



Materials Science

An Indian Journal

Full Paper

MSAIJ, 13(9), 2015 [289-299]

Preparation and characterization of high strength and high porosity porous spinel by decomposing an EX - POTATO known as starch soluble $(C_6H_{10}O_5)_N$ using porous magnesia

Kumar Saurav^{1*}, Manas Ranjan Majhi², Vinay Kumar Singh²

¹Phd Student, Department of Ceramic Engineering, Indian Institute of Technology (BHU), (INDIA)

²Associate Prof, Department of Ceramic Engineering, Indian Institute of Technology (BHU), (INDIA)

E-mail: ksaurav.cool@gmail.com

ABSTRACT

The technique was applied to produce porous Spinel by decomposing an EX potato known as starch soluble $(C_6H_{10}O_5)_n$. Observations of the microstructure reveal variation in pore shape and size. Mean grain sizes are less than 70 nm. Mercury porosimetry measurements reveal a bimodal pore size distribution. A porous spinel body was fabricated from porous MgO using a Novel techniques. Porous MgO was synthesis by heating pellets (MgO:Potato Starch :PVA;60:30:10) at 1100 °C for 1h. The resultant porous MgO was then immersed in an 10mol/L aluminium nitrate solution, dried, and reheated at 1300 °C for 2h to convert it to spinel. After five solution treatments The porosity, compressive strength, Permeability, Thermal conductivity, bulk density are calculated and finally spinel conversion ratio are studied. That by using $(C_6H_{10}O_5)_n$ complex compound, a large fraction of pores can be generated and kept at high temperatures (1300°C) The starting materials for the Porous $MgAl_2O_4$ were synthesized via a sintering mechanism using poly vinyl alcohol and starch. Novel pore-forming agents, Poly vinyl alcohol as well as Magnesia were mixed via a sintering process and were used to fabricate porous spinel ceramics. Porous $MgAl_2O_4$ (spinel) ceramics prepared at different sintering temperatures is studied. © 2015 Trade Science Inc. - INDIA

KEYWORDS

PVA;
Starch;
Sintering;
Decomposition.

INTRODUCTION

Porous ceramics are a class of highly reticulated ceramic material that covers a wide range of structures, such as foams, honeycombs, interconnected rods, fibers, or hollow spheres. Porous ceramics have attracted an increasing attention due to their expanding technological applications Sin many in-

dustrial areas, such as Thermal and acoustic insulation, Separation/filtration, Impact absorption, Catalyst supports, Lightweight structures, Porous burners, Energy storage and accumulation, Biomedical devices, Gas sensors, Sonar transducers. High-temperature (>1000 °C) thermal insulating products are fundamental in reducing the energy costs in the cement, steel, aluminum, iron-al-

Full Paper

loy and petrochemical industries. Among the suitable materials for this purpose, porous ceramics are outstanding because they combine intrinsic ceramic properties, such as chemical inertness and refractoriness, with low thermal conductivity. Besides saving energy, the diminished heat loss to the environment also improves working conditions minimizing the employees' stress as a result of their exposure to high temperatures. Porous ceramic products cover wide range of advanced ceramic materials, which can be oxides ceramics: alumina, zirconia, or non-oxides ceramics: carbides, borides, nitrides, silicides^[1-4]. The properties of porous ceramic product depend on three main factors: the properties of the ceramic material of which the product is made; the topology (connectivity) and shape of the pores; and the relative density of the product. Novel pore-forming agents as well as other starting materials were produced in situ via a solution combustion process and were used to fabricate porous MgAl₂O₄ ceramics. Meanwhile, pore formers and other starting materials for porous ceramics used in the conventional methods were first prepared separately and then mixed.

Among the techniques used to produce these materials (such as the addition of foaming agents and organic compounds), the pore generation via phase transformation presents key aspects, such as easy processing and the absence of toxic volatiles. In this study, this technique was applied to produce porous ceramics by decomposing an EX potato known as starch soluble (C₆H₁₀O₅)_n. Porous MgO ceramics prepared at different sintering temperatures is studied^[4-8]. A porous spinel body was fabricated from porous MgO using a Novel techniques. MgO with 68% porosity was fabricated by heating compact from platelets at 1300°C for 1h. The resultant porous MgO was then immersed in an 10mol/L aluminium nitrate solution, dried, and reheated at 1300 °C for 2h to convert it to spinel. After five solution treatments The porosity, compressive strength, bulk density, permeability, thermal conductivity are calculated and finally spinel conversion ratio are studied.

Decomposition of starch -

The incorporation of organic compounds induce pore formation after their burn out, when previously mixed with inorganic ones. Individual organic particles (such as non dissolved starch, wood flour or seeds) or a Ex potato starch can be used for this purpose. Physical Properties of ex potato starch.

Physical state at 20 °C	-Solid
Colour	-White powder
Density [g/cm ³]	- 1.5
Solubility in water [% weight]	-Insoluble in water
Loss on drying (at 105 deg C)	-Max 10%
Sulphated ash	-Max 0.5%
Chloride (Cl)	-Max 0.04%

Poly vinyl alcohol

Polyvinyl alcohol (PVOH, PVA, or PVA I) is a water-soluble synthetic polymer. It has the idealized formula [CH₂CH(OH)]_n. PVA has a melting point of 230 °C and 180–190°C (356-374 degrees Fahrenheit) for the fully hydrolysed and partially hydrolysed grades, respectively. It decomposes rapidly above 200 °C as it can undergo pyrolysis at high temperatures. PVA is close to incompressible. PVA is an atactic material that exhibits crystallinity. In this case, a fraction of smaller pores greater than those obtained by simply mixing these raw materials can be attained.

