Universidad Zaragoza
1542

Institut Européen des Membranes

SILICON CARBIDE-BASED CAPILLARY MEMBRANES for GAS SEPARATION and WATER TREATMENT

Done by –**MENGISTU Meron Mulatu**

Supervisors: **Dr. CERNEAUX Sophie**

&

Dr. BERNARD Samuel

24 June-2014

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ACKNOWLEDGEMENTS

Glory be to the almighty God, who always guide me throughout my life. Next I offer my deep gratitude to my supervisors Dr. CERNEAUX Sophie and Dr. BERNARD Samuel who supported me throughout this project with a valuable comments and encouragement that enabled me to get a wider understanding of the subject. I also want to thank Mr. Anthony Ballestero for his help during the experimental work. Without their support it would have been impossible to accomplish it.

It is an honour to thank EM3E, UNIZAR and IEM stuff members and laboratory technicians for their assistance and support to accomplish this thesis.

Finally I would like to thank my family and all my friends who encouraged me thorough out the project.

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1. INTRODUCTION

Membrane technology is an emerging technology that has become very important in the development of different industrial processes for sustainable growth. Membrane can be defined as a barrier that separates two phases, through a selective transport of one component over the other (figure 1). There are different ways to classify synthetic membranes, for instance depending on nature of the material; they can be grouped as inorganic such as ceramics or metals and organic such as polymers. On the other hand according to their shape they can be classified as tubular, flat and hollow fibres membranes (A.G. Fane, Rong Wang et al. 2011).
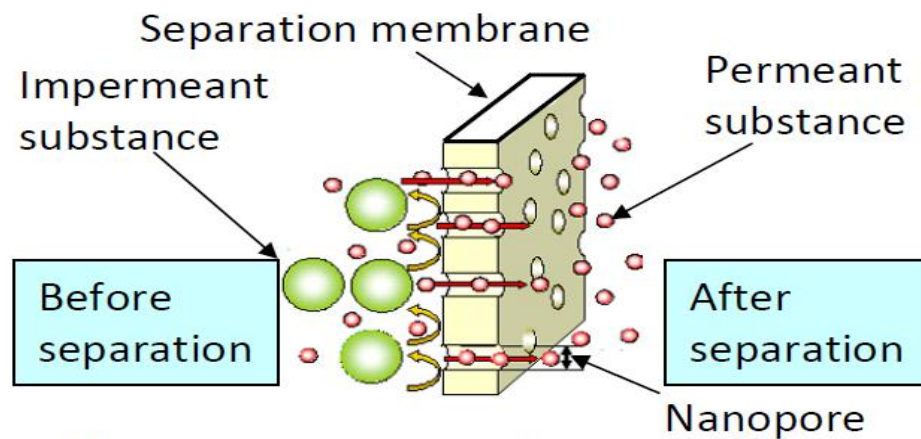
Figure 1. Schematic representation for definition of membrane (Huang, Lee et al. 1994)

IUPAC classification of membranes according to pore size are macroporous (>50nm), mesoporous (2-50nm) and microprous (<2nm). The pore size determines its industrial application (figure 2). Macroporous membranes are used for microfiltration and ultrafiltration processes, while mesoporous membranes can be implemented in ultrafiltration, nanofiltration and gas separation processes. Microporous and dense membranes are used for gas separation and industrial reaction process (Li 2007).
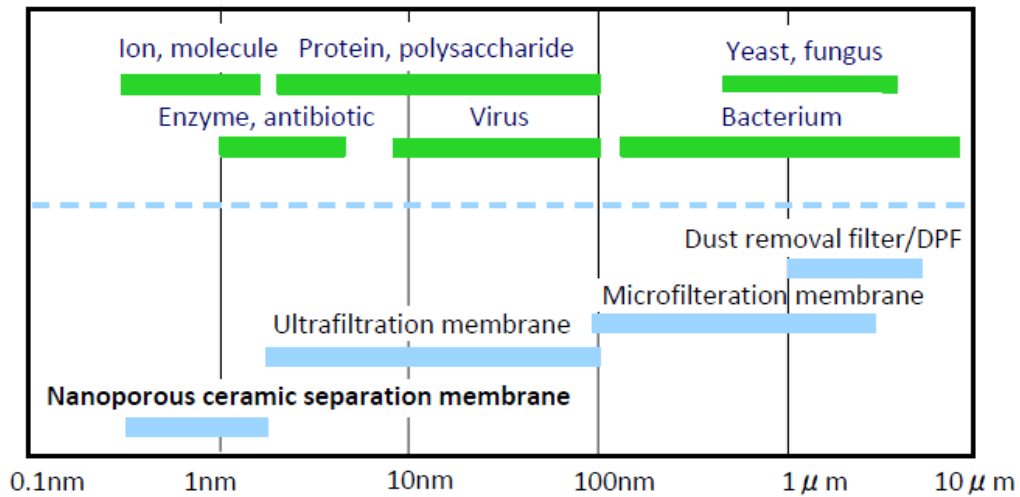
Figure 2. Size of separated substance and pore diameters of separation membranes (Huang, Lee et al. 1994)

Inorganic membranes are multilayers system that are synthesised in different steps (figure 3); a macroporous is first prepared to give the system a mechanical strength (layer 4). Then one or more intermediate layers (2 and/or 3) will be placed before a final deposition of the dense or separation layer (Li 2007).
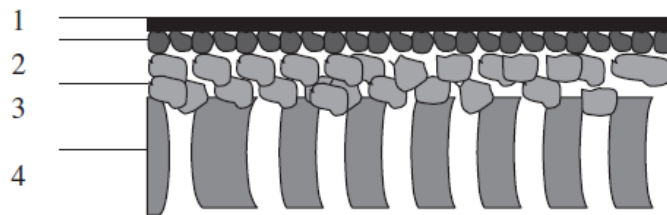
1 Active separation layer (dense or <2nm)

2 Separation layer (2-50nm)

3 Intermediate layers (50-1000nm)

4 Porous supports (1-15µm)

Figure 3. Schematic representation of multilayer inorganic membrane (Li 2007)

Alumina and oxygen containing ceramics are common inorganic membranes used industrially. However in recent years there is a demand for the use of ceramics in harsh industrial environments, such as high temperature, corrosion and heavy loads. These conditions do not allow the use of

oxide ceramics; this gives an opportunity for non-oxide ceramics such as silicon carbides due to its excellent thermal and chemical stability. Industrial process such as desalination of sea water and methane gas reforming are examples of such harsh industrial conditions (K. Yamada and Mohri 1991).

