The Characterization of Silica-Nickel Oxide (SiO$_2$-NiO) Foam with Different NiO Composition and Sintering Temperatures

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ABSTRACT

The porous Silica-Nickel Oxide (SiO$_2$-NiO) ceramic had been fabricated by polymeric replication method, which produced high porosity with large interconnections. The influences of NiO composition on the morphology and properties of foams, including the compressive strength were studied. Polyurethane (PU) as the template was cut into a cylindrical shape of 12.5mm and 26.0 mm height. The PU template was impregnated in the prepared ceramic slurry which was a mixture of distilled water with Carboxymethyl Cellulose (CMC), Polyethylene Glycol (PEG), Silica (SiO$_2$) and Nickel Oxide (NiO). The composition of SiO$_2$ was fixed at 55 wt.% with varied NiO content of 2 wt.%, 4 wt.%, 6 wt.% and 8 wt.%. The impregnated PU template was then dried in the drying oven and later the sintering process at temperatures of 1000ºC, 1100ºC and 1200ºC. The morphology of ceramic foam was analysed by Scanning Electron Microscopy (SEM) and Electron Dispersive X-ray Spectroscopy (EDS), while properties of sintered foam were determined by porosity and density test, and compressive test. The window cell size was observed within 200-800 µm with porosity and density results was in the range of 54.48-66.21% and 0.81-1.21 g/cm^3, respectively. The compressive strength of ceramic foam obtained was within 0.42-1.16 MPa.

Keywords: *Reticulated, Engineering Ceramic, Gas Exchange, Polymeric Replication*

Introduction

Highly porous ceramic materials are important for diverse applications such as membranes, molten metal filters, catalytic reaction supports, thermal insulation, cathodes, anodes and orthopaedic implants which lead to the development of numerous processing routes [1]. Various fabrication methods are available to prepare macro porous ceramic or ceramic foam such as direct foaming, sacrificial fugitives, polymer replication, freezing casting and partial sintering [2]. All these methods have their own merits and drawbacks. Thus, suitable methods selection plays as significant role in the success of porous product fabrication with relatively high strength, high resistance to chemical attack, high temperature resistance, and high structural uniformity [3]. As an example, polymer foam replication method can produce reticulated porous ceramic with ultra-high porosity and large interconnections [4].

The pore size can be easily controlled by varying the polymer size and it has been declared as its attractive value and thus become the reason for wider applications in industry [5]. In particular, Montanaro *et al.,* 1998 stated that the porous network structures have relatively low mass, low density, low thermal conductivity, and even offer higher permeability [3]. Nowadays, the applications of porous ceramics are broadening in industrial market by adding additive as catalyst. The properties of ceramic foams which are sponge-like structures that consist of open accessible pore in the range of 10 to 100 per inch, with high interconnected window cells ranging from 75% up to 90% make them very attractive to be applied as catalyst supports [6]. There are few examples of supported metal catalysts which are nickel (Ni), platinum (Pt), palladium (Pd), rhodium (Rh), and ruthenium (Ru) [7]. All these elements are active and stable but very expensive. However, nickel based catalysts is the most favourable in the process of steam reforming of methane because of the high activity and plentiful resources of nickel [8].

In current study, SiO_2 and NiO were chosen as the starting materials in order to obtain porous ceramics products using the polymer replication template which requires a slurry preparation. The impregnation of polyurethane template (PU) was considered as crucial step because improper technique will affect the final product [9]. The research is focused on the effect of sintering temperature towards the morphology and mechanical properties of the porous SiO_2-NiO ceramic.

Experimental Procedure

The polymeric foam replication method was developed a decade ago and patented by Schwartzwalder and Somers [10]. The fabrication of porous ceramics by this method generally involves impregnation of an open-cell polymeric foam into a prepared ceramic slurry followed by burning-out of

