Chapter 1

Introduction – Applications of Porous Ceramics

Porous materials in various forms have been in use by human beings in different applications for long times. Among various types of porous materials, the demand of porous ceramics is increasing rapidly day by day, particularly in high temperature challenging areas, with the advancement of engineering and technological applications. Major thrust of research includes innovations in synthesis and processing methods, tailoring of structure and properties, modeling of various materials' structures and processing parameters, novel characterization tools etc.

As per the nomenclature, porous ceramics refer to dispersion of pores (void/air spaces) in a ceramic matrix of connected solid network. In porous ceramics void space is deliberately introduced to fulfil certain functions. Depending on the connectivity of the pores, porous ceramics can either contain closed pores (zero connectivity) or open pores (interconnected). Porous ceramics with open pores are identical to the closed ones except the presence of large channels of interconnection between the pores. The unique structure of porous ceramics with open pores has the main advantage of its' flow through' capability and access of the internal surface of pores. Liquids and gases can flow through the structure with minimal resistance. As per the nomenclature recommended by the IUPAC,[1] according to which porous materials can be classified according to the size (mean dia.) of the pores as macroporous (pore diameter > 50 nm), meso porous (pore diameter between 2-50 nm) and microporous (pore diameter < 2 nm).

The properties of all porous ceramics are strong function of their microstructure. The microstructural parameters which play a critical role include volume fraction of porosity, pore size, shape and orientation, extent of interconnection, characteristics of the pore surface and interface etc.[2] The presence of air phase in porous ceramics helps in significant weight reduction and imparts special mechanical properties vastly different from its bulk material. Porous materials are known to possess specific properties such as high temperature resistance, low relative density, low specific heat, low thermal and electrical conductivity, high specific surface area, low thermal mass, high chemical inertness, high thermal shock resistance, high specific strength, low thermal conductivity, high electrical resistance, wear resistance etc. Use of porous ceramic materials allows simultaneous optimization of stiffness, strength, energy absorption, overall weight, thermal conductivity, surface area, and gas permeability. As such, these materials are highly desirable for a wide range of engineering and technological applications such as thermal, structural, chemical, biomedical, filtration, electrical/electronic, aerospace, defense applications etc. A detailed description related to the use of porous ceramics in various applications is given below.

1.1. Thermal Applications

A. Insulation

Thermal insulation is an important part of almost all manufacturing and processing units where the operating temperature is much higher than the ambient temperature. Without use of thermal insulation, it is almost impossible to run high temperature processes. Also, thermal insulation is a basic part in kilns and furnaces that operate at high temperatures on a continuous basis. Porous ceramics with closed pores are intended for use as energy efficient thermal insulation materials in high temperature furnaces. In comparison to fibrous insulation, which is most commonly used, porous ceramics are more environmental friendly and non-hazardous. Because of significantly low thermal mass of porous ceramics, they are promising materials for operating conditions with faster heating and cooling cycle. Porous ceramics for use in refractory thermal insulation can be produced in the form of bricks, boards or other cast shapes (Fig. 1.1). When these are used for thermal insulation in the construction of buildings, then these are being produced from fly ash and concrete.

Benefits of porous ceramics for use as thermal insulation include longer life, uniformity in firing atmosphere, less shrinkage in insulating layer, chemical inertness, cost effectiveness and free from fibers.

Fig. 1.1 Foam cement insulation board[206]

Porous ceramic thermal insulators to be used in heating applications are designed and built to resist high temperatures and fast thermal cycling. It is recommended that only cordierite and alumina (all grades) be used in high temperature applications due to their impressive thermal stability. Porous insulators for heating applications are neither glazed, metalized nor coated, as all these treatments reduce the performance of the porous ceramics.

Apart from the insulation application, the other high temperature applications of porous ceramics includes supports for electronic element in furnaces, kilns, ovens and heaters, weight bearing components for loads in high temperature environments etc.

B. Kiln furniture

One of the major component during production and processing of materials at high temperature is the energy consumption. Thus, it is advisable to make efficient use of the total kiln volume. Therefore, it is a standard practice to load the kilns to the maximum possible extent and this is achieved by stacking the components to be fired. At the same time, uniform temperature distribution is also another important criteria to minimize the inconsistency in product quality.

