Special Review

Review

Research and Development of Ceramics-related Components and Materials at Toyota Central R&D Labs., Inc.

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ABSTRACT This paper briefly reviews ceramics-related activities at Toyota Central R&D Labs., Inc. A new concept called "anion-substitution ceramics" was created in the process of research aiming to improve the energy conversion efficiency of heat engines, which led to the development of high-temperature structural ceramic components. Novel surface treatments for steel using diffusion and chemical reactions have been developed and widely used industrially for tools and molds to form carbide surface layers with excellent adhesion strength. Basic research on clay minerals has not been limited to the development of adsorbents, but has also led to the development of unique hybrid materials consisting of polymers and ceramics in the inorganic/organic boundary region. This research has also led to the creation of periodic mesoporous organosilicas as well as inorganic mesoporous materials. Newly developed ceramic powders have helped to boost the performance of catalysts for emission control of combustion engines. Physics-based research into ceramics and the development of manufacturing processes have contributed to a number of distinguished achievements with the capability to facilitate the realization of a sustainable society, such as visible light sensitized photocatalysts, ultrahigh-quality silicon carbide single crystals, high performance lead-free piezoelectric ceramics, and so on.

KEYWORDS Ceramic Components, Clay Minerals, Hybrid Material, Silicon Nitride, Emulsion Combustion Method, Silicon Carbide Single Crystal, Lead-free Piezoelectric Ceramics

1. Introduction

Ceramics, such as porcelains, glass, bricks, and cement, are hard, rust-free non-metallic inorganic materials that are resistant to heat and friction. They are widely used in industry as well as in daily life. Advanced ceramics, which mostly use high-purity artificial raw materials and are produced by automated processes, have developed remarkably in the latter half of the 20th century. Quality-controlled advanced ceramics have been mainly used as components of electric/electronic devices and machinery. Depending on the application, these materials are referred to as electronic-, structural-, optical-, bio-ceramics, and so on, demonstrating the importance and diversity of ceramics in modern life. Advanced ceramics are sometimes used as coatings that improve the surface hardness and lubrication properties of components, as well as in bulk applications for accomplishing various functions. Unfortunately, as most advanced ceramics are used in electronic components, sensors, and actuators inside equipment and factories, there is little opportunity to see them directly in daily life.

Although many specific application examples of advanced ceramics have already been reported,(1) it should be noted that the development of high performance electronic ceramics and high-capacity ceramic powders for the electrodes of secondary batteries has contributed to the miniaturization and high performance of portable equipment such as personal computers and smartphones. Modern vehicles commonly use two types of advanced ceramics: structural ceramics in fundamental components such as gasoline engine spark plugs, diesel engine glow plugs, monolithic catalyst filters, window glass, and the like, and electronic ceramics in essential components for safe and comfortable driving, such as engine knock sensors, exhaust gas oxygen sensors, and so on. Electronic ceramics are being increasingly used as sensors, actuators, and secondary battery materials as electronic controls increase and the electric motorization of vehicles progresses.

This review introduces the ceramics-related technologies innovated at Toyota Central R&D Labs., Inc. (TCRDL), including sintered ceramics, single crystals, powders, coatings and hybrid/composite materials. Expert researchers in various fields have worked on the development of materials and components, and have created new technologies leveraging the advantages of ceramics. The first half briefly outlines noteworthy technologies concerning ceramics-related developments that were primarily conducted by researchers at TCRDL. The second half briefly describes the technical details of four research projects after 1980 in which the author participated. These are (1) structural ceramics: the development of injection molding of silicon nitride (Si_3N_4) for high-temperature engine components, (2) ceramic powders: the development of a new process to produce homogeneous and morphologically unique metal oxide powders, (3) ceramic single crystals : the development of a manufacturing process of ultrahigh-quality silicon carbide (SiC) single crystals for semiconductor substrates to enable highly efficient power control of electric vehicles, and (4) electronic ceramics: the development of environmentally conscious high-performance lead-free piezoelectric ceramics to reduce the use of harmful substances from vehicles.

2. Research and Development of Ceramics-related Materials at TCRDL

Research and development of ceramics at TCRDL were launched and driven for about twenty years by Osami Kamigaito. It started from the development of high-temperature structural ceramics with high mechanical strength, with the aim of increasing the efficiency of heat engines in the late 1960s.[2] As understood from the Carnot cycle, the energy efficiency of a heat engine such as a gas turbine increases as the operating temperature rises. For rotating bodies such as gas turbine blades, a small specific gravity has the advantage of generating a small inertia moment and is a favorable property for high speed rotation. Non-oxide ceramics such as Si_3N_4, aluminum nitride (AlN), and SiC, which have covalent bonding properties, were considered as suitable candidates to meet these requirements. These substances are not present in nature and were known to be intrinsically difficult to be sintered. After the acquisition of these substances as high-quality artificial powders, a feasibility study began by searching for sintering additives to promote densification.

In the process of investigating the sintering of Si_3N_4, a novel anion-exchange substance which essentially alters the physical properties of Si_3N_4 was explored at TCRDL. This new concept was reported to academia in 1971. Conventionally, the properties of ceramics had been modified by partially replacing only cations (metal ions) that coordinate with oxygen in oxide ceramics. Yoichi Oyama and Osami Kamigaito found a new solid solution by adding alumina (Al_2O_3) to Si_3N_4.[3] They synthesized a solid solution with the same crystal structure as Si_3N_4 by partial substitution of both cationic silicon (Si) and anionic nitrogen (N) with aluminum (Al) and oxygen (O) respectively at once. The solid solution was named SIALON (chemical formula: $Si_{6-Z}Al_ZO_ZN_{8-Z}$) by British researchers[4] who independently found the same substance almost at the same time. The discovery of SIALON contributed to the improvement of the oxidation resistance and high temperature mechanical properties, as well as the densification of the hard-to-sinter substance Si_3N_4. Furthermore, Hideyuki Masaki and Osami Kamigaito[5] discovered magnesium spinel ($MgAl_2O_4$) as an effective sintering additive for Si_3N_4 and succeeded in the sintering of dense and strong ceramics in a nitrogen atmosphere.

