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Producing porous ceramic by different techniques

Graduation project submitted to materials

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SUPERVISOR CERTIFICATION

I certify that the preparation of this project entitled "

Producing porous ceramic by different techniques"

Prepared by

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Was made under my supervision at Babylon University-College of Materials Engineering –Department of Ceramics and Building

Materials Engineering in partial fulfillment of the requirement achieve graduate degree in materials engineering

Signature:

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2021_2022

Abstract

a lot of efforts have been devoted on the processing of porous ceramics in order to control the pore size, pore shape along with substantial improvements of properties.

In present study porous Alumina ceramic was prepared using (i) partial sintering, (ii) replica templates, (iii) sacrificial fugitives techniques. Each technique need many experimental works to control the porosity, pore size , pore shape and mechanical properties.

The results show that using more than 6% sacrificial fugitive (yeast in present work) produced very brittle samples while porous samples from partial sintering technique have better handling property.

The Aim of Project

The aim of this study was preparing porous alumina ceramics using three techniques: Sacrifical template , Replica methods and Partial sintering

The physical properties including density and porosity as well as the mechanical properties represented by compression strength should be performed on the prepared samples, followed by comparing these properties for porous samples produced by the different methods .

Chapter One

Theoretical part

1.1 Introduction

Porous ceramics are now used for wide variety of industrial applications from filtration, absorption, catalysts, and catalyst supports to lightweight structural components. In these decades, a great deal of research efforts has been devoted for tailoring deliberately sizes, amounts, shapes, locations, and connectivity of distributed pores, which have brought improved or unique properties and functions of porous ceramics. The merits in using porous ceramics for these applications are generally a combination of intrinsic properties of ceramics themselves and advantages of dispersing pores into them. The former include heat and corrosion resistances, wear and erosion resistance, unique electronic properties, good bioaffinity, low density, and high specific strength, and the latter are low density, low thermal conductivity, controlled permeability, high surface area, low dielectric constant, and improved piezoelectric properties.

Porous ceramic has been prepared by various methods, including: freeze casting, chemical foams method, extrusion molding, replica method and pore-forming agent method. Among these techniques, the pore-forming agent and replica methods are the most frequently used methods to fabricate porous ceramics with a controlled microstructure (porosity and pore size). Many pore-forming agents such as core-shell microspheres, bioactive yeast, carbon black, yeast fungi, and starch have been used.

Finally it can be concluded that porous ceramics are very important materials which can be used in a wide range of structural and functional applications. Great efforts are required for ensuring the good mechanical strength of highly porous materials. Pores are generally considered as stress concentrators and deteriorate the mechanical strength of material. By carefully controlling and tailoring the microstructure of porous ceramic materials we can obtain the materials with improved properties.

1.2. Porous ceramic structures

Porous ceramics possess a number of suitable properties, which combine the features of ceramics, and porous materials such as low density, lightweight, low thermal conductivity, low dielectric constant, thermal stability, high specific surface area, high specific strength, high permeability, high resistance to chemical attack and high wear resistance . Either porous ceramics are reticulate (interconnected voids surrounded by a connection of ceramic) or foam (closed voids within a continuous ceramic matrix). Reticulated porous ceramics are usually used for molten metal, industrial hot-gas filters, catalyst supports, and diesel engine exhaust filters.

Pore size and porosity percentage are controlled by the particle size distribution of starting ceramic powders, fabrication techniques, types of binder used, concentration of binder and sintering conditions respectively.

Generally, the particle size of raw ceramic powder should be geometrically in the range between two to five times larger than that of pores in order to provide the desired pore size. The Porosity percentage reductions with increased making conditions such as pressure, sintering temperature and time. Furthermore, the fabrication influences such as the amount and type of additives, green densities, and sintering conditions (temperature, pressure atmosphere, etc.) significantly affect for the porous ceramics microstructures.

1.3. Classifying Porous Ceramics

In general, porous ceramics may be divided into two main classes : honeycomb ceramics and ceramic foam . The former has polygonal columnar pores that form a two-dimensional array , and the latter has hollow polyhedron pores that form a three-dimensional array. Figure shows two ceramic foams with different pore structures, both of which were made from compounded oxides.

