

Automotive and industrial applications of structural ceramics in Japan

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Abstract

This paper reviews the status of structural ceramics in Japan. Until around 1980, successful applications of these materials were limited to wear-resistant parts and structural components working under very low stresses. Considerable work has been done over the years on applying ceramics to mechanical parts used under higher stresses. This led to some successful applications of silicon nitride to automotive components, including turbocharger rotors and glow plugs. However, the recent market for silicon nitride automotive components has not been as large as was expected. Cordierite honeycombs for catalysts and diesel particulate filters made of silicon carbide are becoming more important applications in Japan.

It is noteworthy that the Japanese market for structural ceramics has been steadily increasing since 1985, with the leading applications being apparatus for purifying the exhaust gas of automotive engines and parts for semiconductor manufacturing equipment. Alumina, for example, is widely used for vacuum process chambers. High-purity alumina is also used for the components of liquid crystal device manufacturing equipment and various mechanical parts. The recent applications of structural ceramics in Japan summarized in this review include vacuum process chambers for manufacturing semiconductor and liquid crystal devices, wear-resistant ceramics used for steel-making, optical lens forming and cutting tools, refractory tubes for casting aluminum alloys, and automotive applications.

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1. Introduction

The general advantages of structural ceramics, such as alumina, silicon nitride, silicon carbide and zirconia, in comparison with steel are light weight, chemical and thermal stabilities at elevated temperatures and excellent wear resistance. In addition, the high yield stress of ceramics enables the production of precisely machined parts that maintain their accurate dimensions over long periods of use. This is due to the strong chemical bonds formed in ceramics, although it also leads to unreliable mechanical properties responsible for brittle failure. The brittle behavior of ceramics has generally restricted their applications to structural components. Successful applications until around 1980 were typically wear-resistant parts like thread guides and ceramic cutting tools, and structural components used under very low stresses such as ceramic pumps and blowers.

Considerable work has been done on applying ceramics to mechanical parts working under relatively high stresses. In the 1980s, silicon nitride was successfully applied to some auto-

motive components, including turbocharger rotors and glow plugs.^{1,2} These applications actually resulted from various technical advances achieved through research and development work done on ceramic gas turbines. Such advances included (i) enhancement of the fracture toughness of ceramics, (ii) development of process technologies for suppressing the generations of flaws responsible for brittle failure, (iii) development of techniques for designing ceramic components with reduced maximum stresses, and (iv) progress in assuring the strength of components and in inspection techniques for detecting flaws. These advances were based on the application of fracture mechanics as well as the findings of intensive studies of ceramic gas turbines. Applications of silicon nitride to automotive engines, however, gradually decreased in the 1990s. Instead, the application of high-purity alumina was gradually expanded to the parts of equipment for producing semiconductor devices and liquid crystal displays.

This paper reviews recent advances in applications of structural ceramics in Japan.

2. Market for structural ceramics in Japan

The beginning of the Japanese market for structural ceramics dates to around 1980, and the market has expanded steadily

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Table 1
Shipments of structural ceramics in the Japanese market³

	Fiscal year			
	1985	1990	1995	2003
Alumina	105	172	203	372
Zirconia	12	53	82	73
Silicon nitride	13	45	43	45
Silicon carbide	10	28	23	49
Aluminum nitride	–	–	–	40
Others	20	88	117	135
Total	160	387	468	715

Millions of euros; 1 euro = 163 yen.

since then except for several years in the early 1990s.³ Table 1 summarizes the market trends for individual ceramic materials in terms of the value of shipments from 1985 to 2003. High-purity alumina accounts for the largest portion of the structural ceramics market, exceeding the total for zirconia, silicon nitride and silicon carbide combined. The recent increase in shipments of high-purity alumina is due to its application to equipment for manufacturing semiconductor devices and liquid crystal display panels. High-strength zirconia ceramics, typically made with the addition of yttria, are used for wear-resistant parts, cutting blades and ferrule connectors for optical fibers.