EXPERIMENTAL

Fine magnesium oxide (Thomas baker pvt ltd, India, 0.10 mm in diameter and 98% pure,) was used as a sintering additive. Ex potato starch (.50 mm, lobachemie pvt ltd) and PVA was also added to the starting materials as a pore former. All powders used as pore-formers were previously dried at 100 °C during 24 h. After this step, their density and surface area were measured in Accu Pyc 1330 helium pycnometer and BET equipment (Micrometrics, USA), respectively. The surface area of porous MgO are found 100 m²/g. Lightly Calcined (fine powder) magnesia and EX Potato Starch - C₆H₁₀O_{5N} (loba chemie pvt ltd. mumbai) were mixed and then poly vinyl alcohol (fine powder) are mixed. The batches

were comprised of Porous MgO (60;30;10-MgO;Starch;PVA) were attrition milled for 3 h and then dried at 100°C for 24 h. The powders were shaped in pellet (piece of small shot) form using hydraulic pressing machine (uniform pressing). The applied load are 15 tonn respectively for sample. The samples were fired at temperatures 1100°C. The heating rate was maintained at 3°C/min and soaking period was 2 hour. The sintered sample was immersed into the aluminium nitrite solution for 1 h under vacuum, removed, and then dried at room temperature for 24h. The resultant sample was reheated at 1300 °C for 2h in air. This solution immersion and reheating treatment was performed up to five times. After each solution treatments are characterized by XRD,SEM, DTA, TGA, Thermal Conductivity, Permeability. The Bulk density, Apparent porosity,compressive strength and linear shrinkage are measured the physical analysis of the sample. Similar to the decomposition of organic matter, this technique is based on generating pores through the volume reduction that follows the decarbonation reactions^[8-13]. After firing, the porosity of the samples was measured by the immersion method (kerosene oil as immersion fluid, five samples). Their Porosity is one of the factors that influences the physical interactions and chemical reactivity of solids with gases and liquids for many industrial applications. The examples of industrially important porous materials include catalysts, construction materials, ce-

ramics, pharmaceutical products, pigments, sorbents, membranes, electrodes, sensors, active components in batteries and fuel cells, and oil and gas bearing strata and rocks. The volume fraction of porosity can be defined as the fraction of void space relative to the apparent total bulk volume of the sample. Porosity in materials originates from different processing and synthesis routes. Synthesis of porous crystalline materials, such as magenesia compound and metal organic frameworks, leads to highly regular intra crystalline pore networks in addition to inherent voids imparted by the presence of vacancies, grain boundaries, and inter particle spaces^[13-16]. As a simplified measure, pore size (or width) is referred to the smallest dimension within a given pore shape, that is, the width between two opposite walls for a slit-shaped pore and the diameter for a cylindrical pore.

DTA–TG analyses were carried out using a Netzsch STA409 equipment.

RESULTS AND DISCUSSION

Porosity and bulk density

The makeup of a porous body with solid, open pores and closed pores, and how water absorbed into the open porosity (by vacuum or boiling) presents when weighed either suspended or soaked. The Apparent Porosity, are calculated from the Dry, Soaked and Suspended weights as follows-

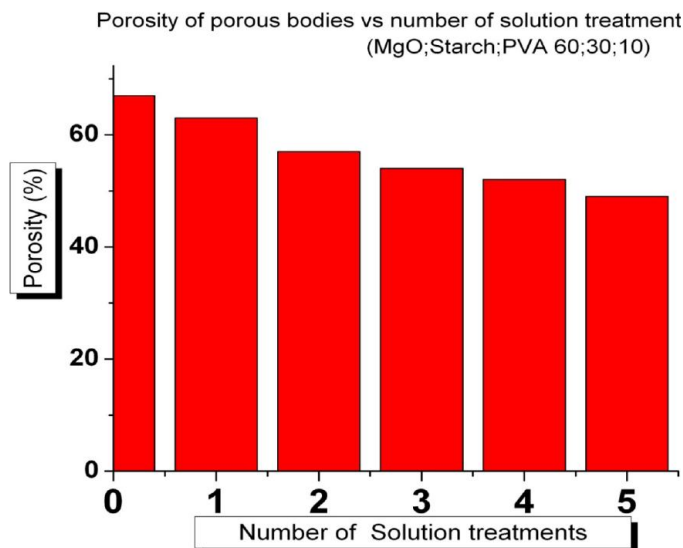


Figure 1 : Percentage porosity of Porous MgO vs number of solution treatments

Full Paper

$\% AP = (\text{Soaked Weight} - \text{Dry Weight}) \times 100 / (\text{Soaked Weight} - \text{Suspended Weight})$

Figure 1 shows MgO porosity vs. the number of solution treatments. The porosity of the samples decreased with increasing number of solution treatments. The porosity of a pure porous magnesia body without solution treatment was approximately 68%. After five solution treatments, the porosity of the samples decreased to 46.0% on average. The flows of weight percentage of MgO seemed to decrease the porosity. The bulk density of refractory materials are measured, using the Archimedes buoyancy technique with dry weights, soaked weights and immersed weights in water (mercury, xylene or denatured alcohol if the refractory is water sensitive).

The plotting figure and comparing them at temperature 1300°C after each solution treatments

$BD = \text{Dry Weight} / (\text{Soaked Weight} - \text{Suspended Weight})$

Figure 2 shows bulk density MgO bodies vs. the number of solution treatments. The bulk density of the samples increased with increasing number of solution treatments. The density of a pure porous magnesia body without solution treatment was approximately 1.9 gm/cc. After five solution treatments, the bulk density of the samples increased to 2.5 gm/cc on average. the density are increased due to mass transport of MgO and alumina.