In most arid regions of the world where surface and ground water are not available, a reliable way of fresh water production is necessary. To overcome this and other shortage of water supply, sea water and brackish water purification as well as waste-water treatment represent alternative and promising ways. Sea water is abundantly available and it is the most promising water sources, but its salt content being very high, that makes desalination a complex, expensive and energy demanding process. One of the traditional water desalination technologies is multi-effect distillation, which is an energy intensive process. Thus these technologies are limited to regions that have sufficient energy and financial resources (Bart Van der Bruggen and Vandecasteele 2002).
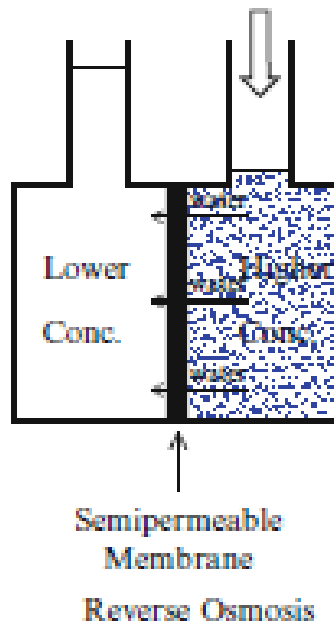
Figure 4. Reverse osmosis (A.G. Fane, Rong Wang et al. 2011)

Reverse osmosis (RO) is a membrane technology that is used for sea water desalination without heating mechanisms. In this process a high pressure is applied and force water through a semi-permeable membrane (figure 4). It has low water production cost compared to the traditional methods. To make RO feasible the salty water should first pass through pre-treatment section to remove suspended solid in order to avoid membrane fouling. Ultrafiltration (UF) and microfiltration (MF) can be used for pre-treatment before RO to remove big particles (figure 2), by using membrane that can withstand the harsh conditions (Bart Van der Bruggen and Vandecasteele 2002; Akili D. Khawaji, Ibrahim K. Kutubkhanah et al. 2008).

Organic polymeric membranes such as polyvinyl chloride (PVC), polyether sulfone (PES), polyvinylidene fluoride (PVDF) are typically used in MF and UF processes for pre-treatment. However these membranes face rapid fouling problem by seawater. It is well known that silicon carbide membranes that are potentially unexplored membranes, have a superior chemical, thermal and mechanical stability, which gives an opportunity to implement under MF/UF pre-treatment process for the next RO process (Jia Xua, Chia-Yuan Changb et al. 2010).

On the other hand to minimize fossil fuel consumption an alternative energy source is being under development. Renewable energy sources such as sun and wind have a great potential to substitute non-renewable energy. However they are intermittent unlike the energy demand, so that the requirement of cost effective and energy efficient storage system is mandatory. Hydrogen is a clean fuel that is used as an energy carrier; as a result its demand is being increased very rapidly. It is suggested that hydrogen can be used as an alternative fuel that can be used in place of fossil fuels (Fukushima, Zhou et al. 2006).

The most common way of producing hydrogen is by using steam methane reforming reaction (reaction 1), which is an endothermic reaction occurring at about 800°C. To favour the production of hydrogen over methane thermodynamically it is necessary to work at high temperature and pressure during the reaction (Fukushima, Zhou et al. 2006; Zhoua, Fukushima et al. 2011).

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO \qquad \Delta E = \frac{206.0 kJ}{mol} \qquad (1)$$
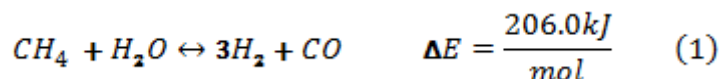
In addition, it is required to have a separation technique for purification of the produced hydrogen form bi-products and impurities, usually by adsorption technology. Consequently due to the high temperature and complicate purification process requirements, production of hydrogen is expensive (Fukushima, Zhou et al. 2006; Zhoua, Fukushima et al. 2011).

A high temperature membrane reaction can simplify the system of steam methane reforming reaction and also lower the minimum required temperature to $500^{o}C$. Using membrane reactor, the reaction and selective separation can be done in one step, that helps the equilibrium shift towards the production of pure hydrogen by avoiding simultaneously a high applied temperature and lower the production costs (Kazuhiro Yoshida, Yoshio Hirano et al. 2001; Fukushima, Zhou et al. 2006; Zhoua, Fukushima et al. 2011).

Taking into account hydrogen production reaction, the membrane used for this process must have a good stability and reliability at high temperature and steam environment. Because of their low thermal resistance polymeric membrane are not applicable for methane reforming reaction. Metallic membranes such as palladium have high hydrogen permselectivity, however hydrogen embrittlement and coke formation are the major drawbacks of using this membrane reactor under steam and carbon based gases (Fukushima, Zhou et al. 2006).

Due to their high temperature resistance, good mechanical strength and chemical stability under steam, ceramic membranes are competent for a harsh industrial condition. Oxide ceramic membranes such as silica have high hydrogen permselectivity under dry and high temperature environment, but in the presence of water vapour the permeability of the membrane decreases mainly due to the condensation of water vapour inside the pores (Kazuhiro Yoshida, Yoshio Hirano et al. 2001).

