Effect of Porosity on Thermal Conductivity and Flexural Strength of Ceramic Foam

Dr. Shihab Ahmed Zaidan [iD]
Applied Sciences Department, University of Technology/Baghdad
Dr. AbdalKhalaq F. Hamood
Production and Metallurgy Engineering Department, University of Technology/Baghdad
Sara Nabil Ibrahim
Applied Sciences Department, University of Technology/Baghdad

ABSTRACT

Refractory ceramics used for thermal insulating applications should be porous; containing large number of air cells.This work addresses a highly porous local ceramic prepared via simple and low cost process (direct foaming method) by using Iraqi raw material (kaolin) and egg white as a binder and a foaming agent. Porosity, thermal conductivity and flexural strength were obtained after sintering of the specimens at 1100 and 1300 $^{\circ}$C. The prepared ceramic foam contained a large amount of spherical microspores; it has high porosity (68.1-80%), low thermal conductivity (0.2-0.6) W/m.K with flexural strength range (0.4-2.8) MPa. The direct foaming method, using egg white foam, proved to be an efficient and feasible method for producing highly porous ceramics with good mechanical properties for thermal insulating applications.

INTRODUCTION

Due to energy costs and environmental concerns in recent years, an increasing interest in the development and use of insulating refractories have been observed. Insulating refractories are always associated with highly porous structures and low thermal conductivity. Although their primary goal is to reduce overall energy consumption and heat losses, these materials can also play an important role in the control of temperature in various industrial processes [1].In general, some ceramics become more effective thermal insulators at high temperatures when designed with smaller pore size and higher porosity and preferably closed porous microstructure [2].In recent years, great progress has been made in direct foaming methods, where gas bubbles are dispersed into a suspension either by stirring or by in situ gas evolution (through chemical reactions). The resulting foam is subsequently set with the help of a binder or heat that will retain the bubble-containing structure [3].
Iraqi raw material (kaolin) was used to produce insulation foam ceramics. A simple and low cost procedure (direct foaming method) was adopted, which is simply explained by the incorporation of gas into ceramic slurry. This was achieved by (1) chemical blowing agent (sodium bicarbonate) and (2) physical blowing agent (egg white foamed by mechanical stirring).
The advantages of using Egg white are :
❖ Egg white performs dual functions, of both foamier and binder.
❖ No other organic additives in significant quantity are required, thus keeping the amount of organic material in the dried green foam small and reducing the amount of material that has to burn out later.

❖   Observation of aqueous foams for similar or lower concentration of egg white in solution indicates that it provides higher foam stability than Cetyltrimethylammonium bromide (CTAB), a commonly used foaming agent.

❖   Egg white was used in food processing, so it is nontoxic and environment friendly [4].

Ceramic foam

Ceramic foam is a class of highly porous materials that are used for wide range of technological applications. It can be classified as lightweight materials that exist as a cellular structure composed of a three-dimensional network of struts [5]. As shown in figure (1). It is a brittle material comprising of large void cells, with linear dimensions in the range of 10μm to 5mm [6]. Ceramic foam is generally divided into 2 types:

1. Macro cellular foam, typically presents cell size larger than 50μm and cell densities <10^9 cells/cm^3.

2. Micro cellular foam, have closed cells with cell densities greater than 10^9 cells/cm^3 and fully grown cells smaller than 50μm [7].
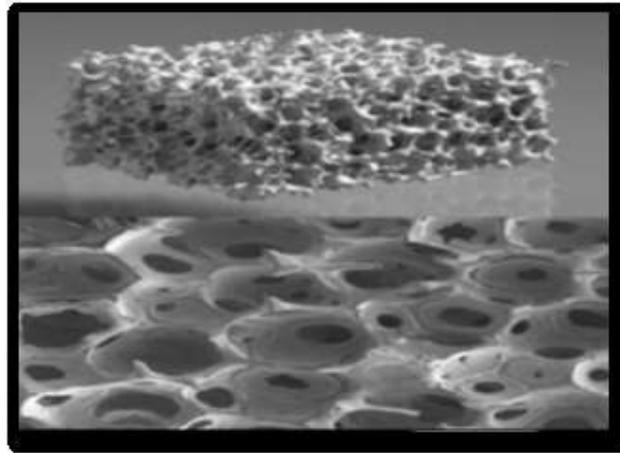

Figure (1): Ceramic foam with its special micro-macro structure [8].