Spinel formation

The formation of the porous spinel from porous

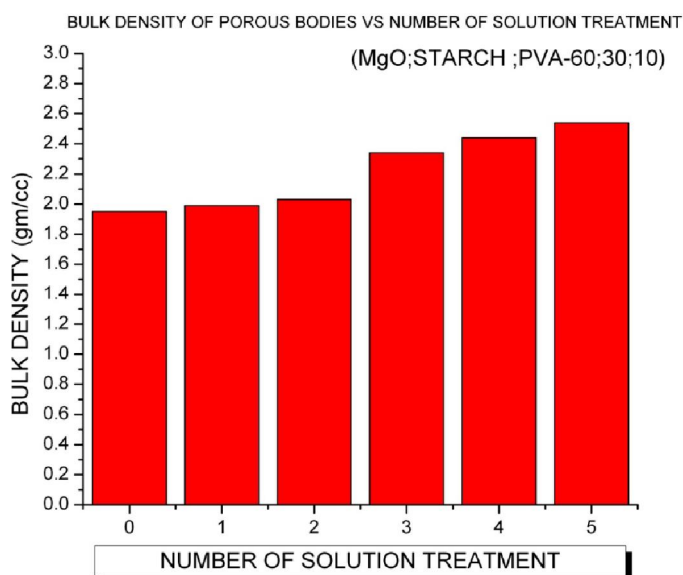


Figure 2 : Bulk density of porous MgO vs number of solution treatments

DTA Curve for Porous MgO-Al₂O₃ (Spinel) after 5th solution treatment

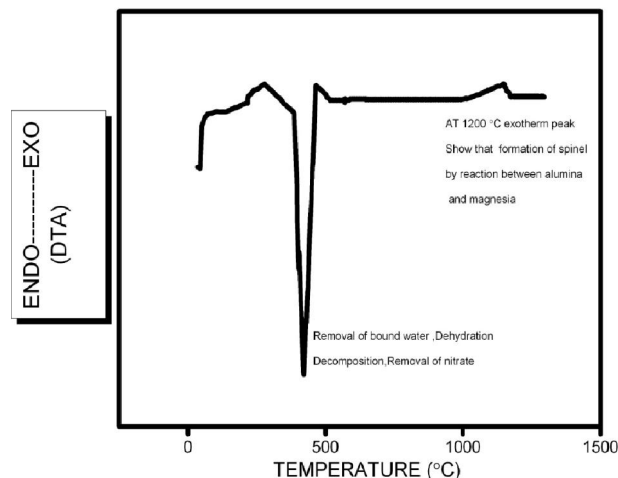


Figure 3a : DTA of porous MgO after fifth solution treatments

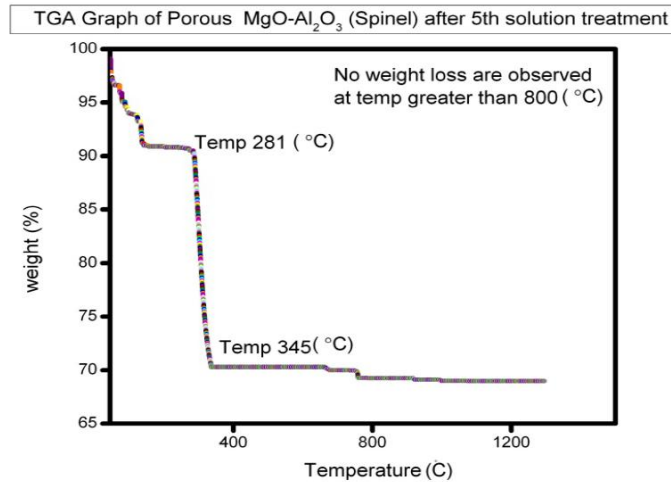


Figure 3b : TGA of Porous MgO after fifth solution treatments

XRD Patterns of Porous MgO bodies vs number of solution treatments.

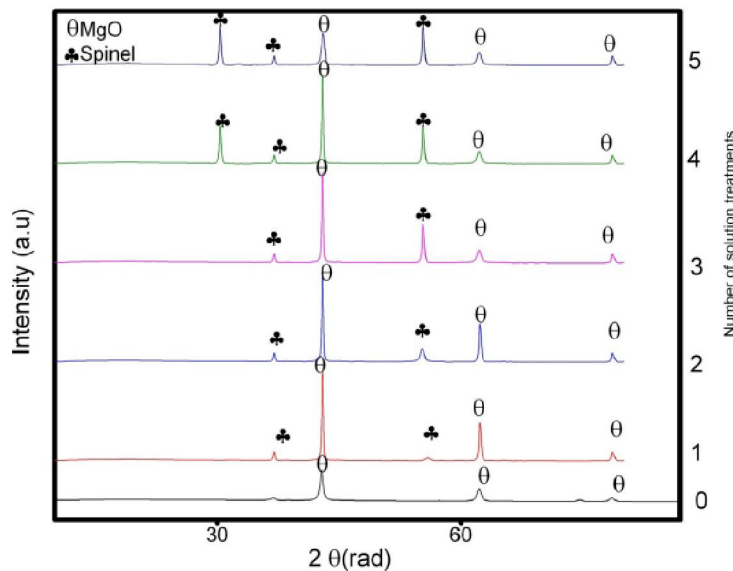


Figure 4 : XRD of Porous MgO with solution treatments

MgO and aluminium nitrate solution after fifth solution treatments was studied. Figure 3 a and Figure 3 b shows DTA–TG analyses of the mixture, where the endothermic bands observed at 281°C and 345 °C were attributed to dehydration and nitrate removal and removal of bound waters, respectively. At 1200 °C a small exothermic effect was detected associated with nucleation and formation of spinel by reaction between alumina and magnesia. This fact was confirmed by SEM and XRD diffraction studies. No distinct weight Loss is observed at temperature higher than 800 °C because of the mass formation of spinel.

