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SPECIAL FEATURES

Material Research for Solving Environmental Problems

Environmental Purification using Photocatalysis

—The challenge of developing a visible light-sensitive photocatalyst—

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Photocatalysts can efficiently decompose organic contaminants by means of a strong oxidizing ability which is generated when the photocatalysts are irradiated by light. Much attention is therefore paid to these materials so as to develop an environment-friendly technology to purify polluted air and water without electricity or other energy sources. At present, active development of products which utilize the deodorizing, anti-microbial, anti-pollutant, and anti-fogging effects of titanium dioxide (TiO_2) is already underway.

However, TiO_2 displays a high activity only when it is irradiated by UV light , where the light wavelength is shorter than 400nm. In particular, the oxide is not suitable to decompose the contaminants in indoor environments where there is a little of UV light, for example, in the case of sick house syndrome. Therefore, the key to indoor applications of photocatalysts is research and development of a visible light-sensitive photocatalytic material.

Our group began developing new types of visible light-sensitive photocatalysts using a material design method based on crystallographic science, and has succeeded in developing a number of new photocatalysts which display a high activity in decomposing organic substances when irradiated by visible light.

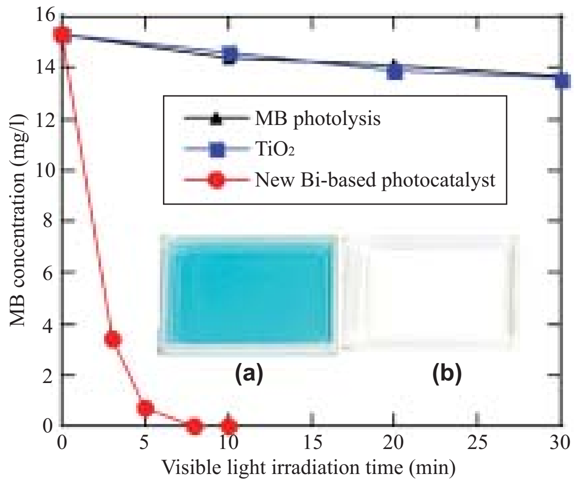

Fig.1 Decomposition of methylene blue (MB) on a new Bi-based photocatalyst under visible light irradiation Photo (a), before irradiation; (b), after irradiation with visible light for 8 minutes.

Figure 1 shows the decomposition of methylene blue (MB) with time on a Bi-based oxide photocatalyst, in comparison with MB decomposition on TiO_2 and MB photolysis. On TiO_2, the MB decomposition rate was extremely slow in the visible light range and showed no significant difference from MB photolysis. However, in the presence of the newly developed photocatalyst, MB was completely oxidized and decomposed, and the MB solution changed from blue to colorless (transparent), as shown in the inserted figures (a) and (b), in a remarkably short time of 8 minutes when exposed to visible light.

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Detoxification of Organic Chemical Substances using Photocatalysts

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Photocatalysts are materials which act to decompose certain chemical substances in the presence of light. Following the recent discovery that titanium dioxide (TiO_2) effectively decomposes chemical substances in the presence of UV light, application to a variety of fields has been expected, including decomposition of environmental endocrine disrupters, purification of atmospheric pollutants, and decomposition and removal of dioxins, etc. Beginning in 2000, NIMS launched a research project to study the decomposition/ detoxification of harmful chemical substances using photocatalysts.

Three categories of catalysts are included in the NIMS research; the above-mentioned TiO_2, zinc oxide (ZnO), and hollandite compounds (tin oxide-based compound oxides).

In the category of TiO_2 catalysts, a high efficiency photocatalyst was developed by producing a porous thin film on a glass plate and embedding TiO_2 to the inner pore walls, greatly increasing the catalyst concentration per unit of area. The thin catalyst layer formed on the glass plate is transparent and transmits light. Although the catalyst layer is thin, its highly-porous open structure gives it a large specific surface area, and the fact that it is transparent means that the photocatalyst can utilize light from various directions. As a result, a high decomposition rate, 13 times greater than that of commercially-available high efficiency titanium oxide catalyst P25, was obtained in acetaldehyde decomposition tests (Fig. A).