Foam structure

The main structural characteristics that comprise foams are ligaments (referred to as struts), cells and nodes. These are illustrated in Figure (2). Size, shape, direction, anisotropy and uniformity of these features have significant influence on the bulk properties of the material. The ligaments and nodes together establish the framework and structural integrity of the foam, whereas the cells contribute largely to the porosity and density of the bulk material [9].
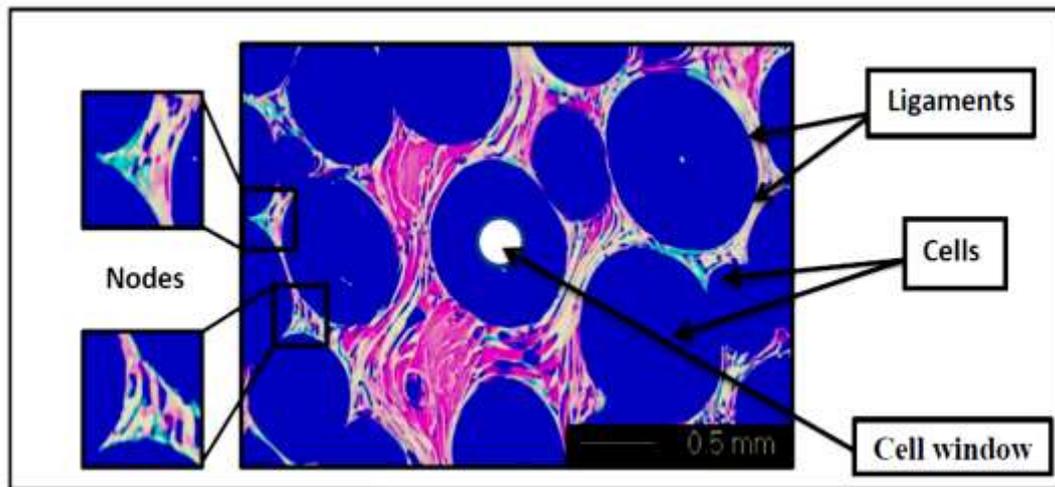
Figure (2): Illustration of ligaments, cells, and nodes within foam [9]

Experimental
Materials
Kaolin clay was brought from the stat Establishment of Geological Survery and Mining of the Ministry of Industry and Minerals, Baghdad, Iraq. The procedure for preparing rocks consisted of "grinding" using "jaw crushing machine" then "Balls milling". The resulted powder was then sieved by using a sieve shaker, to yield particle size ≤63 µm. The particle size distribution for the resulted powder is shown in the table (1). Some of the prepared Kaolin was burned, at a temperature of 1100 ºC for two hours to obtain grog and then added to the mixture in order to reduce the plasticity and theshrinkage.

Table (1): grading of kaolin powder

Sieve Size (µm)	63	45	32	25
Passing %	58.8	37.07	3.8	0.3

  Egg white powder (ovalbumin), manufactured in Switzerland, has been used as the binding and foaming agent. Two different concentrations were used, a more dense (1:4) and a diluted (1:8) as compared to water respectively.
The egg white powder was dissolved in water at room temperatureto make solutions A (with a ratio of 1:4 of egg white to water) & B (with a ratio of 1:8 of egg white to water), then mixed for two minutes using an electrical hand mixer to get the foam.
    In addition commercially available baking soda has been used as a source of sodium bicarbonate ($NaHCO_3$) as a chemical blowing agent, to produce bubbles inside the kaolin slurry.

Sample preparation
  The processing of kaolin foam was carried out following several steps. The first step involves preparation of slurry. Concentrated ceramic slurries were prepared by mixing kaolin powder (particle size ≤ 63µm) with water in 5 different ratios. [the total kaolin powder consists of 50% unburned and 50% burned at 1100ºC]. The slurry was ball milled for 3 hours with alumina balls as the grinding media, resulting in a well dispersed homogenized material. Experimental trials were conducted with different percentages of kaolin to water ratio in order to reach the optimum quality. Separate experimental trials were conducted involving different kaolin to water ratio. Based on such trials, it was found that the practical range of viscosity of kaolin slurries was (60%≥kaolin ≥30%).

This was followed by addition of sodium bicarbonate to each ratio and mixed carefully; air bubbles generated in the kaolin slurry were recognized.

The second step involves the preparation of egg white foam as described above in two concentrations, and adding them to the kaolin slurry samples then mixing them carefully to maintain the air bubbles inside the mixture. The increase in the volume of the kaolin slurry due to the air bubbles is shown in fig (3). The compositions of all Specimens are shown in table (2).

The third step involved the casting of the foamed slurry in a rectangular and a circular silicon rubbermolds, which were dried in an oven under 70ºC for 14 hrs.

