Reviews

Materials Chemistry Issues Related to Advanced Materials Applications in the Automotive Industry

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The driving force behind the research on advanced materials has largely been aerospace and defense applications. In such applications the customer-induced limitations and infrastructural economic factors are secondary to the application-oriented parameters. Automobiles, on the other hand, represent the primary consumers of advanced materials in civilian applications. Automobiles are high-technology, low-cost machines which need to be robust for various climatic conditions and driver behavior. Advanced materials play an important role in the design and fabrication of various components of automobiles, and the use of new materials continues to increase. Recent interest in developing highly fuel efficient vehicles with low emissions has focused efforts toward materials, designs, and devices and is spurring research into advanced materials for weight reduction. The goal is to achieve fuel efficiency by weight reduction and a more efficient powertrain. In this review article, we summarize the efforts of the 1970s and the 1980s on the development of ceramic gas turbine engines with emphasis on materials processing and properties. This is followed by a discussion of metal−matrix composites and reinforced plastics, the structural materials of current interest. The materials issues related to automotive exhaust reduction catalysts are discussed since materials continue to play an important role in designing catalysts to meet the new EPA regulations. The understanding of materials chemistry is expected to play an important role in designing new materials and developing new processes that can be used economically to mass produce vehicle components. We also summarize reports based on ceramic precursor technology and sol−gel processes that show promise in the fabrication of automotive components.

Introduction

Automobiles are probably the most common high-technology machines that an average person operates on a daily basis in developed countries. Since the early days of automobile development, the basic vehicle design has consisted of an engine, wheels, a steering wheel, brakes, and driver and passenger compartments. The first noticeable change occurred in the driver and passenger compartments from stagecoach-type designs to closed compartments over a century ago. Improvements over the past several decades have brought major changes in automobiles. Compared to early automobiles, today's vehicles are aerodynamic, have a large number of safety features, employ a variety of advanced materials and composites in various parts, and contain several electronic components. The driving forces for research are (i) improvement in quality in a highly competitive market, (ii) environmental issues, (iii) economics, and (iv) government regulations.[1] Recent interest in developing highly fuel efficient vehicles with low emissions has focused efforts toward materials, designs, and devices. The two commonly used acronyms ULEV and PNGV refer to "ultralow emission vehicles" and "partnership for a new generation vehicle (a cooperative program between GM, Ford, Chrysler, and the Department of Energy)" and represent the goals for emissions and fuel economy. The ULEV need to meet non-methane organic gases/CO/NO_x emission standards of 0.04/1.7/0.2 g/mile for 50 000 miles and of 0.055/2.1/0.3 g/mile for 100 000 miles. The PNGVs need to attain fuel efficiency of 82.5 miles/gal. New materials and technologies will be needed to meet these goals. It is important to mention that the adoption of a technology is not just an addition to a vehicle; it requires major changes in the overall design of the vehicle itself.[2]

The traditional materials of interest to the automobile industry have been (i) metals which form most of the body and engine components, (ii) organic polymers which are plastics and rubbers for internal trim, dashboards, tires, wipers, bumpers, and some body components, (iii) oils, and (iv) paints.[3] Over the years, the use of electronics in cars has increased and is expected

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to grow further. It was recognized quite early that the reduction in the weight of an automobile for both gasoline and diesel engines, and burning diesel at elevated temperatures (1315 °C) will result in improved fuel efficiency and reduced tail-pipe emissions. At present, materials limitations prevent the operation of diesel vehicles at high temperatures. The fuel efficiency of the modern gasoline vehicle is achieved by a reduction in the weight of the automobile and the treatment of emissions with a three-way catalyst. Further improvements of modern gasoline vehicles can be achieved with the use of advanced materials to reduce the weight of vehicles without compromising safety.

The purpose of this review is to summarize the research on the automotive applications of advanced materials. In the 1970s, ceramics were proposed as the materials of choice[4] because they provide the ideal combination of being lightweight and able to function at high temperatures. This led to the fabrication of gas turbine and adiabatic diesel engines. However, those efforts were largely abandoned due to the limited reliability of ceramics, their catastrophic failure, and the exorbitant cost of machining them. There is still some interest in these devices for PNGV, although nonadiabatic diesel engine based technologies offer better fuel economy and will become suitable for mass production provided advances in catalysis can bring NO_x and particulate emissions to acceptable levels.

In the following sections, we will summarize earlier efforts on the ceramics in gas turbines and adiabatic engines. This will be followed by the description of the materials of current interest. Space requirements force us to limit our discussion to metal matrix composites, fiber-reinforced plastics, and automotive catalysts. Other important applications of ceramics are in optical coatings,[5] energy-storage materials and energy-conversion materials,[6] and chemical sensor devices[7] which will not be discussed here. Since this review emphasizes applications, we will first describe devices prior to materials related issues. This will be followed by the summary of earlier efforts, ongoing research that could have an impact in automotive industry, and future directions. Since the number of publications and patents on automotive applications of materials is very large, we limit our discussion to the review of the relevant work rather than attempt to create a comprehensive summary.

Some recent reports based on ceramic precursor technology and sol−gel processes show promise in designing vehicle components and are described along with the discussion on the processing of materials. An obvious omission is CVD-based developments. For automotive applications, the CVD-based processes are limited to electronics, optical, and chemical sensor applications due to economic reasons.[8]

Structural Ceramics in the Automotive Industry

Structural ceramics need to tolerate high stress at low strain, implying that they should have a high elastic modulus. The commonly used parameter for the comparison of various materials is the specific modulus (elastic modulus/specific gravity) which expresses usable strength per unit weight. Table 1 shows the specific modulus and melting point/decomposition point of some materials. High-temperature strength, chemical stability, low thermal expansion and good thermal shock resistance of materials also constitute selection criteria. Thus silicon carbide and silicon nitride are the only acceptable materials because aluminum nitride is unstable in moisture, alumina does not have good thermal shock resistance, beryllium oxide is toxic, carbon has a low oxidation stability, and boron nitride is difficult to fabricate.

Table 1. Specific Modulus of Some Important Materials[a]

material	specific modulus (10^4 MN m^{-2})	MP/dec P (°C)
SiC	17.2	2600
AlN	10.3	2450
Si_3N_4	11.7	1900
Al_2O_3	9.0	2050
BeO	12.4	2530
BN	4.8	2700
C	42.0	3500
SiO_2(vitreous)	3.1	1710
steel	3.8	1500
Al	3.0	660

[a] From: Dobson, M. M. *Silicon Carbide Alloys*; Evans, P. E., Ed.; The Parthenon Press: Lancashire, England, 1986; p 2.

Although a ceramics based gas turbine engine and parts of the adiabatic engine were fabricated in the 1970s, they are not in use because ceramics are quite brittle and have intrinsic cracks which grow under stress.[9] Here we provide a brief description of the gas turbine and adiabatic engine with emphasis on the materials needs. Structural materials for these engines were identified to be partially stabilized zirconia (PSZ), silicon carbide (SiC), silicon nitride (Si_3N_4), lithium aluminum silicate (LAS), and magnesium aluminum silicate (MAS) with operating temperatures ranging from 800 °C for PSZ to 1500 °C for SiC. We will limit our discussion to the fabrication processes, properties, and limitations of silicon carbide and silicon nitride materials which were employed with some success. At present, a Si_3N_4 turbocharger rotor is in production and is used in several Japanese automobiles.[10]

We will limit our discussion of ceramic precursors for silicon carbide or silicon nitride to those which have been employed either in the fabrication of complex shapes or as binders. There are only a few examples of the applications of ceramic precursors in the fabrication of complex shapes. These examples do not show the advantages of ceramic precursor pyrolysis over classical methods to obtain SiC or Si_3N_4 components. A green body made of preceramic polymer undergoes significant density changes (factor of 2−3) and weight loss in the form of gaseous byproducts. The compacting of the green body causes shrinkage and gas evolution which introduces porosity. The maximum volume[11] change during polymer−ceramic conversion is given as

$$\psi = \alpha\beta - 1$$

where α is the mass of ceramic/mass of polymer and β is the density of polymer/density of ceramic.

Maximum porosity (π) during a volume-invariant conversion is given as

$$\pi = 1 - \alpha\beta$$

In most polymer−ceramic conversions, significant volume change and porosity formation are observed. In the case for all organosilicon polymers, $\alpha\beta$ is smaller

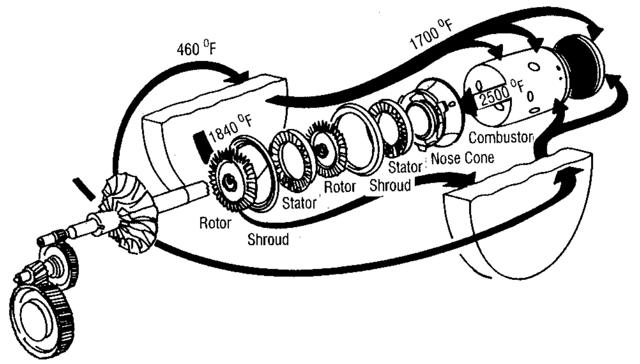


Figure 1. Gas flow path of a vehicular gas turbine made of ceramics.

than unity, suggesting that the fabrication of fully dense bodies is probably impossible without shrinkage.[12,13]

Active filler-controlled pyrolysis of preceramic polymers overcomes the problems of shrinkage and massive porosity associated with fabrication of ceramic components from preceramic polymers.[13] In this approach, active fillers react with the pyrolysis byproducts of preceramic polymers. Thus, this approach combines the classical method approach with ceramic precursor technology since the reaction of active fillers with gaseous byproducts proceeds under the reaction conditions of classical methods. This method seems to be more suitable for the preparation of ceramic composites and fabrication of composite components. Unfortunately, the physical properties of materials prepared by this method have not been determined.

Gas Turbine Engine. Turbines have been in use in power plants, aircraft turboprops, helicopter engines, aircraft jet engines, marine engines, and hydrofoil craft engines and are considered a proven technology. These turbines are usually fabricated from costly superalloys, which makes them too expensive to be useful in a high-volume, low-cost industry such as automobiles. A ceramic-based turbine, on the other hand, could be prepared in large volumes at an acceptable cost. A vehicular gas turbine made of ceramics was developed in the 1970s and 1980s, and its entire gas flow path is shown in Figure 1.[4] The objective of this research was to exclude cooling and demonstrate that the components can survive a 175 h duty cycle at 1055 °C and 25 h at 1372 °C involving several starts and shutdowns. A design of this type was expected to offer several advantages such as low exhaust emission, multi-fuel capability, a simple low-maintenance machine, and low oil consumption.

Initially, the ceramics of choice for the gas turbine engine were silicon nitride and silicon carbide. Later, silicon nitride (both reaction-bonded and hot-pressed) was found to be more suitable in the fabrication of various components.

Adiabatic Engine. Figure 2 shows a simplified schematic adiabatic engine descried by Bryzik and Kamo and developed under tank-automotive command and the Cummins Engine Co. program.[14] The engine is adiabatic in a thermodynamic sense, but there is still some heat loss. The diesel combustion chamber is insulated to allow operation at near adiabatic conditions. In addition, the thermal energy lost to the exhaust system is converted to useful power by turbomachinery and there is no conventional forced cooling.

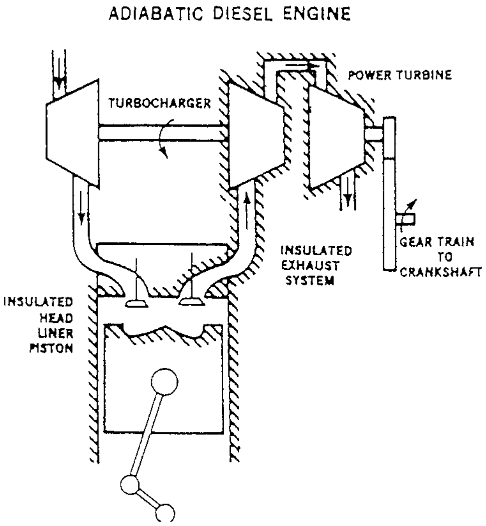


Figure 2. Adiabatic engine. Reprinted with permission from SAE Paper Number 830314, copyright 1983 Society of Automotive Engineers, Inc.

The insulated components are the piston, cylinder head valves, cylinder liner, exhaust valves, and exhaust ports. Thus the reduction in the lost energy and elimination of a conventional cooling system results in improved fuel efficiency and economy. Feasibility studies have been concentrated in the 250−500 HP range for military trucks. The materials for the application in adiabatic engines need to have the following characteristics: insulation capability, high expansion coefficient, high temperature capability, high strength, fracture toughness, high thermal shock resistance, low-friction and wear characteristics, and low cost. The material properties are as follows: temperature limit (°C) >982, fracture toughness (K_{IC} in MPa) >8.0, flexural strength (MPa) >800, thermal conductivity (K) <0.01, thermal shock resistance (ΔT, °C) >500, and coefficient of expansion (10^{-6}/°C) >10.[14] Partially stabilized zirconia (PSZ) was considered to be a suitable material due to its good thermal shock resistance and flexural strength.[15] Ceramic coatings were found to be acceptable for insulation or corrosion resistance in high-temperature applications.[16]

Another material of interest in developing low-friction, unlubricated diesel engines was silicon carbide.[17] The interest in silicon carbide stems from properties such as wear resistance, lightweight, high-temperature stability, low coefficient of friction, potential low-cost fabrication, and corrosion resistance. A solid silicon carbide cylinder and pistons were tested for 47.5 h and performed reasonably well. Ultimately, failure occurred due to the failure of the piston/piston pin connection.

Lithium aluminosilicate, $LiAlSi_4O_{12}$ (β-spodumene), was also investigated for manufacturing components of the ceramic diesel engine.[17] Pistons and liners fabricated from lithium aluminosilicate were tested by the light-load firing test. After 3 min, the piston disintegrated and the liner cracked. The failure mechanism is believed to involve the metal-to-ceramic interface.

Materials for Gas Turbine and Adiabatic Engine Components

The preceding discussion provides information on the selection criteria for the materials for the gas turbine and adiabatic engine components. In this section, we describe structural details, classical method of preparation, and properties of silicon nitride and silicon carbide. A large number of ceramic precursor routes for silicon carbide and silicon nitride are known and are summarized in a recent book.[18] Some recent developments in the use of preceramics as binders show promise and will be discussed. At least one report claims reproducible shrinkage when preceramics are used as binders; this might reduce machining and the cost of fabricating components. If fabrication does not require machining and results in achieving properties comparable to those achieved with the injection molding process, ceramic precursors as binders may be competitive.

Silicon Nitride. Excellent strength, thermal shock resistance, and oxidation behavior make silicon nitride a material of choice for gas turbine engines.[19] Silicon nitride was first prepared by Wöhler in 1857. Subsequently, its preparation from the carbothermal nitridation of silicon oxide, direct nitridation of silicon, and the decomposition of silicon amide [$Si(NH)_2$] was reported. Silicon nitride exists in α- and β-forms consisting of 8- and 12-membered rings of silicon and nitrogen that form interleaved sheets. Each silicon atom is surrounded by four nitrogen atoms and occupies a tetrahedral site. The α-form, in addition, contains 0.04 oxygen/silicon. Of these two phases, β-Si_3N_4 is a long-grained material with high fracture toughness, and α-Si_3N_4 is equiaxed grained with low fracture toughness.[20] Thus a high volume fraction of α-Si_3N_4 is necessary for the fabrication of high-strength parts.[21] The $\alpha \rightarrow \beta$ phase transformation is related to the formation of elongated grains with high aspect ratio, which is believed to increase fracture toughness to about 6 MPa $m^{1/2}$.[22] Grain growth is a function of sintering additives, impurities, and Si_3N_4.[23] Highly elongated grains develop by gas-pressure sintering with a fracture toughness of 9−11 MPa $m^{1/2}$.[24] Toughness increase is also accomplished by whisker reinforcing.[25] The toughening contribution of whiskers, involving frictional motion along the interface, is described by the following equation:[26]

$$DK_{fb} \approx \{(\sigma_r)^2 d_w f\gamma_r E_c/24E_r\gamma_i\}^{1/2}$$

where $\gamma_r/\gamma_i = \mu\sigma_r/\tau_{db}$. The terms σ_r, d_w, $f\gamma_r$, E_r, γ_i and τ_{db}, E_c, and μ represent tensile strength, diameter, volume fraction, fracture energy, and Young's modulus of the reinforcing phase, interfacial debonding energy, Young's modulus of the composite, and the friction coefficient along the interface, respectively. The whisker pullout toughening contribution is described as follows:

$$DK_{po} \approx \{(\sigma_r)^3 d_w f\gamma_r E_c/12E_r\tau_i\}^{1/2}$$

where τ_i is the shear resistance of the interface.