Ceramic membranes are of high interest in areas such as environment and energy. Indeed, depending on their nature, oxide or non-oxide, their porous texture and microstructure, their crystallinity, they are employed in various applications going from more or less complex aqueous media to solid and gas separations and treatment. However, the industrial development of non-oxide ceramic membranes remains limited due to high cost of production that includes raw materials and thermal treatments at high temperature very energy-demanding. Nevertheless, their

properties in terms of mechanical resistance, corrosion resistance, thermal and chemical stabilities remain unique.

More and more drastic recommendations on the treatment and recycling of industrial wastewater for example but also gases still imply the development of new materials highly resistant under harsh environments. To assess these requirements, non-oxide ceramic materials based on silicon carbide/nitride are envisaged.

Silicon carbide (SiC) and silicon nitride (Si_3N_4) are intensively studied especially for their thermo structural applications. Concerning membranes processing different synthesis routes are described in literature. Most of them involve synthesis using hard template or biotemplates to prepare hollow fibers. Shaping of ceramic supports may be performed by warm pressing to yield flat supports but also extrusion and phase inversion to elaborate tubular supports. Finally, preceramic polymers may be deposited over macroporous supports to yield selective filtration layers after pyrolysis.

2. OBJECTIVES

The main objective of this project was to synthesize silicon carbide (SiC)-based ceramic membrane with a controlled microstructure and composition, by taking into account the current water purification and hydrogen permselectivity issues. To prepare non-oxide support and membrane, two strategies were developed.

The first route was to use conventional powder technology to elaborate the support and the filtration layers, using commercially available SiC powders and organic additives to enable the formation of a porous and mechanically resistant material. The preparation of porous supports with a capillary geometry has for objective to enhance the volume to surface ratio and thus to improve transport fluxes and exchanges at the solid/liquid interfaces. The identified drawbacks mainly their mechanical resistance and accessible porosity, are directly correlated to the nature and quantity of the different organic additives and/or minerals involve in the paste formulation. In addition, it has a strong impact on the advancement of the sintering stage of the final ceramic similarly to the temperature and atmosphere applied during the thermal treatments.

The second route was to develop new SiC precursors containing at the atomic level an additional element such as boron (B) that will help the sintering of the final ceramic and thus decrease the firing temperature and production costs. Boron containing SiC precursor (Si/B/C) were synthesized following the preceramic polymer route by varying the boron content to determine the optimum composition that will be selected and used for large scale synthesis. In addition, SiC macroporous support mixed with different pore forming agent and sintering conditions were synthesized in different shapes from commercially available SiC powders.

3. STRUCTURE and PROPERTY of SILICON CARBIDE

Silicon carbide has different crystalline structures called polytypes that are built up by a stacking of identical SiC crystal at a different sequence (figure 5). Each polytype is stable at different temperatures. Generally the polytypes can be divided into β-SiC (Zinc blend) as a low temperature form (1500-1800°C) cubic phase and α-SiC as a high temperature (>1500°C) hexagonal phase (SHAFFER 1969).
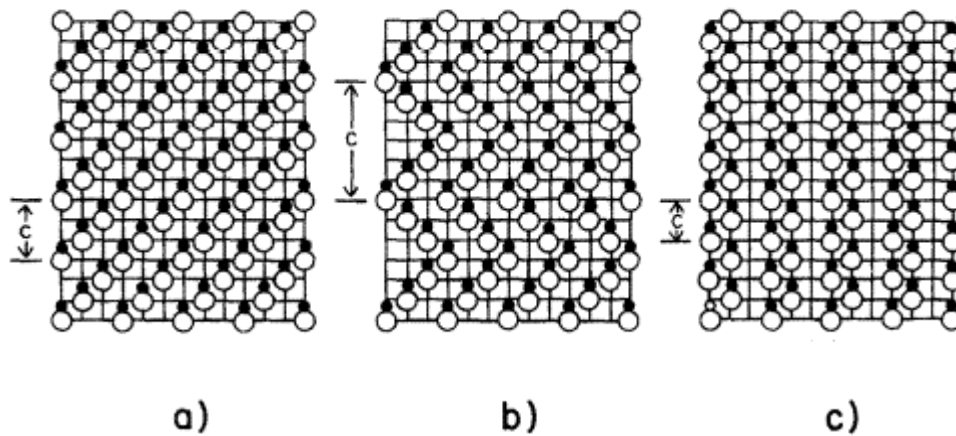
Figure 5. Common SiC polytypes on [1120]plane, a)3C polytypes (Zinc blend structure) b)6H polytypes c)2H polytype (Wurtizie structure) (Jason Guth and Petuskey 1986)

β-SiC is found in a cubic shape (3C) while different hexagonal (2H, 4H and 6H), rhombohedral (15R) and other shapes are categorized in α-SiC. The numbers indicate the stacking sequence repetition while C, H and R stand for cubic, hexagonal and rhombohedral shapes, respectively. For example, according to Ramsdell's notation, on the (111) plane β-SiC has a stacking sequence of ABCABC…while for 2H also called wurtzite type, on the (0001) plane, it has a stacking sequence of ABAB… In all polytypes, the Si:C atomic ratio is 1:1and each atom is tetrahedrally bonded to a heterogeneous neighbouring atom (Inomata 1991).

3.1   Thermal Stability of SiC Polytypes

The stability and /or formation of SiC polytpes depend on the temperature. At temperatures below 1400°C, 2H polytypes are formed. When the temperature increases up to 1500°C, 2H-structure will transform into another polytype but to a similar crystal appearance. If the temperature increases further, its crystal appearance will also transforms and 3C, 4H and 6H will be formed irreversibly (Inomata 1991).

3C is formed at early stage of crystallisation and when temperature reaches and exceeds 1600°C, it will be transformed to α-SiC polytypes (except 2H) by recrystallization. 4H has a probability of formation at approximately 2000°C and at temperatures ranges between 2200°C and 2600°C; 6H is more stable than the other polytypes. Though 15R has also a probability to be formed at temperatures greater than 2000°C, 6H is more stable compared to 15R (Inomata 1991).