Ceramics were known to be brittle materials and it was necessary to overcome the drawback of abrupt destruction, which occurs without warning signs such as plastic deformation, to enable the practical use of structural ceramics. Many researchers all over the world worked to improve the fracture toughness of ceramics under the principle of crack propagation interference by means of the formation of rod-like grains, dispersion of secondary-phase fine grains, use of non-equilibrium crystalline phase grains, and the like. However, ceramics are fundamentally brittle, unlike steel and other ductile materials that break after yielding. Ceramic failures depend on the size and position of the defect at the fracture origin in the component, and are statistically processed by the Weibull distribution. Therefore, considering this statistical treatment, it was necessary to establish the principle of lifetime prediction and the proof test procedure of ceramics under real-world conditions[6] to enable the use of structural ceramics with confidence. Nobuo Kamiya and Osami Kamigaito[7] introduced a thermal fatigue life prediction theory for brittle materials to ensure reliability when using ceramics, and experimentally confirmed it through thermal shock experiments. New materials such as advanced ceramics were put into practical use as automotive components only after long-term reliability could be ensured. The result of this basic research influenced the design of ceramic components installed on vehicles. For example, it was applied to zirconia oxygen sensors installed in exhaust pipes and Si_3N_4 engine components manufactured by injection molding.

Another main subject of ceramics research in the 1970s focused on the recycling of window glass in end-of-life vehicles. This research was carried out in response to the need for recycling technology in anticipation of increasing automotive waste as vehicle use became more widespread. Technology was established to fabricate foam glass as a thermal insulator shown in **Fig. 1** through melting and foaming of waste glass. The project was conducted in collaboration with Toyoda Boshoku Corp. (now Toyota Boshoku Corp.) from around 1973.[8] Because the product consisted of thin-glass-wall closed pores, it was neither water-absorbing nor breathable, and was given the name Celoam (an abbreviation of "cellular foam"). Utilizing excellent strength and heat insulation characteristics, it was applied as the bottom parts, liquid-proof barrier linings, and piping insulation materials, and the like of liquefied natural gas storage tanks all over Japan. It was also used in household goods, walls to prevent dew condensation of large grain warehouses, and so on.

Researchers who had studied how to improve the surface properties of steel developed an epoch-making method to form a hard ceramic coating on the surface of steel. Tohru Arai and colleagues developed a novel surface treatment named the Toyota Diffusion Coating Process (TD process) in 1969, in which vanadium carbide (VC), niobium carbide and chromium carbide are formed on carbon-containing materials.[9] The process involved simply soaking a workpiece in a molten salt bath comprising mainly borax and carbide forming elements under an ambient atmosphere. A firmly adherent and dense carbide layer with a practical coating thickness of 5 to 15 µm can be grown on the substrate by the reaction between carbide-forming metal elements dissolved in molten borax and carbon atoms diffusing through the coating layer from the substrate. The Vickers hardness (Hv) of this VC coating is 3000 or more, which is far harder than hardened steel (Hv of about 700) or cemented carbide (Hv of about 1500). A carbide layer formed in this way is very hard and has excellent resistance to wear, seizure, scuffing corrosion, oxidation, and the like. The process is quite useful to improve the performance of dies, tools, knives, and machine components, and has been widely utilized in various fields of industry such as vehicle and electric appliance manufacturing, steel making, metal working, casting, wire making, and textile machinery fields.

One inconvenient process in this molten salt method was the hot water washing process to remove solvent adhering to the workpiece. A major improvement in the original TD process was achieved in the 1980s by the development of a large-scale fluidized bed furnace process that enables continuous treatment and prevention of solvent adhesion. This second-generation TD process improved the working environment and shortened the total process time. The technology has been started patent licensing since 1990 and applied to various components such as molds and the like.

Technology to form a low-friction coating on the surface of complicated metal components entered a new stage at the end of the 1980s at TCRDL with the development of a silicon-containing diamond-like carbon coating (DLC-Si). The developed process allows the high-speed formation of a coating with high adhesion strength using a relatively inexpensive plasma CVD method. Several DLC coatings of different recipes had already been developed around the world by that time. However, these could not be adopted in automotive components because of high process costs and the low adhesion strength of the coatings. Initially, although the DLC-Si coating was suitable for mass production, its adhesion strength was

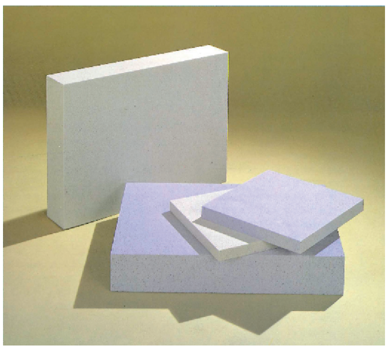

Fig. 1 Appearance of Celoam: A closed-pore inorganic insulation material.

not at a practical level. After various investigations of interface treatments, such as the formation of an intermediate layer, adhesion strength was found to be drastically improved by the introduction of plasma etching pretreatment of the workpiece, and a practical DLC-Si coating technology was finally established in 1997. The developed coating was a highly reliable hard film with heat and seizure resistance. It was applied to mainly sliding components because of its low friction coefficient and high durability during oil lubrication, and has been put into practical use in engine components, driving components, molds, tools, and the like since 2004. **Figure 2** shows a DLC-Si coated intelligent torque-controlled coupling clutch[10] developed in cooperation with JTEKT Corp., which was awarded the National Commendation for Invention in 2009.