Ceramic kiln furnitures made of various materials in different shapes and sizes, used to meet the above requirements as well as to support the load and prevent deformation of the components are being fired at high temperatures. Kiln furniture has been commonly used in firing of potteries, engine spark plugs, electronic ceramic components etc. (Fig. 1.2).

Fig. 1.2 Kiln furnitures made of various materials[206]

Though kiln furnitures composed of dense ceramics are also used in practice, use of porous ceramics holds much greater promise considering the advantages in terms of the low thermal mass, greater thermal shock resistance, reduced interaction with the materials being fired and greater uniformity in temperature. The porous kiln furniture currently in use is composed of mainly cordierite, steatite, fused silica, high alumina, mullite, recrystallized silicon carbide, or stabilized zirconia etc. with porosity in the range 50-90%.[3] These are widely used in firing kilns in the production of mosaic, square bricks, tableware ceramics, sanitary ware ceramics, roofing tiles, magnetic materials and advanced ceramics.

C. Combustion

Porous ceramics find applications as burners for air heating systems, in steam generators, gas turbine combustion chambers etc (Fig. 1.3).

Fig. 1.3 Porous ceramics for combustion application[206]

Porous ceramic burner is characterized by higher burning rates, increased flame stability with low noise emissions and controllable homogeneous combustion zone temperatures etc.[4] The above characteristics lead to a reduction in NO_x and CO emissions.

The following advantages make porous ceramics suitable for a variety of domestic and industrial applications:

- High power turndown ratio of up to 1:30.
- High power density with heat loads per cross section up to 8 mWm^{-2} under atmospheric pressure for methane/air mixtures.
- High combustion stability due to the heat capacity of the porous ceramics.
- Geometrical flexibility allowing good adaptation to application demands.

1.2. Structural Applications

A. Light weight support

One of the challenging application is space mirror as it demands use of materials that are not only light weight but also rigid and exhibit low co-efficient of thermal expansion. The above requirements are met through use of porous ceramics as support materials for dense highly polished ceramic materials with desirable optical properties. Porous SiC ceramics have been used in supporting a thin layer of highly polished SiC reflector material (Fig. 1.4).

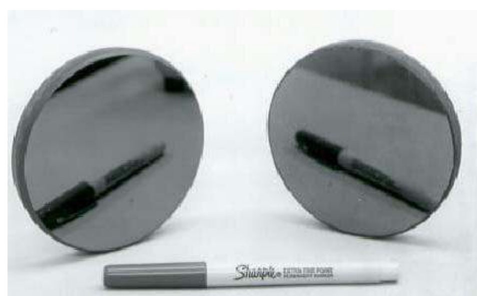

Fig. 1.4 Light weight space mirrors with porous SiC used as a support for dense polished SiC reflecting layer [207]

B. Construction application

Ceramics are generally useful in civil engineering design to minimize the weight of structures (constructions), where highest possible strength and stiffness are required (combination of structural applications and use of light weight materials). Compared to their dense counterparts, porous ceramics can exhibit high fracture toughness and gradual damage accumulation instead of catastrophic failure.

One of the common examples is porous concrete, which is produced by mixing aqueous foams with concrete slurries followed by setting it like conventional concrete. Porous concrete is able to make thermally insulating, sound and fire proof structures. Use of porous concrete helps obtaining construction of building/structures at a comparatively faster rate than the conventional concrete. Porous concrete finds uses in walls and floors as sound proof partitions, in walls and roofs for its thermal insulation property and filling of trenches dug in roads when pipes are laid or repairs are carried out.

C. Acoustic insulation application

Sound absorbing porous materials represent a very important engineering material class and their uses involve a large range of applications e.g., in architecture and thermo-acoustic insulation of engines and pump chambers etc.

Combustion chambers of gas turbines, water pumps and thermal insulation of motors require insulation of emitted sound waves. For obtaining promising sound absorbing properties, it is known that a microstructure with controlled air flow resistance and high interconnected porosity is necessary because an open porous microstructure allows the penetration and propagation of the sound waves through the material. When the sound waves enter these special microstructures of porous ceramics, their amplitude is decreased by friction when moving through the tortuous passages. The sound is absorbed by transforming sound energy to thermal energy.