3.2   Crystallographic Properties

Highly pure 3C forms yellow transparent crystal, whereas the rest of polytypes are colorless. Depending on the presence of impure elements such as aluminum and nitrogen as a solid solution the crystal will be coloured green or blue. Under pressurized atmosphere and at 2830°C temperature SiC decomposes into graphite and molten silicon (Inomata 1991).

Sintered SiC ceramics have a superior strength at high temperatures, thus they are considered as the most promising heat resistant materials. SiC has covalent bond with only 12% of ionicity. This covalent bond is the source for the high strength property. Fundamentally SiC is brittle; however sintered SiC is one of advanced materials that are used at high temperature of 1300°C and above (Inomata 1991).

4. SYNTHESIS METHOD for SiC-BASED NON-OXIDE CERAMICS

4.1 Powder Routes for SiC Synthesis

Silicon carbide is conventionally synthesized following the Acheson's method (A. G. Acheson, British Patent, 1892, 17911), in which silica sand or siliceous rocks are reacted with petroleum coke at high temperature ($2100\text{-}2400^{\circ}C$) in an electric furnace according to reaction 2.

$$SiO_2 + 3C \rightarrow SiC + 2CO \qquad (2)$$
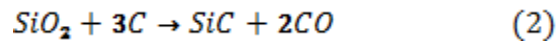
Usually α-SiC is obtained by this method even though β-SiC can also be obtained by this method at lower temperature ($1500\text{-}1800^{\circ}C$) (K. Yamada and Mohri 1991).

Acheson's method has drawbacks, starting from the high temperatures input, since impurities usually remain from the raw materials used such as Fe, Ti and present in siliceous rock. Indeed, these impurities will not be vaporized at high temperature so that they will be present in the synthesized SiC powders as impurities. In addition, the synthesis is done under carbon rich conditions; therefore after synthesis free carbon will also be available as an impurity. In addition as a result of insufficient mixing during reaction, silicon and silicon dioxide are both present in the final product, which results in abnormal grain growth (K. Yamada and Mohri 1991). Above all the mentioned quality problems it is also an environmentally hazardous process since at $1500^{\circ}C$ and above there is NO_x formation and emission (Riedel 1995).
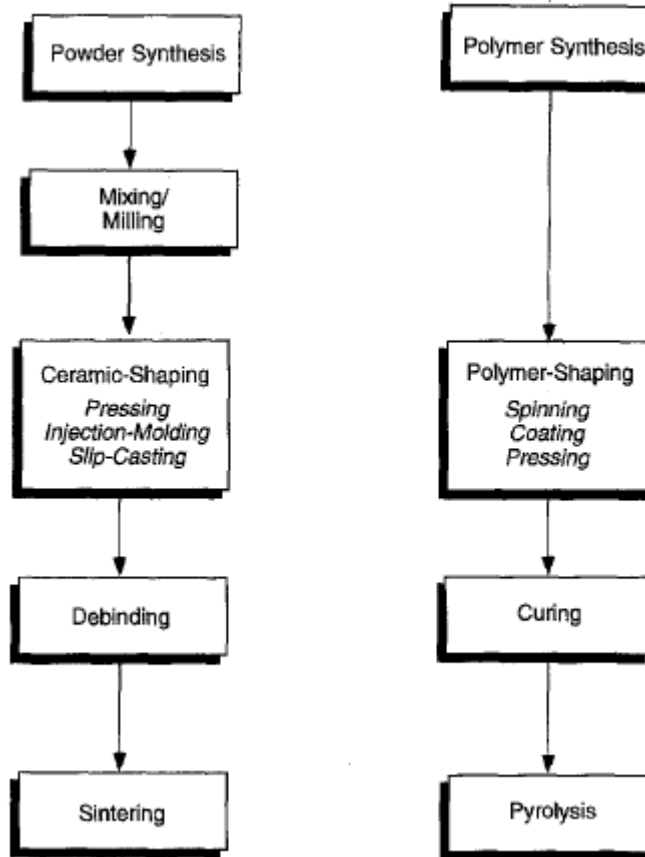
Figure 6. Schematic diagram of powder route (left) and molecular route (right) for ceramic membrane synthesis (Riedel 1995)

Particle size obtained by Acheson's method varies widely, and by controlling temperature it is possible to obtain coarse α-SiC and fine β-SiC. Figure 6 shows a schematic diagram for ceramic synthesis through powder route. The step includes SiC powder mixing with different additives and solvents, followed by shaping and sintering. Ceramic membrane synthesized from a powder requires shaping and sintering at higher temperature ($1000^{o}C$-$2500^{o}C$) to obtain a porosity of 35-50%. These steps will be discussed in chapter 6 (Riedel 1995; Greil 2000).

4.2   Molecular Routes for SiC Synthesis

Report about production of non-oxide silicon carbide-based ceramic synthesized from molecular precursor started in the early 1960s. In 1970s, pyrolysis of preceramic polymers such as polysiloxane, polycarbosilane and polysilazanes to ceramic fibers of SiC/Si_3N_4 for a high temperature application was presented. Afterwards, numerous researches have been done on polymer derived ceramics (PDCs) and a significant progress has been achieved(Riedel 1995; Colombo, Mera et al. 2010).

To obtain tailor made SiC-based ceramic it is important that the starting precursor or powder is highly pure and has a controlled composition at the atomic level. In the previous synthesis method of SiC, the powder method, in addition to the economic and environmental problems, it is impossible to control the composition and purity of the powders. By using polymer pyrolysis it is possible to synthesize highly pure non-oxide ceramic from a molecular precursor. Compared to the conventional powder synthesis method molecular precursor has many advantages. It is possible to control the microstructure such as homogeneity, multicomponent and pore size and porosity; and also membrane shapes such as films, continuous fibers, and monoliths are synthesized by the molecular methods that are difficult to obtain through the conventional methods. Specifically for polymer pyrolysis the synthesis is done at lower temperature (800^oC-1200^oC) that has benefit over the powder technology both economically and environmentally (Riedel 1995; L. V. Interrante, K. Moraes et al. 2002; Colombo, Mera et al. 2010).