In research on ZnO, an innovative method of utilizing visible light as well as UV was devised. A fine-grained membrane was formed by adding nanosized tungsten and nitrogen compounds to the Zn compound and spraying this mixture on a heated substrate. In decomposition tests with acetaldehyde under visible LED blue light, this N-added tungsten-Zn oxide-type catalyst (N-added WO_3-ZnO) achieved a decomposition rate more than twice as fast as the above-mentioned P25 catalyst (Fig. B).

With hollandite compounds, efforts are being made to improve catalyst performance by high purification. In tests using one type of highly toxic dioxin-related compound (PCP), decomposition with the P25 catalyst was limited to only 44%, but in contrast, 94% decomposition was achieved in the same time with high purity hollandite (Fig. C).

We are now carrying out joint research with businesses and others with the aim of developing practical uses for these three new types of catalysts in applications which take advantage of their respective strengths.

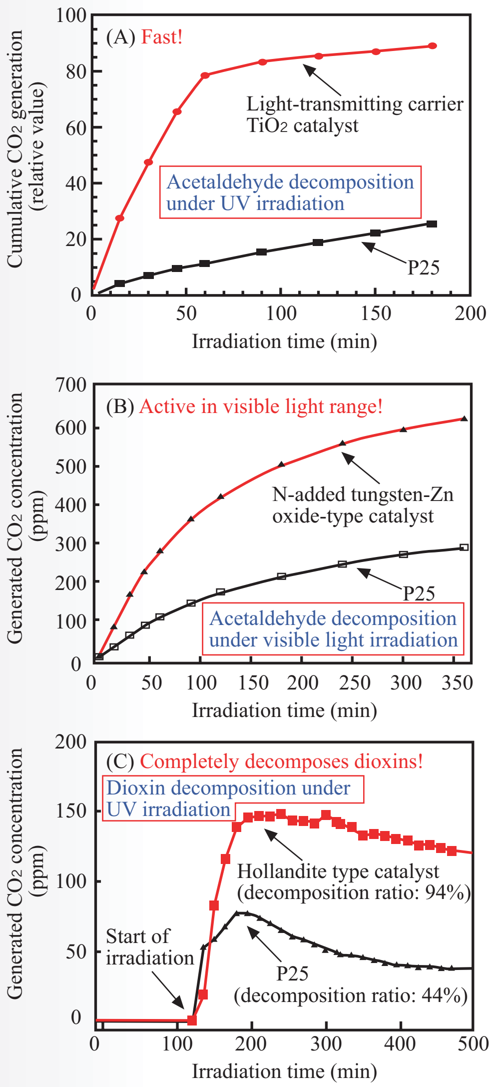

Fig. Performance of test photocatalysts in decomposition of toxic organic substances (Using CO_2 generated by decomposition of organic substance as index of reaction).

Utilizing Impurities to Strengthen Recycled Resources

—Upgrade recycling creates high strength steel from ordinary scrap—

Yoshiaki Osawa
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One important task for building a recycling-based society is improvement of material recyclability. However, the increasing use of composite materials and combinations of heterogeneous materials to create higher performance products causes serious problems in the recycling stage. For example, scrap containing large quantities of hard-to-remove metallic impurities called "tramp elements" is generally buried in landfills without recycling. In particular, the development of effective uses for scrap containing impurities has been strongly desired in recent years due to the shortage of waste disposal sites, among other reasons. Eco-Circulation Processing Group is therefore developing new processes which positively utilize impurities as strengthening elements. The following describes scrap utilization processes for recycled steel containing (1) copper and (2) aluminum. The former applies powder metallurgy technology (PM) to steel scrap containing copper impurities, which is typically generated when automobiles are recycled, while the latter applies casting technology to steel scrap containing aluminum, which is a product of can recycling.

In the shredder process, steel recycled from scrapped automobiles is contaminated with copper from small motors, harnesses, and other components built into cars. Because it is difficult to remove copper from steel with conventional refining techniques, we investigated a method of applying PM technology to form a microstructure containing finely dispersed copper. First, iron powder with a micro-

Design of High Performance Electrolytes in Solid Oxide Fuel Cell using Nano Structure Control

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Ecomaterials Center (EMC)

Compact, high-output fuel cells have been proposed as one solution to the problems of reducing CO_2 emissions and meeting rising energy demand, and are now the object of intense R&D work. Possible applications now under study include power sources for private power generation by individual households and small businesses, power supplies for next-generation humanoid robots, etc.