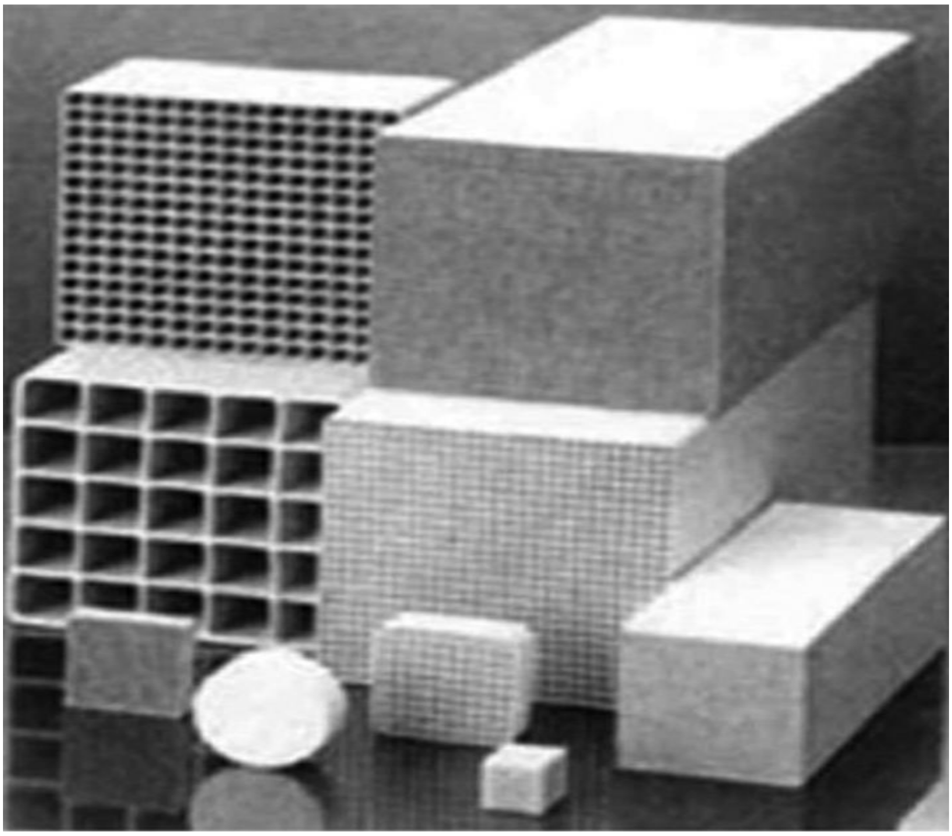


Figure (1) . An optical photograph showing two dimensional honeycomb ceramic products

There are two sorts of ceramic foam:
the open-cell, reticulated ceramic foam and the closed-cell, bubblelike ceramic foam . When the solid species constituting the foamed body is comprised only of pore struts, the connective pores will generate reticulated structures, resulting in open-cell ceramic foams. When pores are separated by solid cell walls, the closed-cell ceramic foam will be achieved. Such differences can be clearly seen by comparing the fluid penetrability of these two sorts of foamed bodies. The distinction between the two types depends on whether the pore is enveloped by solid cell walls or not . In addition, there are half open-cell ceramic foams. Apparently, some ceramic foams have both open and closed pores.

These porous structures take on a relatively low level of bulk density and thermal conductivity, as well as varying levels of fluid penetrability which is high for the open-cell body. By properly matching the ceramic raw material to the preparation technique, porous ceramics may be created that have relatively high levels of mechanical strength, corrosion resistance, and stability under high temperatures that can satisfy the demands of severe conditions