After that, the process was followed by the sintering at 2 different temperatures of 1100ºC and 1300ºC for 3 hours with soaking time of 2 hours using a programmable furnace (Nabertherm-p310-Germany).The rate of heating and cooling was (6.1) $^\circ$C / min for 1100°C and 7.2°C/min for 1300°C). A foamed specimen, before and after sintering, is shown in fig (4).
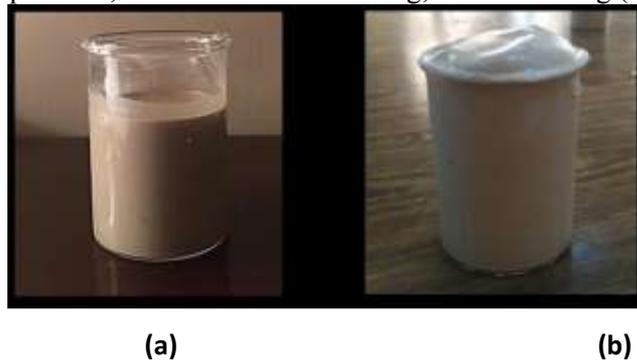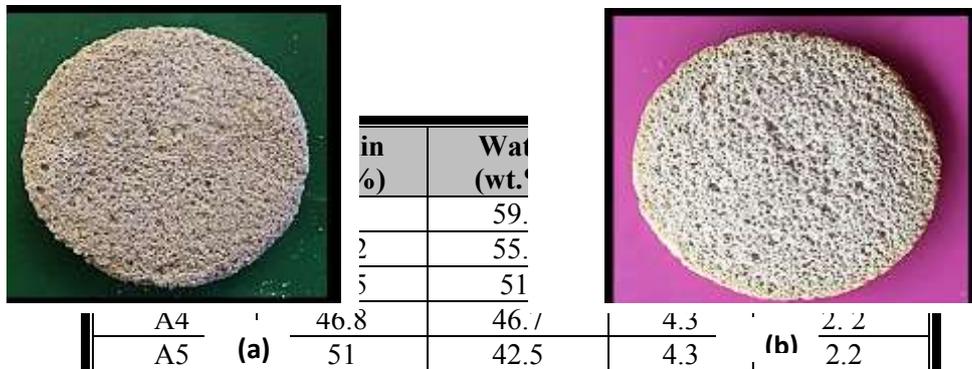

(a)   (b)

**Figure (3): Side view pictures show (a) kaolin slurry before adding egg white.
(b) Final mixture after adding egg white.**

	in (%)	Wat (wt.		
		59.		
	2	55.		
	5	51		
A4	46.8	46.7	4.3	2. 2
A5	51	42.5	4.3	2.2

Figure(4):Specimen (a) before sintering, (b) after sintering.

Table (2): Compositions of specimens (Key specimens)

B3	43	51.6	4.3	1.1
B4	47.3	47.3	4.3	1.1
B5	51.6	43	4.3	1.1

Measurements

The apparent porosity (A.P) of the sintered samples were measured by the Archimedes drainage method, using ASTM (C373).

Flexural strength was measured in a 3-Point Bending Test Using LARYEE Testing Machine (Computer control electronic universal testing machine WDW-100). The dimensions of bar-shaped specimens are ($6\times2\times1$ cm^3).

Leė s disk method was used for determining the thermal conductivity (K) [10].This investigation was carried out using (40*20) mm cylindrical specimens according to the standard specifications of the instruments using Lee's disk type (Griffin & George Ltd - Germany).

Results & Discussions:

Porosity is the dominant factor affecting the performance of ceramic materials. The porosity of the direct foaming method was controlled through the control of viscosity, which could be determined by the kaolin concentration and egg white protein concentrations. Figure (5) shows the apparent porosity versus kaolin additives sintered at (1100) ºC and (1300) ºC. From these figures it can be seen an apparent decrease in porosity with increasing kaolin amount. This is attributed to the decrease of air bubbles in the mixture, mainly due to the decrease of egg white and sodium bicarbonate relative to Kaolin for the same group. [Both are responsible for generating the bubbles which make the porosity]. When the viscosity increased, the total amount of air incorporated into more viscous slurry was less than that incorporated into less viscous slurry. Therefore, fewer pores formed from more viscous slurry. Also between G.A and G.B, for the same sintering temp, it can be seen that the porosities of G.A are less than G.B. Although the differences are not large, this difference is due to the changing in egg white solution viscosity. In G.A, the amount of egg white and viscosity of egg solution are higher than viscosity in G.B. so the porosity decreased as the egg white solution viscosity increased. By comparing between Fig (5_ a,b) and Fig (5 c,d), one can see that as the sintering temperature increased (1100 ºC - 1300 ºC), the porosity decreased, this can be attributed to the decreasing micro pores that occurred due to the densification. The specimen preparation and cell size in ceramic foams is very sensitive to the baking conditions [4]. Any variation in temperature of drying oven (caused due to the fluctuations of electrical current) leads to the collapse of specimens. One specimen affected by the changed in temperature so that another one was prepared in order to avoid the incorrect results.