polymeric foam through sintering process which yields ceramic foam as the replica of the original polymeric foam used [9]. The works flow were summarized in flowchart as shown in Figure 1.
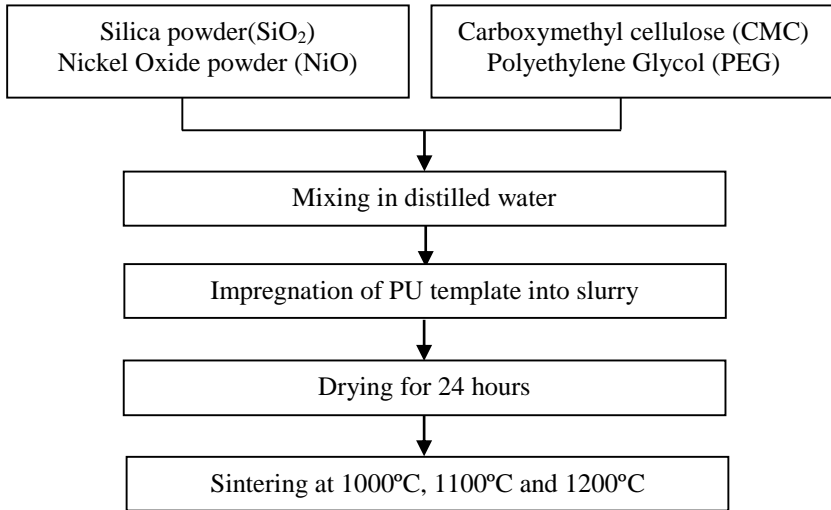
Silica powder(SiO$_2$) Nickel Oxide powder (NiO)	Carboxymethyl cellulose (CMC) Polyethylene Glycol (PEG)

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            Mixing in distilled water

       Impregnation of PU template into slurry

              Drying for 24 hours

      Sintering at 1000ºC, 1100ºC and 1200ºC
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Figure 1: Fabrication steps of porous ceramic foam by polymer foam replication method

Results and Discussion

The final product of porous ceramic depends on the starting material compositions and firing temperature. The morphology of the porous ceramic such as pore size, pore distribution, microstructure and compressive strength of the porous ceramic final product are hereby discussed.

Characterisation of Foams

Table 1 shows the composition of SiO$_2$ and NiO after the foam has been omitted during   sintering process at 1200ºC as analysed by Electron Dispersive X-ray Spectroscopy (EDS). It was observed that the mass of nickel has increased as the initial NiO composition was increased after sintering process. The increment of nickel content obtained by EDS confirmed that higher deposition of catalyst which is nickel particles on the surface of foam. Therefore, as deposition of catalyst on the bigger pores got higher, the higher goes the hydrogen generation rates [17].

Table 1: Results of EDS test for different NiO composition which has been sintered at 1200ºC.

Nickel Oxide Composition (wt.%)	Mass (%)		
	Silica (SiO_2)	Nickel (Ni)	Oxygen (O_2)
2	51.96	6.04	42.00
4	50.24	6.46	40.50
6	47.04	18.67	34.29
8	44.90	24.33	30.77

Thus, based on Table 1, it is confirmed that the content of both SiO_2 and NiO, as mixed did not show any reductions or decompositions upon sintering.

Colour of Foams

The final product of porous ceramic depends on the starting material compositions and firing temperature. The morphology of the porous ceramic such as pore size, pore distribution, microstructure and compressive strength of the porous ceramic final product are hereby discussed.

In this study, the colour of the samples changes when subjected to different sintering temperature. Figure 2 shows the colour difference of the SiO_2-NiO foam upon sintered at different temperatures. The colour change from dark grey to green was postulated due to the presence of NiO. However, it can be proved by the presence of excess NiO particles which shown in Figure 3. The changes of NiO colour from dark grey to green indicates that sintering started at below 773K which equal to 499.85°C, whereas with increasing green tones ranging from brown grey to grey-green and green-grey to olive green as sintering temperature increased [11]. The colour changes of the SiO_2-NiO foam with different sintering temperature was summarized in Table 2, while Figures 2(a), 2(b) and 2(c) represent the SiO_2-NiO foam after sintering.