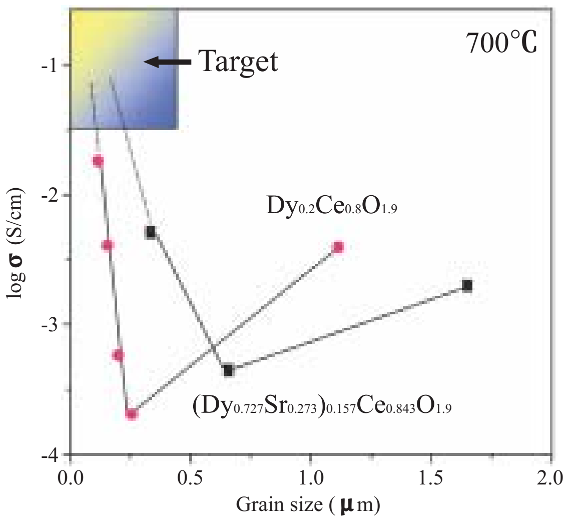

Fig.1 Relationship between grain size and conductivity.

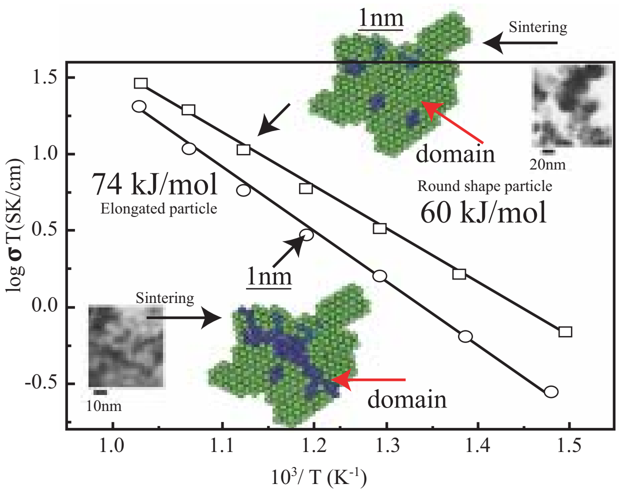

Fig.2 Influence of sinter particle morphology and domain size on conductivity.

Because high-output will be a requirement in this type of compact fuel cell, R&D on solid electrolytes for fuel cells with high outputs in the 500℃-700℃ temperature range is indispensable.

In the present research, rare earth doped ceria attracted our attention as a candidate solid electrolyte which is suitable for fuel cells operating at temperatures of 700℃ and under. We attempted to improve the performance of doped ceria compounds through a process which involved synthesizing nano powders and controlling the powder morphology, analyzing the refined structure at the nano-level, and studying its effect on conduction properties.

With nitrate as the starting material, we were able to modify the powder morphology from a spherical shape to a columnar shape at the nano-size level by the coprecipitation method, using ammonium carbonate or ammonium hydrogen carbonate as a precipitant.

Figure 1 shows the relationship between the grain size of high density sintered bodies manufactured from spherical particles at various sintering temperatures from 1000℃ to 1450 ℃, and conductivity (measured by the DC 3-pont method). Although it had previously been thought that conductivity would decrease as the grain size was reduced, the conductivity of dense sintered bodies with a nano-order grain size is expected to exceed that of micron-order dense sintered bodies.

Next, as shown in Figure 2, we found that powder morphology strongly influences conductivity in dense sintered body. TEM observation and other investigation results showed that minute regions in the sintered body called domains, which comprise from 20 to 50 atomic units, have a profound relationship with the manifestation of this property. Thus, our aim is to realize high performance in a solid electrolyte by controlling the distribution and size of these nano-order domains.

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structure containing copper precipitated at the 10 nanometer order is produced by rapid solidification using a high pressure water atomizing method developed by NIMS. Next, hardening forming is performed at low temperature (873K) to maintain the rapid solidification structure of the powder. Our research to date has revealed that material with extremely high strength (approximately 900MPa) can be obtained by strengthening with a dispersed structure of nanometer-size copper.