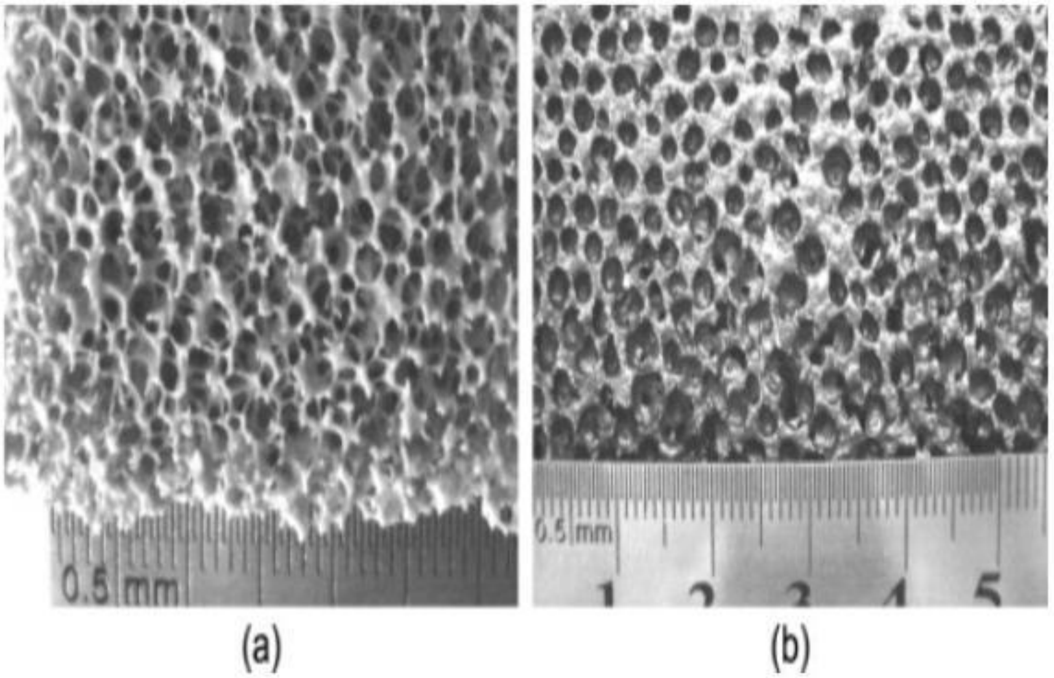


Figure (2). Three-dimensional ceramic foams: (a) an open-cell reticulated ceramic foam, (b) a closed-cell bubblelike ceramic foam.

Porous ceramics can be classified according to the size of their pores, as follows

1. Microporous material, for pore sizes of less than 2 nm
2. Mesoporous material, for pore sizes of 2–50 nm
3. Macroporous material, for pore sizes over 50 nm

This classification standard has not been adopted abroad because the rules about using porous materials vary widely from country to country.
Ceramic foam is an important part of porous ceramics, and the open-cell type of ceramic foam, which is a new type of highly porous ceramics, has a three-dimensional, reticulated structure with connective pores, resulting in great specific surface area, high fluid contact efficiency, and a small loss of fluid pressure . In particular, these materials have many connective pores and capillary holes and have high specific surface energy on the inside, so they perform well in terms of filtration and adsorption under low fluid resistance loss conditions. They can be used in many fields, including metallurgy, chemical engineering, environment protection, energy, and biology, for such applications as metal melt

filtration, high-temperature gas purification, and catalyst support . Moreover, the porosity, density, fluid resistance loss, and penetrability of these materials can be modulated by various processing techniques, and the commonly used material species includes alumina and cordierite. Cordierite is used as a raw material with the primary purpose of improving the heat fluctuation resistance of products, and alumina is used to increase a material’s strength and thermal stability. As the demand of thermal stability heightens for such products, porous silicon nitride and silicon carbide ceramics also have been developed .

Porous ceramics have several common characteristics :

1. *Good chemical stability*. Choosing the appropriate material species and techniques can make porous products suitable for various corrosive conditions in which the products are expected to function.

2. *Great specific strength and rigidity*. The shape and size of pores in porous ceramics will not change under gas pressure, liquid pressure, and other stress loadings.

3. *Fine thermal stability*. Porous products made of heat-resistant ceramics can filtrate molten steel or high-temperature burning gas.

These excellent characteristics promise a great future for porous ceramics being used in a wide variety of applications, and make such materials adaptable in many areas, including chemical engineering, environment protection, energy source, metallurgy, and electronic industry. The specific cases for which porous ceramics are suitable depend on both the composition and structure of the products. At first, porous ceramics were used as filtration materials to filtrate bacteria belonging to the microorganism. Once the level of controlling the fine pores of porous ceramics was increased, the resulting products gradually became used in more and more applications, including separation, dispersion, and adsorption; and they are presently being used in many industrial areas, including the chemical engineering, metal smelting, petroleum, textile, pharmaceutical, and foodstuff machinery industries. Also, these porous ceramics have been used increasingly in sound-absorbing materials, sensitive components, artificial bones, and tooth root materials.

1.4. Applications of porous ceramic materials

Pore-ceramic is a new type of ceramic material, also known as pore-functional ceramics. It is a kind of ceramic material with a large number of interconnected or closed pores in the body after it is shaped and fired at high temperature.