By comparison between egg white additives (1.1%) and (2.2%) it is apparent that there was no significant increase in porosity, that means that the maximum value of porosity obtained from adding egg white by these two percentage was 71-80% at 1100 ºC   and (67-79.5%) at 1300 ºC.

It is well known that the porosity of a ceramic material is regarded as one of the most important factors affecting the thermal conductivity coefficient. Thermal conductivity versus kaolin foam

specimens sintered at 1100 ºC is presented in Fig (5 a,b). It shows a general increase of thermal conductivity with decreasing porosity.

At higher sintering temperature (1300 ºC), the micro pore content was reduced due to densification as shown in figure (5_ c,d) and this consequently led to an increase of its thermal conductivity.

A general rule states that closed pores tends to be more effective in thermal conductivity, as it increases with increasing viscosity (higher Kaolin). However it was recognized in this study that the total porosity tends to decrease with increasing viscosity. This leads to conclude that the number overwhelms the type of pores, and this is the reason behind increasing the thermal conductivity as the kaolin percentage increases.

The foamed compositions showed very low values of thermal conductivity, ranging from (0.23-0.47 W/m.K) for specimens sintered at 1100 ºC and from (0.4-0.66 W/m.K) for specimens sintered at 1300 ºC.

Figure (6) show the graph of flexural strength versus kaolin percentage for 2 egg white percentages, at sintering temperatures of 1100 ºC and 1300 ºC respectively. It is clearly seen that the flexural strength increases with increasing the kaolin percentage in the specimens for the same sintering temp. This is due to the increased interconnections forces provided by Kaolin and the corresponding decrease in porosity. Porosity has a significant role to influence the flexural strength of sintered kaolin foam. The flexural strength is inversely proportional to the porosity [4] and this reason explains why the flexural strength values ofG.A were higher than Flexural strength values of G.B for the same sintering temp.

Also by comparing fig (6_a,b) and fig (6_ c,d) as sintering temperature increases the flexural strength of foamed specimens also increase. Previous works indicated that changes of foam strength as a result of grains grew up that led to the foam had more contacting areas which became the main reason for causing the improvement of foams strength at that time. As the particle grew up and turned into the large grains, it solidly bonded together which increased the flexural strength [11] of sintered kaolin foams.

Abrupt changes, sometimes, can take place, mainly due to the existence of micro-anomalies such as micro-cracks. A general value of (0.5-1.2) MPa at 1100 ℃ and (0.7-2.8) at 1300 ℃ MPa was computed in this study presumed to make sense.

Microstructural properties (SEM Images): Figures (7_a),(7_b), (7_c),(7_d) showed the microstructure of A1,A5,B1,B5 respectively.

❖   As the kaolin percentage increased (slurry viscosity increased) it's clearly seen that:

1.   The cell volume of A1,B1 was higher than cell volume of A5,B5 and this led to increase the total porosity of A1 and B1.

2.   The cell windows in specimen A1,B1 were more than in A5,B5 and this is mean that the open pores in A1,B1 were more than in A5,B5, and the porosity became more open as the amount of porosity increased due to decreasing in slurry viscosity.

3.   The porewalls and struts were generally thin in A1 and B1 sintered at 1100 ℃.It is obvious that pore wall of B5 and A5 thicker than A1 and B1

That's mean as the kaolin additives increased (slurry viscosity increased) the pore walls became thicker.

4.   The nodes in A1,B1, were denser than in A5,B5 due to increasing in kaolin percentage which led to increase the dense area free from pores.

❖   By compared between G.A and G. B for the same temp. ,one can understand that the cell volumes and cell windows in B1,B5 were higher than in A1,A5, this is due to the changing in viscosity of egg white as the amount of water adding to egg white in G.B was twice the amount of water adding to egg white in G.A

G.A[1:4], G.B[1:8]   [egg white : water]

The pore walls, struts and nodes in G.A were thicker than in G.B this is for the reason of decreasing in egg white viscosity, it was more obvious in A5 and B5.