On the other hand, large quantities of scrap containing a mixture of ferrous alloys and aluminum alloys, which are the most commonly used metallic materials, are also generated by recycling. For example, the tops of steel beverage cans are made of an aluminum alloy, and even assuming a shredder is used, about 60% of the can-top remains attached to the can body. Our attention was drawn to the fact that the allowable content of alloying elements is relatively high in cast iron, except in certain special cases, suggesting the possibility of using recycled steel cans as a material for cast iron. The results of our study showed that carbides form in the aluminum content range of 10~16%, which substantially improves wear resistance, as shown in the figure. We also observed improvement in high-temperature oxidation resistance characteristics due formation of alumina on the cast iron surface, and improvement in the damping property, which is thought to be due to magnetic domains.

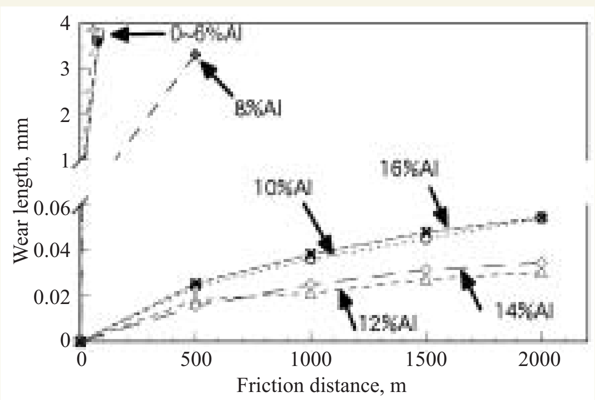

Fig. Wear resistance of Al-containing cast iron.

As demonstrated by these examples, impurities in recycled material can be positively utilized by applying ingenuity in the manufacturing process. This thinking is one key to "upgrade recycling," in which used products, which had conventionally been considered waste, are recycled upward into higher performance, higher value-added products.

Water Purification with Superconducting Magnets

—High volume purification of water containing trace amounts of arsenic and endocrine disrupters—

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High Magnetic Field Center, NIMS

Kazunari Mitsuhashi
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University of Tsukuba

Hidehiko Okada
Advanced Science and Technology Institute of Iwate

A superconducting magnetic separation system was developed to enable high volume, high speed purification of dilute suspensions of environmental endocrine disrupters in water. In this technique, called "magnetic seeding," special whiskers are formed on micron-sized magnetic particles to adsorb endocrine disrupters, which become entwined in the whiskers and are then captured by a magnetic force.

Endocrine disrupters are chemical substances which disrupt the functioning of hormones in the body. Approximately 65 types are thought to exist, including nonyl phenol, which is a raw material for industrial detergents, bisphenol A, which is used in plastic tableware and similar products, the dioxins, and others. Among these, Japan's Ministry of the Environment has designated nonylphenol as an endocrine disrupter in shellfish, and there is concern that it also affects the human body.

In response to the global problem of environmental endocrine disrupters, the Magnetic Field Applications Group developed a technology for efficiently adsorbing and separating these substances by the magnetic separation method employing a superconducting magnet. Using the experimental device shown in the picture, we demonstrated that water containing bisphenol A or nonylphenol can be purified to 1/10 the original concentrations of these substances when passed through a superconducting magnet at a flow rate of 20L/min, and further, that the magnetic seed substance can be reused any number of times.

As features of the Bi2223 superconducting (sc) magnet used here, the strength of the magnetic field can be changed far more rapidly than with metal-type sc magnets, enabling high efficiency adsorption/separation.

We also installed this magnetic separation system at a geothermal power plant in Iwate Prefecture (in northeastern Japan) and are currently conducting research on a purification technology for effective use of geothermal water. In this collaboration project, we developed a magnetic seeding substance which adsorbs toxic arsenic and succeeded in purifying geothermal water to below the standard concentration for effluents established by Ministry of the Environment. This demonstrated that geothermal water can be detoxified sufficiently for release into rivers. By enabling direct use of geothermal water, which had previously been impossible, this technology will greatly expand the potential of geothermal power as a new energy source.

Because magnetic separation does not generate used filters, and therefore does not cause secondary waste, it has the advantage of environment-friendliness. It is also suitable for a wide variety of applications, as it can be used in extreme environments characterized by high/low temperatures, acids/alkalis, and radioactive substances.