The market for silicon nitride expanded in the 1980s with its application to automotive engine parts, though the market recently has been relatively smaller than what was originally expected. The market for silicon carbide has recently expanded, mainly as a result of its application to diesel particulate filters. Although the major application of aluminum nitride has been as a functional ceramic applied to the heat sink of semiconductors, its use as a structural ceramic began from around 1996 when it was first applied to semiconductor production equipment. The major application under the “Others” category in Table 1 is for cordierite ceramics applied to catalyst honeycombs, which support fine particles of precious metal catalysts for purifying the exhaust gas of gasoline engines. Annual sales of this material have reached around 20 billion yen (approximately 120 million euros) recently.

Table 2 shows the value of shipments of structural ceramics for various products in the Japanese market in fiscal 2004 and 2005.^{4,5} Many ceramic parts are used in severe environments

Table 2
Shipments of recent structural ceramic products in Japan^{4,5}

Product	FY 2004	FY 2005
Communication and electric products	67	85
Semiconductor production equipment	182	207
Liquid crystal display production equipment	73	74
Precision mechanical parts	11	12
General mechanical parts	101	104
Non-ferrous alloy making equipment	12	14
Automobile parts	168	184
Others	84	82
Total	699	761

Millions of euros; 1 euro = 163 yen

for producing semiconductors and liquid crystal display panels, where the parts are exposed to plasma and reactive gases. High-purity alumina is commonly used for insulators and electrostatic wafer chucks in these devices, as is aluminum nitride, and silicon carbide is also used for other components of the heat-treatment equipment for Si wafers. Automotive applications also contribute to the overall ceramics market. Cordierite ceramics for catalyst honeycombs account for the major portion of automotive applications, with a relatively small contribution made by silicon nitride used for engine parts. The market for general mechanical parts is the third largest and includes wear-resistant parts such as thread guides and mechanical seals. Magnetic head sliders for hard discs and optical connectors are included in the category of communication and electric products. Al₂O₃–TiC composites are used for magnetic head sliders, and ZrO₂ is used for ferrule connectors for optical fibers. The category of precision mechanical parts includes both the mechanical parts of precision machines like ceramic bearings and production machinery parts such as ceramic surface plates for producing precision machines. The category of non-ferrous alloy making includes thermocouple protection tubes.

3. Application to the components of industrial production equipment

3.1. Semiconductor production

In the semiconductor production process, high-purity silicon carbide is used for the parts of diffusion furnaces, where silicon wafers are heat-treated. High purity is required to suppress the migration of impurities.^{6,7} This property is particularly important for silicon carbide wafer boats and for the liner tubes that shut out diffusive impurities. The high thermal conductivity of silicon carbide is advantageous for homogenizing the local temperature gradient. The general procedure for producing high-purity silicon carbide is as follows. High-purity reaction-sintered silicon carbide is produced from compacts of high-purity silicon carbide powder, and high-purity liquid silicon is infused into the compacts at elevated temperatures. Finally, the surfaces are coated with chemically vapor deposited (CVD) SiC.

Fig. 1 shows typical silicon carbide boats used in the heat-treatment process for Si wafers. Fig. 2 shows a scanning electron micrograph of the cross-section of a wafer boat, which indicates that the boat material consists of reaction-sintered silicon carbide covered with dense CVD SiC on the surface.⁷ While fused silica has been extensively used for diffusion furnaces, the major advantages of using SiC for wafer boats are its thermal stability at elevated temperatures and a coefficient of thermal expansion closer to silicon than that of fused silica. During heat cycles, the latter property suppresses the generation of debris, which might otherwise result from sliding movement due to a thermal coefficient mismatch.⁷

High-purity alumina is used for the parts that support silicon wafers in the vacuum chamber where the etching of semiconductors is done.⁸ This is due to the material's excellent performance in corrosive and plasma environments. The requirements for such materials are (i) to have excellent resistance to halogen