❖   The comparison between two sintering temperatures for the same specimens A1,A5,B1,B5 sintered at 1100 ^{o}C shown in fig(7a, 7b, 7c, 7d) and A1,A5,B1,B5 sintered at 1300 ^{o}C shows in fig(8a, 8b, 8c, 8d) shows that :

1.   As the sintering temperature increased the pore walls and struts became thicker and denser. And this is led to the increasing in foam density as explained before.

2.   Volume of cells decreased as the sintering temp increased also due to the densification of micro pores.

CONCLUSIONS

Most important parameters that strongly affect on Insulation Ceramics are porosity and thermal conductivity.

1. Higher porosity means lower thermal conductivity of material; this is lead to high efficiency in thermal insulation. When porosity increased, thermal conductivity decreased too.

2. Increasing porosity doesnot mean getting better insulating materials, unless accompanied by good mechanical properties, so it can be useful in different application and to prevent breakage while performing different tasks.
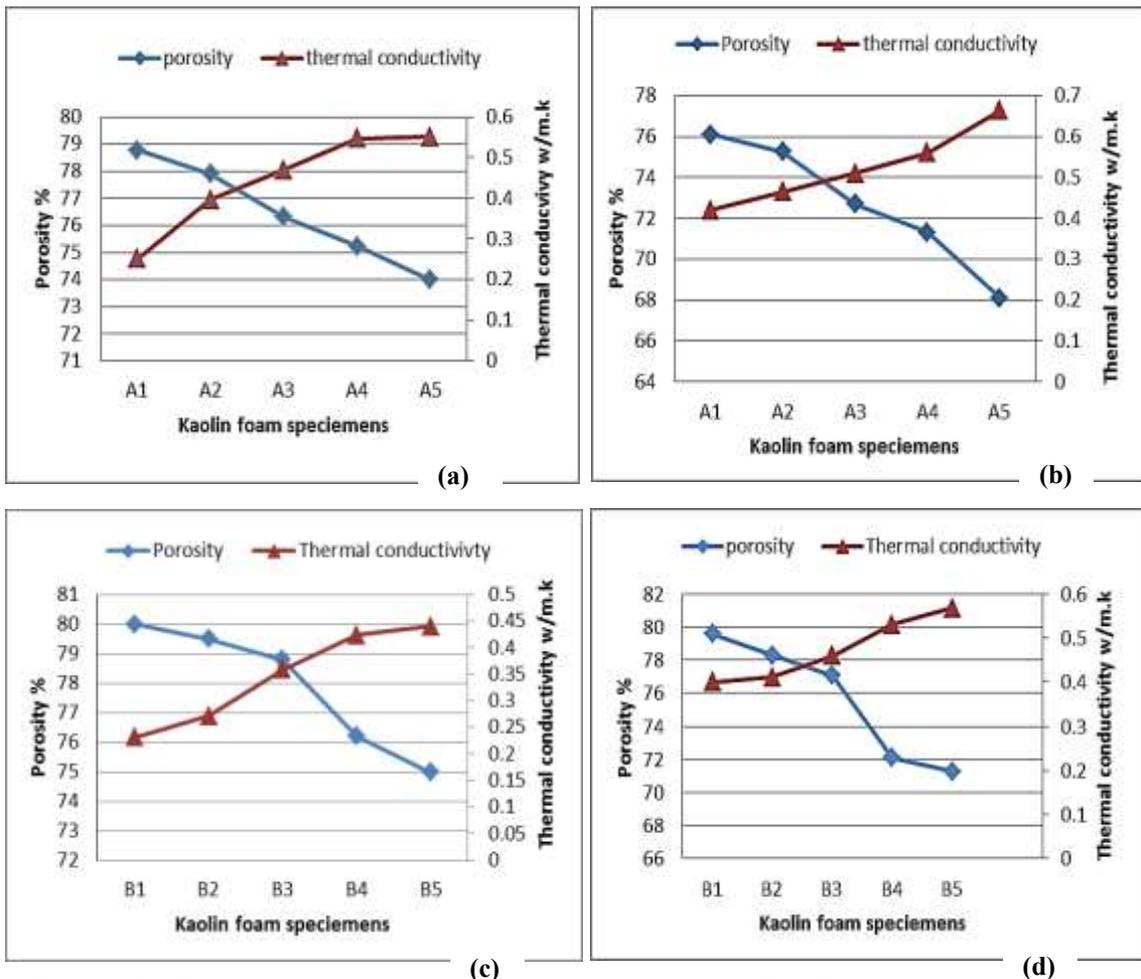