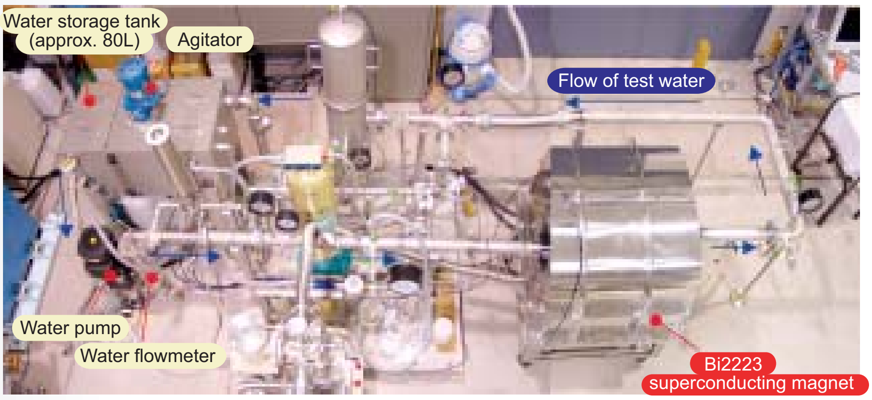

Fig. Experimental water purification device using a superconducting magnet.

Cooperation with Pohang Research Institute of Science and Technology (RIST) in Korea

On July 29, 2003, the Materials Engineering Laboratory (MEL) signed an MOU for cooperative research in the field of smart materials with the Pohang Research Institute of Science and Technology (RIST) in Korea. The goal of this agreement is to develop practical applications for smart materials, which have been the object of basic research at both institutes to date, through a synergy of the respective technical strengths of the two parties. Concretely, development of processing technologies will be conducted at RIST, using ferrous shape memory alloys developed by MEL, and MEL will be responsible for damage assessment of smart boards being researched at RIST. This agreement opens the way for a new form of research on smart materials, with the two institutes serving as core laboratories for research in Korea and Japan, respectively.

Reliable Analysis Technology Supporting Lead-Free Solder Packaging

Yoshiharu Kariya
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—Toward development of high-reliability, low-environmental load micro connections—

Proposed directives for Restrictions on Harmful Substances (RoHS) and Waste Electric and Electronic Equipment (WEEE) have finally been approved by the European Council and are scheduled to take effect in 2006. Full-scale practical application of lead-free soldering is being introduced as part of these moves.

Pb-free soldering in electronics is not simply a matter of eliminating lead from the product; mechanical reliability, including fatigue of solder joints and similar properties are also critical. This is particularly important in the fine interconnections used in LSI packages. The CTE (thermal expansion coefficient) mismatch between Si chip and organic substrate (2.6ppm/K and 18ppm/K, respectively) imposes a significant cyclical inelastic strain into the solder joints as shown in Fig. 1, due to the Joule heat generated by Si chip operation and external temperature changes. Ultimately, this can lead to fatigue damage of solder joints, as illustrated in Fig. 2. Although electronic boards contain an extremely large number of such joints, the failure (electrical open) of a single solder joint could render an entire electronic assembly inoperable. Moreover, when electronic components are used for control and safety devices in transportation, device failure can result in serious accidents.

At present, efforts to develop practical Pb-free solder center on Sn-Ag-Cu system alloys, which offer comparatively high reliability. However, with increasing miniaturization of electronic packages, Pb-free solder alloys with higher fatigue durability are needed. In developing the packages to meet these higher reliability requirements, test and analysis techniques which enable accurate evaluation of the mechanical reliability of extremely small joints are indispensable.

The Eco-Device Group developed a micro fatigue testing machine which makes it possible to apply a cyclical strain load to fine pitch LSI package interconnections and a computer-based high-accuracy stress and inelastic strain analysis technique, supporting the development of Sn-Ag-Cu family with enhanced fatigue durability. At present, we are using these analysis technique not only in the development of higher-reliability Pb-free soldering materials, but also in the development of packaging techniques which achieve both further size reduction and lower environmental loads by using materials other than solder alloys, such as conductive adhesive.