Porous ceramics can be divided into foam ceramics, honeycomb ceramics and granular ceramics according to the pore-forming methods and voids. The corresponding porosity is as follows:

Porous ceramic materials due to its unique porous structure and small volume density, high specific surface area, low thermal conductivity, and ceramic materials themselves unique high temperature resistance, high strength, good chemical stability and other characteristics, has been widely used in environmental protection, energy saving, chemical, smelting, food, pharmaceutical, biological medical and other fields.

Porous ceramic materials are used in filtration and separation devices

1.4.1 Porous filter ceramic tube

The filter unit composed of porous ceramic plate or tubular products has the characteristics of large filtration area and high filtration efficiency.It is widely used in water purification, oil separation and filtration, organic solution, acid and alkali solution, other viscous liquid and compressed air, coke oven gas, steam, methane, acetylene and other gas separation.Due to the advantages of high temperature resistance, wear resistance, chemical corrosion resistance and high mechanical strength, porous ceramics are increasingly showing their unique advantages in the application fields of corrosive fluids, high-temperature fluids and molten metals.

Porous ceramic material is used in sound absorption and noise reduction device

1.4.2 Honeycomb ceramic sound-absorbing material

Porous ceramics as a sound-absorbing material is mainly to use its diffusion function, that is, through the porous structure of sound waves caused by the air pressure to disperse, to achieve the purpose of sound-absorbing.Porous ceramics as sound-absorbing materials require small pore size (20 ~ 150 m), high porosity (more than 60%) and high mechanical strength.Porous ceramics have now been used in high-rise buildings, tunnels, subways and other places with high requirements for fire prevention, TV transmission centers, cinemas and other places with high requirements for sound insulation.

1.4.3 Porous ceramic material is used as catalyst carrier

Since porous ceramics have good adsorption capacity and activity, the conversion efficiency and reaction rate will be greatly improved after the reaction fluid passes through the porous ceramic channel after the catalyst is covered.

Porous ceramic materials used for sensitive components

1.5. Processing Methods for the Preparation of Porous Ceramics

Processing Methods for Macroporous Ceramics

The processes for manufacturing macroporous ceramics can be divided into following four categories and the

process schematic is shown in Fig.

(i) Partial sintering

(ii) Replica templates

(iii) Sacrificial fugitives

(iv) Direct foaming

1.5.1 Partial sintering

Partial sintering of powder compact is the most con- ventional and straightforward route to fabricate porous ceramic materials. In this technique, particles of powder compact are bonded due to surface diffusion or evapora- tion-condensation processes enhanced by heat treatments. A homogeneous porous structure forms when sintering is terminated before fully densification occur. Pore size is controlled by the size of starting powders whereas poros- ity is controlled by the degree of partial sintering. Generally, in order to provide the desired pore size, the size of raw powder should be geometrically in the range two to five times larger than that of pore. The mechani- cal properties depend largely on degree of neck growth between grains, as well as porosity and pore size. Sev- eral processing approaches have been developed to enhance grain bonding and improve strength of porous ceramics. Oh et al. [19] and Yang et al. [20] fabricated porous Al_2O_3 and Al_2O_3 based composites by the pulse electric current sintering (PECS) technique and found that the strength was substantially improved due to the formation of thick and strong necks.