TCRDL started basic research focusing on the utilization of clay minerals in 1980. Yoshiaki Fukushima and Shinji Inagaki found the swelling phenomenon of a smectite clay mineral, montmorillonite, in a polymer matrix in 1987 for the first time.[11] This finding resulted in an innovative development of Nylon-Clay Hybrid (NCH). The developed hybrid polymers demonstrated high tensile strength and modulus, high thermal distortion resistance, and low gas permeability. Arimitsu Usuki has already reviewed in detail the development and automotive applications of NCH.[12] Yoshiaki Fukushima and colleagues also studied the adsorption properties of a microporous clay mineral, sepiolite, which resulted in the development of humidity conditioners and deodorants.[13] Shinji Inagaki and colleagues synthesized a highly ordered mesoporous silica with a honeycomb-like pore structure derived from a layer silicate kanemite[14] and named it as FSM (Folded Sheet Mesoporous material). FSM was developed by modification of synthesis procedure for a layered nanoporous material reported by Kazuyuki Kuroda and colleagues, Waseda University.[15] Mesoporous silica is regarded as a promising material due to its characteristic adsorption properties, as well as due to the potential of utilizing uniform mesopores as minute reaction fields and the like. It is interesting that two mesoporous silica materials with the same structure but manufactured by different processes were developed and disclosed at the same time by researchers at TCRDL in Japan and at Mobil R&D Corp. in USA,[16] just like SIALON was independently and simultaneously discovered by the researchers of TCRDL and in the UK. Further remarkable progress was achieved by Shinji Inagaki and colleagues[17] who succeeded in synthesizing periodic mesoporous organosilicas (PMOs) in 1999. PMOs are a versatile inorganic/organic hybrid with well-defined nanoporous structures and high functionalities of the organosilica framework. Various organic species ranging from hydrocarbons to metal complexes are introduced into the pore walls of PMOs. They reported a crystal-PMO[18] schematically shown in **Fig. 3** with molecular scale periodicity of phenylene groups in the framework to Nature in 2002. This significant finding triggered the study of mesoporous materials throughout the world. These newly developed hybrid materials are expected to exhibit unprecedented properties due to their structural specificity, and it has already been confirmed that they demonstrate ionic conduction, luminescent properties, and the functions of a light-harvesting antenna.

In the field of electronic ceramics, TCRDL contributed to the development of resistor plugs for gasoline engines in 1975 to prevent the generation of electromagnetic noise from the spark plug and to

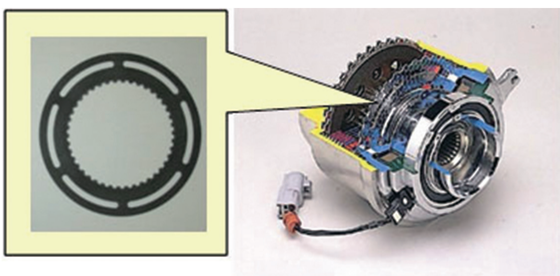

Photo Credit: JTEKT Corp.

Fig. 2 DLC-Si coated ITCC clutch.

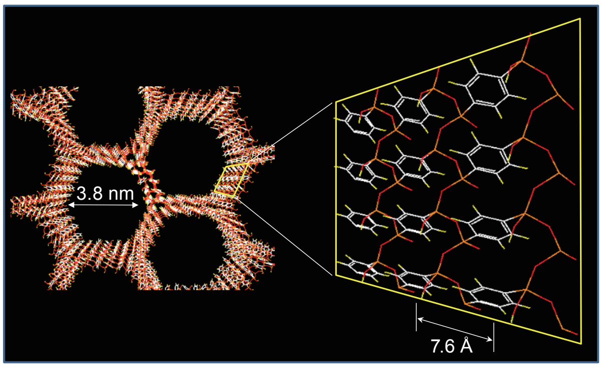

Fig. 3 Structural model of crystal-like periodic mesoporous benzene-silica.

ensure the sound operation of electronic equipment. In addition, TCRDL analyzed the characteristics of zirconia-based oxygen sensors and contributed to their commercialization in 1976. Oxygen sensors are absolutely necessary to control the exhaust emission of automobiles by catalytic systems. Since 1990, the major research subjects for ceramics have shifted from structural ceramics to electronic ceramics. Taking advantage of the accumulated structural ceramic technology, new research topics such as highly reliable utilization technology for piezoelectric ceramics were implemented. Material explorings of high performance lead-free piezoelectric ceramics for actuators were started as well as that of new mechanical quantity sensors. Microwave heating was studied for sintering of ceramics. Process development was also started to achieve SiC single crystal for wide band gap semiconductor substrates, to synthesize original metal oxide powders, to make crystal-axis-oriented ceramics, and the like.

The exhaust gas purification catalyst is an indispensable item for vehicles equipped with an internal combustion engine, and its continuous improvement has been one of the most important research projects at TCRDL. Catalyst researchers cooperated with engine engineers to create new ideas for improving the performance of the exhaust emission control system and worked closely with Toyota Motor Corp. and Cataler Corp. to continually improve the exhaust gas purification catalyst. In case of gasoline engines, a three-way catalyst plays a principal role. It simultaneously converts three major harmful emission gases, nitrogen oxides (NOx), carbon monoxide (CO), and fuel residues (HC: unburned hydrocarbons) into nitrogen, water and carbon dioxide gases. Noble metal fine particles such as platinum and rhodium play a catalytic function. The ceramic catalyst carriers on which these noble metal fine particles are loaded play an important role not only in maintaining catalytic activity for a long time but also in assisting the function of the noble metal catalysts. Since the three-way catalyst has high cleanup performance when the exhaust gas composition is in the vicinity of the theoretical air-fuel ratio, it is quite important to control the atmosphere of the catalyst against variations in the composition of the exhaust gas due to the operating conditions. The catalyst carrier has attracted attention for the purpose of adjusting the noble metal atmosphere, and a ceria-zirconia (CeO_2-ZrO_2) solid solution powder with a high oxygen storage capacity (OSC) was developed in the early 1990s.[19] Furthermore, the manufacturing method and layout of the OSC powder were successively improved to achieve high-performance exhaust gas purification. As shown in **Fig. 4**, the sintering of noble metals in a three-way catalyst can be effectively suppressed through these developments, and as a result, the initial purification performance can be maintained for a long period of time.[20] This material greatly contributed to improving the durability of automotive exhaust gas purification systems.