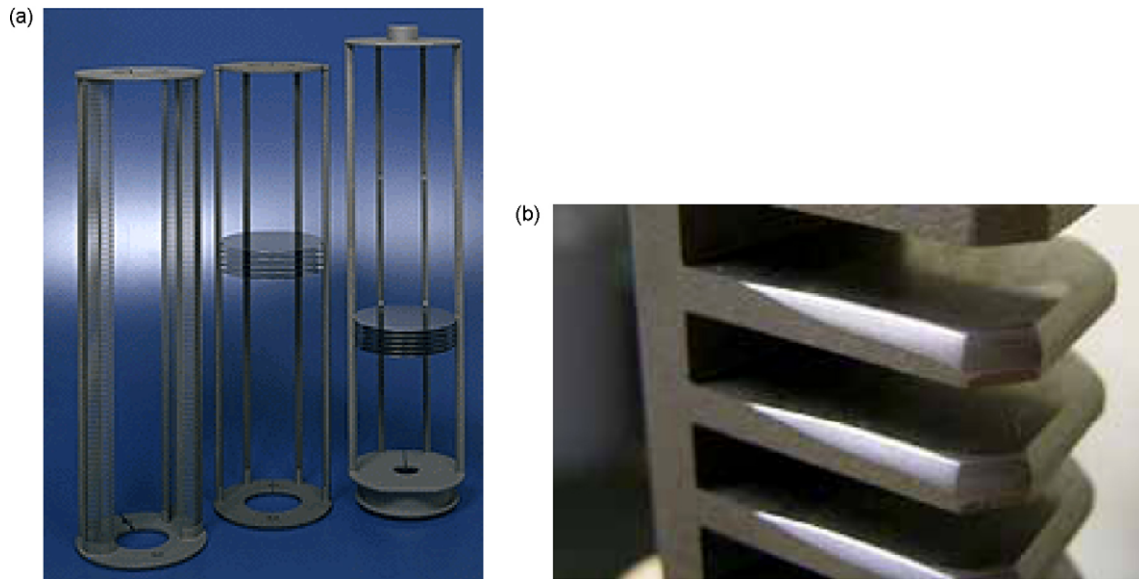


Fig. 1. Typical silicon carbide wafer boats for heat treatment of Si wafers.⁷ (a) A view of the boats with Si wafers and (b) a magnified view of a wafer support.

gases in the plasma environment, (ii) to be free of hazardous elements that degrade the performance of semiconductors, and (iii) not to release any evaporating gases that obstruct the vacuuming procedure. Fig. 3 shows examples of the dense ceramic components of the manufacturing equipment for semiconductor devices and liquid crystal display panels.⁸

Applications of aluminum nitrides are expanding and include electrostatic wafer chucks, susceptors and substrate heaters for supporting silicon wafers in the CVD, PVD, stepper and etching processes.^{6,9} In comparison with alumina, the advantages of using aluminum nitride for supporting silicon wafers are, firstly, its high thermal conductivity that helps to homogenize the temperature gradient, and secondly, a reduction of the particle generation rate owing to less frictional movement between the silicon wafers and AlN susceptors during repeated heating and cooling processes. Because the thermal expansion coefficient of aluminum nitride is very close to that of sili-

con, frictional movement between the wafers and susceptors is reduced.

Ceramics with zero or a low thermal expansion coefficient are used for the parts that support silicon wafers in steppers.⁸ Such ceramics are suitable for this application because steppers must maintain the right position of the silicon wafers independent of temperature changes. Furthermore, the materials for supporting silicon wafers in steppers must be lightweight and have high rigidity, and electric conductance is desirable in order to eliminate static electricity.