Thus, toughness increases with increasing whisker contribution and whisker diameter. High whisker strength is needed to sustain frictional forces resisting whisker pullout. Since silicon nitride grains can also act like reinforcing whiskers, there is substantial research in progress to optimize grain size.[27]

The structure of the interface between reinforcing grains and the matrix is very important for silicon nitride sintered components. The interface between the matrix and the reinforcing phase should be already debonded or should separate as the crack tip approaches. Analysis of crack propagation in whisker-reinforced silicon nitride has been carried out by Hutchinson.[28] Finally, machining also affects the toughness of silicon nitride bodies. For example, Tajima and Urashima report that the coarse diamond abrasion of fine-grain silicon nitride reduces its strength from ∼1500 to ∼800 MPa.[29]

The fabrication of components from silicon nitride powder is generally carried out by slip casting, injection molding, or compression molding. Each method provides components of different characteristics. For example, slip cast Si_3N_4 has high strength, injection molded Si_3N_4 material shows good thermal shock resistance, and compression molded Si_3N_4 materials exhibit high hardness, good wear resistance, and low thermal expansion. After fabrication, the components are machined, which substantially increases their cost.

Reaction-Sintered Silicon Nitride. In reaction sintering, silicon powder is isostatically pressed, injection molded, or slip-cast after demping with an organic binder. The nitridation of the compact is carried out at 1300−1450 °C. The process is unique in that no dimensional changes occur during nitridation. In general, reaction bonded silicon nitride components have high porosity. The properties of the reaction bonded silicon nitride components also depend on the quality and particle size of the silicon powder, and temperature of nitridation. For example, the modulus of rupture of a sample prepared at 1400 °C from −400 mesh silicon powder is 23 400 ± 1380 psi.[30] The modulus of rupture of a sample prepared from 10 μm silicon nitridation at 1450 °C is 32 000 ± 4350 psi.[31] Flame spraying also furnishes samples with a high modulus of rupture (33 900 ± 2200 psi,[32] above 40 000 psi[33]). Purity (98−99% vs 99−99.99%) does not seem to affect bend strength.[30] The materials for fabrication of a gas turbine engine should be capable of operating at 1260 °C with a stress of 10 000 psi for 200 h while undergoing less than 0.5% creep strain.

The primary advantage of injection molding is that complex shapes can be fabricated with minimum finish machining. However, the strength of injection molded silicon nitride components is far less than the stress in the disk of the wheel of a turbine rotor. Injection molding of silicon powder containing 0.02 wt % calcium gave a material of desired specification upon nitridation at 1282 °C with 1.8% H_2 containing N_2.[34] The improved creep resistance is attributed to a fine-grained microstructure and increased refractories at the grain boundary phase.

In slip-casting, a stable suspension of silicon powder is poured into an absorbent mold. The mold absorbs most of the liquid, and the cast thus formed is subsequently dried and sintered. The highest density cast is obtained from the lowest viscosity suspension. The nitridation results in high-density silicon nitride ware. The density and modulus of rupture of samples nitrided at 1093 °C for 18 h, 1260 °C for 24 h, and 1460 °C for 18 h were 2.73 g/cm^3 and 40 000 psi.[35]

Hot-Pressed Silicon Nitride. Hot-pressed silicon nitride is sufficiently strong for the fabrication of rotor disks. Hot-pressed silicon nitride powders can be fully densified in the presence of small amounts of hot-pressing aids.[36] Terwilliger and Lange suggest that at high temperatures a liquid phase is formed which promotes densification by a solution-reprecipitation mechanism.[37] The microstructure of the silicon nitride powder influences the strength and fracture energy of hot-pressed silicon nitride.[21]

The grain boundary governs the mechanical properties of the components at high temperatures. A liquid phase, proposed to be magnesium silicate, forms on the grain boundaries when hot pressing is done in the presence of MgO.[38] The formation of magnesium calcium silicate has been shown by the Auger analysis of the fracture surface. A depth profile of the samples also suggests incorporation of oxide impurities in the boundary phase.[39] Thus, hot pressing aids and oxide impurities can be expected to influence the high-temperature strength of hot-pressed silicon nitride. For example, a sample of α-Si_3N_4 from Westinghouse containing about 100 ppm calcium was hot pressed with 5 wt % MgO and was found to have a flexural strength of 60 Ksi at 1400 °C.[40]

Ceramic Precursors in Fabrication of Silicon Nitride Bodies. The past 10 years have seen an explosion of research on ceramic precursors for silicon nitride materials.[18] A large number of papers and patents claim the suitability of ceramic precursors in the fabrication of components of various shapes and forms. Unfortunately, information on actual fabrications of components and their properties is nonexistent. Ceramic precursor routes would be ideal if the precursors (i) are soluble in common organic solvents and can be molded into the shape of the components and (ii) form silicon nitride in high yields. However, shrinkage and high porosity can be expected due to densification and gas evolution, respectively. A more practical application of a ceramic precursor is as a binder which was first employed by Yajima for silicon carbides.[41]

In a patent, Lukacs claims that a mixture of silicon nitride powder, poly[(methylvinyl)silazane], $[(CH_3SiHNH)_{0.8}(CH_3SiCH{=}CH_2NH)_{0.2}]_n$, and sintering aids can be injection molded and cured at 150 °C.[42] After curing, densified and sintered silicon nitride bodies are obtained which retain the shape of the article. Unfortunately, there is no information on the properties of the silicon nitride components. Schwark et al. report the application of isocyanate modified polysilazane[43] prepared from the reaction of phenylisocyanate with $[(MeSiHNH)_{0.8}(CH_2{=}CHSiMeNH)_{0.2}]_x$ as a binder. In this process, the polymer is mixed with silicon nitride and sintering aids and injected at 3500 MPa into a heated (>150 °C) mold.[44] The resulting silicon nitride green bodies with 8 wt % binder exhibit a four-point strength above 8 MPa. On firing, a shrinkage of less than 10% is observed. The flexural strength and fracture toughness of the sintered silicon nitride bodies are claimed to be comparable to traditional injection molded bodies, although no data are presented.

Riedel et al.[45] prepared ceramic parts from polysilazane NCP 200 which are first thermally treated to an infusible, trisilylated nitrogen structure:

$$[-RSiH-NH-]_n \xrightarrow{350\ ^\circ C} [-RSiH-NH-]_{n-m}[-RSiN-]_m + mH_2$$

The infusible material is then powdered and isostatically pressed to form green compacts which are then pyrolyzed under argon or ammonia to obtain SiCN or Si_3N_4 parts, respectively. These parts are X-ray amorphous and crack-free and attain 93% density. The mechanical strength is 375 MPa and Vickers hardness is 9.5 GPa for SiCN-based parts.

Table 2. Some Properties of Silicon Carbide

type	Young's modulus (10^4 MN m^{-2})	coeff of thermal expansion α (10^{-6} °C^{-1})	thermal conductivity K (wm^{-1} °C^{-1})
sintered (α)	40.7	4.8	100−150
reaction bonded (20% v/v free Si)	34.5	4.4	100−50
SiC fiber−Si composite	34.0		70
CVD	41.4		
REFEL SiC	41.3	4.3	84−39
sintered Si_3N_4 (alumina additive)	27.6	3.2	28−12

Silicon Carbide. The low fracture toughness of silicon carbide has limited its applications in the automotive industry, but it has found some use in automobile exhaust-valve systems and turbocharger rotors.[46] The possible number of polytypes for silicon carbide have been calculated to be 93 813 567,[47] and approximately 200 polytypes have been identified.[48] The common polytypes are 2H, 6H, 15R, and 3C. The chemistry of sintering aids and metallic impurities influence $\beta \rightarrow \alpha$ phase transformations.[49] The toughness of silicon carbide can be improved by sintering with alumina, and the high toughness has also been correlated with the aspect ratio of grains.[50] Aluminum-doped β-SiC powders also show similar grain structure in sintered bodies.[51] The proposed sintering mechanism suggests the formation of aluminum silicate which promotes liquid-phase sintering.[52]

There are several known methods for the fabrication of SiC components. The sintering of pure SiC powders shows no shrinkage. Pressureless sintering of SiC is considered to be an important development.[53] This is done with B and C addition, but the fracture toughness of these materials is low. Control of composite microstructure by liquid-phase sintering has also been attempted.[54] Injection molding is considered to be suitable for mass-scale production and is described in detail. Some properties of silicon carbide, prepared by various methods, are summarized in Table 2.

Injection Molding of Silicon Carbide Components. Silicon carbide components need to have a Weibull strength of 80 Ksi and a Weibull modulus of 16 to be considered suitable. The fabrication process needs to be simple and suitable for mass production. Considering these two parameters, injection molding was recognized to be method of choice. In this process, a powder of silicon carbide and sintering aids is suspended in an organic binder and the resulting slurry is injection molded into complex shapes. After removal of the binder, the green body is sintered to obtain the final compact. The method employed by Whalen et al. to fabricate turbochargers is described here.[55]

Commercial β-silicon carbide (Ibiden UF lot 0166), amorphous boron (Starck lots 3506), and lampblack carbon (Monsanto TL 246) were first analyzed to determine purity. The silicon carbide contained 1.6 wt % oxygen which is typical of ultrafine powders (due to the SiO_2 coating) and 0.7 wt % free carbon. The carbon and boron also showed some oxygen due to adsorbed moisture. The mean particle sizes for SiC, B, and C were 1.18, 2.70, and 5.62 μm, respectively. Polytype analysis of SiC was carried out by X-ray diffraction. The SiC was primarily 3C (85%) and the remaining material was a disordered phase. The SEM micrographs showed that the particles were equiaxed and rounded with a few grains showing well-defined cleavage faces.

A 55.5 vol % powder (97% SiC powder, 2% carbon black, and 1% amorphous boron) was mixed with a 44.5 vol % thermoplastic binder. The mixture was warmed and homogenized in a high-shear Haake mill. The homogeneous mixture was injection molded into test bars. The dewaxing of the bars was carried out under vacuum conditions. The resulting bars showed a mean warpage of 0.001 94 in. and mean linear shrinkage of 3.89%. The bars were sintered at 2100 °C in vacuum for 10 min. The average density of the bars was 94% of theoretical density (3.17 g/cm^3) as sintered and increased to 95.5% after machining.

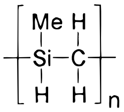
The bars showed reduced oxygen (0.006%) and excess carbon (2%). The higher carbon content is due to the addition of carbon black as a sintering aid. The microstructure of the bars was comprised of uniform particles of 6 μm with evenly distributed small pores and no evidence of needle or feather morphology which is typical of oversintering. There was a random distribution of low density inclusions of sizes up to 80 micrometers. The X-ray diffraction analysis showed 52.9% 3C SiC with a balance of disordered SiC. At room temperature, the mean modulus of rupture, Weibull characteristic, and Weibull modulus were 43.3 Ksi, 45.8 Ksi, and 8.0, respectively. The flexural stress rupture measurements at 1400 °C and applied stress of 25 and 30 Ksi showed behavior typical of heterogenous materials with a failure time range of 5−163 h.

SEM analysis shows four types of defects in the sintered bars. The first type of defect is caused by poorly sintered SiC particles. This defect has nearly spherical 25−30 μm shapes and is probably formed from agglomerates which do not contain sintering aids. The second type of defect is caused by grain growth which is also spherical in shape. The third platelike flaw is a mixture of grain sizes and shapes comprised mainly of boron and low levels of carbon. The fourth type of flaw is caused by iron impurities introduced during one of the mixing steps. Each of the four types of defects can act as an initiation site for failure.

Strength improvements of 40% in Weibull characteristic strength and 31% in the Weibull modulus were achieved by statistical process control to reduce defects. Turbocharger rotors were molded by this process to obtain crack-free rotors.

Ceramic Precursors in Fabrication of Articles. A large number of known precursors can be converted to silicon carbide.[18,56] Several of these polymers are soluble in common organic solvents and can be employed to make various shapes and forms. The ceramic yields from some of the polymers are quite high and the silicon carbide produced is relatively free from impurities. There is very little information on the properties of the silicon carbide powder that can be produced from these routes and practically no information on the fabrication of the components or the properties of the fabricated components. There are some important results on the fabrication of ceramic components using ceramic precursors as binders which will be summarized here.

The application of ceramic precursors as binder is not a new concept. Yajima showed that α-SiC (particle size 3 μm, purity 99.99%) mixed with polycarbosilane (average mol wt 800)[57] can be pressed into green bodies (10 × 30 × 4 mm). These green bodies can then be sintered at 700−1400 °C without shrinkage or expansion.[58]



$$\left[\mathrm{Si(Me)(H)}-\mathrm{C(H)(H)}\right]_n$$

The bending strength of the sintered bodies was 61.7 MN m^{-2} at 1100. The optimum amount of polycarbosilane (PC) was found to be 10% by weight and the resulting bodies had a bending strength of 61.7 MN m^{-2}. The bending strength of the bodies increased on "polycarbosilane impregnation". The density of the sintered bodies increased to 83% and bending strength to 250 MN m^{-2}.

Semen and Loop report the fabrication of silicon carbide parts from silicon carbide powder and a proprietary polysilazane binder from Ethyl Corp.[59] The ceramics contained over 20 vol % porosity with a pore size of ≤10 nm and had high bending strength (550 MPa), low density (2.25−2.35 g/cm^3), high reliability (Weibull modulus of 12), and good fracture toughness (3.5 MPa.m$^{1/2}$). Structural studies show that the composite parts contain amorphous Si−N−C materials which form a high-porosity matrix with low pore dimensions. The matrix materials remained stable even after heating to 1400 °C in nitrogen. Thermal aging improved the bending strength probably due to the collapse of pores and healing of critical surface flaws by the oxide surface layer. An important claim of this work is that the net-shape structural ceramic parts can be made with very close dimensional tolerances because linear shrinkage is reproducible and low (2−4.5%), and green machinability is very good.

Hot pressing of fine-grained silicon carbide, obtained from the pyrolysis of polycarbosilane, was carried out by Kodama.[60] The resulting ceramic bodies achieved >99% of theoretical density, 534 MPa flexure strength, 5.1 MPa.m$^{1/2}$ fracture toughness, and 2556 HV Vickers hardness. However, this method does not offer advantages over classical methods in the fabrication of parts.

Fiber-Reinforced Plastics

The greatest driving force for increased use of composite plastics in automotive applications is weight reduction for PNGV. The goal is to reduce body panel weights by ~50%. The relative weight of a given part requiring a particular stiffness can be estimated from the density and flexural modulus of the material. Estimates to typical weight savings relative to cold rolled steel are given in Table 3 for various types of composites. Actual weight savings are very design specific. Weight savings from using plastics on nonstructural parts are generally greater than indicated in Table 3 since performance is not limited by stiffness.