(a)

(b)

(c)

(d)

Figure (5): Effect of porosity on thermal conductivity: (a) For G.A. sintered at 1100 º C. (b) For G.A sintered at 1300 ºC. (c) For G.B. sintered at 1100 ºC. (d) For G.B. sintered at 1300 ºC.
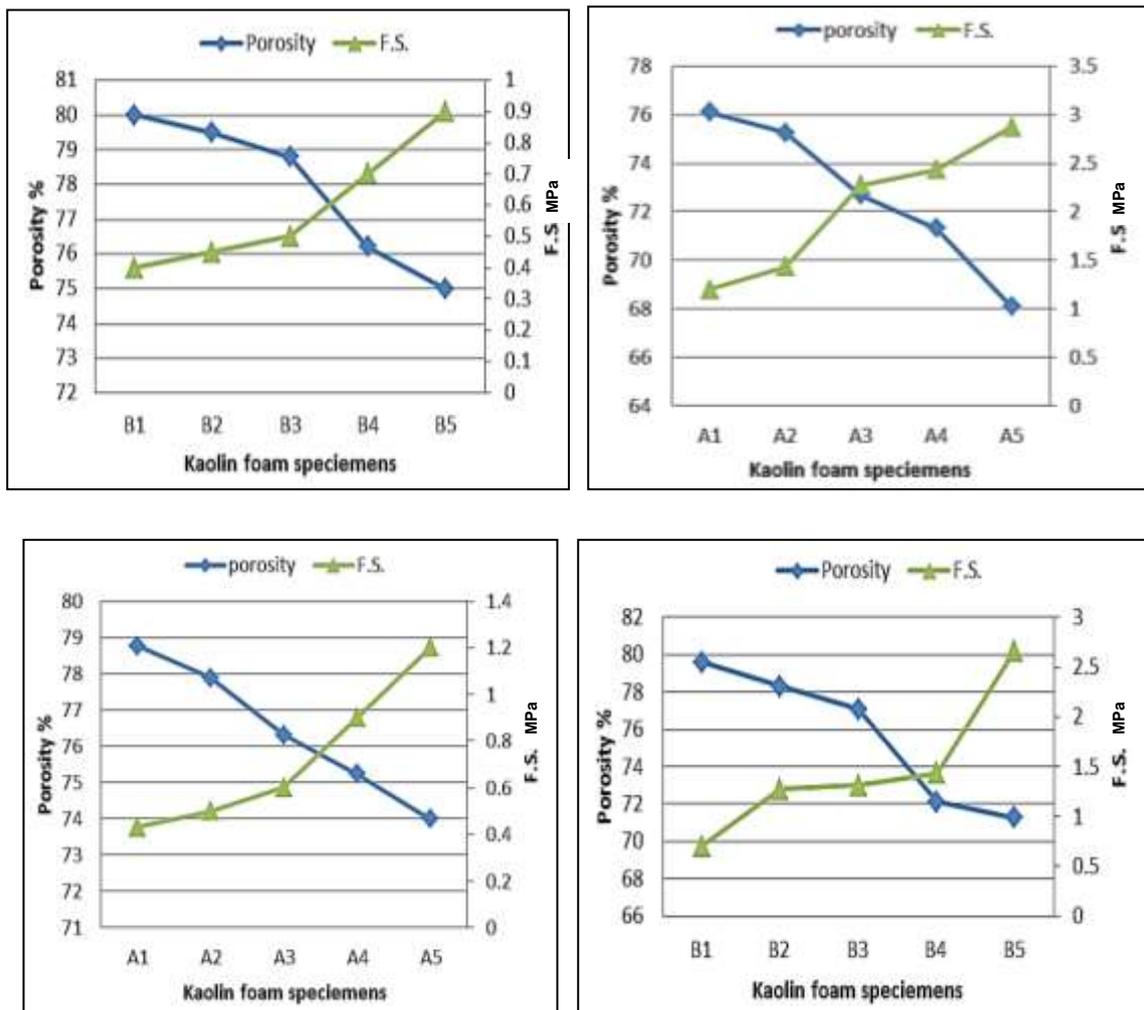
Figure (6): Effect of porosity on Flexural strength: (a) For G.A. sintered at 1100 ºC.