1.3. Chemical Applications

Catalyst and adsorbent supports

Porous ceramics can either have catalytic properties or can be used as a catalyst support. Accordingly, they are used as catalyst carriers in vehicle exhaust systems and in chemical process industry. As catalyst carrier, porous ceramics increase the production efficiency of methane.[5] Various catalysts such as Pt, Rh, Pd, Ru etc. are coated on porous ceramics, which chemically fight against pollutants like carbon monoxide (CO), hydrocarbons (HC), oxides of nitrogen (NO_x) and convert these into harmless substances like carbon dioxide (CO_2), nitrogen (N_2), and water vapor (H_2O). Porous ceramics coated with platinum as a thin layer are being used in catalytic converters.

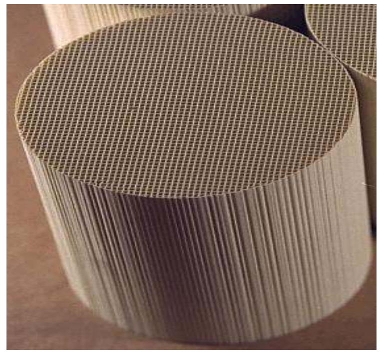

Fig. 1.5 Ceramic catalyst substrate for catalyst and adsorbent supports[209]

Ceramic catalysts and adsorbents or catalyst supports are used in the form of extruded honeycombs, open-cell highly porous ceramics or as bulk solids (pellets, beads, specific geometries). Porous ceramics offer advantages if high capacities, low flow resistance, very good heat dissipation as well as good lateral mixing of reaction media are required. By coating the porous structure with selected adsorbents and/or catalytically active materials (e.g. zeolites, hexa aluminates, active carbon, precious metals, transition metals) the ceramic support material can be functionalized. It is sufficient to apply thin layers on the substrate in order to obtain comparable adsorption results or catalytic conversion as in the case of bulk solids.

Catalyst substrate is a crucial component which influences the performance, robustness and durability of catalytic converter systems. A good catalyst substrate should meet the following criteria: high geometric surface area (GSA), low heat capacity and thermal mass, high operating temperature, low coefficient of thermal expansion, good coatability, reasonable strength and good oxidation resistance. A porous ceramic catalyst substrate is shown in Fig. 1.5. These are manufactured in an extrusion process.

1.4. Filtration Applications

A. Metal filtration

As porous ceramics possess excellent properties like high temperature resistance, strong chemical corrosion resistance, large surface area etc. these are widely used in molten metal filtration to remove undesirable impurities, non-metallic inclusions and foreign materials from the melt prior to casting. Metal filtration ensures high quality of cast products. If not removed, these impurities lead to defects such as cracks, pin holes, poor surface finish etc. in the cast part and lead to rejection of the cast parts. During filtration, impurity particles larger than about 30 μm are separated. These impurity particles agglomerate in the form of a cake which itself adds to filtration. Most of the porous ceramic filters (Fig. 1.6) are fabricated through replication of polyurethane foam structure.

Fig. 1.6 Ceramic foam filters for metal filtration[206]

The basic materials of ceramic filter includes alumina, zirconia and mullite etc. These porous ceramics (ceramic foam) for metal filtration applications are typically 75% porous.[6] Apart from impurity separation, porous ceramic filters perform multi functions like reduce turbulence level of molten metal filling the mold, increase the filling and feeding capacity of the melt, reduce processing time and tool abrasion, improve casting yield etc.

B. Fluid (air, gas, liquid, acid) filtration

Filtration of fluids such as air, gas, liquids and acids at high temperature is another important application of porous ceramics. Various processes like separation of combustion gases for reuse across secondary turbines, hydrocarbon processing of gas streams above the dew point etc. are a few examples of removal of particulates from the fluids. The advantage of porous ceramics is that these have the flexibility of customizing the porosity and pore microstructure as per the requirement of the flow (Fig. 1.7).