Fused silica is also used for the crucibles employed in the Czochralski process of producing single-crystal semiconductors and for the supports used in the heat treatment and dry etching processes of semiconductors. Graphite materials are used for heating elements and the parts of ion implantation devices.⁷



Fig. 2. A scanning electron micrograph of the cross-section of the SiC material. The material is reaction-sintered silicon carbide covered with dense CVD SiC on the surface.⁷



Fig. 3. Examples of dense ceramic components of manufacturing equipment for semiconductor devices and liquid crystal display panels.⁸

3.2. Steel making and aluminum casting

The basic process for making steel is as follows. First, coal is carbonized in a coke oven to produce coke. Powdered ferrous ore mixed with limestone is then sintered in a sintering machine to produce lumps with suitable dimensions. The ferrous ore is then reduced with coke in a blast furnace to produce a melt of cast iron. The cast iron is then converted to molten steel in a steel converter or in the Linz-Donawitz process of a basic oxygen furnace by introducing oxygen into the cast iron melt. The molten steel is cast to produce steel slabs that then are hot- and cold-rolled to form steel sheets. The surfaces are occasionally covered with a zinc plating for protection against corrosion.

The tubes used for transferring powders such as ferrous ore and coal are lined with a ceramic material for protection against erosive wear. The blowers used for transferring and collecting the powders also require ceramic liners to protect the blades from wear. Alumina is widely used for such parts, though silicon nitride is applied in particularly severe environments.¹⁰ Fig. 4 shows typical ceramic-lined tubes used for transferring powdery materials in the steel-making process. Ceramic plates are bonded on the inner surfaces of steel tubes to improve wear resistance.¹⁰

Silicon nitride rollers are used for transferring steel sheets on rolling lines.¹¹ Roller bearings are used in the zinc plating bath in which cold-rolled steel coils are immersed at 500 °C in the process of making zinc-coated steel. Stainless steel roller bearings coated with cemented carbide had been widely used previously, but SiAlON has been applied recently to improve productivity on plating lines.¹²

SiAlON is also used for the stalks and sleeves that transfer molten aluminum to the dies in low-pressure casting and die-casting processes.¹² Cast iron had been used previously for the stalks in low-pressure casting, but suffered a short lifetime due to iron immigration into the melt. This problem has been improved by the use of SiAlON sleeves. Fig. 5 shows SiAlON stalks for the low-pressure casting process of molten aluminum. The stalks are supported vertically in the aluminum melt.¹¹



Fig. 4. Ceramic-lined tubes used for transferring powdery materials in the steel-making process.¹⁰ Ceramic plates are bonded on the inner surfaces of steel tubes to improve wear resistance.

Sleeves made of hot-rolled die steel for aluminum die casting require a large amount of lubricant between the sleeve and plunger to push the melt out during the casting process. Steel sleeves have recently been changed to ceramic-lined ones, in which a ceramic tube is inserted inside the metal tube. Consequently, the amount of lubricant is considerably reduced, and it is also effective in eliminating casting defects. Fig. 6 shows a typical SiAlON sleeve used in aluminum die casting.¹¹

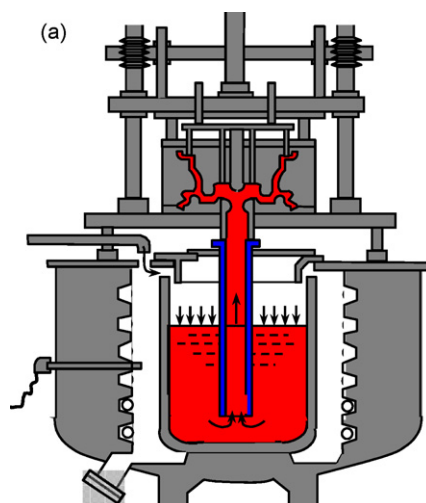


Fig. 5. SiAlON stalks for the low-pressure casting process of molten aluminum.¹¹ (a) Schematic diagram of the low-pressure casting furnace with the stalk located at the center of the furnace and (b) SiAlON stalks.

