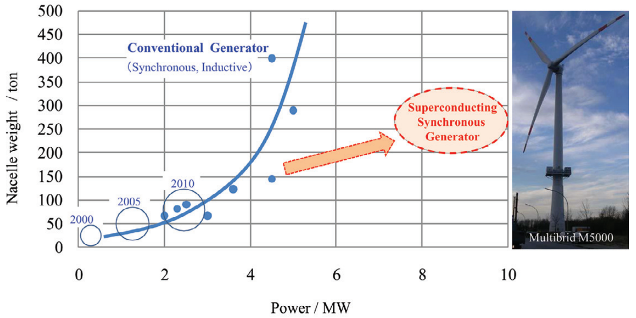


Fig.12 Relationship between the power and nacelle weight on the wind power generators
Right picture shows 5MW system (rotor diameter : 116m, height of hub : 98.5m).

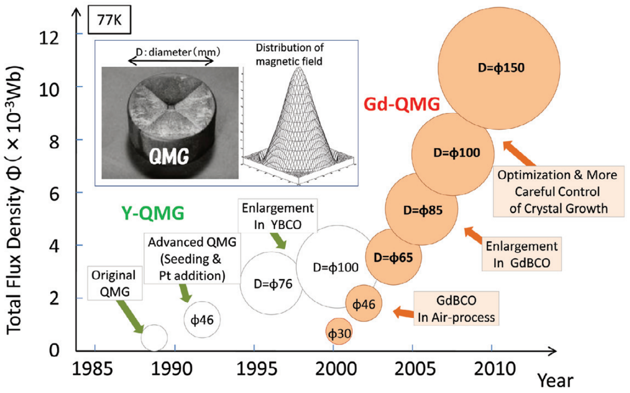


Fig. 13 Progress of total flux and size on a QMG bulk superconductor

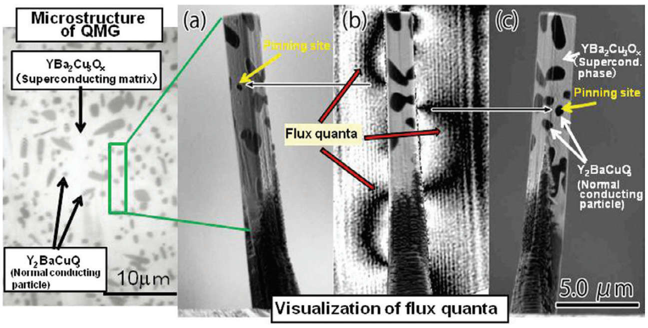


Fig.14 Magnetic flux quanta pinned at normal particles in QMG bulk superconductor

As shown in **Fig. 13**, Nippon Steel has made many improvements to the properties of its superconducting bulk materials by changing the RE from Y to Gd and controlling the raw material powder and crystal growth conditions. At present, it is possible to obtain strong magnetic fields of even 10-T class relatively easily by cooling the bulk material to 30K to 50K in a refrigerator.[19] It is the "pinning" of a quantized magnetic flux (fluxon) in the superconductor that is the microscopic mechanism whereby such a strong magnetic field can be generated. **Fig. 14** presents electron holography (reconstructed phase image) showing a fluxon pinned by normal conducting particles (Y_2BaCuO_5) which are finely dispersed in the matrix of the single crystalline superconducting phase ($YBa_2Cu_3O_X$) in the small column-shaped QMG® specimen.[20]

Much is expected of our superconducting bulk material with the above characteristics as a key material not only for wind power generation but also for tidal power generation, ship propulsion motors, current leads, power storage flywheels, compact cryogen-free NMRs, magnetic drug delivery systems, and magnetic separators, etc.

6. Conclusion

Functional materials of the future must contribute, on a timely and sustainable basis, to an “enjoyable and affluent society” and a “society highly conscious of the environment and energy”—concepts that might seem mutually incompatible—while maintaining the desirable property trends of conventional functional materials.

In the long run, it will become necessary for all of us to deal with the serious and thorny problems of population and resources. It is estimated that the world population will increase forty percent in the next forty years. On the other hand, Japan’s population is estimated to decrease thirty percent in that period. At the same time, the country will become an aged society. Looking at energy and mineral resources around the world, Japan will be confronted with an increasingly difficult situation because resource-rich countries will become less generous with their resources and because certain kinds of resources are not inexhaustible. Regrettably, at present, we have neither a clear vision nor a precedent to follow as to how we should face the above situations.

Bearing in mind the remark: “ The light bulb was not invented by a crash program on candles,”21) we should consider how useful materials have come into being. The path of technological progress is not always linearly progressive. In recent years, in particular, many technological breakthroughs have been achieved by continued developmental efforts that are comprehensive and interrelated. We think that a new dynamism is generated by extensive collaboration between materials science and other scientific fields and by the interdisciplinary application of technologies in diverse fields. Such fresh dynamism will help develop advanced materials that meet the needs of and address the many hurdles facing our changing society.

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