Titanium dioxide (TiO_2) is known to possess photocatalytic potential by ultraviolet light irradiation. Its strong oxidizing performance is actually used for the decomposition of harmful organic substances and its superhydrophilic action is used for the antifouling of glass. Since sunlight consists of about 5% ultraviolet light and 52% visible light, many efforts were conducted to realize a photocatalyst responsive to visible light. However, research was mainly devoted to cation substitution of TiO_2, and its improvement was limited. Takeshi Morikawa and colleagues studied the essence of the photocatalytic action of TiO_2 and investigated means to expand its excitation light wavelength from ultraviolet light to visible light. These efforts resulted in the development of a nitrogen-doped titanium oxide ($TiO_{2-X}N_X$) that effectively enabled a photocatalyst with a visible light response in 1999. This catalyst achieves the decomposition and removal of malodorous gas, as well as an antibacterial action by the visible light in a room. This is a typical material design born from the idea of controlling the band gap of semiconductors inherent in TiO_2, and technical information including theoretical calculations by Ryoji Asahi was published in the scientific journal Science in 2001.[21] A useful anion-substituted material

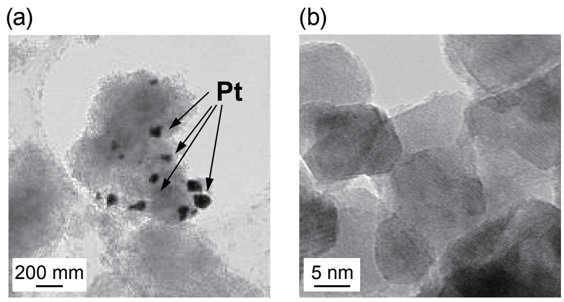

Fig. 4 TEM images of Pt loaded catalyst after ageing: (a) without OSC material, (b) with OSC material.

was invented again at TCRDL following SIALON. This material was commercialized by Toyota Tsusho Corp. in 2003 under the trade name V-CAT. It has expanded the indoor use of photocatalysts for applications such as textile products and furniture with deodorant, antibacterial, anti-fouling functions, as well as for neutralizing volatile organic compounds (VOCs) that are harmful to human health. Development of a visible light photocatalyst later became the beginning of research into artificial photosynthesis at TCRDL.

3. Introduction of Research into Ceramics and Processes

3. 1 Development of Ceramic Engine Components Using Advanced Structural Ceramics

The room temperature bending strength of Si_3N_4 was improved to about 700 MPa due to progress in pressureless sintering technology at TCRDL in 1978. Reflecting this result, TCRDL started developing injection molding technology for ceramics capable of producing complicated shape components in 1980, and jointly developed a pre-combustion chamber made of Si_3N_4 with Toyota Motor Corp. in 1981. The chamber, which is installed in the upper part of the main combustion chamber of diesel engines, is used to perform fuel injection, mixing of fuel mist and air, and spontaneous ignition. Since it is exposed to temperatures close to 1000°C, it requires excellent high-temperature strength and thermal shock resistance. An interdisciplinary project team consisting of researchers of ceramics, polymers, and injection molding was launched in TCRDL for promoting the joint development. The major development issues were (1) defect-free injection molding of a kneaded compound containing a high proportion of ceramic powder, (2) technology for removing organic components (dewaxing) from the molded bodies, and (3) composition design of organic compounds with good formability and easily dewaxing behavior. To overcome these issues, many prototypes were produced and a series of injection molding technologies were established to manufacture Si_3N_4 pre-combustion chambers with few defects up to the level of actual use. At the same time, TCRDL also developed a non-destructive inspection technique for complicated-shaped workpieces using ultrasonic diagnostics. A reliability of Si_3N_4 pre-combustion chamber was ensured through the improvement of an installation method in actual engines and an initial durability test in the engine operation. To prevent fracture of the chamber due to local thermal stress generated during engine operation, a steel ring was shrink-fitted to ensure reliability and durability. In August 1984, Toyota Motor Corp. launched a car with a high-power turbo diesel engine equipped with a Si_3N_4 pre-combustion chamber. **Figure 5** shows the configuration of the chamber installed in a commercial car.

These technologies accumulated during the development of Si_3N_4 chamber were applied to the joint development of a Si_3N_4 turbocharger rotor with Toyota Motor Corp., and the resultant product was commercialized in 1989. The biggest problem in the rotor development was unexpected breakage during operation test. This breakage was found to be induced by collision between the rotor blade tip and airborne particles, and countermeasures were applied to protect the rotor from breakage.

This Si_3N_4 ceramic material was subsequently improved by TCRDL to further increase its high-temperature resistance and strength, and was put to practical use in the hot extrusion molds of engine valves as shown in **Fig. 6**.

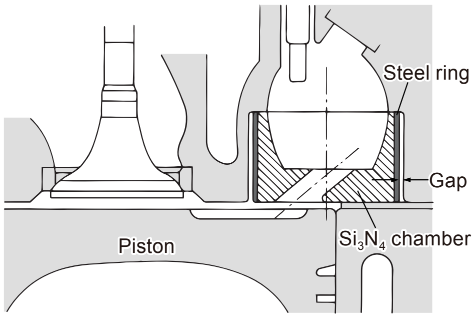

Fig. 5 Installation state of ceramic pre-combustion chamber.

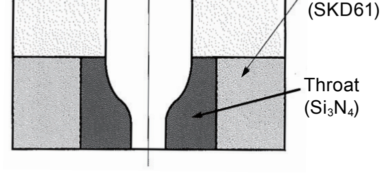

Fig. 6 Hot extrusion ceramic mold for engine valve.

3. 2 Development of Novel Process to Synthesize Characteristic Metal-oxide Powders

The development of a novel ceramic powder synthesis process called the emulsion combustion method (ECM) started in 1994. It was designed to synthesize characteristic spherical fine powder and homogeneous fine raw materials for sintering[22] based on an idea by Saburo Hori. At the time, the emulsion process was well known academically as a wet powder synthesis method of ceramics, and aqueous phase droplets of about 1 μm or less in the oil matrix were used as the isolated chemical reaction field for powder synthesis. ECM is a process developed with reference to an internal combustion engine and instantaneously synthesizing ceramic powders by spraying and burning an emulsion. An overview of the process is shown in **Fig. 7**. Sprayed emulsion droplets of tens of micrometers contain water droplets of less than a few micrometers into which the chemical components of the target product have been dissolved. Oil adjacent to water droplets burns instantaneously and each water droplet becomes an isolated reaction field to form metal oxide particles. Synthesized particles generally have a round shape and a homogeneous component distribution. Because of the short reaction period of this method, metastable crystal phase or hollow particle powders may be synthesized in some cases. ECM is a process with a simple synthesis apparatus, a small number of work steps, continuous operation, and very low contamination. Relatively inexpensive water soluble metal salts, which are obtained in the process of refining metals from ores, are used as raw materials, and complex oxide powders with a uniform component distribution can be synthesized because of the use of liquid raw materials.