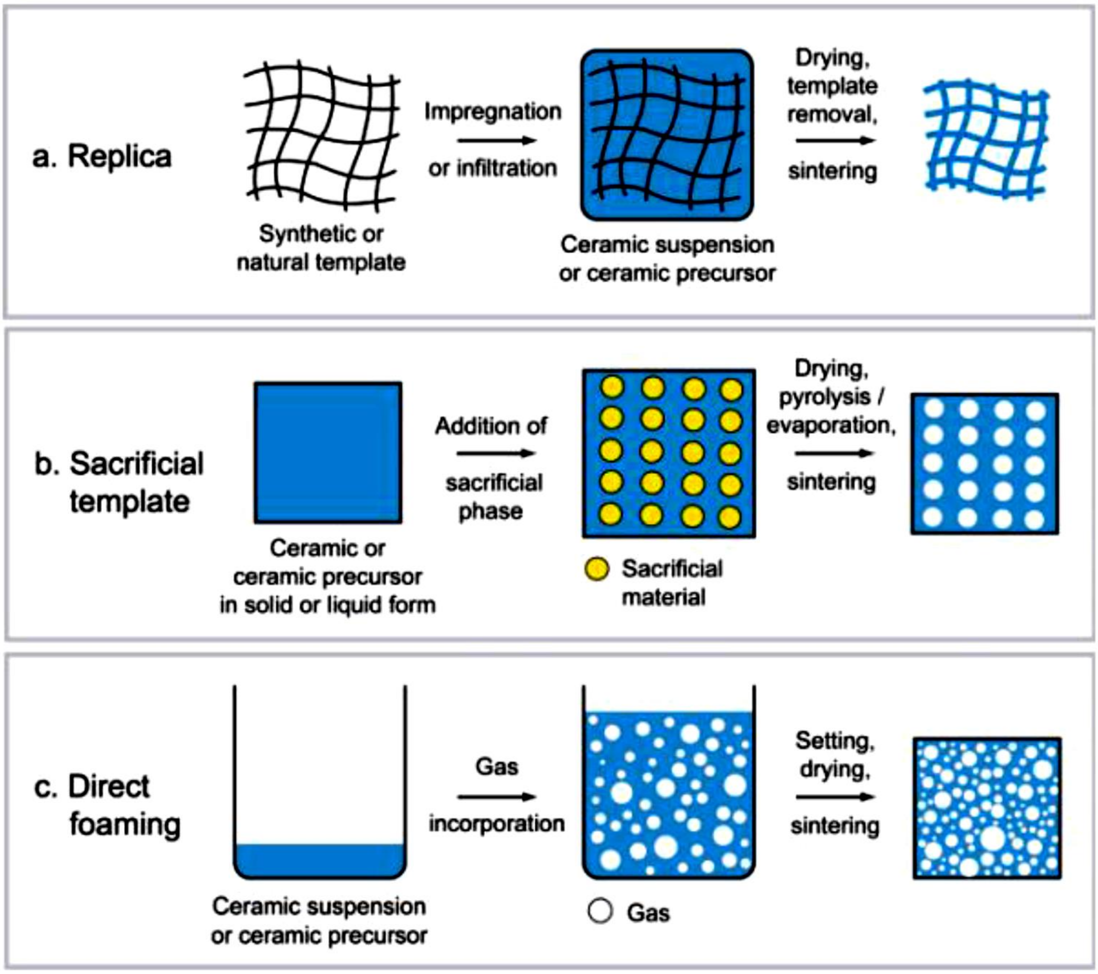


Fig.3. Different processing routes for the manufacturing of macroporous ceramics

1.5.2 Replica templates

Macroporous ceramics having interconnected large pores of high volume porosity and open cell walls have been frequently fabricated by the replica techniques. Replica techniques produce the macroporous ceramics having interconnected large pores of high volume porosity and open cell walls but due to cracking of the struts during the pyrolysis, the mechanical properties of ceramic foams are poor.

The first step of a typical template process is impregnation of a porous or cellular structure with ceramic suspension or precursor solution. The most frequently used synthetic template is porous polymeric sponge such as polyure- thane. Natural resources of porous structures such as woods, corals, sea sponge, etc. have been also used as replica templates. The templates are soaked into a ceramic slurry or precursor solution to impregnate them, and the surplus is drained and removed by centrifugation or roller compression. In this process, the appropriate viscosity and fluidity depending on the cell size are required so that uniform ceramic layer forms over the sponge walls. The ceramic-impregnated templates are dried and then heat treated to decompose the organic sponges. Fol lowing the pyrolysis, the ceramic layers are sintered at higher temperatures for densification. Porosity higher than 90% can be obtained with cell sizes ranging from a few hundred micrometers to several millimeters. The open cells are interconnected, which allows fluid to pass through the foams with a relatively low pressure drop. However, due to cracking of the struts during the pyroly- sis, the mechanical properties of ceramic reticulated foams are generally poor .

1.5.3 Sacrificial fugitives

Porous ceramics can be obtained by mixing appropri- ate amounts of sacrificial fugitives as pore forming agents with ceramic raw powder and evaporating or burning out them before or during sintering to create pores . In this technique, porosity is controlled by the amount of the agents, and pore shape and size are also affected by the shape and size of the agents. However, the removal of the organic template material can be very time consuming and generates harmful by products. The pore forming agents are generally classified as follows:.