Table 2: Colour changes of SiO_2-NiO foam at different sintering temperatures

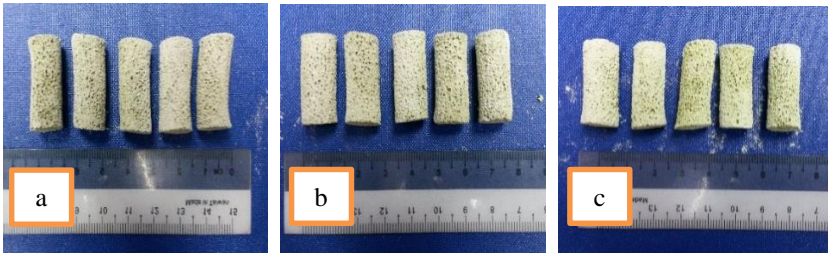| Temperature (ºC)	Colour of SiO_2-NiO foam
1000	Dark grey
1100	Greenish grey
1200	Green

Figure 2: Colour of SiO$_2$-NiO foam after sintering at (a) 1000ºC, (b) 1100ºC, and (c) 1200ºC

Morphological Analyses

The morphology of the porous ceramic that has been sintered at 1000ºC, 1100ºC and 1200ºC observed under Scanning Electron Microscopy (SEM) was shown in Figure 3. The microstructure of the SiO$_2$-NiO as can be seen in Figures 3(a), 3(b) and 3(c) consist of open pore, closed pore and interconnected. The open window cells are interconnected to each other by the struts. Black regions in the Figure 3 indicate the presence of open pore on the foam. The open pores on the porous structure of sample exhibit an interconnected by the struts.

Practically, SiO$_2$-NiO foam which has been sintered at 1000ºC, 1100ºC and 1200ºC showed no obvious differences in their morphological structure and consisted of hollow particles of spherical shape and a large number of units having no regular form. The open pore or window cell size in this study were found to be within the range of 200 – 800 µm. The smallest window cell size was 262 µm and the window cell size increased up to 728 µm which was the highest window cell size observed. This result is found to be similar to the results obtained by the previous researchers [13,14] which obtained the macro porous structure of sintered ceramic foam in the range of more than 400 µm of pore size with high interconnectivity. Thus, SiO$_2$-NiO foam fabricated by polymeric replication technique is suitable to be applied as catalyst support and other applications in other industries. However, the presence of closed cell numbers increased as the sintering temperature increased which can be seen in Figure 3(c). Therefore, it is suggested that, the excess slurry that hasn't removed completely after impregnation of PU template process might contribute to the presence of closed cell. The excess slurry has bridging the struts of the sintered porous ceramic foams together[12].
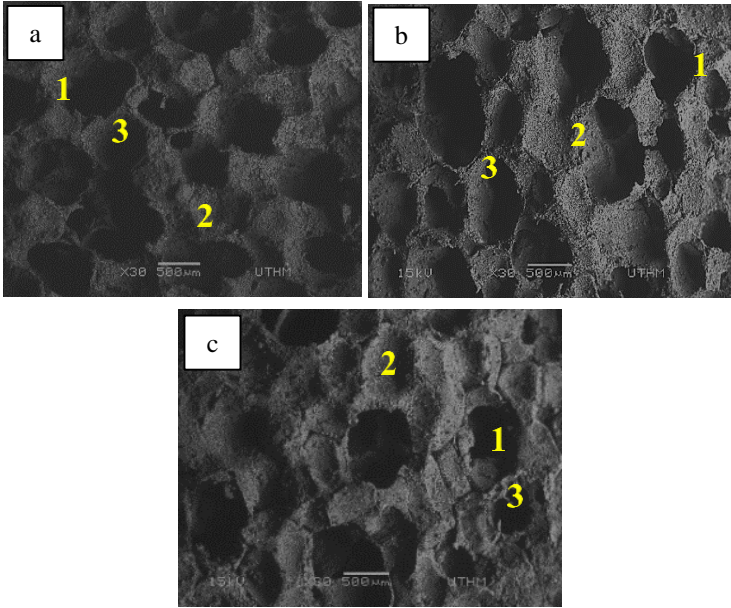
Figure 3: Microstructure of sintered SiO_2-NiO foam at (a)1000ºC, (b)1100ºC and (c)1200ºC with labelled of 1, 2, 3 for open pore, closed pore and interconnected, respectively.