Figure 8 shows the X-ray diffraction profiles of synthesized ZrO_2-CeO_2 powders that can be used as solid electrolytes and as OSC materials for exhaust gas purification catalyst. An aqueous solution of metal components is stirred vigorously in kerosene to form a w/o type emulsion, which is then subjected to spray combustion for the synthesis of a powder. As shown in the figure, almost all the complex oxides have a fluorite-type structure with the same peak layout as CeO_2, and the lattice spacing shrinks as the zirconium increases since the diffraction angle (2θ) of the peaks shifts to a higher angle. From the phase diagram of ZrO_2-CeO_2,[23] two phases coexist for these compositions in equilibrium state. Therefore, ECM is capable of synthesizing metastable solid solution powders. Since the peaks are notably broad in mixed compositions, the crystallite size was considered to be quite small. The crystallite diameter calculated from the X-ray diffraction method was about 10 nm, virtually matching the result of transmission electron microscope (TEM) observation.

Hollow and submicron size Al_2O_3 particles were synthesized by ECM using an aluminum nitrate aqueous solution as a raw material.[24] The particles

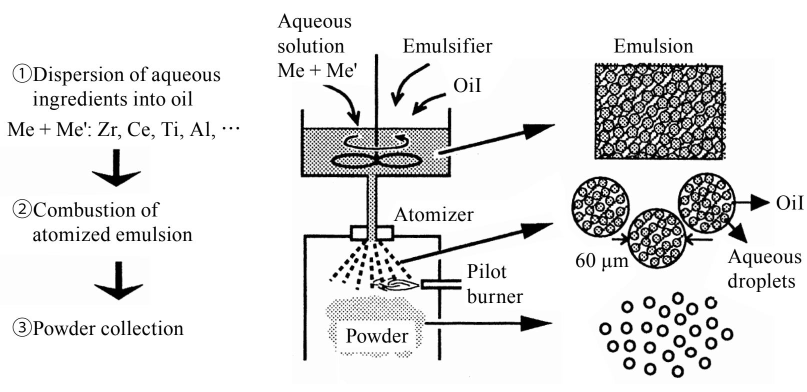

Fig. 7 Schematic diagram of powder production process by emulsion combustion method.

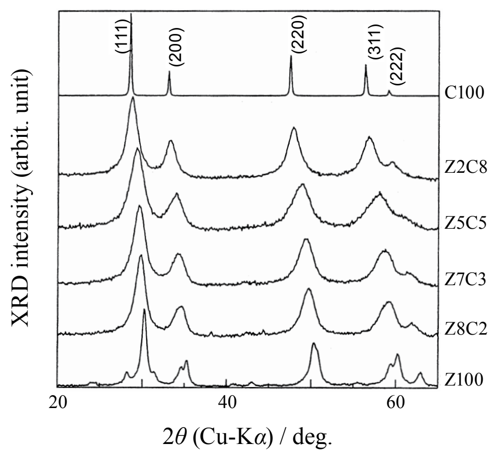

Fig. 8 XRD patterns of ZrO_2-CeO_2 powders synthesized by ECM. C100 is pure CeO_2 and Z100 is pure ZrO_2. Z2C8, Z5C5, Z7C3, and Z8C2 contain zirconium and cerium component in a ratio of 2:8, 5:5, 7:3, and 8:2, respectively.

shown in **Fig. 9** have a shell thickness of 10 to 20 nm and a specific surface area of about 50 m^2/g. The hollow structure and the crystalline phase of γ-Al_2O_3 were maintained up to 1000°C in atmospheric conditions. Conventionally, hollow particles of metal oxides are widely used for lightweight, heat insulating fillers, and the like, with a particle size as large as 30 to 3000 μm in general. Even with the small hollow particles already reported, the particle size is 5 to 20 μm and the specific surface area is less than several m^2/g. Since the hollow Al_2O_3 particles produced by ECM have unprecedented features, there is also interest in the development of fine hollow particles other than Al_2O_3.

ECM was developed with the aim of achieving uniform distribution of chemical components. In addition to the uniformity and reactivity of the synthesized powder, it was also found that a metastable crystal phase and fine hollow particles were synthesized. Applications that make use of these features are likely to be developed in the future.

3. 3 Development of SiC Single Crystals for High Power Semiconductor Substrate

Wide band-gap SiC semiconductors are regarded as promising replacements for Si devices in hybrid and electric vehicle inverters that require a control of large current. Highly efficient power devices can be realized since SiC semiconductors have better thermal stability, higher withstand voltage, and higher thermal conductivity than Si. One major challenge in achieving practical adoption was drastically improving the quality of the substrate SiC single crystals. The performance and reliability of devices using conventional SiC semiconductors could not be improved since crystal defects in the SiC substrate could not be sufficiently reduced. Since 1991, TCRDL started growing SiC single crystals in preparation for the spread of power electronics regarded as essential for vehicles in the future. From the middle of 1990s, this research was carried out in collaboration with Denso Corp.

SiC is a high-temperature ceramic used for the heating element of high-temperature electric furnace. It does not melt and sublimes at about 2800°C under atmospheric pressures. For this reason, the Czochralski process, which is used to obtain single crystals such as Si ingots from a melt, is not applicable to SiC single crystals. Therefore it is usually manufactured by the sublimation-recrystallization method, in which seed crystals are grown by physical vapor deposition at an extremely high temperature of 2000°C or more. Due to the ultrahigh temperature of this process and the many polymorphs of SiC, it is not easy to control the growth conditions and to reduce crystal defects. Crystal defects in a SiC single crystal are classified two types such as microscopic crystal defects called dislocations, and macroscopic crystal defects called hollow core dislocations (micropipes).