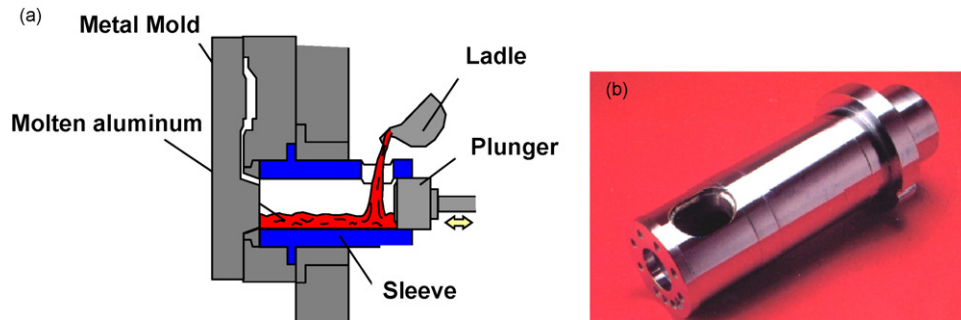


Fig. 6. Die-casting and SiAlON sleeve.¹¹ (a) Schematic diagram of the die-casting structure and (b) SiAlON sleeve where a SiAlON tube is inserted into the metal sleeve.

3.3. Ceramic molds

Optical lenses have generally been produced by cutting and grinding glass. However, non-spherical lenses have recently begun to be used for information and electronic devices. These lenses are produced under pressure in a mold at temperatures over 300 °C. The molds used at such high temperatures are usually made of hard materials such as steels, cemented carbides, and ceramics. Among these materials, silicon carbides coated with CVD SiC are used in particular for high-temperature molding.¹³ Fig. 7 shows a schematic diagram of the lens molding process and the appearance of a lens mold made of precision ceramics.¹³

Press-formed copper alloys are used for the connectors in cellular phones and automobiles. The connector dies were previously made primarily of steel and cemented carbides, but zirconia ceramics with high fracture toughness have been used since around 2000. ZrO₂ ceramics dispersed with tungsten

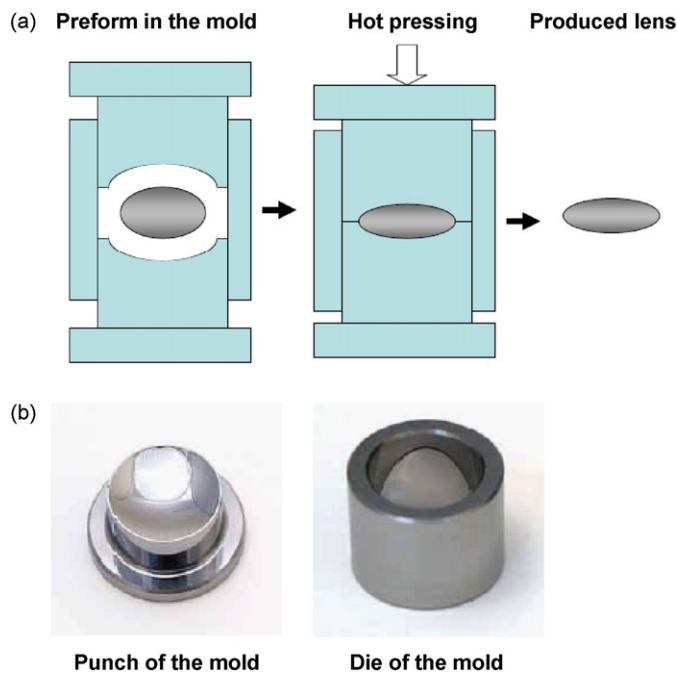


Fig. 7. Precision ceramics for lens molding. (a) Schematic diagram of lens molding process and (b) the appearance of the lens mold and die made of precision ceramics.¹³

carbide (WC) particles are particularly advantageous because their electric conductivity facilitates a wire electrical discharge machining (EDM) process.¹³