Besides that, the morphology of porous structure which includes the content, dimensions, shapes and orientation of porosity can be adjusted by varying the initial slurry compositions [15]. As shown in Figure 3, the number of pore distribution decreased as the sintering temperature increases. However, the pore size would increased as the composition of NiO increase. Thus, the macroporous materials with a thick wall, low porosity and poor pore regularity are due to the excess content of oxide particles [16]. The powder such as particles on the surface of SiO_2-NiO foam as shown in Figure 4(a) is the excess of NiO particles where is the SiO_2-NiO foam sintered at 1200ºC. In the other hand, Figure 4(b) shows a clearer image of SiO_2-NiO foam microstructure with irregular open pore shape, dense strut and excess NiO particles.
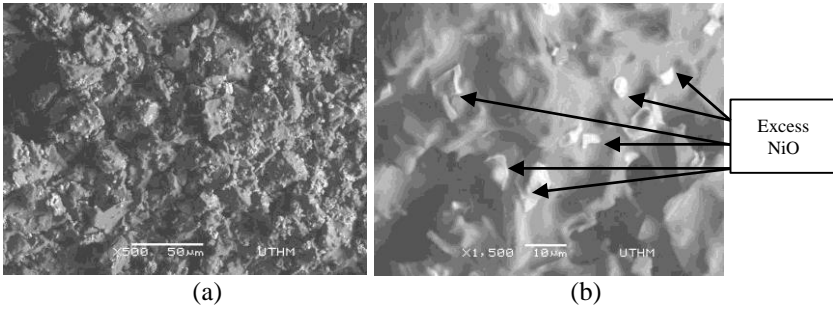
| (a) | (b) |

Figure 4: The microstructure of SiO_2-NiO foam with 8 wt.% of NiO at (a)500X and (b)1500X magnification

Porosity and Density Analyses

The porosity and density of sintered SiO_2-NiO foam were obtained by applying the Archimedes' principal as according to ASTM C773-88. The porosity and density of the SiO_2-NiO foam effects due to varying NiO compositions were plotted as shown in Figures 5(a) and 5(b), respectively.
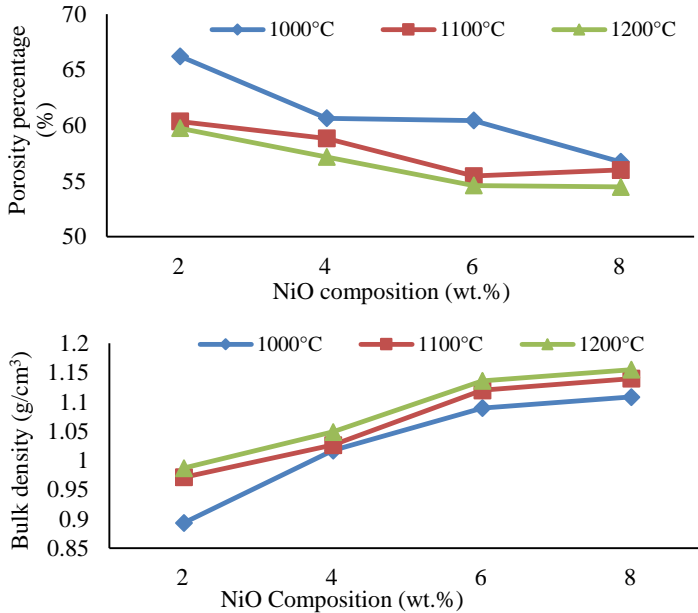

Figure 5: Effects of sintering temperature on porosity and bulk density of 55 wt.% of SiO_2 with different NiO compositions

The result of porosity obtained in Figure 5(a) showed decreasing trend as the composition of NiO were increased due to decreasing number of open pore and presence of closed pore. The highest percentage of porosity was 66.21% for SiO_2-NiO foam with 2 wt.% of NiO, sintered at 1000ºC. Meanwhile, the lowest value was 54.48% with addition of 8 wt.% NiO, sintered at 1200ºC. As the sintering temperature increased, the number of porosity decreased due to the gradual occurrence formation of the neck in which the microstructure will be densed [18, 19]. The struts size measured in Figure 3(c) is 138.44 μm compared to the other two struts size which are 118.08 μm and 123.41 μm as observed in Figures 3(a) and 3(b). This is well supported by the morphology of sintered foam in Figure 3 which showed decreased number of open window as the sintering temperature increased. Furthermore, higher number of open pore cells were observed at lower temperature compared to the pore distribution at higher temperature as can be seen in Figure 3 which led to the higher porosity percentage at lower temperature. This might be due to the increasing of sintering temperature which affected the porosity when the holes left by the binder shrink and pore become smaller [27].