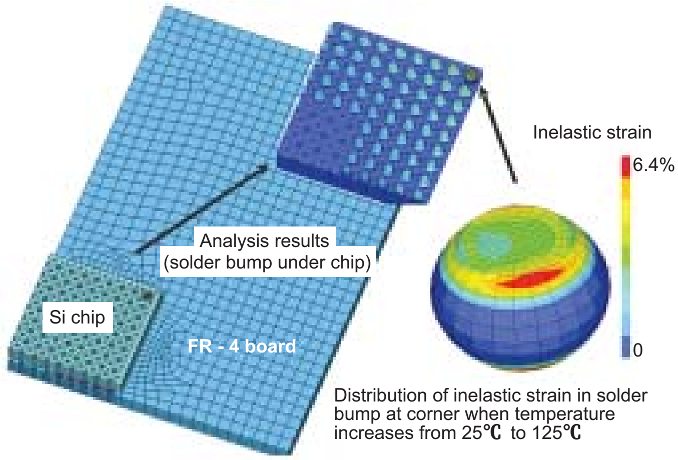

Fig.1 Example of inelastic strain distribution during thermal fatigue in flip chip solder bump by finite element method (FEM) analysis (1/4 symmetrical model; elastoplastic creep simulation). Large inelastic strain can be noted in the solder bump located in the corner.

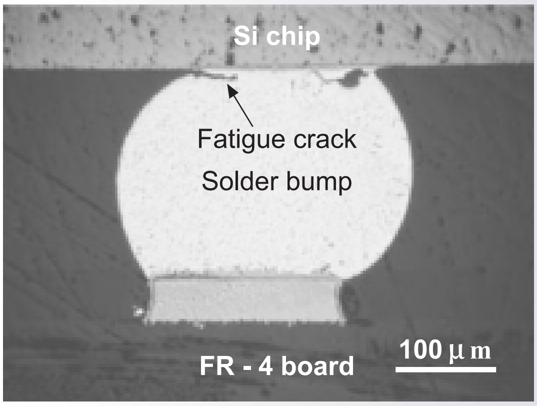

Fig.2 Fatigue crack propagation in solder bump. A fatigue crack can be observed at the point corresponding to the strain concentration in FEM analysis results (after 100 cycles).

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Environmental Purification using Photocatalysis

Figure 2 shows the decomposition curves for acetaldehyde, which is the main component of tobacco smoke, using a new Ba-based oxide photocatalyst. Acetaldehyde is effectively decomposed into CO_2 in a wide range of visible light wavelength up to 640nm.

As can be understood from these examples, high expectations are placed on these newly developed photocatalysts to remove a variety of harmful organic substances.

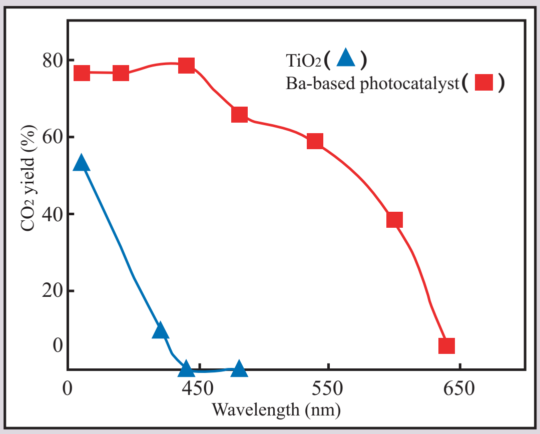

Fig.2 Acetaldehyde decomposition on a new Ba-based photocatalyst under visible light irradiation.

Development of New High Temperature Materials for Ultra-High Efficiency Gas Turbines

Tadaharu Yokokawa
High Temperature Materials Group
Materials Engineering Laboratory (MEL)

Gas turbines are used in numerous industrial fields, including thermal power generation equipment and jet engines, and have become an indispensable part of modern life in Japan. On the other hand, approximately 30% of Japan's total CO_2 emissions can be attributed to thermal power generation. At present, the thermal efficiency of thermal power plants is approximately 40%, but a substantial improvement in this figure, achieving a corresponding reduction in CO_2 emissions, is desirable for preventing global warming. Increasing the combustion gas temperature is extremely effective for improving the thermal efficiency of gas turbines. However, the development of new heat-resistant materials is essential for realizing higher operating temperatures.