Figure 4 shows diffraction pattern of porous MgO

with number of aluminium nitrate solution treatments. Initially after first solution treatment a small peaks of spinel are detected, which indicated that the MgO reacts with alumina and forms spinel. As can be seen, no alumina was detected in any sample, which indicates that the initially precipitated alumina completely reacted with MgO to form Spinel during processing. After five solution treatments huge amount of spinel are formed. The ratio of spinel conversion are calculated by weight gain formula according to the chemically reaction. Actually more than 35% Spinel are formed after fifth solution treatments.

Figure 5a shows an SEM micrograph of a porous MgO sample without any treatments. The sur-

Full Paper

faces of the platelets were rough, but the overall platelet shape remained. The spot develop on the surface indicates the starch evolution during increasing temperature. Figure 5 b shows an SEM micro-

graph of a porous MgO sample with first solution treatments. The white surface suggests that the MgO platelets were partially covered with the precipitated spinel. Figure 5c shows an SEM micrograph

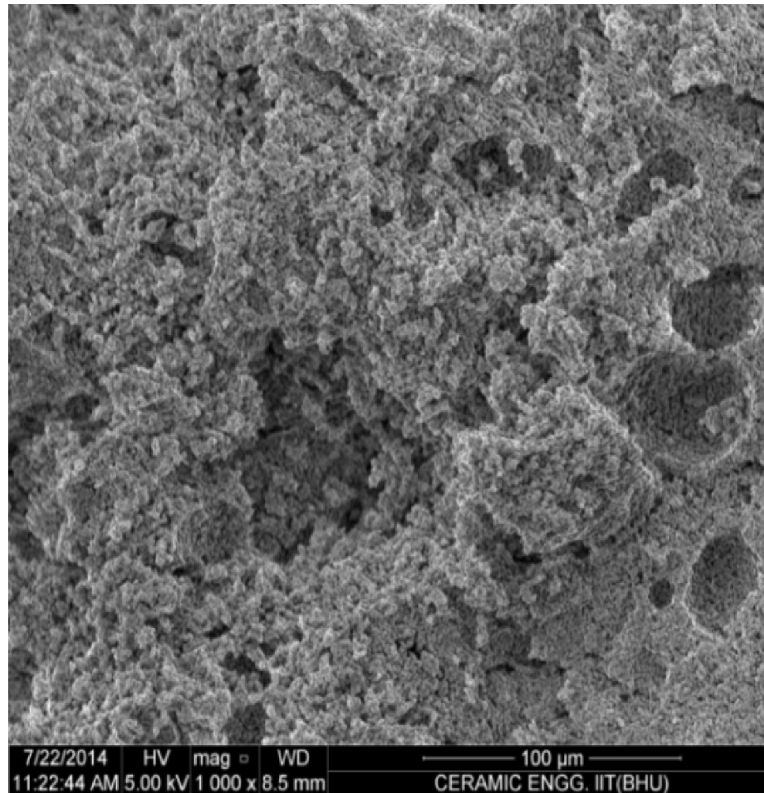


Figure 5a : SEM of Porous MgO with out solution treatments

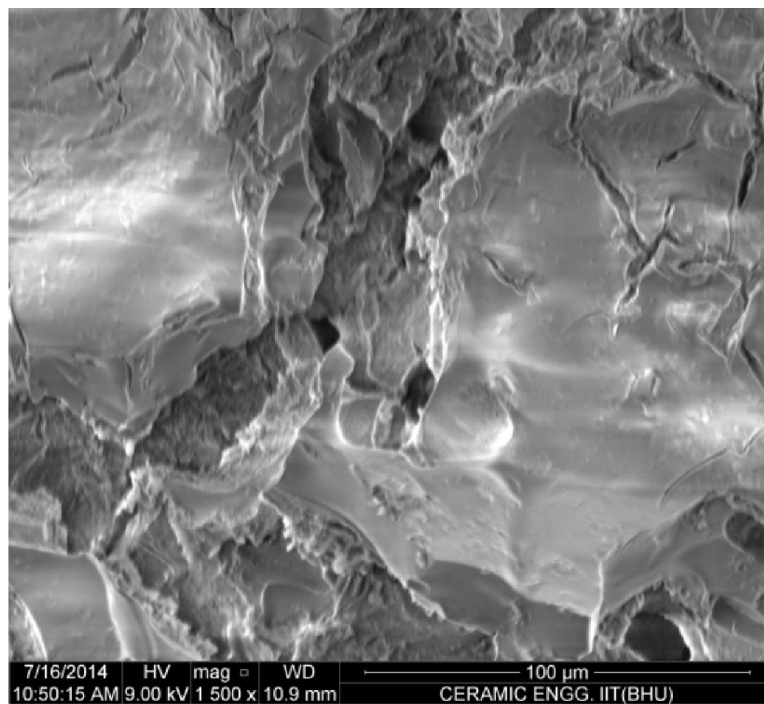


Figure 5b : SEM of Porous MgO with first solution treatments

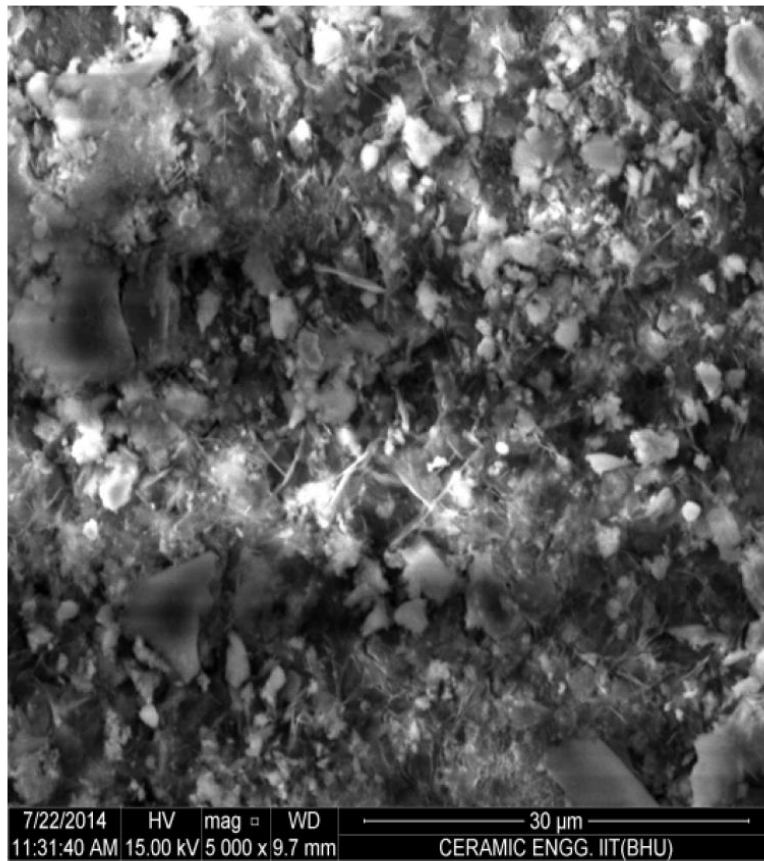


Figure 5c : SEM of Porous MgO with fifth solution treatments

TABLE 1 : Pore volume fraction of the maximum temperature used in following time cycle

Sample	T_{MAX} (hour)	APPARENT POROSITY (%)
POROUS MgO	0	68
POROUS MgO with first solution treatments	24	63
POROUS MgO with second solution treatments	48	57
POROUS MgO with third solution treatments	72	54
POROUS MgO with fourth solution treatments	120	52
POROUS MgO with fifth solution treatments	144	48