617

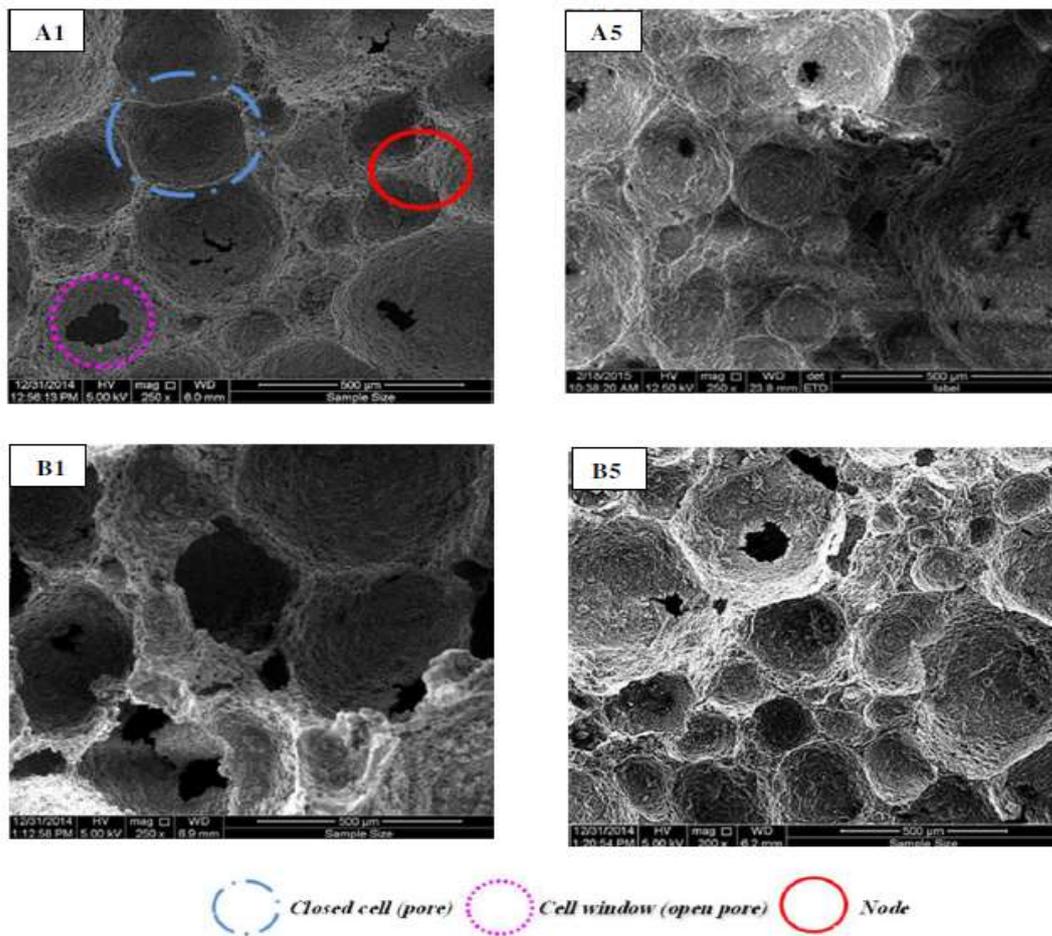**(b) For G.A sintered at 1300 ºC. (c) For G.B. sintered at 1100 ºC. (d) For G.B. sintered at 1300 ºC.**