The selection of polymer for the fabrication of automotive component depends on the physical properties

Table 3. Relative Weight Reduction[a]

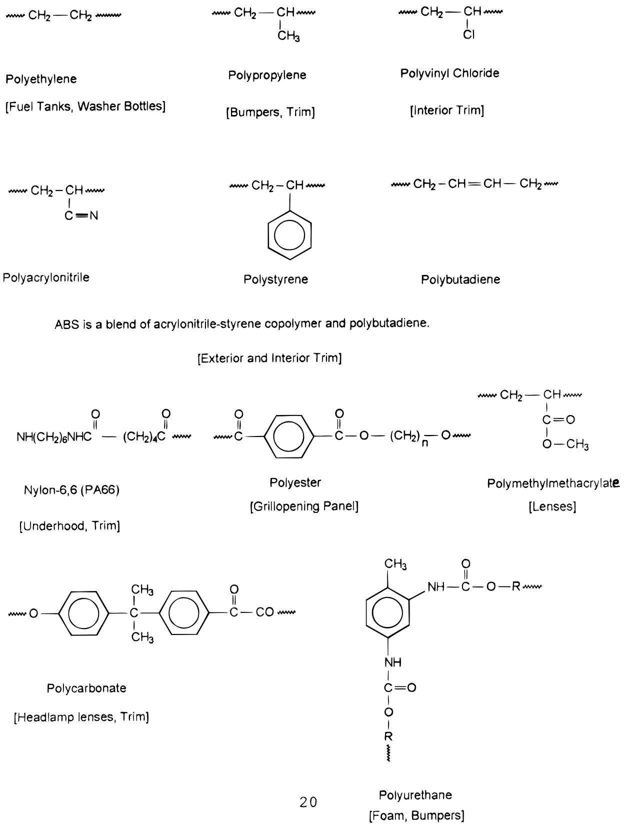
material	relative weight reduction
steel	1.00
aluminum	0.50
unfilled plastic	0.85
40% mineral-filled plastic	0.85
SMC	0.75
40% glass fiber reinforced plastic	0.65
40% carbon fiber reinforced plastic	0.50

[a] These weight reductions are estimates only.

of polymeric materials which span an extremely broad range. For example, the moduli of typical polymers range from less than 0.1 GPa for elastomeric plastics to greater than 10 GPa for reinforced composites. The temperature range of use also varies widely: rubber modified plastics are available which remain ductile down to −40 °C while high-temperature plastics can remain rigid out to 300 °C. This range of properties has led to a large number of different automotive applications for polymeric materials. In total, around 3 billion pounds of polymeric materials were used by the North American automobile industry in 1994. Plastics account for some 15% of the average vehicle's weight. The usage of plastics has doubled in the past 10 years. Much of the increase has been a result of polymers replacing other materials such as steel or glass. In the sections that follow, some of these applications will be described along with future trends.

The wide range of physical properties that can be produced from polymers is a direct result of the large number different polymer types and the resulting microstructures that can be synthesized. To better describe why certain materials are selected for a given application, it is useful to summarize the different classes of polymeric materials and to describe their microstructures. The organic part of a polymeric material consists of long chain polymers with various additives and stabilizers. Where necessary, the polymer is combined with different inorganic fillers and/or reinforcing fibers to form a composite. The most common synthetic pathways are addition polymerization (when the monomer contains a carbon−carbon double bond) and condensation polymerization. Polymer molecular weights ranging from $>10^4$ to 10^6 are realized. More detailed descriptions of specific polymers are given elsewhere[61] (Chart 1).

Chart 1. Typical Polymers Used in Automotive Applications



In a melt, polymer chains assume the shape of random coils. As the polymer cools, it can either maintain an amorphous random coil structure or form crystalline domains. The degree of crystallinity, if any, depends on the monomer and other details of chain structure, such as the number of branch points or other defects. Polymers that are stable in a melt are termed *thermoplastics* indicating that they can be melted and solidified over and over again. Polymers with reactive functionality form permanent crosslinked structures in a melt. These materials are referred to as *thermosets*. These materials cannot be remelted. The temperature range over which polymeric materials can be used depends on the glass transition temperature (i.e., the temperature at which the polymer chain becomes rigid), the crystallization melt temperature, and the degradation temperature.[62,63] The glass transition temperature defines the upper usage limit for amorphous, glassy polymers. It defines the lower use temperature for lightly cross-linked elastomers and rubber modified thermoplastics. The melt temperature is the upper limit for semicrystalline polymers, while the degradation temperature limits all polymers. Semicrystalline polymers are generally ductile between the glass and melt temperatures and brittle below the glass transition temperature.

A wide variety of fillers and reinforcing fibers can be used to modify the physical and mechanical properties of polymers. The most common fillers are talc, mica, calcium carbonate, and carbon black. Glass fibers (both continuous and chopped) are used to increase the modulus of polymeric materials.[64] The most common reinforced composite in automotive applications is sheet molding compound (SMC) which consists of a thermoset polyester resin, calcium carbonate filler, and chopped fiber glass.[65] Carbon fibers provide additional stiffness, but their use has been limited due to high cost.[66] A schematic of composite parts of a graphite fiber composite car is shown in Figure 3.

Fabrication methods depend both on the part and on the material.[67] Thermoplastic materials used in automotive applications are usually formed by injection molding or blow molding. Thermoset materials are formed by reaction injection molding, by compression molding, or in the case of continuous reinforced composites by resin transfer molding. The application of plastic based materials in various automotive components is discussed in this section.

Bumpers. Twenty years ago, all bumpers were manufactured using chrome-plated steel. Today, bumpers on virtually all cars and an increasing number of trucks consist of a plastic cover over a beam that can be either metal or plastic. Bumpers represent one of

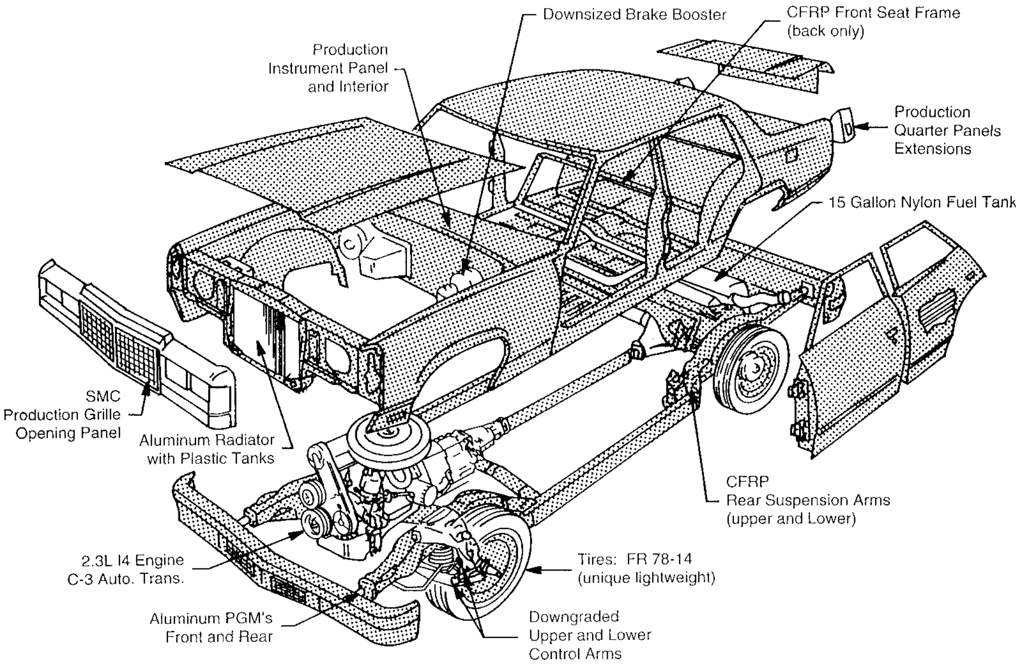


Figure 3. Schematic view of carbon fiber reinforced plastic vehicle with the composite components.

the largest uses of plastics (~400 million pounds/year). Bumpers have both functional (they must be able to withstand low-speed impact) and appearance requirements. The bumper beam is also part of the overall crash energy management system. Good impact performance requires that bumper cover materials be extremely ductile, even at low temperatures.

The first plastic bumper materials were thermoset polyurethanes formed by reaction injection molding (RIM) of a polyol and isocyanate. These materials both cross-link and phase separate during molding to form a tough, but flexible (~0.5 GPa modulus) polymer. RIM urethane bumper covers are still widely used but are gradually being replaced by thermoplastic materials which offer advantages in recycling and cost.

Several different types of thermoplastics can be used for bumpers. For example, a rubber toughened blend of polycarbonate and polybutyleneterephthalate (PC/PBT) can be used to produce a relatively hard, high modulus (2 GPa) bumper. Polycarbonate is a very tough thermoplastic while the PBT provides environmental resistance. Energy management is provided by both the beam and the cover which are adhesively bonded or welded together.

Another type of thermoplastic bumper cover uses a relatively low modulus (~0.5 GPa) rubber toughened polypropylene. This material is gradually replacing RIM urethane bumpers. The choice between hard and soft covers is primarily decided by design issues. Since soft covers deform more easily, they can be mounted flush against the sheet metal body without concern for damaging sheet metal during low speed impact. Soft bumper covers must be mounted over relatively stiff beams for energy management. The key issue for polypropylene-based bumpers is paintability.[68] Polypropylene has a very low surface energy. Special surface treatments or primers are required to achieve good paint adhesion. Current trends in polypropylene based bumpers include introduction of reactive functionality into the polymer chain to promote paintability and developing materials to produce thinner (and, thus lighter) bumper covers. Reducing wall thickness by 25% (3.5−2.8 mm) while maintaining part stiffness requires a doubling of the modulus. Injection molding thin wall parts requires lowering the viscosity of the melt plastic significantly. These developments are being assisted by recent breakthroughs in olefin synthesis. Single site metallocene catalysts offer potential for better control of polyolefin microstructure than is available with traditional Ziegler−Natta catalysts.

Fuel Tanks. Fuel tanks have been traditionally constructed using terne plated steel. Blow-molded polyethylene fuel tanks were introduced about 10 years ago. Plastic fuel tanks offer several advantages over steel including lower weight, greater design flexibility, and, in some cases, decreased cost. Polyethylene tanks have excellent impact and overall durability performance. The major outstanding issue with polyethylene tanks is fuel permeability. Hydrocarbon fuels swell polyethylene by 5−10%. Hydrocarbon diffusion coefficients in polyethylene are of the order of 10^{-8} cm^2/s, leading to a permeation rate of roughly 8 g/day for a typical tank. While this is negligible compared to the overall capacity (~50 kg), it is significant when compared to the amount of hydrocarbon emitted as a result of combustion (<0.2 g/mile). New regulations require significant reduction in hydrocarbon permeation. Fuel tanks will be expected to have permeation rates of ~0.1 g/day. Surface treatment of the inside of the tank by fluorination has been shown to reduce permeability, but the long-term durability of such treatments is not well-known. The best approach to reducing permeability seems to be coextruding a barrier layer as shown in Figure 4. Ethylene−vinyl alcohol copolymers are glassy polymers which greatly reduce hydrocarbon diffusion and solubility. Methanol containing fuels tend to have slightly higher but still acceptable permeation rates due to plasticization of the EVOH by methanol. Key issues are ensuring good adhesion between the barrier layer and the polyethylene and process control to ensure uniform barrier thickness.

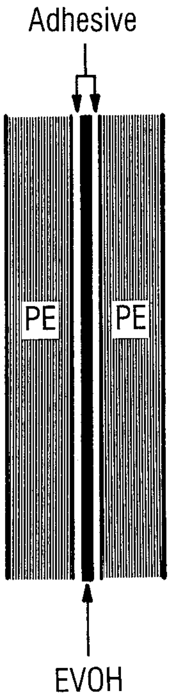


Figure 4. Typical coex wall structure.

Plastic Lenses. Plastics have replaced glass in virtually all lense (taillight, side marker, and headlamp) applications. Two different transparent, amorphous plastics are used. In applications where high impact strength is not required, acrylics (izod impact strength ~0.4 ft lbs/in) are used. In headlamp applications, where high impact strength is required, polycarbonate (izod impact strength ~14 ft lbs/in) is used. The polycarbonate lenses are coated to improve abrasion resistance, provide UV durability, and prevent solvent crazing. As the size of headlamps is reduced, operating temperatures increase, approaching the upper use temperature of polycarbonate. Modified polycarbonates with higher glass transition temperatures may have to be used. Replacement of glass by plastic in glazing applications is the subject of significant research. Issues include improving long-term durability and abrasion resistance, understanding the dynamics of plastic glazing during impact, and engineering glazing components to compensate for the large difference in coefficient of linear thermal expansion (CTLE) between plastic and metal fixtures.

Underhood Applications. Plastics have been widely used as containers, trays, electrical connecters, fan shrouds, etc. As the engine compartment has become more crowded, operating temperatures have risen to as high as 150 °C. This has led to material changes and selective shielding of plastic components. Recently, plastics have begun to be used in more demanding applications such as valve covers and intake manifolds. The manifold application illustrates many of the current underhood development issues and will be described in more detail. Traditionally, manifolds were cast aluminum. Manifolds are extremely complex structures which often cannot be molded as a single piece by conventional injection molding. Complex parts used to be made by a process called lost-core molding. Low-melt-temperature metal cores were inserted into the mold to produce the required shape. Phenolic resins were injected into the mold and cured. The part was removed from the mold and heated to complete cure, melt, and remove the metal cores. Molding costs for this process were fairly high, and the phenolic resin tended to be brittle. This process has been replaced by injection molding two or more pieces using filled nylon and assembling the pieces with adhesives or frictional welding. Injection molding has the advantage that the inside surfaces are very smooth leading to better air flow and performance. A key issue with any high-temperature application is demonstrating long-term (10 year) durability, including dimensional stability.

Body Panels and Other Structural Components. Body panels and other structural automotive components have been traditionally made from steel. SMC was first used on the Corvette in 1952. Continuous reinforced composites were introduced by Lotus in 1956.[69] SMC is the dominant plastic resin for body panels. In 1994, usage exceeded 200 million pounds for the first time.[70] While the use of SMC has steadily increased over the past several years, its usage is still very small in comparison to steel. The use of continuous fiber reinforced composites is limited to very low volume, specialty vehicles. Nonreinforced plastics have also been used in a very limited number of applications. Lower modulus and a relatively high CLTE value limit the application of nonreinforced plastics. Nonreinforced plastics have CLTE values of $\sim 80 \times 10^{-6}$ in./in. C, while composites and metals have values $\sim(10-20) \times 10^{-6}$ in./in. C. High CLTE values require larger than desirable gaps between parts to avoid warping during paint bake.

Metal Matrix Composites

The need to replace iron based metals to reduce the weight of the vehicles has led to the application of light weight metals such as aluminum and magnesium alloys. For example, aluminum–silicon eutectics are quite common in the fabrication of engine components such as blocks and cylinder heads. Pure aluminum cannot be used due to its low melting point and strength, while a 16% silicon containing aluminum alloy normally has the suitable properties. Since the 1960s, it has been known that the mechanical properties of light alloys can be greatly enhanced by reinforcing them with ceramic fibers.[71] These materials, called metal-matrix composites [MMC], are a promising family of next generation structural materials and will be playing a role in replacing metals in the fabrication of car components.[72] In addition to reduced weight, the MMC based components show improved NVH, controlled thermal expansion, and improved thermal and mechanical durability.

Feest defines metal matrix composites as continuous metallic materials containing an artificially introduced second phase.[73] The properties of MMCs depend on the method of fabrication and the nature of the reinforcing material. Continuously reinforced MMCs are superior to the short-fiber/whisker-reinforced MMCs which in turn are superior to matrix metal/alloys. The early MMCs were continuous fiber-reinforced metals with a macrostructure similar to that of the fiber reinforced plastics. High costs prevented any large-scale application of MMCs outside of the aerospace and military industries. Improvements in the fabrication methods and development of cost-effective preforms of short fiber or whiskers reinforcement have led to some civilian applications. For example, pistons for Toyota light diesel engines are in commercial production,[74] and Honda is employing an alumina and carbon-reinforced aluminum silicon alloy cylinder liner.[75]

For the automotive industry, particle-reinforced aluminum composites are of considerable interest SiC, TiC, and Al_2O_3 being the primary reinforcement materials in volume fraction ranging from 5 to 30%. Higher volume fraction materials containing 45−75% of the ceramic component are also of interest for specialized applications such as electronic packaging. Several components such as brake rotors, brake calipers, brake backing pads, drive shafts, cylinder liners, cylinder head inserts, block bearing inserts, mechanical tappets, oil pump rotors, pulleys and sprockets, piston inserts, rocker arms, connecting rods, suspension components, and housings based on MMCs are under development at various automotive industrial research laboratories and may be used in vehicles in the coming 10−15 years.[72] Electronic packaging is another area where MMCs are expected to play an important role since packaged modules must withstand stress caused by the underhood vibrations, high heat, and temperature changes in various climates. Ceramic-based electronic modules are currently in production. A module contains a stack of silicon, solder, copper, aluminum nitride, copper, solder, and a baseplate of copper or aluminum. Since the thermal expansion coefficients of these materials differ considerably, the temperature changes associated with vehicle operation cause considerable stresses. High ceramic content metal matrix composites Cu−SiC and Al−SiC are expected to eliminate the solder, copper, and aluminum nitride layers. For the fabrication of a suitable MMC for electronic packaging, several factors need to be considered: (1) the thermal expansion coefficients of the ceramic phase and metal phase differ considerably, (2) the thermal conductivity of the composite has a nonlinear dependance on the component phases, (3) the thermal conductivity of the composite depends on the particle size and intermixing, and (4) the Kapitza resistance associated with fine particles mandates larger particle size.