of a porous MgO sample with fifth solution treatments, a large amount of white ball are developed which indicate huge amount of Spinel are formed. This suggests that the alumina platelets were fully covered with the precipitated spinel. Pore volume fractions as a function of the time T_{max} are reported in TABLE 1. The micrograph in Figure 5 reveals a homogeneous grain size of less than 100 nm and variation in pore shape and size. At least two different characteristic pore sizes can be identified. The mercury porosimetry measurements confirm that the samples exhibit bimodal pore size distributions, constituted by mesopores with diameter less than

50 nm and by macropores with diameter above 50 nm.

Figure (6a). Porous MgO without solution treatment has high porosity. The five graphs in Figure 6 reveal that the mesopore volume fraction increases with the porosity. The grain size of the Porous magnesia increases from 62 to 70 nm when the applied solution treatments are increased.

Compressive strength

The compressive strength of materials is the most common performance measure used by the engineer in designing buildings and other structures. The compressive strength is measured by breaking cylin-

Full Paper

drical concrete specimens in a compression-testing machine. The compressive strength is calculated from the failure load divided by the cross-sectional area resisting the load and reported in units of pound-force per square inch (psi) in US Customary units or megapascals (MPa) in SI units. Figure 7 shows the compressive strength of the samples vs. the number of solution treatments. By increasing the number of

solution treatments, the compressive strength of the samples increased. After five solution treatments, the compressive strength reached 18.0 MPa. The increasing compressive strength are due to material transport of alumina and MgO.

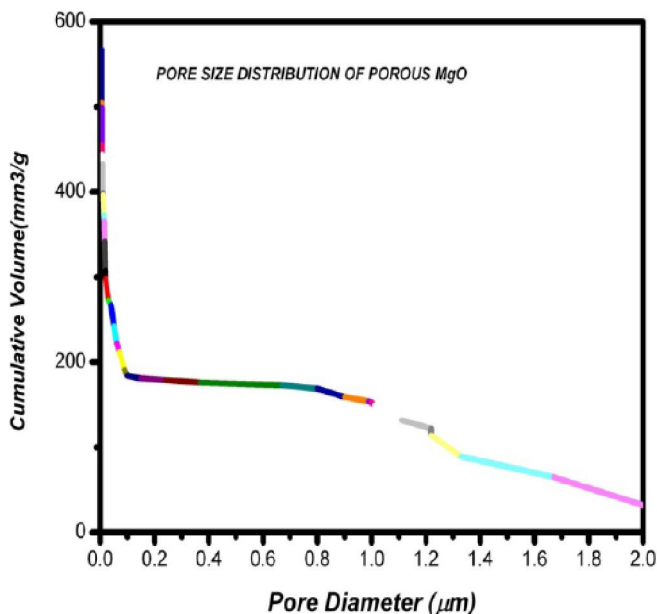


Figure 6a : Pore size distribution of Porous MgO without solution treatments sample contains high (68%) Porosity

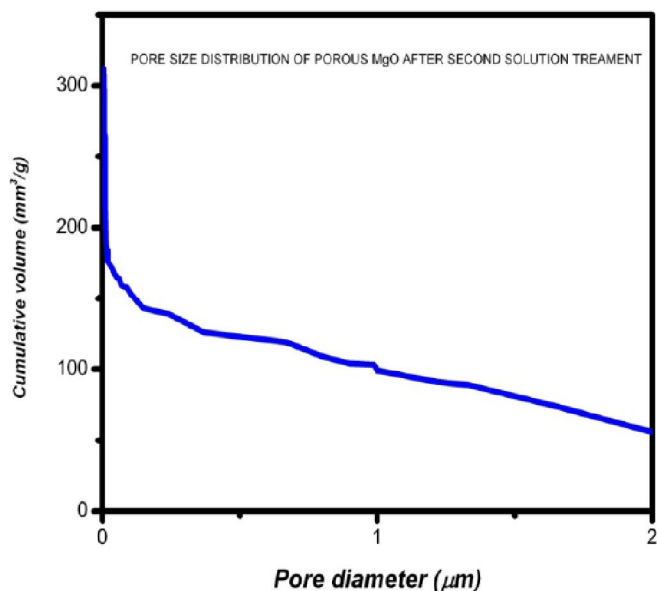


Figure 6c : Pore size distribution of Porous MgO with second solution treatments sample contains (57%) Porosity