A preceramic polymer can be defined as an inorganic/organometallic system that when treated thermally can give ceramic with a controlled chemical composition and a closely defined nano structural organization at lower temperature 500^oC-1500^oC. Common types of organosilyl preceramic polymer are shown in figure 7 (Greil 2000).
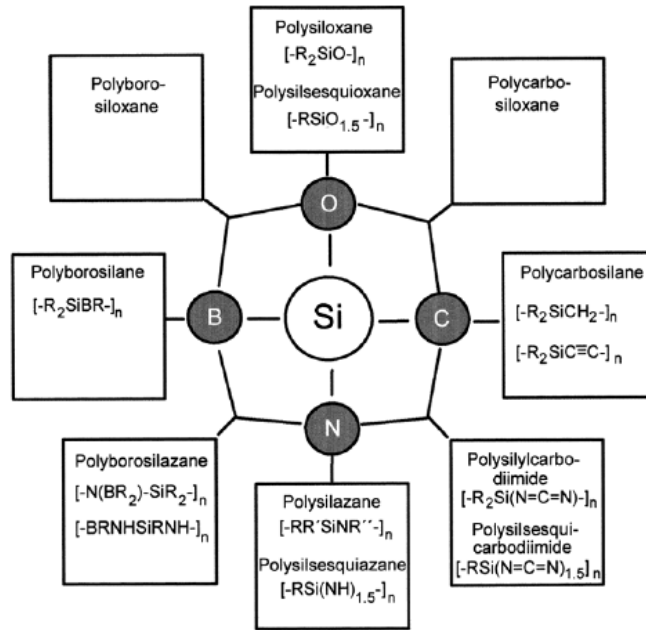
Figure 7. Silicon-based preceramic polymers (Greil 2000)

A general formula for organosilicon and the different possible ceramics obtained by pyrolysis can be seen in figure 8 (Greil 2000; Colombo, Mera et al. 2010).

$$[(R)(R')SiX]_n \xrightarrow{\text{Pyrolysis}} \text{SiC, Si-O-C, Si-C-N, Si}_3\text{N}_4, \text{etc.}$$
$$[(R)SiX_{1.5}]_n$$
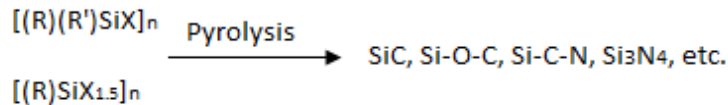
Where R, R' =allyl, alkyl, aryl, arenyl and X can be NH (polysilazanes), CH_2 (polycarbosilanes), O (Polysiloxanes), B (Polyborosilanes).

Figure 8. A general formula for preceramic polymer and different ceramics obtained through pyrolysis (Greil 2000)

X, R' and R groups are important parameters in order to design and modify the preceramic polymer at a molecular level. For further modification of the preceramic polymer these groups are advantageous. For example, a polycarbosilane group that contains a reactive R group such as vinyl/allyl will allow further reaction such as hydroboration reaction for the incorporation of boron in final ceramics (Si/B/C). Similarly, hydroboration and thermal treatment of polyvinylsilazanes

result in S/B/C/N ceramics. Small amount of boron (<1 wt %) incorporation will increase the overall thermal stability and will thus help the sintering of the silicon carbide ceramic. Therefore incorporation of boron in the preceramic polymer enables the homogeneity of the final boron containing ceramic (Riedel 1995; Varaporn Suwanmethanond, Edward Goo et al. 2000; Alexis R. Puerta, Edward E. Remsen et al. 2003).

The functional groups (R and R') attached to silicon atoms will determine the thermal and chemical stability, and also the solubility and rheological property of the preceramic polymer. In addition, they also define the carbon content in the PDC. Therefore the final PDCs microstructure and thus the physical and chemical properties can be varied and modified to an extent that depends on the design of the polymer precursor (Colombo, Mera et al. 2010).

R groups such as hydrogen, aromatic and aliphatic organic groups can be attached to silicon atoms. For further processing, the solubility, thermal stability and viscosity property of the polymers at different temperature are important factors (Colombo, Mera et al. 2010). Generally synthesis of ceramic from polymer precursor involves three steps (figure 6) (Greil 2000; Ralf Riedel, Emanuel Ionescu et al. 2008):

- Preceramic polymer synthesis
- Shaping and curing of the synthesized polymer and,
- Then conversion of the preceramic polymer to ceramic by pyrolysis

4.2.1 Synthesis of Preceramic Polymer

Organo-chlorosilane is most commonly used as monomer for the preceramic polymer synthesis. The different silicon based preceramic precursor synthesized from the monomer is shown in figure 9 (Greil 2000; Colombo, Mera et al. 2010).
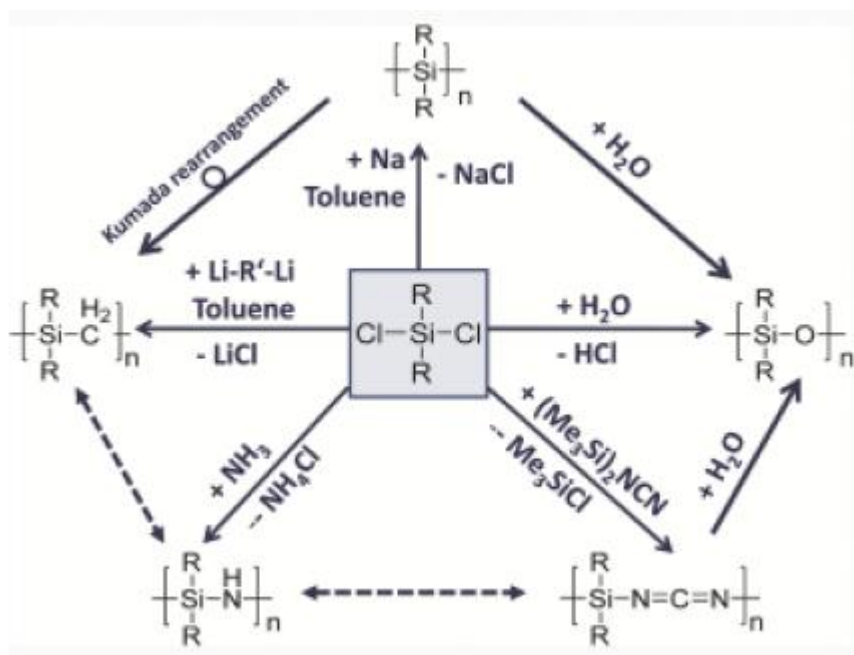
Figure 9. Preceramic polymer synthesis routes from organo-chlorosilane (Colombo, Mera et al. 2010)