The common methods for the fabrication of MMCs are melt stirring[76] and pressureless liquid metal infiltration,[77] pressure infiltration, and powder metallurgy.[78] Other technologies for producing MMCs include semisolid slurry processing,[79] exothermic dispersion, and cospraying.[80] The selection of methods to prepare MMCs depends on a number of factors, including economics and the nature of the raw materials. The low-cost production method starts with molten metal ingots. The ceramic powder is then added to the molten metal with stirring to prepare MMC ingots or bars. Complex shapes of components are fabricated by casting, forging, or extrusion into components. In the powder metallurgy method, powdered metals, mixed with ceramics and binders, are used to fabricate the green bodies of complex shapes which are then subjected to a process to remove the organic binder. Each green body is then fired to obtain the component in finished form. The machining of the resulting composites is substantially less expensive than that of a ceramic-based material. This method provides a superior distribution of the ceramic component in the matrix. Powder metallurgy-based methods are obviously quite expensive, although the resulting MMCs have superior fatigue properties.

Reinforcement Materials. Reinforcing materials are generally ceramic fibers, whiskers, or particles. The selection of a reinforcing material is based on economic factors, chemical stability, and desired properties.[81] Ceramics containing silicon, carbon, boron, or oxygen react with aluminum forming solid solutions or stable compounds.[82] Interaction between the ceramic phase and aluminum is necessary to achieve bonding but excessive reaction results in the formation of interfacial compounds which may degrade the performance of the MMC.[79] For example, the prolonged exposure of silicon carbide to the molten aluminum leads to the formation of Al_4C_3 which deteriorates the performance of the SiC/Al composite. Also, if the temperature of the SiC/Al rises above 710 °C, the excessive formation of Al_4C_3 increases the viscosity of the melt resulting in the degradation of mechanical properties in cast composites and a severe loss of corrosion resistance. Excessive formation of Al_4C_3 makes the melt unsuitable for casting.[83]

Some of the reinforcing materials are unsuitable due to low wettability. In some cases, the wettability can be improved by the additives or coatings. For example, addition of magnesium to the aluminum melt improves the wettability of mica,[84] addition of magnesium and silicon to the aluminum melt improves the wettability of graphite particles,[85] and coating with titanium boride improves the wettability of carbon fibers. The properties of some representative commercially available reinforcing ceramics are listed in Table 4.

Ceramic Precursors in Fabrication of Metal Matrix Composites. The application of ceramic precursors in the fabrication of MMCs has not been extensively studied. Yajima et al. described the first known example of Fe−Cr alloy based MMCs using polycarbosilane as an in situ source of silicon carbide and as a binder.[86] In this process, polycarbosilane was mixed with the iron−chromium alloy and hot-pressed at 1100 °C. The resulting MMC contained Cr_7C_3 and $CrSi_2$ and showed a Vickers microhardness of 345 and an excellent abrasion resistance. Seyferth and Czubarow used poly(methylsilane) (PMS) cross-linked with $((\eta^5\text{-}C_5H_5)_2ZrH_2)_n$,[87] nicalon polycarbosilane (PCS),[88] polysilazane (PSZ),[89] and polysilane containing methyl, vinyl, and hydrogen substituents (PVS) to prepare a variety of MMCs with an aluminum or a titanium matrix.[90] All of the polymers formed MMCs with titanium, but only PMS was suitable for the preparation of aluminum MMCs. At low temperatures, pyrolysis of the precursor took place resulting in the distribution of the amorphous ceramic in the metal matrix. This amorphous phase/precursor reacts with the metals at elevated temperatures forming metal-based ceramics. For example, an aluminum/PMS composite formed an Al_4C_3−Si−Al composite at 1000 °C with improvement in hardness:

$$4Al + 3SiC \rightarrow Al_4C_3 + 3Si$$

The formation of aluminum carbide makes these composites unsuitable for structural application due to the degradation of the properties.

Narula et al.[91] briefly mention the fabrication of TiN-containing MMCs using $(CH_3)_3SiNHTiCl_3$.[92] Narula et al. have also shown that poly(borazinylamine)[93] can be used to prepare a variety of MMCs.[94] The MMCs

Table 4. Materials for Metal Matrix Composites[a]

particulate type	density (g/cm^3)	melting point (°C)	modulus (GPa)	thermal expansion ($K^{-1} \times 10^{-6}$)	size (μm)	cost ($/lb)
TiB_2	4.50	2800	55−574	4.6	>40	17.5
SiC	3.22	2300	450	4.5	1−7	2.0−3.5
TiC	4.95	3000	460	7.6		
ZrC	6.75	3500	350	6.6		
AlN	3.30	2200	320	5.5	>40	21.0
BN	3.48	2500	195	7.5	3−40	35.0
Si_3N_4	3.60	1750	300	3.7		
TiN	5.50	2900		9.4		
ZrN	7.30	3000		7.0		
Al_2O_3	3.97	2015	380	8.0	1−80	0.70
MgO	3.75	2620	275	13.0		
SiO_2	2.65	1610	110	0.55		
TiO_2	4.26	1800	88	6.8		
Whiskers/Short Fibers					diameter	
β-SiC	3.20		410	~4.3	0.05−1.5	140−352
β-Si_3N_4	3.20		379	~3.2	0.1	700

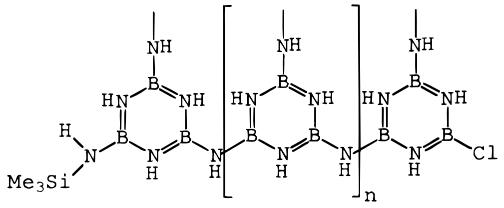
[a] From: Lucas, K. A.; Clarke, H. *Corrosion of Aluminum-based Metal Matrix Composites*; John Wiley & Sons Inc.: New York, 1993.

Table 5. Metal Matrix Composites from Preceramic Precursors

sample	phases	density[a]	hardness
Al/PBA/500	Al, AlN	2.40	25.5 HV
Al/PBA/1000	Al, B, AlN, AlB_2	2.55	51.2 HV
Ti/PBA/1200	Ti, TiN, TiB	4.06	70.0 HRA
Fe/PBA/800	Fe, $Fe_{23}B_6$	4.80	33.2 HV
Fe/PBA/1200	Fe, B, $Fe_{23}B_6$, Fe_3N	6.60	25.0 HRA
Cu/PBA/900	Cu	6.47	37.0 HV
W/PBA/1200	W, W_2B, WN	12.1	35.0 HRA
Ni/PBA/1000		5.1	
Ni/PBA/1200	Ni, Ni_3B	C	
Fe,Cr/PCS/1100			

[a] Density of metals: Al, 2.7; Ti, 4.5; Fe, 7.8; Cu, 8.9; W, 19.3; Ni, 8.9 g/cm3. C = too brittle to determine hardness. HV = hardness, Vickers; HRA = hardness, Rockwell (A).

prepared by this method contain amorphous boron nitride at low temperatures which reacts with metals at elevated temperatures to furnish metal borides:



The advantage of using this precursor is that metal/boride or metal/boride/nitride MMCs can be prepared with a fine distribution of ceramic phases. The properties of some of the MMCs prepared from ceramic precursors are listed in Table 5.

All four reports use powder metallurgy based methods. First, a metal powder and a ceramic precursor are intimately mixed in the presence of a solvent. After the removal of the solvent, the remaining powder is used to fabricate a green body by isostatic pressing. Since ceramic precursors also function as binders, there is no need for the addition of a binder or dewaxing of the green body. The green bodies are then fired to obtain metal-matrix composites. Although the development of this application of ceramic precursors is at the early stages, some of the limitations are obvious. Low-temperature treatment results in MMCs with amorphous ceramic phases which are not desirable. High-temperature treatment leads to the reaction of the metal matrix with the ceramic component. This implies that the precursor should be carefully selected so that the resulting MMCs contains the targeted ceramic phase. Due to the high cost of MMC component produced via powder metallurgy, this method could be most useful in fabricating MMCs for electronic applications and certain specialized structural applications.

Automotive Catalysts

The automotive catalyst is probably the most important example of the successful application of ceramics in the automotive industry. It consists of a ceramic substrate which is coated with a high surface area washcoat containing metals and wrapped in a ceramic fiber bed before being placed in a steel case. The catalysts became integral parts of vehicles to reduce the emissions resulting from the burning of fossil fuel in the fall of 1974 in the USA. The three-way catalyst (TWC) was first installed in 1979. This catalyst simultaneously treats reducing pollutants, CO and HC (uncombusted hydrocarbons), and oxidizing pollutants, oxides of nitrogen. Federal (49 states) exhaust emission standards and California's standards are listed in Table 6.[95] The chemical reactions taking place during catalyst operation are as follows:

Oxidation

$$2CO + O_2 \rightarrow 2CO_2$$

$$2HC + 3O_2 \rightarrow 2CO_2 + H_2O$$

Reduction/Three-Way

$$2CO + 2NO \rightarrow 2CO_2 + N_2$$

$$4HC + 10NO \rightarrow 4CO_2 + 2H_2O + 5N_2$$

Gasoline is a mixture of hydrocarbons containing roughly 20% butanes and pentanes, 35% aromatic compounds, and 45% alkanes and alkynes. Under ideal conditions, the combustion of gasoline in air should produce only CO_2, H_2O, and N_2. However, the exhaust also contains uncombusted hydrocarbons, hydrogen, carbon monoxide, and nitric oxides (product of the reaction of nitrogen with oxygen in the cylinder at combustion temperature).

The driving force behind research on catalysis has been (i) the improvement of the catalyst performance

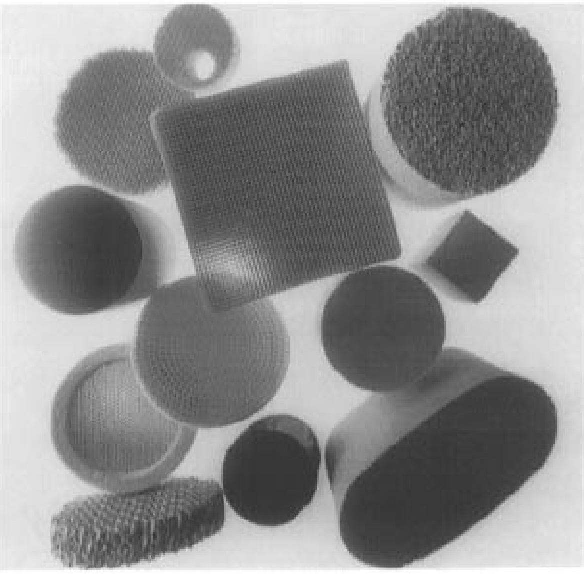


Figure 5. Various shapes of monoliths.

Table 6. Exhaust Emission Standards for Passenger Cars

Federal Standards

	durability mileage/year	exhaust (g/mi) HC/CO/NO$_x$	effective year
precontrol		10.6/8.4/4.1	1968
current	50 000/5	0.41/3.4/1.0	1981
tier I	50 000/5	0.25/3.4/0.4	1994
	100 000/10	0.31/4.2/0.6	1994
tier II	100 000/10	0.125/1.7/0.2	2004

California Standards

emissions (g/mi at 50 000 mi)			
hydrocarbons	NO$_x$	CO	effective year
8.8	3.6	87.0	pre-1966
0.9	2.0	9.0	1975
0.25	0.4	3.8	1994
0.062	0.18	2.8	2003

and (ii) to meet and exceed regulatory requirements. Understanding of the materials issues is quite important and is expected to contribute toward the improvement of the catalysts. We will describe those issues here while limiting the mechanistic aspects of the catalytic interaction of exhaust gases to the current understanding of the process. Automobile catalytic converters are described in a volume by Taylor.[96] The historical development of catalysts can also be found in a paper by Church et al.[97] A specialized review on the studies of the mechanism of the interaction of gases with metals can be found in ref 98.

Two types of catalyst supports have been used in the automotive industry for emission control, monolithic and pelletized. Ford and 3M started working with monolithic substrates by dipping thin papers in ceramic slurries, corrugating, and firing. Corning Glass Works, working with automotive companies, developed the cordierite honeycomb substrate. Honeycomb substrates are now the standard for automobiles and several other companies have prepared their own version of honeycomb type substrates (Figure 5). Cold-start conditions prompted the reinvestigation of metal-based substrates for electrically heated catalyst devices. There are efforts to develop high-temperature substrates.

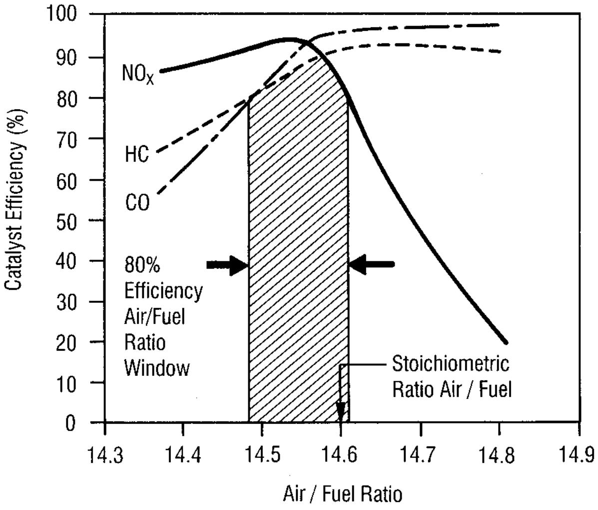


Figure 6. Simultaneous conversion of hydrocarbons, carbon monoxide, and NO$_x$ for three-way catalyst as a function of air-to-fuel ratio.

Monolithic substrates are impregnated with a slurry containing washcoat materials and platinum group metals (PGM). An alumina washcoat containing a variety of other metal oxides provides a high-surface-area medium where the exhaust gases undergo reduction and oxidation on the catalytic metals such as platinum, palladium, and rhodium. The exact volume fraction of metal oxide additives and active metals varies from manufacturer to manufacturer. Earlier catalysts were primarily oxidation catalysts. Engines were calibrated to run on the fuel-rich side of the air–fuel ratio, and air pumps were used to add sufficient oxygen to the exhaust gases. This method treated hydrocarbons and carbon monoxide while nitric oxides were controlled by exhaust gas recirculation. Three-way catalysts have almost replaced the oxidation catalysts. The catalyst is called a three-way catalyst because all three pollutants (HC, CO, and NO$_x$) of the exhaust are treated simultaneously over the same catalyst. This type of catalysis is successful due to improved control strategy, which maintains stoichiometric air–fuel control over varying driving conditions. The catalyst operates at near stoichiometry (defined as ratio of reducing to oxidizing gases in exhaust gases). Figure 6 shows conversion of HC, CO, and NO$_x$ as a function of air–fuel ratio. The narrow window in which conversion of all three gases occurs is close to the stoichiometric point.

Oxygen sensors and feedback control loops play an important role in controlling the exhaust gas mixtures. The exhaust gas oxygen sensor (EGO) is made of an anionic conductive solid electrolyte of stabilized zirconium oxide and has two electrodes made of high surface area platinum.[99] One electrode is installed in the exhaust stream and the other is positioned in natural air to act as a reference electrode. The sensor is an oxygen concentration cell, and the voltage generated across the sensor is described by the Nernst equation:

$$E = E_0 + \frac{RT}{nF} \ln \frac{(PP_{\mathrm{O}_2})_{\mathrm{reference}}}{(PP_{\mathrm{O}_2})_{\mathrm{exhaust}}}$$

where n = number of electrons transferred, F = Faraday constant, and E_0 = standard state voltage.