3.4. Cutting tools¹

Materials used for cutting tools require properties such as: (i) hardness greater than that of the materials to be machined, (ii) an absence of chemical reactions with machined materials, (iii) durability at elevated temperatures resulting from high-speed cutting, and (iv) an absence of brittle failure during machining. Ceramics are usually superior with respect to the characteristics in (i) to (iii), and the improvement of their resistance to brittle failure is thought to make them advantageous as tool materials. However, the market share of ceramic tools remains at only several percent, accounted for largely by cemented carbide followed by TiC cermets. This low level is clearly due to the brittleness of ceramics that causes the tool edges to chip easily. The share of coated tips, consisting of cemented carbide coated with ceramic materials such as alumina and titanium carbide, is increasing. This is due to improvements in material combinations that take advantage of the characteristics of ceramics in (i) to (iii) for the tool surface, while the inside is made of tough cemented carbide that has good resistance to brittle failure.

Nowadays, major applications of ceramic tools are for high-speed machining of cast iron due to the high temperature resistance of ceramic materials. This category includes (i) high-purity alumina, (ii) alumina composites with TiC, ZrO₂, or SiC whiskers, and (iii) silicon nitrides. Among them, silicon nitride is used for rough machining of cast iron and wet machining. This is because silicon nitride has relatively high toughness for a ceramic material, which enables a rather large cutting depth.

4. Automotive applications

4.1. Catalyst honeycomb²

A three-way catalyst system utilizing a precious-metal-based catalytic converter is generally used today to control the exhaust emissions of automotive gasoline engines. To support the proper operation of the catalysts, the air-fuel ratio is controlled within an appropriate range by an electronic system using oxygen sensors. The oxygen sensors have a solid-state electrode made of

Table 3
Developments in processing cordierite honeycomb at NGK Insulators Ltd.²

Cell structure ^a	12/300	6/400	4/400	4/600	3/400	3/600	2/900
Wall thickness (μm)	300	150	100	100	75	75	50
Number of cells per unit cross-sectional area (cell number/cm ²)	47	62	62	93	62	93	140
Apparent density (g/cm ³)	0.6	0.4	0.25	0.3	0.2	0.25	0.2
Surface area per unit volume (cm ² /cm ³)	20	30	30	35	30	35	45
Year of production start	1976	1979	1995	1996	1999	1999	1999

^a Wall thickness in mils (1/1000 in.) and number of cells/in.².

zirconia ceramics, and the catalysts are supported on a cordierite honeycomb produced by extrusion forming. The cell surface of the honeycomb is covered with fine alumina particles coated with fine particles of precious metal catalysts on the surface.

Since exhaust gas catalysts only work at elevated temperatures, the catalyst temperature must be raised rapidly to the light-off level after the engine is started. To accomplish that, the system was improved by reducing the thickness of the honeycomb walls, in addition to modifying the chemical composition of the catalysts and reducing the dimensions of the catalyst particles. The development history shown in Table 3 indicates that the wall thickness of NGK honeycombs was 300 μm in 1976, which was reduced to just 50 μm in 1999. Fig. 8 shows catalyst honeycombs with different cell densities.

4.2. Diesel particulate filter²

The advantages of diesel engines in comparison with their gasoline counterparts include low fuel consumption and resultant low emissions of carbon dioxide, a greenhouse gas responsible for global warming. This performance is due to diesel engine characteristics such as (i) explosive burning at higher pressure, (ii) basically lean-burn combustion, and (iii) an absence of pumping (throttle) loss. However, the explosive burning process of diesel engines, which results from injecting fuel into compressed air, gives rise to a problem of particulate matter formation due to incomplete combustion when the explosion occurs before the fuel is completely evaporated and mixed

with air. Particulate matter is thought to be related to the causes of cancer and bronchial asthma, and regulatory standards for engine emissions are becoming more stringent. Since particulate matter must be removed from exhaust gas, diesel particulate filters of the wall flow type are generally installed on diesel vehicles. The wall flow type filter is made of a porous ceramic honeycomb with square cell holes, and either the inlet or outlet end is filled alternatively. As the exhaust gas passes through the porous inlet walls, particulate matter condenses on the outer and inner surfaces of the walls. The major materials of diesel particulate filters are silicon carbide and cordierite.