Chlorosilane is mostly obtained from many silicone industries as a by-product; consequently it is easily available, inexpensive and can be purified by distillation. The preceramic polymer must fulfil some requirements such as appropriate solubility and rheological property for forming process, sufficiently high molecular weight to prevent volatilisation, and the presence of reactivity or functional groups for cross-linking and curing step (Greil 2000; Colombo, Mera et al. 2010).

Poly(organosilanes) [-R,R'Si-]n

Poly(organosilane) has inorganic Si-Si compounds attached to it. It has high thermal stability property and used for silicon carbide ceramic fiber manufacturing. It is mainly synthesised by dehalogenation reaction of organo-chlorosilane as shown in figure 9 (Greil 2000; Colombo, Mera et al. 2010).

Poly(organocarbosilane) [-RR'Si-CH$_2$]$_n$

This group is primarily synthesised from poly(organosilane) (such as poly(methylsilane)) by thermal reorganization called Kumada rearrangement reaction (figure 9). Currently it is used for synthesising silicon carbide fiber in research issue because of its high ceramic yield. Currently different kinds of polycarbosilane are commercially available. Many types of poly(organocarbosilanes) have a complex structure having hyperbranched Si-Si and Si-C structure (Greil 2000; Colombo, Mera et al. 2010).

Boron containing novel preceramic polymers precursors are under research and development for non-oxide ceramics synthesis. It was reported that incorporation of boron in SiC based ceramic improves sintering temperature. Therefore incorporation of boron to a preceramic polymer will improve the homogeneity of the ceramic. For instance it is reported that Si-B-C ceramic has exceptionally high thermal stability against decomposition, oxidation and crystallization up to 1600°C. Moreover it is developed that Si-B-C-N ceramic stability under inert atmosphere was up to 2000°C (Greil 2000; Colombo, Mera et al. 2010).

4.2.2   Shaping and Cross-Linking

A preceramic precursor is a polymer in nature, therefore it obtains a unique characteristic so that it can be shaped in different methods such as fiber drawing and foaming, which are not easily exploited for ceramic powders. For example siloxanes were used to prepare highly porous ceramic foams by saturation with supercritical carbon dioxide, which is a well-known technology (Colombo, Mera et al. 2010).
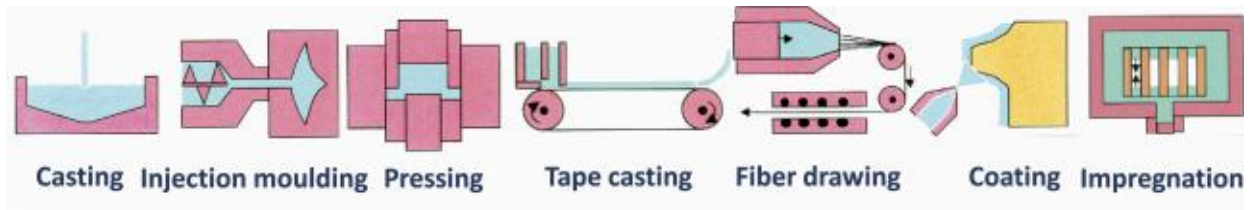
The preceramic polymer can exist in liquid or in solid phase, if it is in solid phase it can be soluble in different organic solvents or can melt at lower temperature ($<150^{o}C$). Figure 10 shows different preceramic polymer forming methods. To make forming possible typically a preceramic polymer that is curable and meltable solid or a dissolved solid, or a cross linkable liquid is used. After forming it is necessary to make the polymer maintain its shape by transforming it in to a thermoset. If the polymer has functional groups such as Si-OH, S-H, or Si-vinyl, spontaneous thermosetting will occur by addition or condensation reaction at low temperature (less than $200^{o}C$) called thermal cross-linking. The curing temperature can be further decreased by using catalysts (Colombo, Mera et al. 2010).

Other curing method that was mostly used in the past is oxidative curing; however it has a disadvantage of excessive oxygen ≈15wt% in the final ceramic product that degrades its stability at high temperatures. Curing without oxygen contamination can also be done by electron beam or $^{\gamma}$-radiation; however it has depth limitation so that it is usually applicable in small dimensional objects such as fibers (Greil 2000).

4.2.3 Pyrolysis

The conversion of organic to inorganic starts at $400^{o}C$ and ends at temperature between $800^{o}C$ and $1000^{o}C$. In addition to the inorganic ceramic the decomposition also results in release of gases mainly C_6H_6, CH_4, CH_3NH_2, etc. This thermal decomposition brings volume shrinkage as high as 50%, that results in pore formation and also defects such as cracks. This brings a limitation for the synthesis of dense ceramic from a preceramic polymer through a direct conversion. Direct conversion is possible for small dimension pieces (few hundred micrometres such as fibers, coating

or foams). To prepare a bulk ceramic usually filler is added prior to shaping. There are different types of filler depending on size/shape such as nanofiber, long fibers, powders that can be ceramics, polymers or metals, etc. Depending on the effect of filler volume, volume shrinkage of the preceramic polymer decreases (Greil 2000; Colombo, Mera et al. 2010).