The trend of bulk density was found to be vice versa with the trend of porosity percentage. The density of SiO_2-NiO increased as the sintering temperature increased due to the decreased number in open pore. Therefore, as shown in Figure 5(b), the SiO_2-NiO foam which had been sintered at 1200ºC showed the highest bulk density compare to the SiO_2-NiO foam sintered at 1000ºC and 1100ºC. The highest value of bulk density obtained was 1.21 g/cm^3 and the lowest value was 0.89 g/cm^3 which had been sintered at 1000ºC. The decreasing trend of bulk density against temperature indicates the foaming process was more consistent and stable at higher temperature [20]. The decreasing of porosity percentage and open pore distribution correlated with the increasing of foam density as the sintering temperature increased.

Compressive Strength Analyses

The compressive strength of the SiO_2-NiO foam with 2 wt.%, 4 wt.%, 6 wt.%, and 8 wt.% NiO content sintered at 1000ºC, 1100ºC and 1200ºC were plotted as in Figure 6.

From the graph in Figure 6, the lowest compressive strength obtained was 0.42 MPa for SiO_2-NiO foam with 2 wt.% of NiO content sintered at 1000ºC, while the highest compressive strength was 1.16 MPa for SiO_2-NiO foam with 6 wt.% of NiO, sintered at 1200ºC. The increasing strength of SiO_2-NiO increased as the composition of NiO increased due to the presence of closed pore at higher temperature as can be monitered by SEM in Figure 3. However, the trend of increased compressive strength for each composition was observed before decreasing at 8 wt.% of NiO composition for each

temperature. As the NiO composition increased, the viscosity of the slurry during slurry preparation increased and this might be one of the reason of decreasing trend observed for SiO_2-NiO foam with 8 wt.% of NiO. This is presumably that at lower composition, the slurry penetrated the PU template easily, while higher composition affects the impregnation process especially to retain their shapes and structures [13]. At higher composition, the slurry became saturated and unable to penetrate into the inner part of the foam away from the edges due to restriction of slurry flow as a result of high viscosity ceramic slurry.
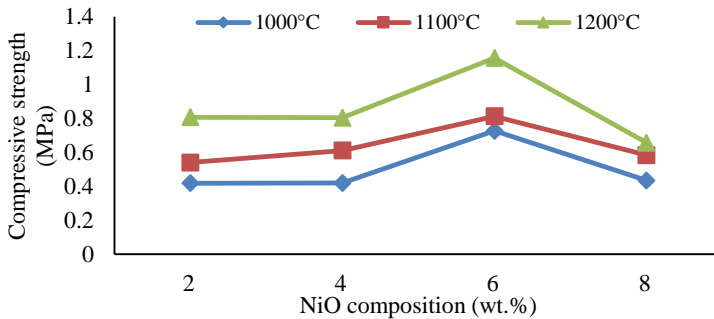

Figure 6: The compressive strength of porous ceramic with different NiO content which was sintered at different temperatures

The compressive strength of SiO_2-NiO foams with 8 wt.% of NiO dropped significantly for every sintering temperature. The same trend was observed for fabricated SiO_2-NiO foams which have been sintered at 1000°C and 1100°C. Figures 7(a) and 7(b) show the stress-strain curve obtained for the SiO_2-NiO foam with 6 wt.% of NiO and 8 wt.% of NiO, respectively.

Figure 7 shows that both of the SiO_2-NiO foams exhibit brittle behaviour which is remarked by the linear increment of stress before the value dropped. The linear increase corresponds to the typical linear elastic behaviour for brittle foam before progressive cells collapse at solid phase by brittle crushing of the struts between the pores. Moreover, brittle fracture is also correlated with crystalline structure which has lower modulus of elasticity compared to plastic and polymer [21].

Pore distributions also affect the mechanical properties of the porous ceramic [22]. As expected, the compressive strength of the SiO_2-NiO foam was increased as the temperature increased. A discussion by [23] stated that, the mechanical properties of porous ceramics were controlled by the number of porosity and will decrease with increasing pore volume fraction.