4.3. Automotive parts¹

Table 4 shows typical applications of silicon nitride to automotive engine parts. It is clear that such applications were actively promoted in the early and mid-1980s. Examples include glow plugs for starting diesel engines more quickly, turbocharger rotors (Fig. 9) for enabling quick acceleration response by employing lightweight ceramics, and wear parts for cam followers such as rocker arm pads and tappets (Fig. 10). These applications were promoted by an extraordinarily strong interest in ceramics in Japan at that time, referred to as the “ceramic fever.” Some ceramic parts were subsequently removed from the next generation of automobile models because the improved performance did not justify the higher production cost.

Lightweight exhaust valves would be advantageous as dynamic parts because of their lower inertial mass at high engine

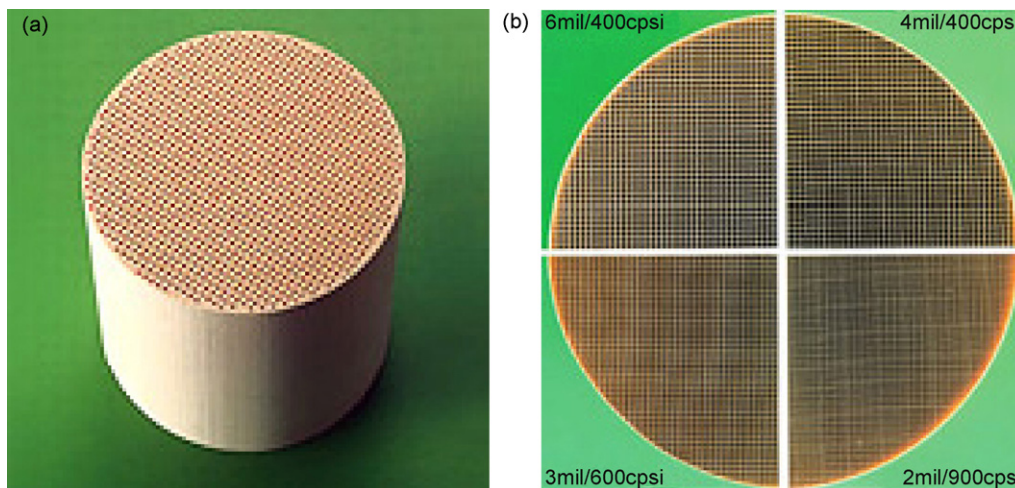


Fig. 8. Catalyst honeycombs with different cell densities (courtesy of NGK Insulators Ltd.). (a) Typical catalyst honeycomb and (b) four honeycombs with different cell structures (see also Table 3).

Table 4
Ceramic parts used on commercial vehicles in Japan¹

Ceramic parts	Materials	Advantages of using ceramics	First application
Diesel engine glow plugs	Silicon nitride	Quicker engine start	1981
Hot plugs for diesel engine swirl chamber	Silicon nitride	Reduction of noise and unburned fuel in exhaust gas	1983
Rocker arm pads (cam followers)	Silicon nitride	Improvement in wear resistance	1984
Turbocharger rotors	Silicon nitride	Improvement in acceleration response	1985
Tappets for diesel engines (cam followers)	Silicon nitride	Improvement in wear resistance	1993
Exhaust control valves of twin turbochargers	Silicon nitride	Improvement in transient characteristics by minimizing gas leakage	1993