Inert or reactive fillers can be used for different purposes. Inert fillers such as SiC, Si_3N_4, BN or B_4C powders, mainly decrease shrinkage by providing a means of escape for the gases generated during pyrolysis. However active fillers such as metallic or intermetallic such as B, Si, CrV, AlN, Ti, $CrSi_2$, $MoSi_2$ etc. react with gases that are produced in the polymer to ceramic conversion. Also they react with the ceramic residue to generate nitrides, carbides, silicides or oxides when heated. During polymer to ceramic conversion metal fillers will expand in volume up to 50% that will compensate the shrinkage and results in a near-net-shaped conversion. Polymeric fillers also can be used as sacrificial filler, because complete decomposition will takes place during pyrolysis (Greil 2000; Colombo, Mera et al. 2010).

Depending on the composition in the polymer, crystalline phases such as SiO_2, Si_3N_4, SiC, B_4C, BN and precipitation of excessive carbon at different temperature might occur. The temperature is higher for boron containing ceramics such as SiBCN, which is above $1600^{o}C$ while for SiC it is between $800\text{-}1000^{o}C$ (Greil 2000).

5. MACRO POROUS SiC MEMBRANE PROCESSING ROUTES

In membrane technology, the active separation layer is usually thin and requires to be supported over a mechanically resistant support. Therefore, to deposit a thin active layer for micro and ultrafiltration, a macroporous support that has an important property in addition to the mechanical strength is vital. Porous silicon carbide (SiC) ceramics have special properties such as high thermal conductivity and low thermal expansion coefficient, excellent mechanical strength, good chemical resistance and high thermal shock resistance. This gives an opportunity for porous SiC to be applied in the industry as a macroporous support for harsh industrial treatments (Varaporn Suwanmethanond, Edward Goo et al. 2000).

There are different processing methods, such as partial sintering, replica, sacrificial template, direct foaming and bonding techniques. Each of these techniques brings different microstructure, pore size and porosity, consequently mechanical strength, fracture toughness and other properties will be different (Jung-Hye Eom, Young-Wook Kim et al. 2013; Kwang-Young Lima, Young-Wook Kima et al. 2013).

5.1   Partial Sintering Method

Partial sintering is a well-known and used, simplest and most conventional method for SiC macroporous synthesis (figure 11). In this method SiC powders are bonded and become compact through or because of surface diffusion, evaporation-condensation, recrystallization or solution re-precipitation.
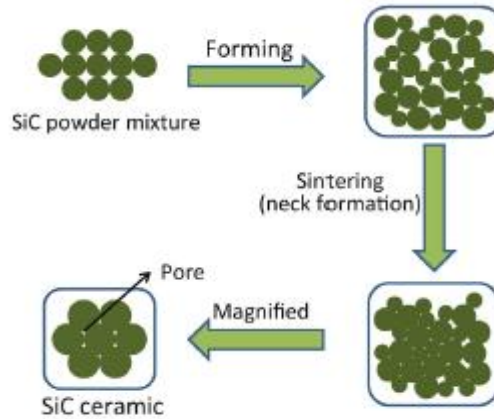
Figure 11. Partial sintering (Jung-Hye Eom, Young-Wook Kim et al. 2013)

In this method, full densification is prohibited or retarded. This can be done by controlling temperature, particle size of the powders and sintering additives. Common conditions for partial sintering are low temperature, coarse particle size and sintering without additive. Porosity obtained by this method is usually less than 65% and pore size between 0.1 to 10µm (Jung-Hye Eom, Young-Wook Kim et al. 2013).

5.2   Sacrificial Template Method

Pore formation can be enhanced by using pore forming agent. An appropriate amount of pore forming agent will be mixed with SiC powders and removed before or during sintering (figure 12). The obtained pores are a result of negative replica of pore forming template. Some examples of pore forming templates are organics such as corn starch, ceramics and metals.
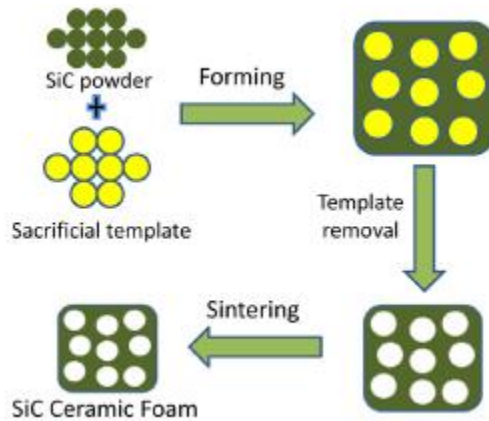
Figure 12. Sacrificial template synthesis method (Jung-Hye Eom, Young-Wook Kim et al. 2013)

Removal and extraction of the template from the mixture is usually done by thermal decomposition at temperature ranging from 200-1000°C. Other removal methods are chemical leaching and oxidation for silica and carbon, respectively. Porosity, pore size and shape are controlled by the type of template used (Jung-Hye Eom, Young-Wook Kim et al. 2013).