1. Synthetic organic matters such as polymer beads, organic fibers.

2. Natural organic matters such as potato starch, cellu- lose, cotton.

3. Metallic and inorganic matters such as nickel, car- bon, fly ash, glass particles.

4. Liquid such as water, gel, emulsions.

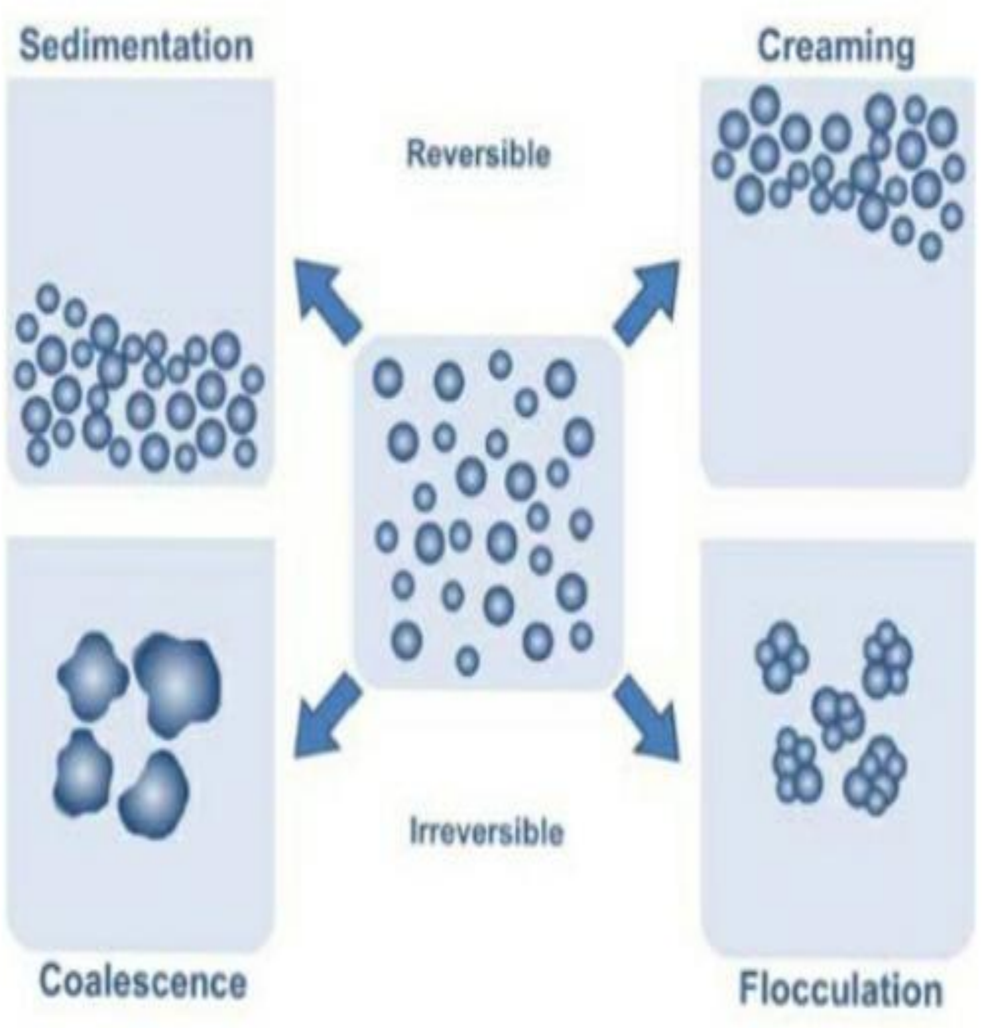
Porosity is controlled by the amount of the agents, and pore shape and size are also affected by the shape and

size of the agents respectively when their sizes are large in comparison with those of starting powders or matrixgrains. This approach is useful particularly for obtaining high open porosity. The agents, however, need to be mixed with ceramic raw powder homogeneously for obtaining uniform and regular distribution of pores.

1.5.4. Direct foaming

In this method, porous materials are fabricated by foaming the ceramic slurry by mechanical agitation or in situ evolution of gases followed by drying and consolida-tion to obtain high strength porous materials]. This

approach probably yields the widest range of cellular structures and hence properties, but they are generally less open than the replicated foams. This technique allows low cost and easy production of highly porous ceramic materials, up to more than 95% porosity. The total porosity of directly foamed ceramics is proportional to the amount of gas incorporated into the suspension or liquid medium during the foaming process. Liquid foams are thermodynamically unstable systems due to their high gas-liquid interfacial area. Several physical processes take place in wet foams to reduce the total Gibbs free energy of the system, resulting in large pores in the final porous bodies, leading to foam destabiliza- tion. The foam lifetime can be increased to a few minutes or several hours by adsorbing long-chain surfactants. Remarkably stable foams exhibiting lifetime of several days and weeks can be prepared through the adsorption of colloidal particles on the surface of air bubbles.