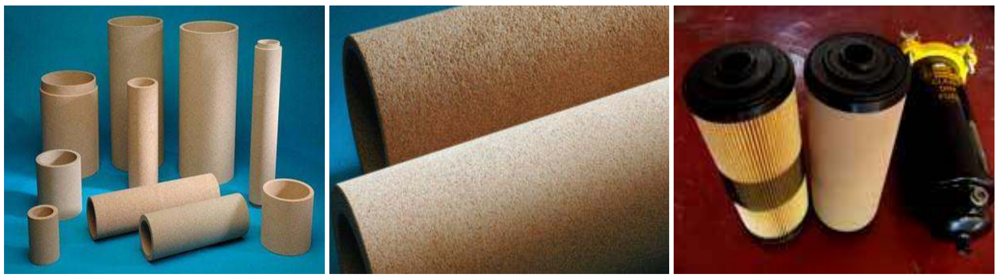

Fig. 1.7 Ceramic foam filters for fluid filtration[210]

Other applications include hot gas candles, mixed filtration-acidic or alkali applications, filtration system in advanced combustion and gasification, protection of gas turbines from particle fouling and erosion, advanced coal or bio mass-based power application, cleaning of process gas to meet emission requirements, in heat exchangers cooling/heating, food filtration applications, mineral processing etc. An ideal porous filter should have the following characteristics: excellent thermal shock resistance, low co-efficient of thermal expansion, excellent binding strength, excellent wear resistance, excellent resistance to acid, fires and sparks, etc.

1.5. Electrical/Electronics Applications

A. Fuel cell application

Porous ceramics play an important role in fuel cells engineering. Solid oxide fuel cells (SOFCs) are mostly constructed from ceramic materials as these have to be operated at high temperatures in the range of 900-1000˚C. These are used (i) to support delicate electrolyte membranes, in which mechanical integrity and effective diffusivity to fuel gases is critical (ii) as gas diffusion layers, where electronic conductivity and permeability to both gas and water is critical (iii) to construct fuel cell electrodes, in which an optimum combination of ionic conductivity, electronic conductivity, porosity and catalyst distribution is critical.

For successful operation of the fuel cells, both cathode and anode need to be porous to allow transport of reacting gases and allow oxygen molecules to reach the electrode/electrolyte interface respectively. Anode is typically made of porous nickel/yittria stabilized zirconia (Ni/YSZ) cermet and cathode is typically a porous perovskite material such as doped lanthanum strontium manganate ($La_{1-x}Sr_xMnO_3$).[7] The porosity in anode and cathode materials is generally created by use of fugitive materials that burnout during high temperature treatment. Fig. 1.8 shows an anode supported SOFC geometry, as well as microstructure of the porous anode and cathode material.

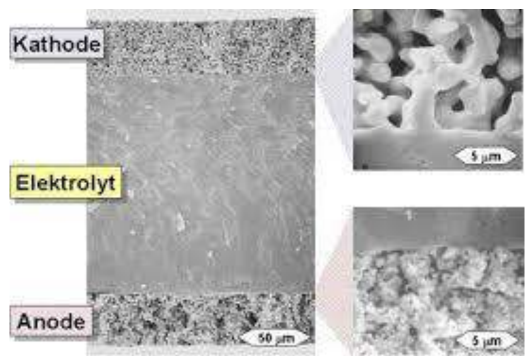

Fig. 1.8 Engineering porous materials for fuel cell applications[211]

Porous materials play two key roles in fuel cells technology. The first is that of transporting gases to/from the fuel cell electrodes. In SOFCs, porous ceramics are commonly used to provide the mechanical support for thin and delicate ceramic oxide electrolytes. In many cases these porous materials also play an important role in current collection on the anode or cathode side.

The second vital role of porous materials is within the fuel cell electrodes, be these anode or cathode. In SOFCs, the electrodes play a vital role in minimizing losses attributable to electrode kinetics and in some cases mass transport. This is achieved by maximizing the length of the so-called triple phase or three-phase boundary (TPB), a term describing the conjunction of a pore space, an ionically conducting phase, and an electronically conducting phase. In practice this is achieved by the use of porous electrode structures containing both ionically and electronically conducting materials.