When oxygen deficiency in the exhaust results in the depletion of the sensor's surface oxygen, the sensor indicates change in voltage. Under oxygen-rich conditions, surface oxygen does not deplete and the sensors indicates a high concentration of oxygen. The voltage signal is fed into a fuel injection control device which adjusts the air−fuel ratio according to the strength of the signal. Modern sensors, modified to be more tolerant of catalyst poisons, are called heated exhaust gas oxygen sensor (HEGO).[100]

There is a time lag associated with adjusting air−fuel ratio due to the time required to process the sensor signal. Thus, the catalyst alternatively operates in slightly rich and slightly lean conditions. This results in the corresponding needs for a small amount of oxygen and the removal of a slight excess of oxygen. In other words, an oxygen storage component is also needed for stoichiometric operation of the catalyst during the time lag between oxygen sensing by the EGO and the adjustment of air−fuel ratio. This component consists of materials such as cerium oxide in the washcoat, which can easily undergo oxidation to remove excess oxygen or reduction to provide oxygen.[101] PGM with cerium oxide also catalyzes the reactions of CO and hydrocarbons in the rich mode and the reaction byproduct hydrogen contributes toward NO_x reduction to nitrogen.

Rich Conditions

$$CeO_2 + CO \rightarrow Ce_2O_3 + CO_2$$

Lean Conditions

$$Ce_2O_3 + {}^1/_2O_2 \rightarrow CeO_2$$

Some important developments are necessary to continue improvement of the automotive catalyst devices. Unfortunately, the current catalysts do not become operational until the so-called light-off temperature, at which point the catalyst converts at least 50% of the pollutants. During a cold start, it takes about 1 min for a catalyst to achieve this temperature. There are several possible approaches to alleviate this problem which require complex hardware, e.g., recirculation, hydrocarbon traps, exhaust gas igniters, burners, electrically heated catalyst devices, etc. Out of these, two approaches can involve materials chemistry. The first approach requires a catalyst which operates during cold start due to its close proximity to the exhaust manifold. For catalyst to remain effective in this location, the substrate, washcoat, and metal component need to be stable at high temperatures. The second approach relies on fast heating of the catalyst to the light-off temperature using an electrically heated catalyst device.

The catalyst life and effectiveness for high-temperature operation also needs to be addressed. The temperature rises considerably during fast acceleration, heavy vehicles such as trucks operate at high temperatures, and close mounting of the catalyst will require a high-temperature catalyst. In a close-coupled configuration, the catalyst is mounted near the engine, which implies that it will be exposed to high-temperature exhaust and will operate at high temperatures. The current catalyst operates at 600 °C under normal urban driving. High speed or heavy loads increase the operating temperature to 800 °C. Finally, a lean-burn NO_x catalyst will be needed for lean-burning diesel and gasoline vehicles. These issues will be discussed further under separate sections with emphasis on issues of interest to the materials chemist starting with the components of a three-way catalyst.

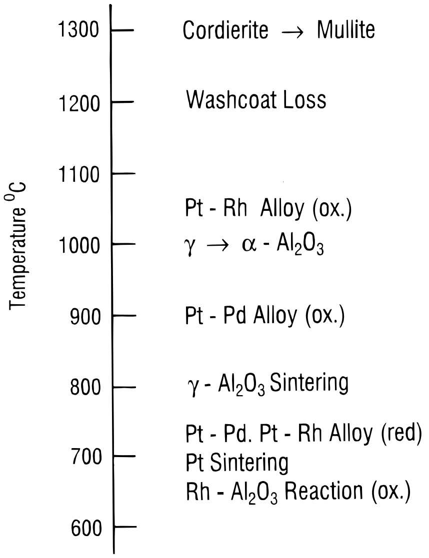


Figure 7. Approximate temperature ranges of catalyst deactivation processes.

Substrate. The current substrate is made of cordierite (magnesium aluminosilicate) and is typically a rectangular honeycomb with 400 cells/in.2, 6.0 mil wall thickness. Some of the relevant properties of cordierite are as follows: density 2.0−2.53 g/cm^3, melting point 1470 °C, thermal expansion coefficient (25−1000 °C) (1.4−2.6) × 10−6/°C, Young's modulus 139−150 GPa ((20−22) × 106 psi), Flexural strength (25 °C) 120−245 MPa, relative dielectric constant 5.0 K.[102]

The cordierite transforms to mullite when temperatures approach 1300 °C, begins to soften at 1400 °C, and melts at 1450 °C (Figure 7). Mullite is brittle and subject to cracking. Softening and melting irreversibly destroy the substrate structure. Such extreme temperatures are not common in automobile operation but occur during severe engine misfires. Thus a substrate which can withstand higher temperatures is needed not only for prevention of catastrophic failure during misfires but also for sustained higher temperature operation such as Autobahn driving, heavy-duty trucks, etc. There is also interest in metallic substrates for high-performance vehicles because they can be prepared with thinner walls. This design reduces backpressure and decreases power losses.

Washcoat. The commercial washcoat consists of a high-surface area alumina containing a variety of proprietary metal oxides which stabilize the surface area of alumina, provide oxygen storage, and assist in suppressing undesirable products such as H_2S. The thermal deactivation of alumina begins at 800 °C and phase changes start to take place above this temperature which result in reduced surface area, increased density, and the collapse of the pore structure. At 1200 °C, the washcoat delaminates from the substrate (Figure 8).[103] A washcoat which can withstand high temperatures without undergoing morphological and structural changes will be needed for a close-coupled catalyst.

Incorporation of alkaline-earth metals and rare-earths in alumina is known to stabilize the surface area at

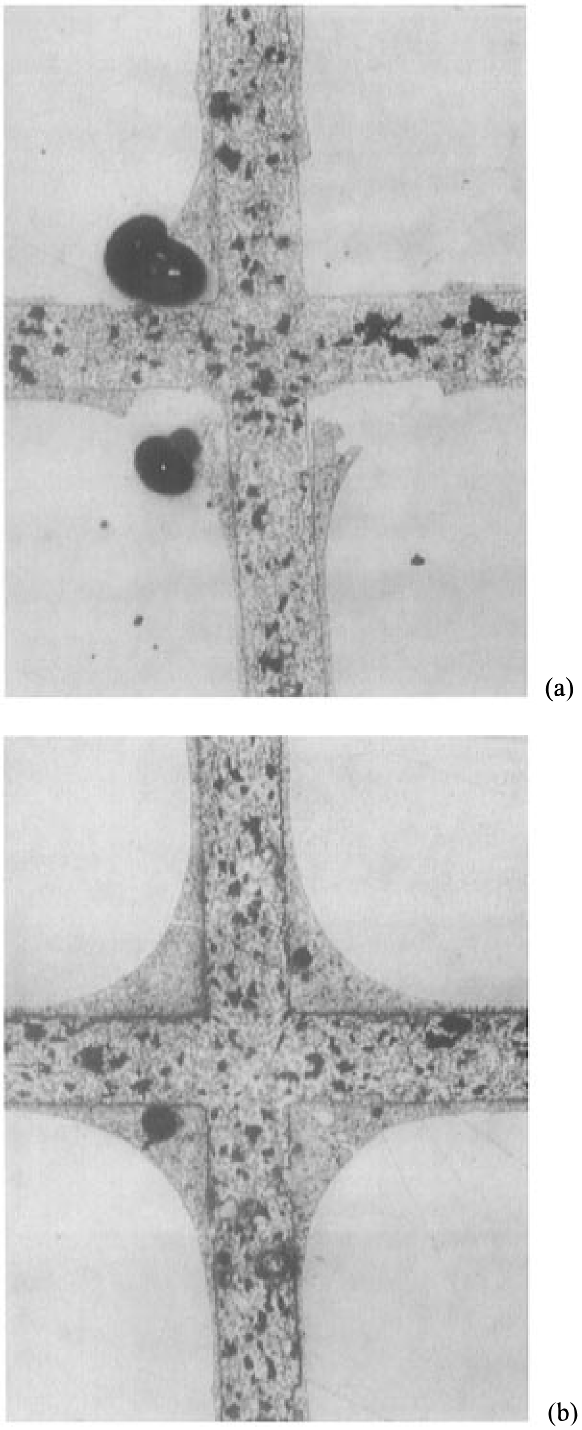


Figure 8. (a) Catalyst aged at temperature above 1000 °C in alternating soot deposition burning cycles and (b) fresh catalyst.

elevated temperatures.[104] Lanthanum[105] and barium oxides[106] are commonly added to the washcoat due to their effectiveness. Silica is also known to stabilize the surface area but introduces undesirable acidic properties.[107] Ceria is considered to be effective[108] as a stabilizer but less than barium oxide or other rare earth oxides.[109]

The precise mechanism of stabilization is not understood but there are two proposed pathways. Beguin et al.[107] proposed that silica replaces the surface hydroxy groups of alumina with the less mobile SiOH group. This hinders the alumina sintering process which occurs by elimination of water from the reaction of neighboring hydroxy groups as suggested by Johnson.[107] Lanthana stabilization is proposed to involve the diffusion of anion vacancies. Ozawa et al. suggest that La^{3+} ions substitute in the alumina lattice which hinders bulk and surface diffusion.[110] Mizukami et al. propose that the increase in cation size reduces mobility, which prevents sintering.[111] It is generally believed that a mixed surface phase is formed which has been identified[112] to be lanthanum β-aluminate, $La_2O_3{\cdot}11Al_2O_3$, as suggested by Matsuda et al.[113] Machida et al.[106] and Arai[114] observed hexaaluminate phases in barium oxide stabilized alumina.

Church et al. investigated the influence of various additives on the surface properties of alumina exposed to high temperatures.[104] Under these conditions, Ca^{2+}, Yb^{3+}, and Sm^{3+} were ineffective, Pr^{3+} and Sr^{2+} were moderately effective, and La^{3+} and Ba^{2+} were the most effective. Hexaaluminate type phases are observed in alumina stabilized with either La^{3+} or Ba^{2+} after heating at 1200 °C. Samples show hydroxy groups which closely resemble those of pure alumina. About 30% of the alumina surface is believed to be made of a capping layer of stabilizers.

There are several known methods for the preparation of stabilized alumina. The preparation of lanthanide stabilized alumina from a mixture of lanthanide alkoxides and aluminum alkoxides has been reported by several authors.[115] Alkaline-earth-metal-stabilized alumina has also been prepared from the hydrolysis of a mixture of alkoxides.[116] Solid-state preparation of lanthanide–aluminum oxides has been investigated and β-alumina $Ln_2O_3{\cdot}5Al_2O_3$, perovskite type $LnAlO_3$, monoclinic $2Ln_2O_3{\cdot}Al_2O_3$, and metastable orthorhombic Ln_2O_3-rich phases have been identified.[117] However, surface properties of these materials are not reported. A sample of γ-alumina modified with La showed a surface area of 12 m^2/g after heating at 1200 °C for 5 h.[118] The activation energy of γ-alumina to α-alumina was 581–583 kJ/mol for pure and Ce-modified alumina and 635–655 kJ/mol for La-, Sr-, and Yb-modified alumina. Lanthanum inserts itself in the lattice and Ce stays on the surface as CeO_2. The preparation of lanthanide containing alumina is also accomplished from coprecipitation of hydroxides from their salts and calcining.[119] Kato et al. report structural transformation as a function of a ratio of La/Al on calcining at 1200 °C.[120] The samples with a La/Al ratio of 2/98 show κ-Al_2O_3 and θ-Al_2O_3, 5/95 contains La-β-Al_2O_3, 10/90 comprises $LaAlO_3$ and La-β-Al_2O_3. The 2 and 5 mol % lanthanum additions are most effective in retention of surface area in the 1000–1400 °C temperature range and are 33 and 37 m^2/g after calcining at 1200 °C, respectively. Increasing lanthanum content above 10% reduced the surface area. The retardation of sintering was caused by La-β-Al_2O_3 and not by $LaAlO_3$ as suggested by Schaper et al.[121]

Compared to commercial alumina, sol–gel processed materials are expensive. There is some cost reduction because the washcoat can be loaded on the honeycomb substrates as a uniform layer without filling up the corners of the channels (Figure 9).[122] Recent studies focus toward using heterometallic alkoxides as precursors.[123] The samples derived from $La[Al(OR)_4]_3$, $Ce[Al(OR)_4]_3$, or their mixtures exhibit a surface area of 40 m^2/g after calcining at 900 °C. The structural

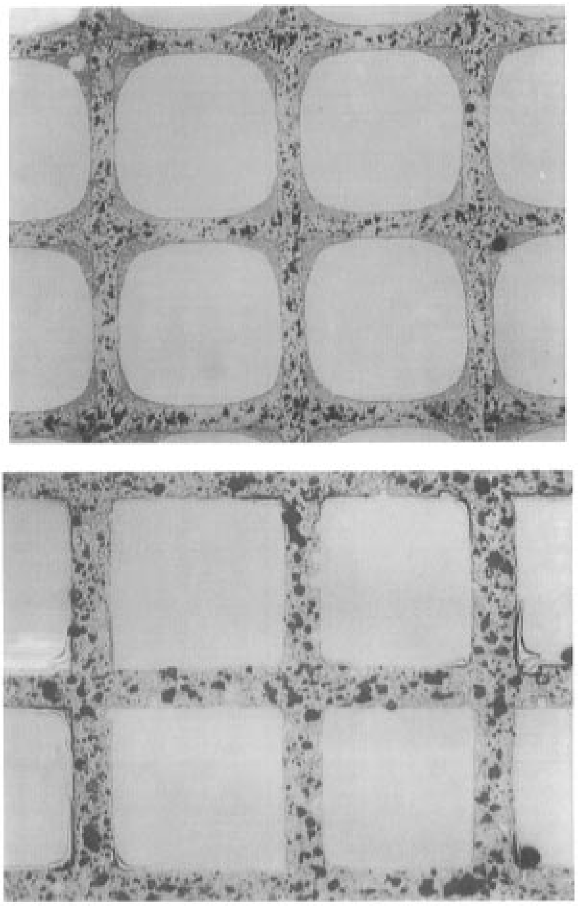


Figure 9. Commercial and sol−gel processed washcoats in honeycomb substrates of automotive catalysts.

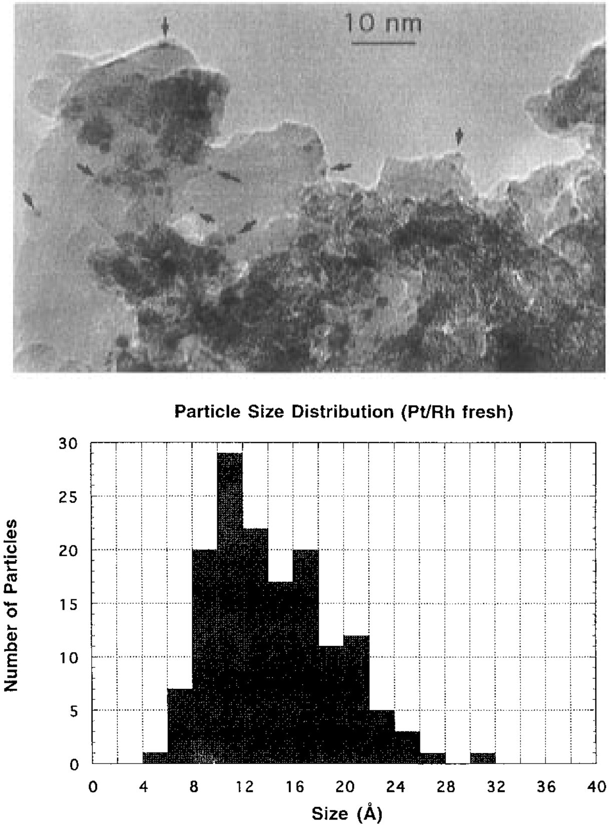


Figure 10. (a) Micrograph of a fresh Pt/Rh TWC. A few ultrafine Pt particles are marked by arrows. (b) Particle size distribution of a fresh Pt/Rh TWC measured by TEM.

chemistry is quite different.[124] The lanthana−alumina samples remain amorphous below 700 °C with the separation of $LaAlO_3$ at 900 °C. The ceria−alumina samples show separation of CeO_2 at 600 °C, and lanthana−ceria−alumina samples show separation of CeO_2 at 700 °C. No new crystalline phase is observed after calcining ceria−alumina or lanthana−ceria−alumina samples at 900 °C. Incorporation of alkaline earths in alumina from heterometallic alkoxides has also been investigated.[125] The mechanism of the hydrolysis of heterometallic alkoxides is not well understood, although current studies suggest that bridging alkoxy groups are replaced with hydroxy groups in the early stages of hydrolysis.[123]

Metals. The noble metals, Pt and Rh, are deposited from their salt solutions by impregnating the washcoat. Subsequent heating results in decomposition of the salts. The particle size of metals on a fresh catalyst is ~13 Å (Figure 10). After 50 000 miles of operation of an average vehicle, the particle size increases to ~57 Å.[126] This thermal sintering results in reduced catalytic sites and thermal deactivation of the catalyst. Deactivation of metals also takes place due to the interaction of metals with the washcoat.