The High Temperature Materials 21 Project in which our group is engaged has succeeded in developing an Ni-based single crystal superalloy with the world's highest temperature capability of 1100℃ (temperature at which material can be used for 1000 hours under 137MPa stress without creep rupture). The newly developed superalloy (TMS-162) is strengthened, based on a NIMS alloy design program, by increasing molybdenum (Mo) addition and refining the interfacial dislocation network formed at the conformity interface between precipitates in the alloy and the matrix (Fig. 1), and the microstructure is stabilized by increasing ruthenium (Ru) addition. Using this alloy, the turbine inlet gas temperature can be increased from the current 1100~1300℃ (blade temperature capability, 900~950℃) to 1700℃, making it possible to construct a liquefied natural gas (LNG)-fired ultra-high efficiency combined cycle power plant with total thermal efficiency exceeding 60%. (As shown in Fig. 2, because turbine blades are used with internal cooling, the blade surface temperature is normally lower than the turbine inlet gas temperature.)

A 20% improvement in the total thermal efficiency of thermal power plants, as described above, would reduce CO_2 generation per unit of electric power by more than 30%. This means that total CO_2 emissions in Japan could be reduced by 10% by adopting ultra-high efficiency combined cycle power generation at the country's large power plants, which would make a very large contribution to achieving the 6% target for reduced CO_2 emissions set for Japan under the Kyoto Protocol.

In other power engineering applications, this alloy will make it possible to develop high output/high efficiency jet engines and cogeneration systems (power generation + waste heat boiler), and thus can be expected to substantially reduce environmental loads, while contributing to effective practical measures to prevent global warming and effectively use energy resources.

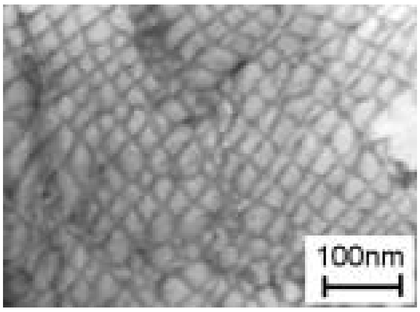

Fig.1 Transmission electron microscope (TEM) photograph of Ni-base single crystal superalloy strengthened by refining the interfacial misfit dislocation network between precipitates and the matrix to 25nm, with stabilization of the microstructure by ruthenium addition.

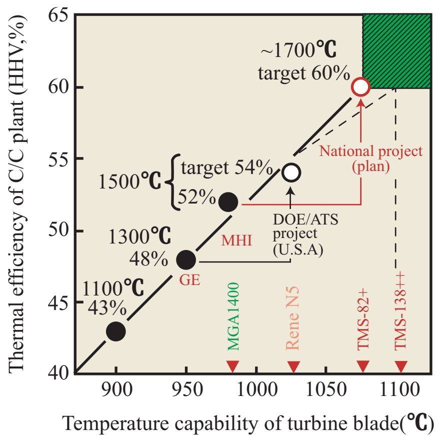

Fig.2 Relationship between thermal efficiency in combined cycle power generation and service temperature of turbine rotor blade (red, alloys developed by NIMS; area in green at upper right, development target of this project).

Cooperation with Bratislava Welding Laboratory in Slovakia

The Steel Research Center (SRC) concluded an MOU for research cooperation with the Slovakia's Bratislava Welding Laboratory (VUZ) on July 3, 2003. The aim of this arrangement is realize more active research cooperation and information exchanges in connection with advanced welding metallurgy in the field of safe materials and to accelerate the development of practical applications, particularly through cooperation in research on evaluation techniques for high-performance welding materials, such as low transformation temperature welding materials, etc. Another important aim of this MOU is to establish an exchange program with a European partner creating opportunities for young researchers of NIMS. Further expansion of this program is expected in the future.

Research Related to Development of Heat-Resistant Steel for Thermal Power Plants with Reduced CO_2

Hirokazu Okada
Heat Resistant Design Group
Steel Research Center (SRC)

In recent years, reduced emissions of CO_2 gas have been required from the viewpoint of preventing global warming. A large reduction in these greenhouse effect gases (GHG) could be achieved by improving the generating efficiency of fossil fired power plants. Because the temperature of the steam (currently approximately 600℃) used to drive steam turbines must be increased to around 650℃ to achieve this, it is necessary to develop materials with improved high temperature strength, and particularly, improved creep characteristics (creep: phenomenon of deformation and rupture in long-term service at elevated temperatures).