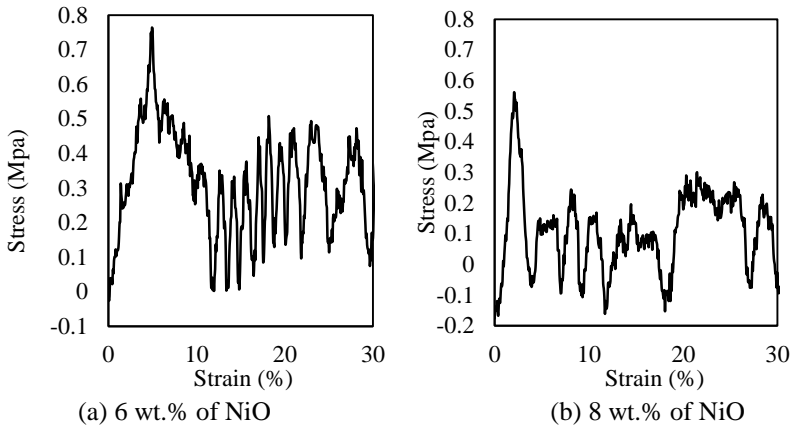(a) 6 wt.% of NiO   (b) 8 wt.% of NiO

Figure 7: Stress-strain curve for different NiO composition at 1200°C

Additionally, the dropped of compressive strength might be due to higher NiO loading. This is well supported by Hermida *et al.,* 2013, Cai *et al.,* 2014 and Nikoli´c *et al.,* 2015 which noted that structural collapse and significant drop in the well-defined framework mesoporosity are due to local blockage of pore channels and agglomeration of higher nickel nanoparticles loading at high temperature [24, 28, 29]. Besides that, the mechanical strength of the sintered body is highly dependent on the foam's microstructure, especially on defects such as pores and cracks [25]. The presence of cracks on the surface of SiO_2-NiO foam as shown in Figure 8 would lower the mechanical properties of the sintered foam.
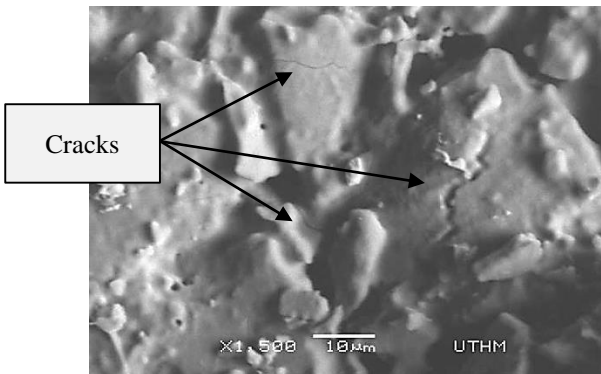

Figure 8: Cracks as observed on the surface of SiO_2-NiO foam with 8 wt.% of NiO composition sintered at 1200°C

The presence of triangularly shaped hole inside the struts contribute to stress concentration at the edges, as well as cracks which is the other reason for limited strength of SiO_2-NiO foam [26]. Porous foam with low strength and fracture toughness is resulted due to foam fabrication technique of replication technique. High number of porosity and thin skeletons limit their structural application and thus more sensitive towards structural stress [27].

Conclusion

Polymeric foam replication method is one of the fabrication methods which are capable of producing the final porous ceramic with larger pore size with open window cell in range of 200-800 µm. The pore distribution decreased as the sintering temperature is increased from 1000ºC to 1200ºC. The decreasing of open pore cells observed on the morphology of sintered foam affected the result of porosity percentage and density. Decreasing trend of porosity percentage was observed as the sintering temperature and NiO composition increased while the trend for bulk density indicates otherwise. Moreover, the compressive strength dropped at 8 wt.% of NiO content due to the excess nickel content. Thus, it can be concluded that the best sintering temperature is 1200ºC with 6 wt.% of NiO content. Fabrication of SiO_2-NiO foam using polymeric replication technique is capable of producing high porous microstructure and of resulting good properties with lower fabrication cost which can compete with other techniques such as direct foaming, gel-casting and sacrificial fugitives. A further study of SiO_2-NiO foam in methane reforming will be carried out.

Acknowledgement

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