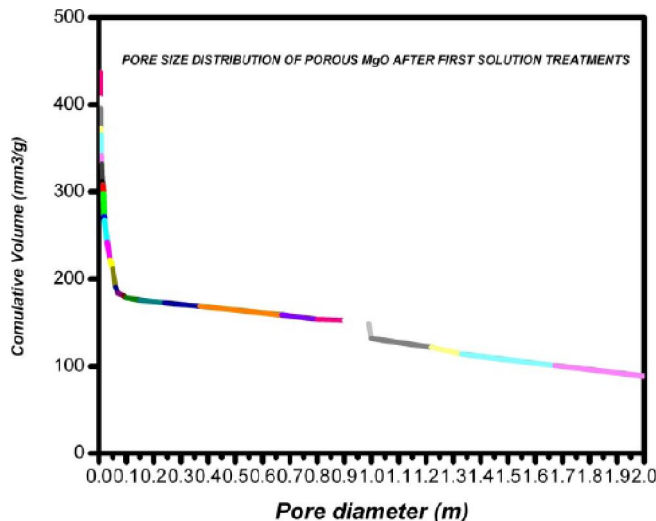


Figure 6b : Pore size distribution of Porous MgO with first solution treatments sample contains (63%) Porosity

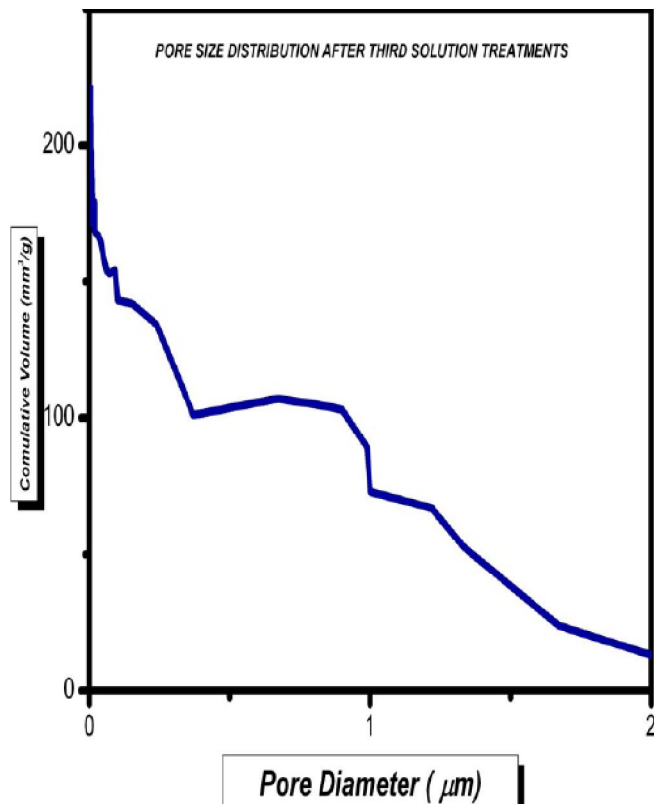


Figure 6d : Pore size distribution of Porous MgO with third solution treatments sample contains (54%) Porosity

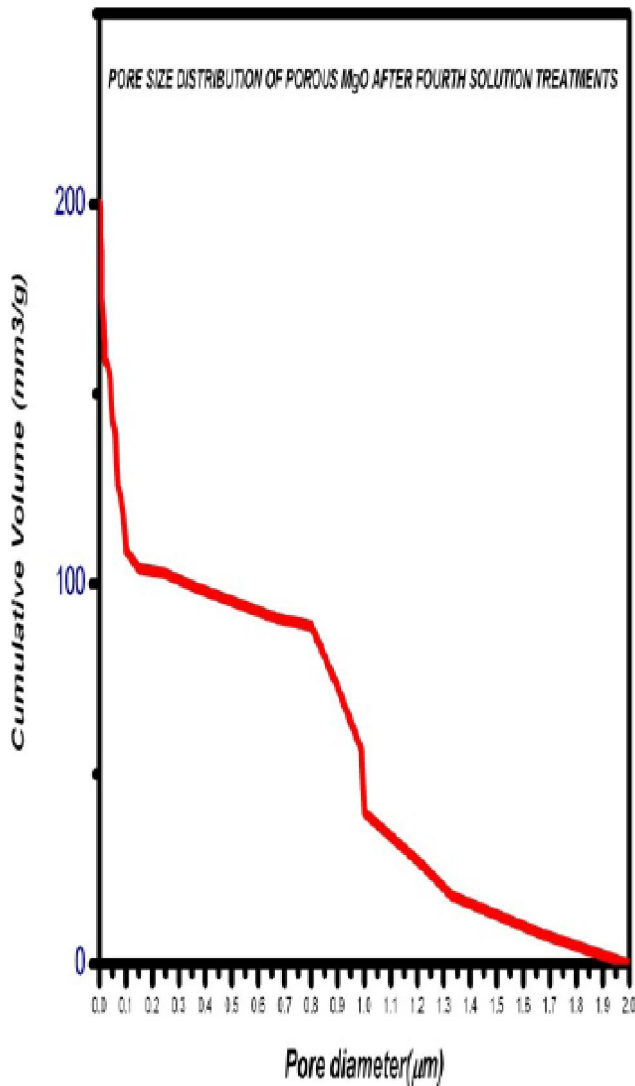


Figure 6e : Pore size distribution of Porous MgO with fourth solution treatments sample contains (52%) Porosity