SiC becomes various different crystal structures depending on the synthesis conditions. The polymorphs are represented by symbols such as 2H, 4H, 6H, and the like in hexagonal system, 3C in cubic system, and 15R in rhombohedral system. In single crystal growth, the conditions must be strictly controlled to form a single type of crystal. A hexagonal-structured SiC typically has two growing directions, namely the axial direction of the hexagonal prism and the direction perpendicular to the axis. The former is called c-face growth, and the latter is referred to a-face growth. As a result of careful examination of the defects of single crystals produced under various synthesis conditions, Daisuke Nakamura found that a-face grown single crystals have a characteristic anisotropic defect structure and came up with an idea to synthesize a high quality SiC single crystal called the Repeated A-Face (RAF) growth process. This process comprises the following steps: (1) the first SiC single crystal "A1" is prepared by a-face growth of the original seed crystal, (2) using "A1" as a seed, a-face growth is performed again in the direction perpendicular to the growth direction of "A1" to make a second seed "A2", (3) the previous step is repeated up to N times until the crystal defects decrease below a certain critical level, (4) finally, an "AN" seed is formed by c-face growth. This process is schematically shown in **Fig. 10**. Each time a single

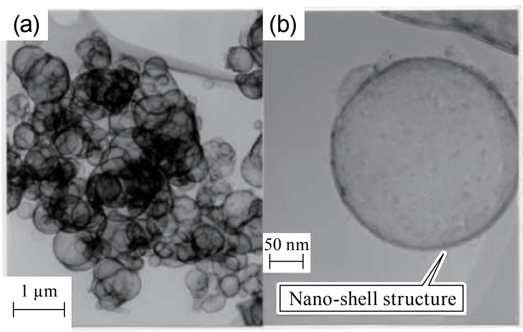

Fig. 9 TEM images of alumina hollow particles.

crystal is grown with the a-face growth direction changed by 90°, the number of crystal defects passed on from the former seed decreases, and a single crystal is finally grown with extremely few dislocation defects. By verifying this idea in experiments, a process was established to synthesize ultrahigh-quality SiC large single crystals.

Micropipe defects can be seen with an optical microscope, but fine crystal defects such as dislocation defects cannot be observed optically. To achieve quantitative defect analysis of a SiC substrate, two 4H-SiC single crystals were compared: a 2-inch diameter RAF substrate and a 1.2-inch conventional substrate. In a visual evaluation, both are shiny circular disks, and it is impossible to find a difference in quality. The analysis was carried out by an X-ray topography method using synchrotron radiation at SPring-8.[25] The RAF substrate in **Fig. 11**(a) is clearly much more homogeneous than the conventional substrate in Fig. 11(b). In addition, no micropipe defects were found in the RAF substrate, and the dislocation density was reduced to 1/100 of the level in the conventional substrate or less. A more detailed investigation identified two types of microscopic crystal defects: screw dislocations that are almost parallel to the direction of the c-axis, and basal plane dislocations with a complicated networking parallel to the bottom surface. In images, the former defect was observed as dots and the latter as arcs of white or black. Almost no basal plane dislocations were observed in the RAF substrate. Together with the other evaluation results, it was proved that the SiC single crystal manufactured by the RAF process has neither micropipe defects nor small-tilt-angle grain boundaries, with a dislocation density as small as 75 cm^{-2}, and almost no distortion of the crystal lattice over the entire substrate.

To examine the reliability of the SiC device, a PIN diode was manufactured and applied to current stress testing for about 4 hours under constant current conditions. **Figure 12** shows the results. With the PIN

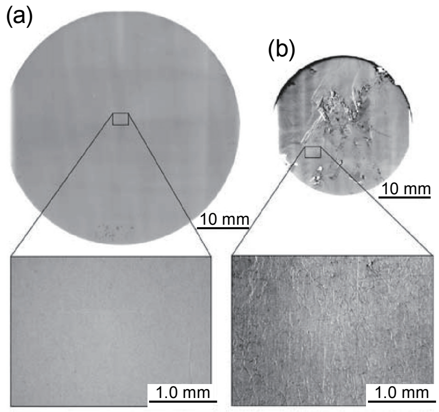

Fig. 11 Synchrotron radiation XRD topography of (a) RAF substrate and (b) conventional substrate.

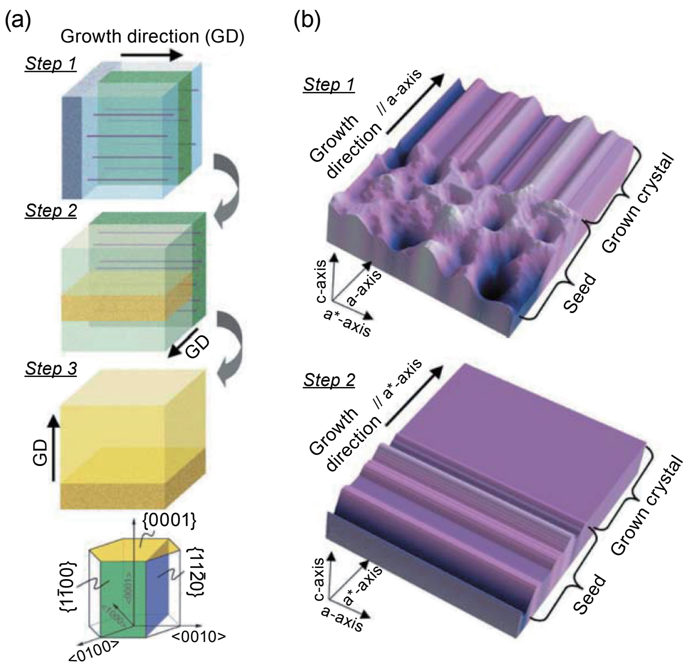

Fig. 10 Schematic illustration of RAF process and the reduction of defects.

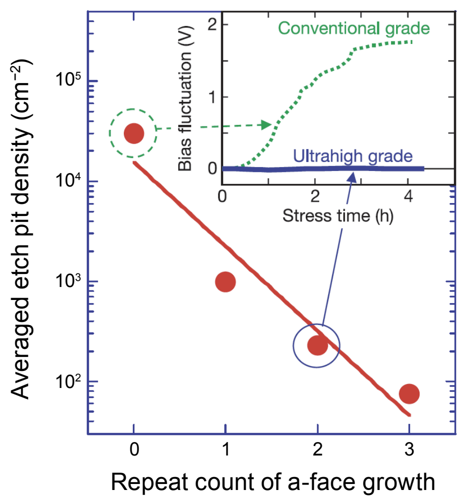

Fig. 12 Etch pit density of SiC substrate. The inset shows the forward bias fluctuation of PIN diodes fabricated using RAF and conventional substrates.

diode using the conventional substrate, the forward bias gradually drifted under constant current density conditions of 160 Acm^{-2}, whereas the PIN diode fabricated using the RAF substrate did not change even at 300 Acm^{-2}. Consequently, it was considered that stable operation was maintained for a long time even under high current stress.