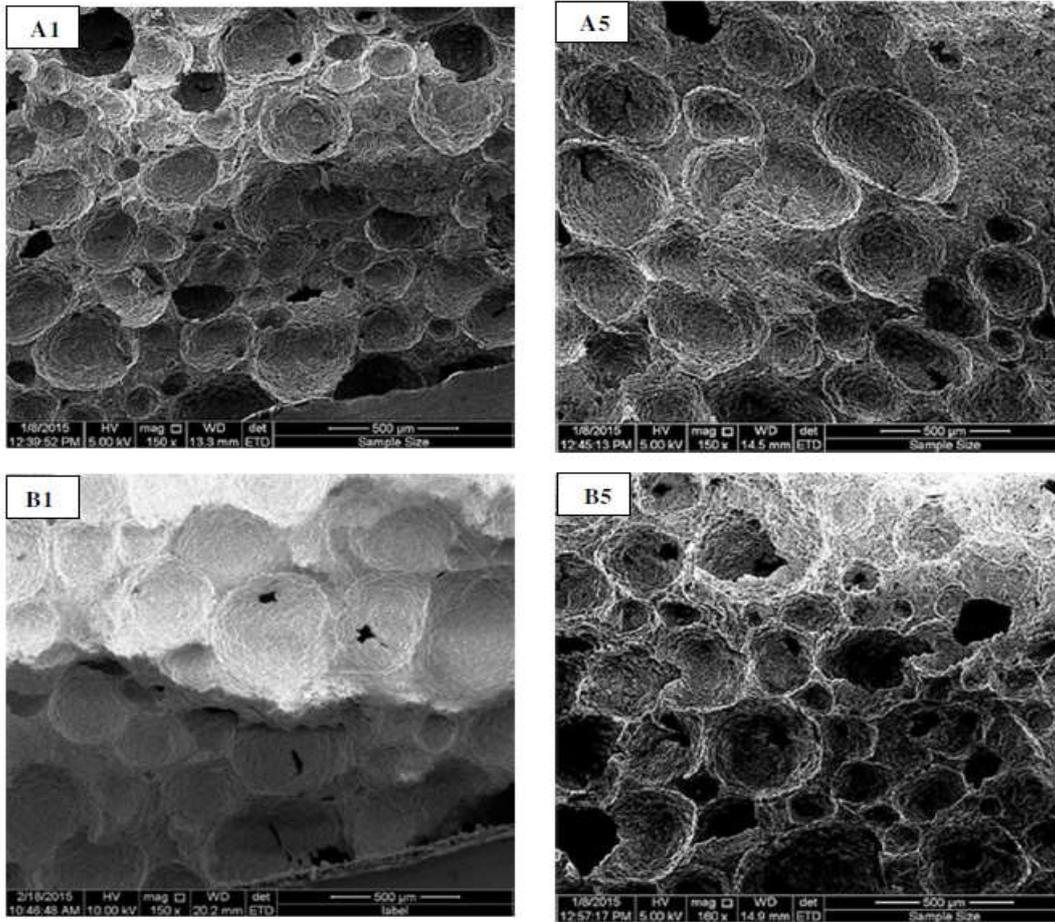Figure (7): SEM graph of [A1,A5,B1,B5] specimens (1100) °C.

Figure (8): SEM graph of [A1,A5,B1 and B5] specimens Sintered at (1300) ᵒC.

REFERENCES:

[1] Scheffer, M., P. Colombo, P."Cellular ceramics: structure, manufacturing, properties and applications", Wiley-VCH, Weinheim ISBN-13: 978-3527313204, (2005), PP (35–56).

[2] Martynenko, G.M.,Maltsev, S.M., Zabolotnyil, S.A.,'' Ceramoconcrete refractory and heat-insulating components in ferrous and nonferrous metallurgy'', Refractories and Industrial Ceramics,Vol. 50, No. 3, (2009), pp(163-165).

[3] V.R.Salvini,B.A. Sardurkov R.F.K. Gunnewiek, D.S.Rosa, V.V. Pandolfelli,'' Porous ceramics with Tailored properties'', American Ceramic Society Bulletin, Vol. 86, No. 3, (2007), pp (9401–9405).

[4] S. Dhara, M. Pradhan, D. Ghosh and P. Bhargava.'' Nature inspired novel processing routes for ceramic foams'', Advances in Applied Ceramics, Vol. 104, No.1, ,(2005) ,pp(9-21).

[5] J. Luyten, S. Mullens, J. Cooymans, A. M. De Wilde, I. Thijs and R. Kemps,'' Different methods to synthesize ceramic foams'', J. Eur. Ceram. Soc., (2009) Vol.29, pp(829-832).

[6] S. Sharafat, N. Ghoniem, M. Sawan, A. Ying, B. Williams, Breeder foam : An innovative solid breeder material for fusion application, J. Am. Ceram. Soc. 81 (2006),pp (455-460).

[7] Lisa biasetto,'' functional ceramic foams from preceramic polymer'',(2005).

[8] LinnéaAndersson,"Shaping Macroporous Ceramics - templated synthesis, X-ray tomography and permeability'', Doctoral Thesis , ISBN 978-91-7447-180-9 (2011).

[9] Jennifer Elizabeth Mueller, ''Determining the role of porosity on the thermal properties of graphite foam'', Master thesis submitted to the faculty of the Virginia Polytechnic Institute and State University,(2008).

[10] P. Philip and L. Fagbenle, "design of lee's disc electrical method for determining thermal conductivity of a poor conductor in the form of a flat disc", International J. of Innovation and Scientific Research, Vol. 9 No. 2 Sep. 2014, pp. (335-343).

[11] H. Yong-sheng, L. Jian-bao, W. Qiang-min and K.Tang, '' The effect of sintering temperatures on alumina foam strength.''Journal of The Ceramic International, (2002), Vol. 28. pp. (755-759)