Rhodium primarily catalyzes NO_x reduction and contributes toward the oxidation of CO during catalyst warmup.[127] Its deactivation occurs in the oxidizing environment at >600 °C.[128] The thermal behavior of rhodium−alumina has been extensively studied and at least three different mechanisms for its deactivation have been proposed. The first model suggests that aggregation of Rh at 827 °C takes place;[129] however, Auger electron spectroscopy, electron energy loss spectroscopy, and thermal desorption spectrometry rule out this possibility.[130] The second model suggests the reaction of Rh with alumina;[131] there is no evidence to either support or oppose this hypothesis.[130] The third model suggests high-temperature oxidation and diffusion in alumina.[131,132] Auger studies seem to support this model and suggest that the Rh remains near the surface. The original amount of rhodium can again be made available by reduction in a hydrogen atmosphere for an hour at 800 °C followed by oxidation for an hour at 500 °C.132

Several strategies have been devised to prevent the reaction of Rh with washcoat materials, but these technologies are considered confidential by the catalyst suppliers. One of the strategies is to employ zirconium oxide as a washcoat since it has a lower reactivity toward rhodium than does alumina. Generally, Rh is segregated from CeO_2 by depositing multiple layers of washcoat with Rh and CeO_2 in different layers, in order to prevent their reaction with each other. The stabilization of CeO_2 with the oxides of zirconium, barium, and lanthanum has also been studied as a means to prevent the reaction with Rh.[133] The interaction of Rh_2O_3 and reactive alumina can be substantially slowed by the use of more refractory metal oxides such as zironia.[134]

Since rhodium is very expensive, efforts have been in progress to replace it with other metals. Considerable success has been achieved in developing new palladium-based three-way catalysts. Research from Allied Signal Inc. shows that the Pd catalyst can attain an activity close to that of rhodium for the oxidation of CO and hydrocarbons but is not as effective in the

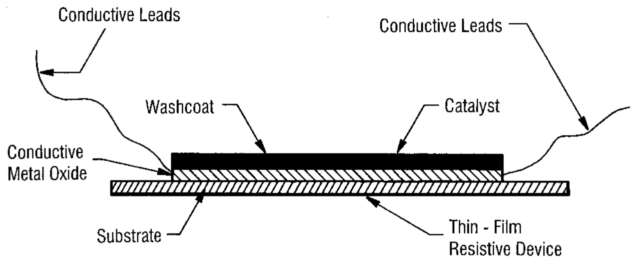


Figure 11. Electrically heated catalyst device.

reduction of NO_x.[135] In general, palladium-based catalysts contain a very high loading of lanthanide oxides and palladium[136] to compensate for the deficiency in NO_x reduction. Muraki claims that the interaction of lanthana with palladium leads to improved hydrocarbon conversion on the rich side of engine operation.[137] Shelef and Graham believe that the enhanced activity of palladium in the presence of lanthanide oxides is directly related to the oxygen storage capacities of lanthanide oxides.[138] The Pd/Rh catalyst replacing platinum was introduced in vehicles in 1989 and a palladium only catalyst has been released in some 1995 models.[139] Among other efforts, alumina sols have been employed to load lanthanum palladium oxides on the catalyst to keep palladium in close contact with lanthanum.[140] Three-way catalyst behavior was observed some 10 years ago from a Pt(Pd)/MoOx(WOx) catalyst; however, this catalyst failed due to the high sulfur content of gasolines and due to the loss of molybdenum and tungsten oxyhydroxides with emissions.[141] Reduced sulfur in reformulated gasolines has led to the renewed efforts in this direction and the laboratory tests show promise.[142]

Electrically Heated Catalyst Devices. During the cold start of the engine, the catalyst is not operational and the emitted exhaust gases are untreated. These emissions can contribute up to 70% of hydrocarbons and CO tailpipe emissions. Several technologies have been proposed[143] to reduce the cold-start emissions. Electrically heated catalyst devices have shown some promise in reducing the emissions.[144] A brief review of various technologies can be found in ref 145. There are several ways to electrically heat the catalyst. The first approach involves heating the substrate which is made of metal.[146] In this method, power consumption is high, requiring a second battery which leads to reduced fuel economy. The second design uses a screen-printed platinum layer on an alumina substrate to simultaneously heat the washcoat and catalyze the exhaust gas reactions.[147] A third design of interest is shown in Figure 11. This design employs placing a thin layer of conducting oxides, nitrides, or carbides on the honeycomb substrate below the washcoat.[148] In a concept design, a fluorine-doped tin oxide layer was placed on a substrate and was coated with titanium oxide by the sol–gel process. The resulting device required low power (50 W) to reach 500 °C in less than 10 s. The low power need is due to low thickness (less than 5000 Å) of conductor and washcoat. This is a low-cost, low-power alternative to the commercial designs. However, for this design to be translated into a commercially viable catalyst, several important improvements need to take place. First, the deposition of conducting metal oxide by the sol–gel process on complex substrates needs to be optimized. Second, a thin nonporous protective layer needs to be deposited over the conducting layer to prevent the reaction of exhaust gases with the conducting layer which could result in catastrophic failure. For the application of non-oxide conductors such as doped silicon carbides, titanium nitride, zirconium nitride, etc., a nonporous protective layer becomes more important to prevent oxidation of the conductors. Currently, there is no economically viable method of mass production. A low cost approach could employ ceramic precursors since the sol–gel process manufacturing method can be modified to prepare ceramic precursor coatings which can then be pyrolyzed to obtain non-oxide conductor films. Unfortunately, there is only one demonstrated report[149] on coating of coupons although there are some examples of coating fibers[150] and particles[151] and several claims in the patent literature. In this approach, alumina coupons were coated with $Me_3SiNHTiCl_3$ from its THF solution and fired to convert the precursor film into titanium nitride film.[149] However, an extensive amount of work needs to be done to find the optimum conditions by studying the effects of concentration, rate of withdrawal, and pyrolysis temperature on the thickness, uniformity, adhesion, hardness, porosity, and conductivity of the films deposited by this method.

Lean-Burn NO_x Catalyst. Since most vehicles operate near stoichiometry, the development of catalysts has been directed toward treating the exhaust of stoichiometric carburation in spark-ignited engines.[152] Thermodynamically efficient lean-burn engines and compression-ignited diesel engines provide better fuel economy, but their exhaust cannot be treated by conventional catalysts. Lean-burn engines operate at a air–fuel ratio of 21–23 as compared to 14.7 for stoichiometric engines and offer up to 10% gain in fuel efficiency.[153] The high efficiency of diesel engines comes from very lean combustion, resulting in high particulate and NO_x emissions. In addition, diesel exhaust is lower in temperature than the stoichiometric engine exhaust imposing another requirement that the catalyst should be effective at low temperatures.

Among the various catalysts, the zeolite-based catalysts have received the most extensive attention for NO_x treatment form the exhaust of both gasoline and diesel engines based vehicles. Selective catalytic reduction of NO_x has recently been reviewed by Shelef with focus on the zeolite-based catalyst.[154] The first patent on this catalyst was granted in 1981 to treat exhaust gases containing NO_x, CO, and HC with copper zeolites.[155] Since then a large number of papers and patents have been granted on the zeolite-based catalysts which are claimed to be effective in treating lean-burn NO_x emissions. A summary of the results on Cu zeolites can be found in an article by Iwamoto and Hamada.[156] While the decomposition of NO_x over Cu-ZSM-5 is faster than over conventional catalysts, it is not fast enough for practical applications. The proposed mechanism of the decomposition of NO over Cu-ZSM-5 involves the high temperature conversion of cupric ion to cuprous ions, adsorption of NO molecules on cuprous ions, and decomposition of the adsorbed ions to nitrogen and oxygen molecules.[157] The reaction of NO_x over Cu-ZSM-5 reaches a maximum in the 450–550 °C temperature range and is dependent on the nature of the catalyst, type, and concentration of HC, time onstream, and space velocity. Carbon monoxide is one of the reaction products of the reduction.

There are several durability issues related to the activity of Cu-ZSM-5 as an automotive exhaust reduction catalyst. Irreversible thermal deactivation occurs at >650 °C with deactivation temperatures decreasing in the presence of water vapors which are normally present in the automotive exhaust.[158] The structural collapse of zeolites and the outmigration of active components is attributed to the deactivation at 650 °C while dealumination is believed to deactivate zeolites at 500 °C.[159] Reactive olefins form carbonaceous deposits while participating in the reduction of NO_x. The deposits impede the gas access to the active sites.[160] Some efforts have been directed toward improving the stability of zeolite-based catalysts. For example, the introduction of certain ions has been investigated to inhibit dealuminations.[161] However, zeolite-based catalysts are still not practical NO_x reduction catalysts.

Several other catalysts which are based on alumina, silica–alumina, zirconia, etc., containing small amounts of Cu or Co have also been investigated but there are no realistic data based on space velocities in the presence of water.[162] Noble-metal catalysts on non-zeolite supports have also been shown to be effective in the low-temperature region and are being considered for diesel applications.[163] However, the reductant is these cases is a mixture of hydrogen and carbon monoxide or a hydrocarbon. Although selective reduction of NO_x is achieved at high space velocities, the addition of reductant species, beyond levels normally found in diesel exhaust, will be required to obtain desired conversions.[164]

Sol–gel processed substrate materials have been investigated as substrate materials for lean-burn NO_x applications since controlled pore sizes can be achieved. Alumina prepared by the Burggraaf method[165] showed a narrow pore size distribution with pore size of 45 Å. Mixing silica sol (5–10 wt % silica in the gel) with Burggraaf's alumina sol and drying to obtain the gel did not change the pore size but improved the thermal stability of alumina. Preparation of alumina gels from a mixture of $(t\text{-BuO})_3Si{-}O{-}Al(O\mathit{i}Pr)_2$ and $Al(O\mathit{i}Pr)_3$ also provided high-temperature stability. Alumina gels, after treatment with silica sol and drying, showed two different pore-sizes (15 and 45 Å). These samples had a BET surface area of 150 m^2/g after aging at 1100 °C. Subsequent steam-aging at 900 °C did not reduce the surface area. Silver deposited on alumina by Burggraaf's method showed a 96% NO_x (cf. Cu-ZSM5, 65%) conversion at 500 °C.[166]

Current diesel lean NO_x technology relies on platinum-based catalysts for the low temperature region (190–250 °C) and on zeolite-based catalysts for high-temperature regions (>350 °C) since diesel engines operates at much lower temperature than gasoline engines. Unfortunately these catalyst are not selective, they oxidize 90% of the hydrocarbons, needed for NO_x reduction. It is important to point out that the diesel exhaust does not contain a sufficient amount of hydrocarbons for NO_x reduction, and additional hydrocarbon fuel needs to be added to the exhaust. Additionally, the exothermic hydocarbon oxidation leads to high bed temperatures, facilitating the conversion of sulfur to sulfates which are emitted as particulates. Recently, Engelhard corporation has announced a proprietary family of catalysts which are effective in reducing NO_x in 150–320 °C range.[167] These catalysts are capable of storing and activating hydrocarbons which then reduce NO_x selectively, thereby reducing the additional hydrocarbon fuel requirement. Degussa AG has also reported their results on platinum based catalysts for low-temperature treatment of NO_x from diesel exhaust.[168] The test results on catalysts supplied by Degussa, Engelhard, and Johnson Matthey can be found in a recent publication from Adams et al.[169]

Future Role of Materials Chemistry

Approximately 30 automobile parts out of 15 000 are made of ceramic materials.[10] The applications of ceramic-based components in low-stress areas can increase significantly provided they can be mass produced at a low cost and exhibit reproducible properties. The discussion presented here shows that it is possible to fabricate ceramic components with acceptable performance if cost is not an issue. Some components can be fabricated at acceptable cost with performance standards and are in manufacture. It should also be obvious that ceramic-based vehicles will not be on the market in the foreseeable future, but the use of ceramic components is slowly increasing. Most of these applications are in advanced components such as electronics, chemical sensors, turbochargers, catalysts, etc. The application of ceramics as structural components has not progressed at the pace envisioned in the 1970s. Obvious reasons are the brittleness of ceramics, the cost associated with the fabrication of the components, the cost of machining, and the lack of low-cost producers. Materials chemistry has offered some alternatives to the traditional processing of materials and it might be possible to develop methods which can be used to fabricate the components at low cost without compromising the properties of the materials. For structural applications, the ceramic powders prepared by ceramic precursor routes do not offer an advantage because they are neither superior to powders made by classical methods nor cost-effective. However, ceramic precursors might play an important role as in situ binders and as reinforcing materials provided that information on (1) shrinkage on pyrolysis of green bodies fabricated from the ceramic powders and ceramic precursor binders, (2) the properties of fabricated components, and (3) information on the failure of the components, becomes available. There is practically no information on the influence on the grain morphology from the controlled chemistry of precursors. This would be an important area of investigation since the elongated grains have been shown to improve the strength of the components fabricated from silicon carbide and silicon nitride.

Automotive applications for polymeric materials extend well beyond traditional interior trim and decorative components. Composites are making significant inroads into body applications traditionally dominated by steel. The potential for weight reduction in structural components using unfilled or mineral filled plastics is relatively small. The actual weight reduction achieved by SMC in comparison to cold rolled steel is typically between 20 and 30%, consistent with prediction. To achieve weight reductions of ~50%, carbon fiber reinforced composites will likely be required. In this regard, it should be noted that in 1979, Ford developed a demonstration vehicle based on carbon fiber composites which achieved part weight savings of 50%. It should also be noted that the vehicle cost over $1 million to build. The main limiting factors in the use of continuous fiber and especially carbon fiber composites are the high cost of carbon fibers and the long processing times to produce dimensionally stable parts. Long processing times limit applications to low volume. Long-term dimensional stability, bonding and assembly, environmental resistance, and design optimization (i.e., taking advantage of the unique, anisotropic properties of continuous composites) are critical research areas.

Another key issue for continued growth of polymeric materials is the ability to recycle. Plastics recycling of automotive components is complicated by the number of different types of plastics that are used. The plastic materials from certain bumpers have been successfully recycled back into other automotive applications.[170] Poly(ethylene terephthalate) (PET) from recycled soda bottles is also being used to replace virgin PET in some applications. Significant materials research is underway both at automotive companies and at their suppliers to promote plastics recyclability.

The fabrication of metal-matrix composites using ceramic precursors is at a preliminary stage. This method seems to reduce the number of steps involved in the fabrication of MMCs from powder metallurgy methods and shows a better distribution of ceramic components in the metal matrix. Unfortunately, the ceramics formed from the decomposition of the precursors are amorphous at low temperatures and react with metals to form carbides which are undesirable for structural applications. Extensive work needs to be done to evaluate ceramic precursors as binders for MMCs. Since there are only a few reports in the literature, a judgement cannot be made. However, it appears that the metal nitride precursors might be more suitable.

The automotive catalyst is the success story of the application of ceramics in the automotive industry. We have presented the needs for future developments in order to meet new regulations. First, a high-temperature substitute for the current packing material is needed for a close coupled catalyst in order to reduce the time for light-off temperature during a cold start. Second, a high-temperature substrate is necessary to withstand the occasional exposure to extreme temperature conditions of sustained high-temperature operation such as autobahn driving, heavy-duty trucks, etc. High surface area washcoat materials which can store oxygen at elevated temperatures without changes in surface properties are also needed. At this time, it seems that palladium will be the metal of choice for the high-temperature operation of catalysts.