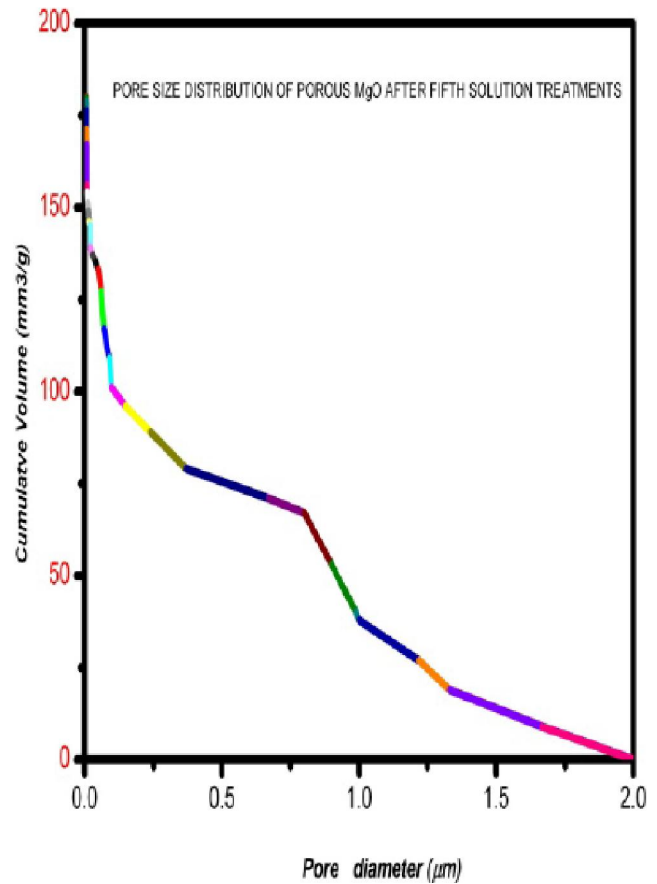


Figure 6f : Pore size distribution of Porous MgO with fifth solution treatments sample contains (48%) Porosity

Thermal conductivity

Incorporation of porosity into a monolithic material decreases the effective thermal conductivity. Figure 8 shows that with increasing solution treatments, the thermal conductivity of the sample

Compressive strength of porous spinel by number of solution treatments

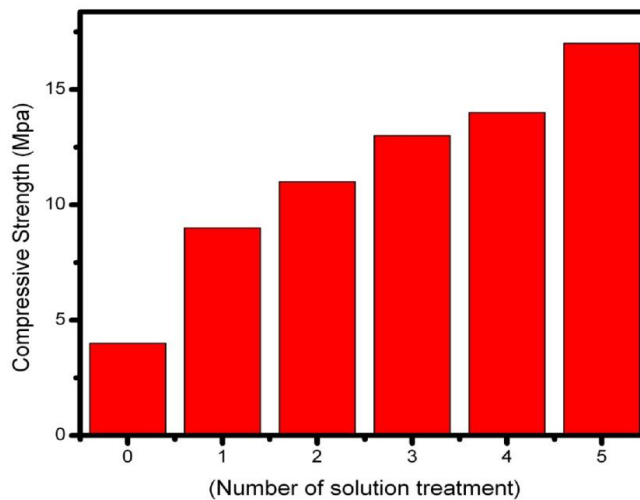


Figure 7 : Compressive Strength of Porous MgO vs number of solution treatments

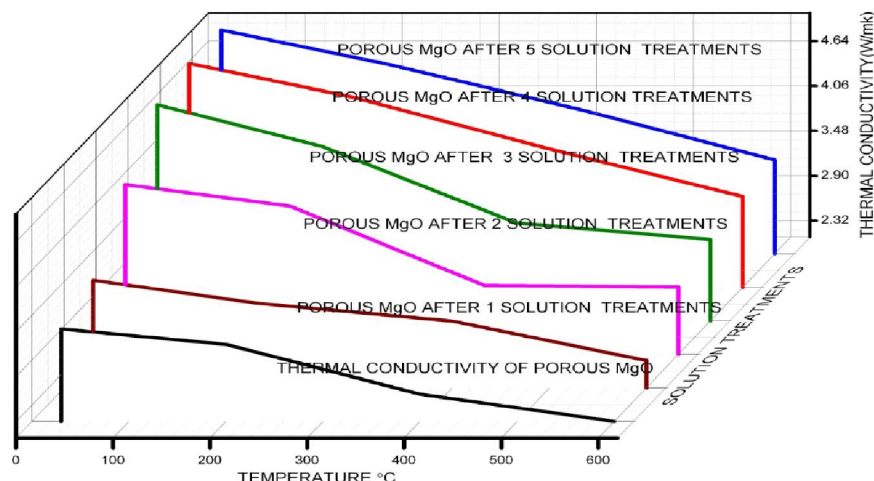


Figure 8 : Thermal conductivity of the Porous MgO each solution treatments

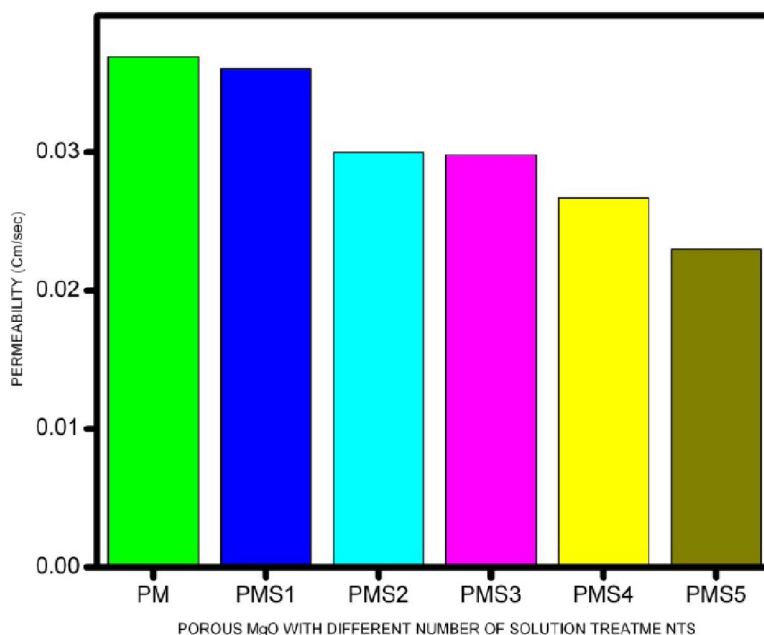


Figure 9 : Permeability of the porous MgO after each solution treatments

increased, finally reaching 4.8W/mK after five solution treatments. In these porous samples, the pore diameter was several micrometers due to the size of the platelets. Furthermore, The temperature remained below 600 °C