Fig(4). Several destabilization mechanisms in foaming of colloidal suspensions.

Literature Review

- Zhiwei Chen et al. 2018, fabricated Porous alumina ceramics by starch consolidation casting using corn starch as a curing agent, Results showed that the porous alumina ceramics with the flexural strength of about 44.31MPa, apparent porosity of about 47.67% and pore size distribution in the range of 1-4 lm could be obtained with SiO2 and MgO additives

Chapter Two

Experimental work

The used materials

Al2O3 powder was used , Yeast as (organic sacrificial fugitives) , polymeric sponge polyurethane as (synthetic porous template) and commercially available poly vinyl alcohol solution (PVA, liquid) as a binder .

Sample preparation

1- Preparation of porous alumina by sacrificial agent

- Powder was prepared by mixing Al2O3 with varying percent of Yeast ( ) Wt%.
- Mixing the powder for (6hr) in the device as shown in figure (1) until getting homogenous mixture.

Fig (1) Mixing device of powders

- To produce the pressing samples, powders were mixed with PVA as a binder and put the mixture in a mold of a diameter (20mm) as shown in figure (2) than using hydrolytic press in load reach about (1Mpa) and remain under this load for time reach (2min) in order to distribution of load for all sample.

Fig (2) Mold shape

- . After that samples were dried in the oven at temperature about (100°c) for (24hr).
- The samples were heated to 600 for 1 hr. in to burn out the yeast than samples were sintered in furnace at temperature about (1200°c) for period reach to (2hr)
- The sample shape was shown in Fig 3

2- Preparation of porous alumina by Replica templates

Ceramic slurry was prepared by stirred alumina powder with PVA. The templates are soaked into a ceramic slurry to impregnate them and the surplus is drained and removed by compression. The ceramic impregnated templates are dried and then heat treated to decompose the organic sponges. We couldn't get the final sample because of some difficulties for using the furn. The soaked templet shape was shown in fig 4

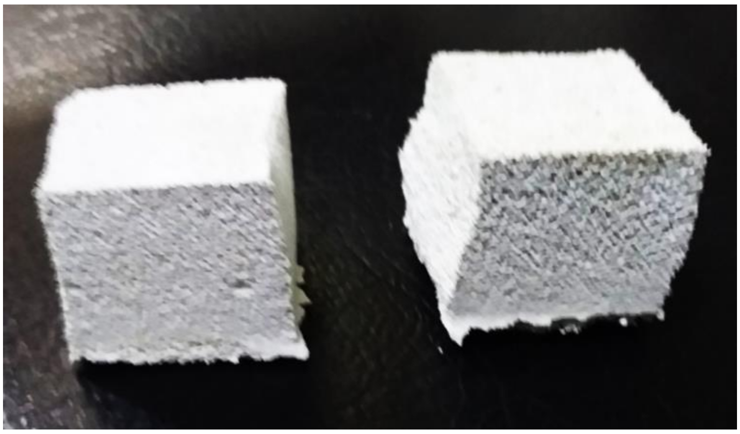


Fig (4) The soaked templet

3- Preparation of porous alumina by partial sintering

Partial sintering of powder compact is the most conventional and straightforward route to fabricate porous ceramic materials. In this technique, particles of powder compact are bonded due to surface diffusion or evaporation- condensation processes enhanced by heat treatments.

- Alumina powder was compacted as a cylindrical sample, powder was mixed with PVA as a binder and put the mixture in a mold of a diameter (20mm) than using hydrolytic press in load reach about (1Mpa) and remain under this load for time reach (2min) in order to distribution of load for all sample.
- . After that samples were dried in the oven at temperature about (100°c) for (24hr).
- The sample was sintered in furnace at temperature about (1100°c) for period reach to (1hr)

The laboratory Tests: -

Particle size analysis

The particle size for both used powders were characterized using Better size 2000 Laser particle size analyzer

Porosity test:

Apparent porosity for the samples were tested according Archimedes method