A series of results on this ultrahigh-quality SiC single crystal growth was published in the scientific journal Nature in the 2004 issue,[26] and its breakthrough achievement was highly praised and contributed to the acceleration of SiC power semiconductor development.

3. 4 Development of Lead-free Piezoelectric Ceramics

The research of piezoelectric ceramics at TCRDL started with reliability studies and material developments of piezoelectric ceramic devices in 1990. Piezoelectric ceramics are widely used for knock sensors, ultrasonic sonar devices, buzzers, and the like, contributing to the improvement of vehicle performance. Many of these are made of ceramics that contain lead, and the development of lead-free piezoelectric ceramics to replace lead-containing materials is strongly required from the viewpoint of reducing environmentally hazardous substances in end-of-life vehicles. A number of studies have been made to improve the performance of piezoelectric ceramics since they were developed around 1950. As a result, the performance of lead-containing piezoelectric ceramics dramatically improved to the practical level by about 1970. On the other hand, many researchers around the world had mainly studied bismuth-based ceramics as leading candidates for lead-free piezoelectric materials that can be used in practical temperature ranges. Although the development of lead-free piezoelectric materials was regarded as important, their performance remained low and hardly improved until the end of the 20th century. For this reason, when the End of Life Vehicle regulations were enacted in Europe in 2003, lead-containing piezoelectric ceramics for engines were excluded because there were no alternative material candidates.

In a study of the composition of lead-free piezoelectric materials at TCRDL, Yasuyoshi Saito developed a new composition niobium (Nb) based perovskite type ceramic in 1998, which achieved a piezoelectric d_{33} constant of 230 pm/V, corresponding to an improvement of about 30% from conventional lead-free piezoelectric materials.[27] The piezoelectric d_{33} constant is a performance index of piezoelectric materials for actuators, and it represents the magnitude of displacement induced by the electric field with respect to the electric field strength. This Nb-based ceramic later became the basic composition of TCRDL's lead-free piezoelectric ceramics development.

Another research subject that aimed to improve the performance of electronic ceramics was started by Toshihiko Tani from process development focusing on crystal-oriented materials since 1995. Crystal-oriented ceramics, textured ceramics in other words, achieve anisotropic single-crystal-like properties in the polycrystals with the aim of maximizing performance in the desired direction, whereas an ordinary ceramic is characterized by isotropic properties. Researchers in Japan and the USA respectively reported textured ceramics in which crystal orientation was achieved by a templated grain growth method when microplates of a target compound can be prepared as aligned seeds. Unfortunately, for practical and useful piezoelectric perovskite-type compounds, the corresponding microplate crystals are rarely produced. In the crystal-oriented ceramic concept developed by TCRDL, microplate crystals are used as aligned reactive templates that topochemically reacts with complementary reactants to form the target composition with maintained crystallographic frameworks. It becomes a dense ceramic in which the crystal orientations of the grains are aligned uniaxially or triaxially. Even when a microplate of the target composition cannot be prepared, this process can be applied using a compositional design between the microplate and complementary reactants, and the target materials for texture engineering have expanded. The technology was named the Reactive-Templated Grain Growth (RTGG) process. In 1996, a Bi-based regular perovskite-type structured piezoelectric ceramics textured by the RTGG process achieved 92% preferred orientation as evaluated by the Lotgering's orientation factor, demonstrating that its piezoelectric properties are 1.6 times greater than conventional isotropic ceramics.[28] In 2000, this process was also proved to be applicable to the basic composition of Nb-based lead-free piezoelectric ceramics which would be studied later in the project.

It was highly appreciated as a technology to promote the development of lead-free piezoelectric ceramics for environmental conservation, and received the Corporate Environmental Achievement Award from the American Ceramic Society in 2004.

TCRDL and Denso Corp. started the collaborative development of high-performance lead-free piezoelectric ceramics as a hundred-week project in anticipation of continuing pressure to remove lead from vehicles. The targeted performance was a high piezoelectric d_{33} constant equal to that of lead-containing piezoelectric ceramics with a Curie temperature of 250°C or above, assuming use in a diesel engine fuel injection actuator, despite minimal prospects of actually achieving these targets. The core technologies of the project were material compositional design and the RTGG process design, and the high-level integration of both technologies was indispensable. In addition to these technical items, the motivation of the research team members was considered as another essential requirement to achieve these high goals. Researchers with excellent knowledge and skills were appointed to the project from within the company and from Denso Corp. Piezoelectric performance was gradually improved through ordinary sintering processes and vigorous composition studies based on the accumulated compositional design strategy. After 100 weeks, the targeted high performance was ultimately achieved using textured lead-free ceramics by the application of the RTGG process to the developed composition. The evolution of the piezoelectric d_{33} performance at room temperature of the developed compositions and their textured ceramics is shown in **Fig. 13** in the relationship between the d_{33} constant and the Curie temperature of the material. The Curie temperature is a measure of the upper operating temperature above which the ferroelectric body loses its ferroelectric property. The developed material is a (K, Na) NbO_3-$LiTaO_3$-$LiSbO_3$ system consisting of uniaxially oriented polycrystals of six metal components, a piezoelectric d_{33} constant of 416 pm/V, a perovskite-type crystal structure, and a 91% Lotgering's orientation factor. **Figure 14** shows the X-ray diffraction patterns of cross-sections of textured and non-textured ceramics of developed composition, and scanning electron microscope (SEM) images of the etched surfaces. The constituent grown grains of the sintered body using the RTGG process exhibit a strong preferred orientation compared with those using the conventional process.

The material technology of this high performance lead-free piezoelectric ceramic was published in the scientific journal Nature in the November 2004 issue.[29] For practical application, there are several issues remaining to be resolved, such as cost reduction and further performance improvement, but this material is expected to be widely applied in environmentally friendly piezoelectric components.