B. Sensors

In electrochemical applications like sensors, oxide based ceramics are considered as the suitable materials to detect the presence of moisture, gases like CO and NO_x etc. The presence of pores in porous sensors determines the optimization of properties like sensitivity, response speed and time etc. Performance of sensors is influenced by the porosity and pore microstructure. Porous piezoelectric ceramics are used to make hydrophones for use in under water systems. Fig. 1.9 shows a typical porous ceramic for use as a sensor.

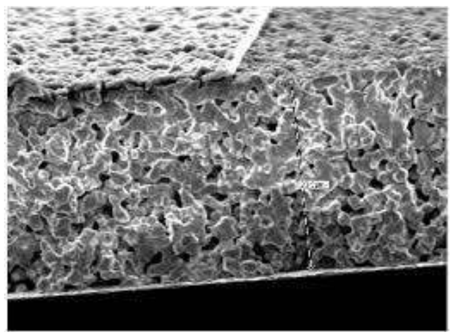

Fig. 1.9 Porous ceramics for humidity sensor[212]

In most electrochemical sensors, like pH electrodes, reference electrodes and ion selective electrodes (ISE) use a porous ceramic plug to maintain a conducting connection between the reference electrode and the test solution.[8] This porous plug is also an important part of the design.

1.6. Biomedical Applications

Human skeleton system is made of bones, most of which are porous in structure. Among various ceramic materials, hydroxyapatite (HA) has been used cinically for many years. It has good biocompatibility with bone contact as its chemical composition is similar to that of bone material. Porous HA ceramics have found enormous use in bio-medical applications including bone tissue regeneration, cell proliferation and drug delivery. In bone tissue engineering it has been applied as filling material for bone defects and augmentation, artificial bone graft material, and prosthesis revision surgery. Its high surface area leads to excellent osteoconductivity and resorbability providing fast bone ingrowth.

Porous hydroxyapatite have been used as implants, which stimulate natural bones. In these porous structures, presence of interconnected pores is essential as it allows the growth of fiber vascular tissues and the attachment of new bones against this structure. There are various techniques reported in the literature[9], which have been developed to produce porous HA with overall structure that is strong enough to withstand the loads encountered in day to day life without being too heavy. Spherical porous HA implants of diameters ranging from 14-22 mm have been used as orbital implants to make false eyes that appear similar to the natural eye balls (Fig. 1.10).

The porosity in orbital implants is designed to be interconnected to support soft tissue in-growth. HA ceramics together with β-tricalcium phosphate have been widely applied as bone substitutes.

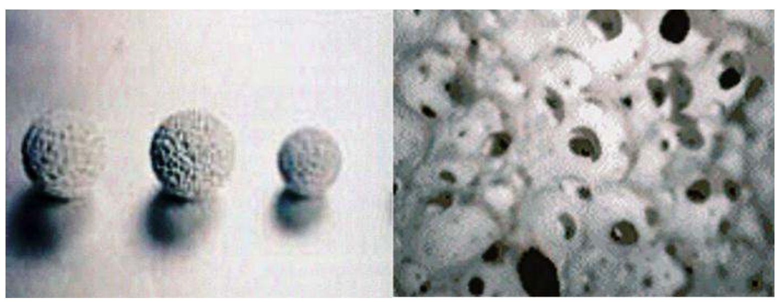

Fig. 1.10 Porous HA eyeball implant and its microstructure[213]

Though, there is a wide range of applications for porous ceramics (a few of which have been described above), each individual application requires ceramic shapes with defined ceramic matrix and pore microstructure which suits the specific requirement. For example, effective thermal insulation application favours products with closed porosity whereas filters and membranes require samples with open porosity. Most of these applications as stated above, require a precise control of porosity, pore size, pore shape, orientation and connectivity.

The requirements for the ceramic matrix and pore microstructure may vary depending on the end use and type of application area. Thus, depending on the application requirement, porous ceramics with controlled pore microstructures are being fabricated via different fabrication routes which will be discussed in detail in the next chapter.