Suitable electrically heated catalyst devices with low-power consumption are not available. We have summarized three designs which have been studied. The application of thin conducting layers under the washcoats seems to be promising for developing an EHC device, but there are no prototypes available for testing. Materials and fabrication methods (for both conducting and protective layers) need to be developed before prototype devices can be fabricated. Lean-burn NO_x catalyst is another area with opportunities which is being extensively investigated.

It is difficult to imagine the high-technology needs of the automotive industry since automobiles have been with us for almost 100 years. However, it is important to remember that a cutting edge technology will require exhaustive testing and modifications to make it suitable for automotive application. It should be obvious that extensive opportunities exist for materials chemists to develop a better understanding of materials behavior and processing for automotive applications.

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References

(1) Korcek, S.; Beardmore, P. In *Proceedings of 6th International Congress of Tribology*; Kozma, M., Ed.; 1993; Vol 1, p 44.
(2) For example, incorporation of antilock brake system to improve the safety of the automobiles required modification of brake system and electronics.
(3) Committee on Materials Science and Engineering for the 1990s: Maintaining Competitiveness in the Age of Materials; Chaudhari, P., Flemings, M. C., Cochairmen; National Academy Press: Washington, DC, 1989.
(4) McLean, A. F. *Ceramics for High-Performance Applications*; Burke, J. J., Lenoe, E. N., Katz, R. N., Eds.; Brook Hill: Chestnut Hill, MA, 1978.
(5) Dislich, H. In *Sol-Gel Technology for Thin Films, Fibers, Preforms, Electronics, and Specialty Shapes*; Klein, L. C., Ed.; Noyes: Park Ridge, NJ, 1988.
(6) Post, R. F.; Fowler, K.; Post, S. F. *Proc. IEEE* **1993**, *81*, 462. Burke, A. F.; SAE International, 1991; p 367. Howard, P. F.; Grenhill, C. J. SAE 931817.
(7) Westbrook, M. H.; Turner, J. D. *Automotive Sensors*; IOP Publishing: Philadephia, 1994. Logothetis, E. M. *Automotive Oxygen Sensors*; Chemical Sensor Technology, 3, Kodansha Ltd., 1991.
(8) The higher cost of CVD is determined by considering this process as a system. Assuming that only one device per vehicle needs to be coated and taking into account only the number of cars sold in US (15 million per year), approximately 7200 devices need to finished per hour (based on 40 h work week with no shutdowns for 52 weeks). This would require simultaneous operation of a large number of CVD units operated by skilled workers. This makes CVD too expensive for coating large components.
(9) Griffith, A. A. *Philos. Trans. R. Soc.* **1920**, *221*, 163.
(10) Taguchi, M. *Adv. Ceram. Mater.* **1987**, *2*, 754.
(11) Greil, P.; Seibold, M. *J. Mater. Sci.* **1991**, *27*, 1053.
(12) Greil, P.; Seibold, M.; Erny, T. *Mater. Res. Soc. Symp. Proc.* **1992**, *274*, 155. Reidel, R.; Passing, G; Schönfelder, Brook, R. J. *Nature* **1992**, *355*, 355.
(13) Greil, P. *J. Am. Ceram. Soc.* **1995**, *78*, 835.
(14) Bryzik, W.; Kamo, R. SAE-830314, 1983.
(15) Swain, M. V.; Hannink, R. H.; Garvie, R. C. Fracture Mechanics of Ceramics; Penn State University, 1981; Vols. 5 and 6.
(16) EPRI Proceedings of the second conference on Advanced Materials for Alternative Fuel Capable Heat Engines, EPRI RD-2369-SR Proceedings, May 1982.
(17) Timoney, S.; Flynn, G. SAE 830313, 1983.
(18) Narula, C. K. *Ceramic Precursor Technology and Its Applications*; Marcel Dekker: 1995.
(19) McLean, A. F.; Fisher, E. A.; Harrison, D. E. AMMRC CTR 72-3 [AD 894 052L], 1972. McLean, A. F.; Fisher, E. A.; Bratton, R. J. AMMRC CTR 72-19 [AD 905 043L], 1972. McLean, A. F.; Fisher, E. A.; Bratton, R. J. AMMRC CTR 73-9 [AD 910 446L], 1973.
(20) Wild, S.; Grieveson, P.; Jack, K. H. *Special Ceramics*; Popper, P., Ed.; British Ceramic Research Association, 1972; Vol. 5, p 385.
(21) Lange, F. F. *J. Am. Ceram. Soc.* **1973**, *56*, 518.
(22) Lange, F. F. *J. Am. Ceram. Soc.* **1979**, *62*, 428.
(23) Hampshire, S.; Park, H. K.; Thompson, D. P.; Jack, K. H. *Nature* **1978**, *274*, 880. Hwang, S.-L.; Chen, I.-W. *J. Am. Ceram. Soc.* **1994**, *77*, 165.
(24) Li, C. W.; Yamanis, J. *Ceram. Eng. Sci. Proc.* **1989**, *10*, 632. Tani, E.; Umebayashi, S.; Kishi, K.; Kobayashi, K.; Nishijima, M. *Am. Ceram. Soc. Bull.* **1986**, *65*, 1311.
(25) Becher, P. F. *J. Am. Ceram. Soc.* **1991**, *74*, 428.
(26) Becher, P. F. *J. Am. Ceram. Soc.* **1991**, *74*, 255.
(27) Li, C. W.; Yamannis, J. *Ceram. Eng. Sci. Proc.* **1989**, *10*, 632. Kawashima, T.; Okamoto, H.; Yamamoto, H.; Kitamura, A. *J. Ceram. Soc. Jpn.* **1991**, *99*, 1.

(28) He, M. Y.; Hutchinson, J. W. *Int. J. Solids Struct.* **1989**, *25*, 1053.
(29) Tajima, Y.; Urashima, K. In Tailoring of Mechanical Properties of Si_3N_4 Ceramics; Hoffmann, M. J., Petzow, G., Eds.; NATO ASI Series; Kluwer Academic Publishers: Dordrecht, 1994; p 101.
(30) Messier, D. R.; Wong, P. *Ceramics for High-Performance Applications*; Burke, J. J., Gorum, A. E., Katz, R. N., Eds.; Brook Hill Publishing Co.: MA; p 181.
(31) Evans, A. G; Davidge, R. W. *J. Mater. Sci.* **1970**, *5*, 314.
(32) Godfrey, D. J.; Lindley, M. W. *Proc. Brit. Ceram. Soc.* **1973**, *22*, 229.
(33) Brown, R. W.; Godfrey, D. J.; Lindley, M. W.; May, E. R. W. *Special Ceramics*; Popper, P., Ed.; British Ceramic Research Association: 1972; Vol. 5, p 345.
(34) Mangeles, J. A. *Ceramics for High-Performance Applications*; Burke, J. J., Gorum, A. E., Katz, R. N., Eds.; Brook Hill Publishing Co.: MA, 1974; p 195.
(35) Ezis, A. *Ceramics for High-Performance Applications*; Burke, J. J., Gorum, A. E., Katz, R. N., Eds.; Brook Hill Publishing Co.: MA, 1974; p 207.
(36) Deeley, G. G.; Herbert, J. M.; Moore, N. C. *Powder Met.* **1961**, 145.
(37) Terwilliger, G. R.; Lange, F. F. *J. Am. Ceram. Soc.* **1974**, *57*, 25.
(38) Wild, S.; Grieveson, P.; Jack, K. H.; Latimer, M. J. *Special Ceramics*; Popper, P., Ed.; British Ceramic Research Association: 1972; Vol. 5, p 377.
(39) Kossowsky, R. *J. Mater. Sci.* **1973**, *8*, 1603.
(40) Lange, F. F.; Iskoe, J. L. *Ceramics for High-Performance Applications*; Burke, J. J., Gorum, A. E., Katz, R. N., Eds.; Brook Hill Publishing Co.: MA, 1974; p 223.
(41) Yajima, S.; Shishido, T.; Kayano, H.; Okamura, K.; Omori, M.; Hayashi, J. *Nature* **1976**, *264*, 239.
(42) Luckacs, A. U.S. Patent 5,190,709, 1993.
(43) Schwark, J. M. *Polym. Prepr.* **1991**, *32*, 567.
(44) Schwark, J. M.; Luckacs, A. *Inorganic and Organometallic Polymers II*; ACS Symposium Series 572; American Chemical Society: Washington, DC, 1994; p 43.
(45) Riedel, R.; Passing, G.; Schönfelder, Brook, R. J. *Nature* **1992**, *355*, 714.
(46) Whalen, T. J.; Baer, J. R. In *Silicon Carbide '87*; Cawley, J. D., Semler, C. E., Eds.; Ceramic Transactions; The American Ceramic Society, Inc.: Westerville, OH, 1989; Vol. 2, p 355.
(47) McLarnan, T. J. *Z. Krystallogr.* **1981**, *155*, 269.
(48) *Gmelin Handbook of Inorganic Chemistry*, 8th ed.; Si-silicon; Springer-Verlag: New York, 1984; supplement Vol. B2.
(49) Shinozaki, S. S.; Hangas, J.; Maeda, K.; Soeta, S. In *Silicon Carbide '87*; Cawley, J. D., Semler, C. E., Eds.; Ceramic Transactions; The American Ceramic Society, Inc.: Westerville, OH, 1989; Vol. 2, p 113.
(50) Suzuki, K.; Sasaki, M. *Research Laboratory Reports*; Asahi Glass Co., Ltd.: Japan, 1986.
(51) Whalen, T. J.; Trela, W.; Shinozaki, S. S. U.S. Patent application in process.
(52) Alliegro, R. A.; Coffin, L. B.; Tinklepauph, J. R. *J. Am. Ceram. Soc.* **1956**, *39*, 386. Lange, F. F. *J. Mater. Sci.* **1975**, *10*, 314.
(53) Prochazka, S. In *Special Cermaics*; Popper, P., Ed.; Brit. Ceram. Res. Assoc.: 1975; p 171.
(54) Mulla, M. A.; Krstic, V. D. *Acta Metall. Mater.* **1994**, *42*, 303. Padture, N. P. *J. Am. Ceram. Soc.* **1994**, *77*, 519.
(55) Whalen, T. J.; Winterbottom, W. L. NASA Contr. Rep. 179477, 1986, under Grant NAS3-24384. Whalen, T. J. NASA Contr. Rep. 180831, 1987, under Grant NAS3-24384.
(56) Laine, R. M.; Babonneau, F. *Chem. Mater.* **1993**, *5*, 260.
(57) Yajima, S.; Liaw, C.; Omori, M.; Hayashi, J. *Chem. Lett.* **1976**, 435. Yajima, S.; Liaw, C.; Omori, M.; Hayashi, J. *Chem. Lett.* **1976**, 551.
(58) Yajima, S.; Shishido, T.; Kayano, H.; Okamura, K.; Omori, M.; Hayashi, J. *Nature* **1976**, *264*, 238.
(59) Semen, J.; Loop, J. G. *Ceram. Eng. Sci. Proc.* **1990**, *11*, 1287. Semen, J.; Loop, J. G. *Ceram. Eng. Sci. Proc.* **1991**, *12*, 1967.
(60) Kodama, H.; Miyoshi, T. *Adv. Ceram. Mater.* **1988**, *3*, 177.
(61) Gardner, H. C.; Margolis, J. Section 2, pp 97−220, of *Engineering Plastics*; Vol. 2 of the Engineered Materials Handbook of ASM; ASM: Metals Park, OH, 1988.
(62) Larramee, R. E. Section 2, p 439, of *Engineering Plastics*; Vol. 2 of the Engineered Materials Handbook of ASM; ASM: Metals Park, OH, 1988.
(63) Shalaby, S. W.; May, P. Section 2, p 445, of *Engineering Plastics*; Vol. 2 of the Engineered Materials Handbook of ASM; ASM: Metals Park, OH, 1988.
(64) Miller, D. M. In Composites; Vol. 1 of the Engineered Materials Handbook of ASM, Metals Park, OH, 1987; p 45.
(65) McCluskey, J. J.; Doherty, F. W. Vol. 1 of the Engineered Materials Handbook of ASM, Metals Park, OH, 1987; p 157.
(66) Hansen, N. W. *Engineered Materials Handbook of ASM*; ASM: Metals Park, OH, 1987; Vol. 1, p 112.
(67) Murray, A.; Johnson, C. F. *Engineered Materials Handbook of ASM*; ASM: Metals Park, OH, 1987; Vol. 1, pp 555, 559, 565.
(68) Ryntz, R. A. *J. Coat. Technol*., in press.
(69) Beardmore, P.; Johnson, C. F. *Composite Sci. Technol.* **1986**, *26*, 251.
(70) Millerschin, E. SMC Automotive Alliance News Release, 1995.
(71) Lucas, K. A.; Clarke, H. *Corrosion of Aluminum-Based Metal Matrix Composites*; John Wiley & Sons Inc.: New York, 1993.
(72) Boardman, B. SAE-Internationals, SAE/SP-90-836, 1990. Metal Matrix Composites; Myers, M. R., Ed.; SAE International, SAE-SP-94-1010, 1994. Allison, J. E.; Cole, G. S. *J. Met.* **1993**, 19. Kozcak, M. J.; Khatri, S. C.; Allison, J. E.; Bader, M. In *Fundamentals of Metal Matrix Composites*; Suresh S., Mortensen, A., Needleman, A., Eds.; Butterworth-Heinemann Publishers: Stoneham, MA, 1993.
(73) Feest, E. A. *Metal Matrix Composites for Industrial Applications*; Materials and Design: 1986; Vol. 7, p 58.
(74) Hamajima, K.; Tanaka, A.; Sugunana, T. *JSAE Rev.* **1990**, *11*. Kubo, M.; Tanaka, A.; Kato, T. *JSAE Rev.* **1988**, *9*.
(75) Hayashi, T.; Ushio, H.; Ebisawa, M. SAE-89-0557, 1889. Ebisawa, M.; Hara, T.; Hayashi, T.; Ushio, H. SAE-91-0835, 1991.
(76) Skibo, M. D.; Schuster, D. M. U.S. Patent 4,786,467, 1988.
(77) Urquhart, A. M. *Adv. Mater. Processes* **1991**, 25. Lynch, C. T.; Kershaw, J. P. *Metal Matrix Composites*; CRC Press: Cleveland, OH, 1972.
(78) Hunt, W. H.; Cook, C. R., Sawtell, R. R. SAE 91-0834, 1991. Hamiuddin, M. *Powder Metall. Inst.* **1987**, *19*, 2.
(79) Mehrabian, R.; Rick, R. G.; Flemings, M. C. *Met. Trans.* **1974**, *5*, 1899.
(80) White, J.; Hughes, I. R.; Willis, T. C.; Jordan, R. M. *J. Phys. Colloq. C3−347*, 1987.
(81) King, J. E. *Advanced Ceramic and Metallic Composites Course Lecture Notes*; University of Cambridge: UK, 1990.
(82) Smithells, C. J. *Metal Reference Book*, 6th ed.; Brandes, E. A., Ed.; Butterworth: London, 1983; p 29. Shunk, F. A. *Constitution of Binary Alloys*, Second Supplement; McGraw-Hill: New York, 1986; p 16.
(83) *Composite Casting Guidelines*; Duralcan Composites: San Diego, 1990.
(84) Nath, D.; Namboodhiri, T. K. G. *Corros. Sci.* **1989**, *29*, 1215.
(85) Krishnan, B. P.; Surappa, M. K.; Rohtagi, P. K. *J. Mater. Sci.* **1981**, *16*, 1209.
(86) Yajima, S.; Shishido, T.; Kayano, H. *Nature* **1976**, *264*, 237.
(87) Seyferth, D.; Wood, T. G.; Tracy, H. J.; Robinson, J. L. *J. Am. Ceram. Soc.* **1992**, *75*, 1300.
(88) Yajima, S. *Am. Ceram. Soc. Bull.* **1983**, *62*, 893.
(89) (a) Seyferth, D.; Wiseman, G. H. *J. Am. Ceram. Soc.* **1984**, *67*, C132. (b) Seyferth, D.; Wiseman, G. H. U.S. Patent 4,482,669, 1984.
(90) Seyferth, D.; Czubarow, P. *Chem. Mater.* **1994**, *6*, 10.
(91) Narula, C. K.; Demczyk, B. G.; Czubarow, P.; Seyferth, D. *J. Am. Ceram. Soc.* **1995**, *78*, 1247.
(92) Narula, C. K. U.S. Patent 5,087,593, 1992. Narula, C. K.; Crosbie, G. M. U.S. Patent 5,350,719, 1994. Narula, C. K. *Mater. Res. Soc. Symp.* **1992**, *271*, 881.
(93) Narula, C. K.; Schaeffer, R. O.; Paine, R. T.; Datye, A.; Hammetter, W. F. *J. Am. Chem. Soc.* **1987**, *109*, 5556.
(94) Narula, C. K.; Czubarow, P.; Seyferth, D. *J. Mater. Sci.*, submitted.
(95) Chang, T. Y.; Chock, D. P.; Hammerle, R. H.; Japar, S. M.; Salmeen, I. T. *Crit. Rev. Environ. Control* **1992**, *22*, 27.
(96) Taylor, K. C. *Automobile Catalytic Converters*; Springer-Verlag: New York, 1984.
(97) Church, M. L.; Cooper, B. J.; Wilson, P. J. SAE 890815, 1989.
(98) Heck, R. M.; Farrauto, R. J. *Catalytic Air Pollution Control: Commerical Technology*; Van Nostrand Reinhold: New York, 1995.
(99) Wang, T.; Soltis, R.; Logothetis, E.; Cok, J.; Hamburg, D. SAE 930352.
(100) Wiedenmann, H.; Raff, L.; Noods, R. SAE 840141.
(101) Harrison, B.; Diwell, A.; Hallett, C. *Platinum Met. Rev.* **1988**, *32*, 73. Fisher, G.; Theis, J.; Casarella, M.; Mahan, S. SAE 931034.
(102) *Engineered Materials Handbook*, Vol. 4, Ceramics and Glasses; Volume Chairman Schneider, S. J., Jr.; ASM International: 1991.
(103) Gandhi, H. S. *Proc. Inst. Mech. Eng.* **1988**, *202 (D4)*, 227.
(104) Burtin, P.; Brunelle, J. P.; Pijolat, M.; Soustelle, M. *Appl. Catal.* **1987**, *34*, 225. Church, J. S.; Cant, N. W.; Trimm, D. L. *Appl. Catal.* **1993**, *101*, 105.
(105) Schaper, H. E.; Doesburg, E. B. M.; van Reijen, L. L. *Appl. Catal.* **1983**, *7*, 211. Schaper, H. E.; Amesz, D. J.; Doesburg, E. B. M.; van Reijen, L. L. *Appl. Catal.* **1984**, *9*, 129.
(106) Machida, M.; Eguchi, K.; Arai, H. *J. Catal.* **1987**, *103*, 385.
(107) Murrell, L. L.; Dispenziere, N. C. *J. Catal.* **1988**, *111*, 450. Johnson, M. F. L. *J. Catal.* **1990**, *123*, 245. Béguin, B.; Garbowski, E.; Primet, M. *J. Catal.* **1991**, *127*, 595.
(108) Ozawa, M.; Kimura, M. *Mater. Sci. Lett.* **1990**, *9*, 291.
(109) Harrison, B.; Diwell, A. F.; Hallett, C. *Plat. Met. Rev.* **1988**, *32*, 73.
(110) Ozawa, M.; Kimura, M.; Isogai, A. *J. Less Common Met.* **1990**, *162*, 297.