To date, the Heat Resistant Design Group has developed a high Cr ferritic type heat-resistant steel with excellent high temperature strength, and at the laboratory level, has discovered materials with properties exceeding those of currently existing products. Figure 1 shows the relationship between applied stress at 650℃ and the time to rupture under stress (creep life) of these new materials in comparison with P92 steel, which possesses the highest strength among conventional ferritic heat-resistant steels. The newly developed materials are a high B steel, which is strengthened by a high boron content of approximately 100ppm, and a nano-nitride steel, which is strengthened with nano-order nitrides. Both materials offer creep strength substantially exceeding that of existing steels.

Power plant piping (steam mains) is large in scale, with outer diameters of 400~600mm, wall thicknesses of 50~100mm, and lengths exceeding 100m, and furthermore, has a welded structure. Therefore, as two basic requirements for practical application, it must be possible to produce large pipes from the developed materials in the manufacturing process, and welds must be tight and display satisfactory creep strength in the weld zone. Figure 2 shows the results of an investigation of the hot formability (hot rolling properties) of the high B steel, which was carried out to evaluate the feasibility of pipe manufacturing. Conventionally, excess boron addition is thought to reduce hot workability. However, this deterioration in mechanical properties is caused by coarse BN inclusions. In the new steel, the formation of BN inclusions is suppressed by reducing the N content to several 10ppm, resulting in excellent temperature ductility, surpassing that of conventional steel, in addition to high strength. Although still on a small scale (OD: 84mm, thickness: 12.5mm), pipes have been successfully trial-manufactured from the high B steel, and research on welding has begun.

In the future, we hope to accelerate R&D aimed at practical application of this new steel, including R&D of welding materials, with the cooperation of private-sector companies.

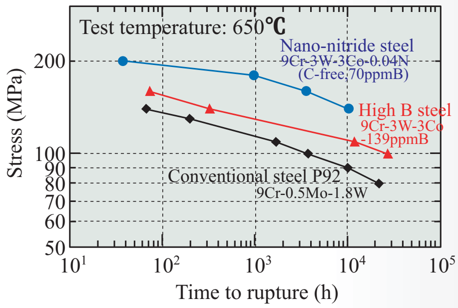

Fig.1 Creep strength of developed steel.

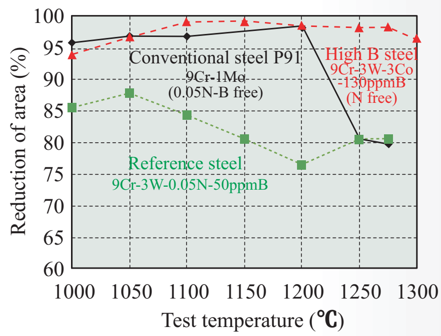

Fig.2 Hot workability of high B steel.

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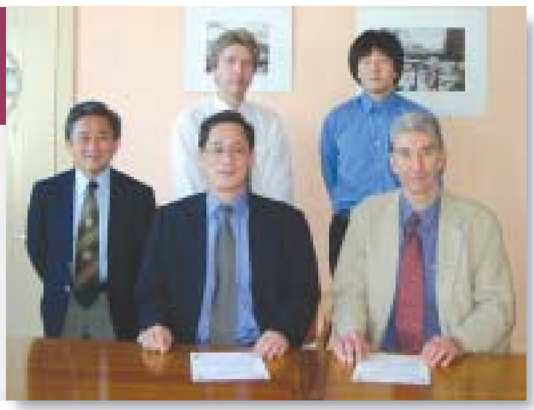
3rd Meeting of NIMS Advisory Board

A meeting of the NIMS Advisory Board was held on August 20-21 at the Hotel New Otani Makuhari in Chiba. At the meeting, leading Japanese and international researchers with expert knowledge of materials science who serve as Advisors to NIMS presented advice and proposals for improving management and efficiency and assigning priorities and directions for research.

This 3rd Advisory Board meeting included Advisors from four foreign countries (US, UK, France, Germany). Reports on the NIMS management system and recent research results were presented, and Advisors offered advice on future policies for establishing NIMS' position as one of the world's top-ranking laboratories.

Research Tie-up with University of Bristol in UK

On June 20, 2003, the Biomaterials Center (BMC) concluded a Memorandum of Understanding (MOU) on research cooperation with the Centre for Organized Matter Chemistry, School of Chemistry, University of Bristol (Professor Stephen Mann). The two institutions plan active human exchanges and exchanges of technical information with the aim of elucidating the mechanism of hard tissue formation in living organisms and, on this base, developing new material synthesis methods.



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