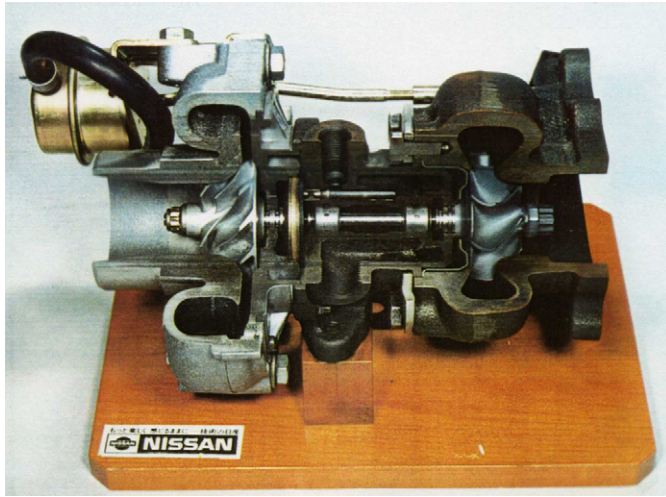


Fig. 9. Ceramic turbocharger rotors.

speeds. There have been strong expectations for the application of ceramics to exhaust valves in view of their light weight and high-temperature durability. Intensive R&D work has been done, and ceramic valves were used on Formula One race cars in the late 1980s, which confirmed the lightweight benefits of ceramic valves. Moreover, Daimler-Benz conducted successful road tests of vehicles with ceramic valves in the 1990s. However, ceramic exhaust valves have yet to be used on production automobiles.

Recent requirements for wear parts include not only wear resistance but also low friction. Creating a low-friction surface is effective in improving efficiency by reducing friction loss. A



Fig. 10. Tappets as wear parts used for cam followers.¹

diamond-like-carbon coating has been applied to valve lifters for that purpose.¹⁴

4.4. Uses in manufacturing processes for automobile parts¹⁵

Ceramics are used in the welding and heat treatment processes in the manufacture of steel parts for automobiles. Alumina welding nozzles have high temperature resistance and are advantageous in plasma welding where the welding nozzle tip reaches high temperatures around 600 °C. The advantages of using silicon nitride nozzles include less adhesion to the metal sputtered from welding materials as well as excellent durability at high temperatures. Silicon nitrides are applied to the squeezing rolls for manufacturing electric-resistance-welded tubes due to their excellent thermal shock resistance, high strength and wear resistance. Work supports used in the induction hardening process for steel parts, such as gears, require excellent wear resistance to ensure a long lifetime, and silicon nitride has been applied to meet that requirement. Bending rolls for metal spinning also require materials with high strength and wear resistance, and zirconia ceramics have been applied here.

5. Concluding remarks

The market for structural ceramics has been steadily increasing, while research activities for these materials have declined in comparison with the very active period of the 1980s, characterized by the “ceramic fever” in Japan. High-purity alumina for the components of the equipment used in producing semiconductor devices and liquid crystal display panels has contributed substantially to the recent market for structural ceramics. Cordierite honeycombs and diesel particulate filters are also important examples of automotive applications. While structural ceramics are used in these applications, the stress levels are relatively low in comparison with gas turbine and turbocharger rotors that were the original uses targeted for these materials.

Extensive research on silicon nitride has led to new areas of application such as ceramic bearings and ceramic springs. Hot-pressed silicon nitride bearings applied to the major shaft of lathe turning machines have contributed to improved precision in these machine tools.¹ In addition, silicon nitride springs capable of withstanding temperatures up to 1000 °C have been developed and applied to the fixtures used in the brazing process, resulting in higher productivity.¹ Alumina has been applied to the single lever mixing valves of cold and hot water supply

systems, precision guides such as air slides, and surface plates. Silicon carbide has been applied to fishing guides. While early applications of zirconia were to knives and scissors, the scope of application has recently been expanded to the ferrule connectors of optical fibers and impellers of slug pumps.¹ Alumina with dispersed TiC particles has been applied to the magnetic head slider of hard discs.

Recent successful applications of structural ceramics have been limited to low levels of stress in severe environments. The next step for the application of ceramics is thought to be uses in severe environments under higher stresses.

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