(111) Mizukami, F.; Maeda, K.; Watanabe, M.; Masuda, K.; Sano, T.; Kuno, K. In *Catalysis and Automotive Pollution Control II*; Studies in Surface Science and Catalysis; Crucq, A., Ed.; Elsevier: Amsterdam, 1991; Vol. 71, p 557.

(112) Haack, L. P.; de Vries, J. E.; Otto, K.; Chattha, M. S. *Appl. Catal. A* **1992**, *82*, 199. Haack, L. P.; Peters, C. R.; de Vries, J. E.; Otto, K. *Appl. Catal. A* **1992**, *87*, 103.

(113) Matsuda, S.; Kato, A.; Mizumoto, M.; Yamashita, H. Proc. 8th International Congress Catalysis, Berlin, 1984, IV; Verlag Chemie: Weinheim, 1984; p 879.

(114) Arai, H.; Machida, M. *Catal. Today* **1991**, *10*, 81.

(115) Watanabe, N.; Yamashita, H.; Kato, A.; Kawagoe, H.; Matsuda, S. Jpn. Kokai Tokkyo Koho JP 63,175,642; *Chem. Abstr.* **1989**, *110*, 64521.

(116) Arai, H. Jpn. Kokai Tokkyo Koho JP 63,119,851; *Chem. Abstr.* **1988**, *109*, 238143.

(117) Mizuno, M.; Yamada, T. Nagoya Kogyo Gijutsu Shikensho Hokoku **1990**, *29*, 157.

(118) Ozawa, M.; Kimura, M.; Isogai, A. *J. Less-Common Met.* **1990**, *162*, 297.

(119) Yamashita, H.; Kato, A.; Watanabe, N.; Matsuda, S. Nippon Kagaku Kaishi, 1986; p 1169. Kato, A.; Yamashita, H.; Mizumoto, M. Matsuda, S. Jpn. Kokai Tokkyo Koho JP 60,266,414; *Chem. Abstr.* **1986**, *104*, 1,122,239. Vidyasagar, K.; Gopalkrishnan, J.; Rao, C. N. R. *J. Solid State Chem.* **1985**, *58*, 29.

(120) Kato, A; Yamashita, H.; Kawagoshi, H.; Matsuda, S. *J. Am. Ceram. Soc.* **1987**, *70*, C157.

(121) Schaper, H.; Doesburg, E. B. M.; Van Reijen, L. L. *Appl. Catal.* **1983**, *7*, 211.

(122) Narula, C. K.; Watkins, W.; Shelef, M. U.S. Patent, 5,210,062, 1993.

(123) Caulton, K. G.; Hubert-Pfalzgraf, L. G. *Chem. Rev.* **1990**, *90*, 969. Hubert-Pfalzgraf, L. G. *Polyhedron* **1994**, *13*, 1118.

(124) Narula, C. K. U.S. Patent 5,134,107, 1992. Narula, C. K. *Mater. Res. Soc. Symp. Proc.* **1992**, *271*, 181. Narula, C. K.; Ying, J. *Chem. Mater.*, submitted.

(125) Narula, C. K. U.S. Patent 5,404,807, 1995.

(126) Yao, M. H.; Liu, D. R.; Baird, R. J.; Usmen, R. K.; McCabe, R. W. *Proc. 52nd Annu. Mtg. Microsc. Soc. Am.*; Bailey, C. W., Garratt-Reed, A. J., Eds.; San Francisco Press: San Francisco.

(127) Schlatter, J. C.; Taylor, K. C. *J. Catal.* **1977**, *49*, 42. Oh, S. H.; Fisher, G. B.; Carpenter, J. E.; Goodman, D. W. *J. Catal.* **1986**, *100*, 360.

(128) Banerle, G. L.; Service, G. R.; Nobe, K. *Ind. Eng. Chem. Prod. Res. Dev.* **1972**, *11*, 54.

(129) Yates, D. J. C.; Prestridge, E. B. *J. Catal.* **1987**, *106*, 549.

(130) Chen, G. C.; Colaianni, M. L.; Chen, P. J.; Yates, J. T.; Fisher, G. B. *J. Phys. Chem.* **1990**, *94*, 5059.

(131) Yao, H. C.; Japar, S.; Shelef, M. *J. Catal.* **1977**, *50*, 407. Yao, H. C.; Stepien, H. K.; Gandhi, H. S. *J. Catal.* **1980**, *61*, 547.

(132) Wong, C.; McCabe, R. W. *J. Catal.* **1989**, *119*, 47.

(133) Usmen, R.; McCabe, R.; Haack, L.; Graham, G.; Hepburn, J.; Watkins, W. L. H. *J. Catal.* **1992**, *134*, 702.

(134) Yao, H. C.; Stepien, H. K.; Gandhi, H. S. *J. Catal.* **1980**, *61*, 547. Stepien, H. K.; Williamson, W. B.; Gandhi, H. S. SAE-800843.

(135) Summers, J. C.; Williamson, W. B.; Henk, M. G. SAE-880281. Summers, J. C.; White, J. J.; Williamson, W. B. SAE-890794.

(136) Eurpean Patent 0,314,057 A1.

(137) Muraki, H.; Shinjoh, H.; Sobukawa, K.; Yokota, K.; Fujitani, Y. *Ind. Eng. Chem. Prod. Res. Dev.* **1986**, *25*, 325. Muraki, H.; Sinjoh, H.; Fujitani, Y. *Appl. Catal.* **1986**, *22*, 325. Muraki, H. SAE 910842.

(138) Shelef, M.; Graham, G. W. *Catal. Rev. Sci. Eng.* **1994**, *36*, 433.

(139) Hepburn, J. S.; Patel, K. S.; Meneghel, M. G.; Gandhi, H. S.; Engelhard, Three Way Catalyst Development Team; Johnson Matthey Three Way Catalyst Development Team; SAE 941058.

(140) Narula, C. K.; Watkins, W. L. H.; Chattha, M. S. U.S. Patent 5,234,881, 1993.

(141) Gandhi, H. S.; Yao, H. C.; Stepien, H. K. ACS Symposium Series No. 178; Bell, A. T., Hegedus, L., Eds.; 1982; p 143. deVries, J. E.; Yao, H. C.; Baird, R. J.; Gandhi, H. S. *J. Catal.* **1983**, *84*, 8. Adams, K. M.; Gandhi, H. S. *Ind. Eng. Chem. Prod. Res. Dev.* **1986**, *22*, 207. Plummer, H. K.; Shinozaki, S.; Adams, K. M.; Gandhi, H. S. *J. Mol. Catal.* **1983**, *20*, 251.

(142) Halasz, I.; Brenner, A.; Shelef, M. *Appl. Catal.* **1992**, *82*, 51. Halasz, I.; Brenner, A.; Shelef, M. *Appl. Catal.* **1993**, *B2*, 131. Halasz, I.; Brenner, A.; Shelef, M. **1992**, *16*, 311. Halasz, I.; Brenner, A.; Shelef, M. *Catal. Lett.* **1993**, *18*, 289.

(143) Whittenberger, W. A.; Kubsh, J. E. SAE 910613, 1991. Hurley, R. G.; Hansen, L.A.; LaCourse, D. L.; Watkins, W. L. H.; Gandhi, H. S.; Whittenberger, W. A. SAE 900504, 1990. Heimrich, M. J.; Albu, S.; Osborne, J. SAE 910612, 1991. Heimrich, M. J. SAE 902115, 1990.

(144) Hurley, R. G.; Guttridge, D. L.; Hansen, L. A.; Pawlowicz, R. J.; Smolinski, J.M.; Gandhi, H. S. SAE 912384, 1991.

(145) Langen, P.; Theissen, M.; Mallog, J.; Zielinski, R. SAE 940470, 1994.

(146) Mizuno, H.; Abe, F.; Hashimoto, S.; Kondo, T. SAE 940466, 1994.

(147) Häffle, E.; Säger, M. WO 92/17692, 1992.

(148) Narula, C. K.; Visser, J. H.; Adamczyk, A. A. U.S. Patent, 5,480,622, 1996.

(149) Narula, C. K.; Czubarow, P.; Seyferth, D. *Chem. Vap. Deposition* **1995**, *1*, 51.

(150) Beck, J. S.; Albani, C. R.; McGhie, A. R.; Rothman, J. B.; Sneddon, L. G. *Chem. Mater.* **1989**, *1*, 433.

(151) Paine, R. T.; Narula, C. K.; Schaeffer, R.; Datye, A. K. *Chem. Mater.* **1989**, *1*, 486. Datye, A. K.; Paine, R. T.; Narula. C. K.; Allard, L. F. *Mater. Res. Soc. Symp. Proc.* **1989**, *153*, 97.

(152) Kummer, J. T. *Prog. Energy Combust. Sci.* **1980**, *6*, 177.

(153) Bonardo, P.; Mortara, W. 23rd FISITA Congr. Paper No. 905117, Torino, May 7−11, 1990.

(154) Shelef, M. *Chem. Rev.* **1995**, *95*, 209.

(155) Ritscher, J. S.; Sandner, M. R. U.S. Patent 4,297,328, 1981.

(156) Iwamoto, M.; Hamada, H. *Catal. Today* **1991**, *10*, 57.

(157) Iwamoto, M.; Yahiro, H.; Tanda, K.; Mizuno, N.; Mine, Y.; Kagawa, S. *J. Phys. Chem.* **1991**, *95*, 3727.

(158) Khara, K. C. C.; Robota, H. J.; Liu, D. *Appl. Catal. B* **1993**, *2*, 225.

(159) Kornatowski, J.; Baur, W. H.; Pieper, G.; Rozawadowski, M.; Schmitz, W.; Cichowlas, A. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 1339.

(160) d'Itri, J. L.; Sachtler, W. M. H. *Appl. Catal. B* **1993**, *2*, L7.

(161) Sano, T.; Suzuki, K.; Shoji, H.; Ikai, S.; Okabe, K.; Murakami, T.; Shin, S.; Hagiwara, H.; Takaya, H. *Chem. Lett.* **1987**, 1421. Suzuki, K.; Sano, T.; Shoji, H.; Murakami, T.; Ikai, S.; Shin, S.; Hagiwara, H.; Takaya, H. *Chem. Lett.* **1987**, 1507.

(162) Kintaichi, Y.; Hamada, H.; Tabata, M.; Sasaki, M.; Ito, T. *Catal. Lett.* **1990**, *6*, 239. Ukisu, Y.; Sato, S.; Muramatsu, G.; Yoshida, K. *Catal. Lett.* **1991**, *11*, 177. Ukisu, Y.; Sato, S.; Abe, A.; Yoshida, K. *Appl. Catal. B* **1993**, *2*, 147. Hamada, H.; Kintaichi, Y.; Sasaki, M.; Ito, T., Tabata, M. *Appl. Catal.* **1991**, *75*, L1. Torikai, Y.; Yahiro, H.; Mizuno, N.; Iwamoto, M. *Catal. Lett.* **1991**, *9*, 91. Hosose, H.; Yahiro, H.; Mizuno, N.; Iwamoto, M. *Chem. Lett.* **1991**, 1859.

(163) Klug, K. H.; Kremer, H. GWF, Gas-Wasserfach: GasErdgas **1992**, *133*, 32. Obuchi, A.; Ohi, A.; Nakamuraa, M.; Ogata, A.; Mizuno, K.; Ohuchi, H. *Appl. Catal. B* **1993**, *2*, 71. Zhang, G.; Yamaguchi, T.; Kawakami, H.; Suzuki, T. *Appl. Catal. B* **1992**, *1*, L15.

(164) Shelef, M. *Catal. Rev. Sci. Eng.* **1975**, *11*, 1.

(165) Leenars, A. F. M.; Keizer, K.; Burggraaf, A. J. *J. Mater. Sci.* **1984**, *19*, 1077. Leenars, A. F. M.; Burggraaf, A. J. *J. Colloid Interface Sci.* **1985**, *105*, 27.

(166) Narula, C. K.; Jen, H.-W.; Gandhi, H. U.S. Patent application, 08/311,298, Sept 23, 1994.

(167) Deeba, M.; Feeley, J.; Farrauto, R. J.; Steinbock, N.; Punke, A. SAE 952491.

(168) Leyrer, J.; Lox, E. S.; Strehlau, W. SAE 952495.

(169) Adams, K. A., Cavataio, J. V.; Hammerle, R. H. *Appl. Catal. B*, in press.

(170) Tao, W.; Golovoy, A.; Zinbo, M.; Bauer, D. R. *SPE 1993 ANTEC Proc.* **1993**, *39*, 3427.

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