Permeability of porous spinel

Permeability is the measure of flow through porosity with in a body,,ability to permit water to flow through its pores or voids. The parameter q in Darcy’s law is called the flow rate or simply the flow (flux). It describes in a unit time, over a unit cross-section area, how much water in terms of volume has been flowed through. Permeability measured of dense refractories gives an indication of how well

that refractory will stand up to slag, melt or gas penetration during service (low permeability = better slag, melt or gas penetration resistance). Falling Head test method are used to determine the permeability. Figure 9 shows that permeability decrease with increase solution treatment. Thus, it was concluded that the Magnesia platelets became more strongly linked due to active mass transport with decreasing porosity, leading to decreases permeability.

CONCLUSION

Porous ceramics for application such as thermal

insulating can be produced by decomposition of EX-Potato Starch such as $(C_6H_{10}O_5)_N$. The suitable choice of raw materials allowed for generation of a great volume of pores during the decomposing of those compound and sintering of material Initially, a porous MgO body with 48 %porosity are build up by heating compact of 60% MgO,30% EX potato starch,10% PVA act as pore former. The resulting pellets are dipped in 1,2,3,4,5 aluminium nitrate solution (the solution treatment are performed up to five times) With increasing solution treatments, the porosity decreased, the compressive strength increase,bulk density increased thermal conductivity increased and permeability decreased. Finally high strength (18 Mpa)high porosity (46%) porous spinel are developed.

REFERENCES

- [1] V.R.Salvini, M.D.M.Innocentini, V.C.Pandolfelli; Optimizing permeability, Mechanical strength of ceramic foams, American Ceramic Society Bulletin, **79(5)**, 49–63 (2000).
- [2] A.R.Studart, U.T.Gonzenbach, E.Tervoot, L.J.Gauckler; Processing routes to macroporous ceramics: a review, Journal of the American Ceramic Society, **89(6)**, 1771–1789 (2006).
- [3] O.Lyckfeldt, J.M.F.Ferreira; Processing of porous ceramics by starch consolidation, Journal of the European Ceramic Society **18(2)**, 131–140 (1998).
- [4] H.C.Park, Y.B.Lee, K.D.Oh, F.L.Riley; Grain growth in sintered MgAl₂O₄ spinel, Journal of Materials Science Letters, **16**, 1841–1844 (1997).
- [5] L.B.Kong, J.Ma, H.Huang; MgAl₂O₄ spinel phase derived from oxide mixture activated by a high-energy ball milling process, Materials Letters, **56**, 238–243 (2002).
- [6] R.Sarkar, S.K.Das, G.Banerjee; Effect of attrition milling on the densification of magnesium aluminate spinel, Ceramics International, **25**, 485–489 (1999).
- [7] Y.Suyama, A.Kato; Characterization and sintering of Mg–Al spinel prepared by spray-pyrolysis technique, Ceramics International **8**, 17–21 (1982).
- [8] C.R.Bickmore, K.F.Waldner, D.R.Treadwell, R.M.Laine; Ultrafine spinel powders by flame spray pyrolysis of a magnesium aluminum double alkoxide, Journal of the American Ceramic Society, **79**, 1419–1423 (1996).
- [9] C.T.Wang, L.S.Lin, S.J.Yang; Preparation of MgAl₂O₄ spinel powders via freeze-drying of alkoxide precursors, Journal of the American Ceramic Society, **75**, 2240–2243 (1992).
- [10] J.Katanic-Popovic, N.Miljevic, S.Zec; Spinel formation from coprecipitated gel, Ceramics International, **17**, 49–52 (1991).
- [11] T.Shiono, K.Shiono, K.Miyamoto, G.Pezzotti; Synthesis and characterization of MgAl₂O₄ spinel powder from a heterogeneous alkoxide solution containing fine MgO powder, Journal of the American Ceramic Society, **83**, 235–237 (2000).
- [12] K.C.Patil, M.S.Hegde, Rattan Tanu, S.T.Aruna; Chemistry of nanocrystalline oxide materials: Combustion synthesis, Properties and Applications, Singapore: World Scientific Press, (2008).
- [13] U.T.Gonzenbach, A.R.Studart, E.Tervoot, J.L.Gauckler; Macroporous ceramics from particle-stabilized wet foams, Journal of the American Ceramic Society, **90(1)**, 16–22 (2007).
- [14] U.T.Gonzenbach, A.R.Studart, D.Steinlin, E.Tervoot, J.L.Gauckler; Processing of particle-stabilized wet foams into porous ceramics, Journal of the American Ceramic Society, **90(11)**, 3407–3414 (2007).
- [15] W.Mista, J.Wrzyszcz; Rehydration of transition aluminas obtained by flash calcination of gibbsite, Thermochimica Acta, **331(1)**, 67–72 (1999).
- [16] Z.Deng, T.Fukasawa, M.Ando; High-surface-area alumina ceramics fabricated by the decomposition of Al(OH)₃, Journal of the American Ceramic Society, **84(3)**, 485–491 (2001).