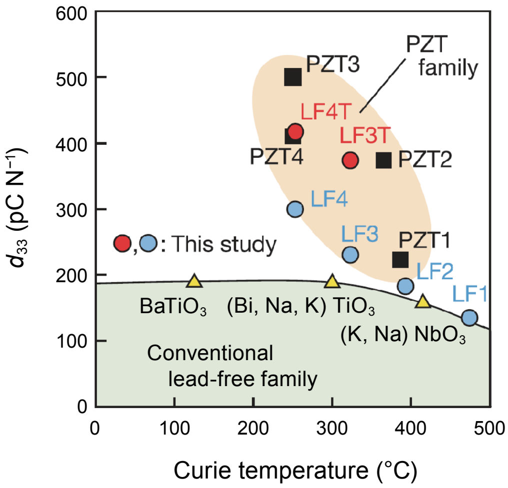

Fig. 13 Improvement of piezoelectric d_{33} performance at room temperature by composition development and crystal orientation.

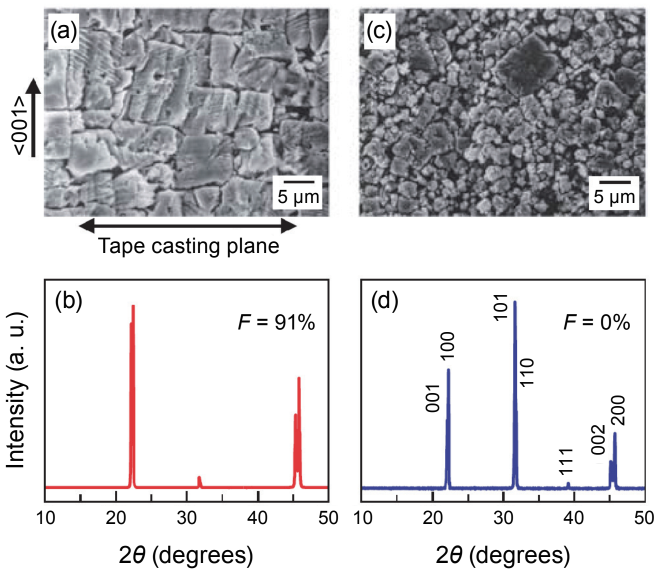

Fig. 14 Comparison of SEM images of etched cross sections and XRD patterns of the cross sections of sintered bodies using the RTGG (left) and conventional process (right).

4. Summary

This review has introduced several examples of research and development of ceramics-related components and materials at TCRDL, including sintered ceramics, single crystals, powders, as well as metal carbide hard films on steel, and inorganic-organic hybrid materials. Since ceramics have various specific electrical and optical properties as well as physical and chemical characteristics such as high hardness and high corrosion resistance, development targets are widely diversified.

All research topics are based on forecasts of future social requirements. Research projects of TCRDL are based on both ideas identified by laboratory researchers and items requested by stakeholder companies. The background to both types includes important technical issues for the future of stakeholder companies, which are aiming to contribute to society through manufacturing. One example was the development of high-temperature structural ceramics and their complicate-shaped components. TCRDL began their research around 1970 in preparation for high-temperature operation of next-generation vehicle engines. Another example is the development of ultrahigh-quality SiC single crystal substrates in anticipation of demand for high electric power control accompanying vehicle electrification. In the future, it is expected that innovative technologies including high-performance rechargeable batteries and power supply system will be created for clean vehicles.

The research style of TCRDL is thought to be advantageous for achieving set goals. In addition to researchers in the fields of ceramics, metals, and polymers, researchers in physics-related fields can work with experts of instrumental analysis. Researchers in material, mechanical, and electronics fields can share internal and external technical information with each other. In addition, cooperation with stakeholder companies greatly promotes the development of useful components and materials. For example, in the development of the diesel pre-combustion chamber, material researchers and processing engineers manufactured prototypes with reference to information on chemical and instrument analysis, as well as non-destructive ultrasonography. The initial durability tests of prototypes made by Si_3N_4 were carried out together with engine experts. Throughout the project, process development was promoted through joint research with engineers from Toyota Motor Corp. In order to overcome important technical issues, it is essential to fully consult with engineers with extensive manufacturing experience and cooperate with researchers including those from academia. In developing the in-vehicle piezoelectric actuators, highly reliable technology was realized through collaboration between Denso's engineers and TCRDL's instrument analysis and material experts.

It should be noted that material development is synonymous with process development. At the research stage of a material, the possibility realizing the expected characteristics is examined using all means based on principles and analysis results without considering the manufacturing cost. In the development stage, it is necessary for an experienced process engineer to optimize manufacturing control factors such as heat treatment conditions for realizing the microstructure with the target characteristics. Even though the same chemical constituents may be used, material properties often differ depending on the manufacturing process. A typical example is the RTGG process, in which the crystal axis orientation of the ceramic is controlled and the ultimate high-performance characteristics can be achieved only through the compatibility of compositional design and process control. In component development, since manufacturing cost is an important element, components with excellent performance are not necessarily put into practical use unless a manufacturing process with a reasonable cost can be realized. The presence and development of people familiar with materials and processing are essential.

Among the many ceramics-related research topics pursued by TCRDL, this review did not have the space to cover the examination of battery materials, or practical applications of thin films such as inorganic electrochromic films, light emitting diodes, and dielectric thin films for electroluminescence. In all cases, it was impossible to make the components without developing excellent manufacturing processes.

To realize a sustainable society through environmentally friendly materials, further improvements in the performance of energy-related equipment are required due to the remarkable advance of high performance functional devices. It is expected that ceramics will play an indispensable role in solid-state rechargeable batteries and solid-oxide fuel cells, while satisfying both safety and high performance requirements. Studies into artificial photosynthesis at TCRDL[30,31] have ingeniously used the semiconductor characteristics of ceramics, facilitating the potential creation of an emerging technology to help realize a sustainable society. A wide range of useful new products are expected to enter practical use, since ceramics demonstrate various functions depending on composition and microstructure. In addition, by exploring the boundaries and leading edge of conventional research fields, it is expected to develop new materials that make the most of the advantages of materials.

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