5.3   Direct Foaming Method

Silicon carbide foam is synthesized by bubble formation inside SiC slurry prepared from SiC powder or preceramic polymer (figure 13). Foaming source can be a blowing agent such as gas evolution that can be introduced mechanically through gas injection or mechanical stirring, or chemically by chemical reaction of solids, liquids or gases that evolves gases during the reaction (Jung-Hye Eom, Young-Wook Kim et al. 2013).
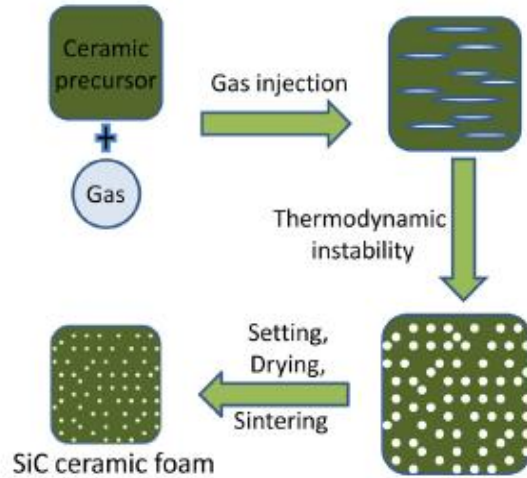
Figure 13. Direct foaming method (Jung-Hye Eom, Young-Wook Kim et al. 2013)

The decomposition of a preceramic polymer evolves volatile gases that can be used as foaming agent. The porosity formed in this case depends on the structure and composition of the precursor that affects the gas evaporation (Jung-Hye Eom, Young-Wook Kim et al. 2013).

A polycarbosilane preceramic polymer and azodicarbonamide (ADA) chemical blowing agent were mixed and heated at a temperature of $250^{o}C$ for two hours under nitrogen flow for enhancing foaming. Then following the procedure of inorganic-organic conversion, the foamed mixture was let to cross –link under static air at a temperature of $200^{o}C$ for 2 hours with a heating rate of $30^{o}C/h$. Final pyrolysis is done under argon flow with heating rate of $5^{o}C/h$ and hold for two hours at a temperature of $1000^{o}C$. Pore diameter that varies from 416 to 1455µm and porosity between 59-85% are obtained by varying the foaming temperature and amount of ADA (Manabu Fukushima and Paolo Colombob 2012).

5.4   Bonding Method

Usually the synthesis of silicon carbide membrane from SiC powders needs a high temperature sintering above $1500^{o}C$, to enable the formation of covalent bonds. Therefore for synthesizing at lower temperature, a preceramic polymer precursor route or using bonding agent in SiC powder route can be used. Silica (SiO_2), mullite ($3Al_2O_3.2SiO_2$), silicon nitride (Si_3N_4) and alumina are

examples of sintering agents that have been investigated. Bonding method can be seen in figure 14 in a simplified way (Jung-Hye Eom, Young-Wook Kim et al. 2013; Kwang-Young Lima, Young-Wook Kima et al. 2013).
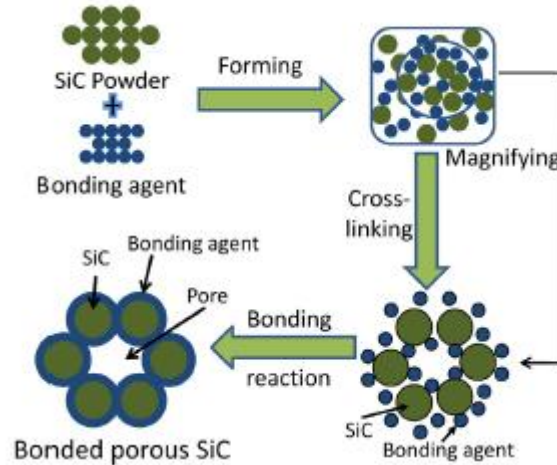
Figure 14. Bonding method (Jung-Hye Eom, Young-Wook Kim et al. 2013)

When SiC is burnt under air at a temperature of 1100-1400°C, amorphous silica is formed and binds the SiC particles together. Similarly Si_3N_4 bonding material is formed when the SiC powders and Si are sintered in a temperature range 1250-1450°C under nitrogen gas. When Al_2O_3 and SiC are fired under air between 1400-1550°C, the silica formed will react with Al_2O_3 to form a mullite crystalline phase. Boron in the form of $Na_2B_4O_7.10H_2O$ is used as bonding agent of SiC powders, and formation of amorphous sodium borosilicate at relatively lower temperature of 800°C enhances bonding of particles by reacting with silica (You Zhoua, Manabu Fukushimaa et al. 2011; Zhoua, Fukushima et al. 2011; Jung-Hye Eom, Young-Wook Kim et al. 2013; Kwang-Young Lima, Young-Wook Kima et al. 2013).

6. PREPARATION of CERAMIC MEMBRANE

Generally there are three steps involved in ceramic membrane synthesis from SiC powder: (i) paste preparation, (ii) forming or shaping and (iii) consolidation of the green body by heat treatment. Paste preparation includes mixing of the silicon carbide powders with organic additives (plasticizer, pore former, lubricant, etc.) and solvent. According to the amount of the prepared paste, it will take few minutes to obtain a homogenized paste by mixing and pugging. Then next step will be preparation of the green body or ceramic precursor by using different shaping methods such as extrusion, roll-pressing or calandering, hot pressing, etc. Densification of the green body called sintering is done by appropriate heat treatment to yield a better mechanical strength (Li 2007; Ralf Riedel, Emanuel Ionescu et al. 2008). In this chapter different forming methods and sintering methods will be explained.

6.1 Extrusion

Extrusion process is applicable both in large and small scales of different membrane support syntheses. Different kinds of inorganic membranes such as capillary tube, honey comb catalyst support and different structural ceramics are synthesized by extrusion process. The requirements of the paste to be extruded are to have a plastic behaviour so that it acts as a rigid solid and resists a small stress before deformation. In the process, a stiff paste is compacted and formed by forcing it slowly through a nozzle. An active separation layer can be deposited in the interior of the capillary tube by slip casting process (section 6.2). The limitation of this method is that cross sectional thickness of the capillary is usually larger than 0.5mm, though it is homogenous (Li 2007).

6.2 Slip Casting

It is one of the most traditional and most commonly used techniques and ceramic preparation method. Slurry prepared from a well-mixed powder suspended in a solvent is poured into a porous support; the particles will aggregate at the surface of the support while the solvent will be absorbed by capillary suction into the pores (figure 15) (Li 2007).
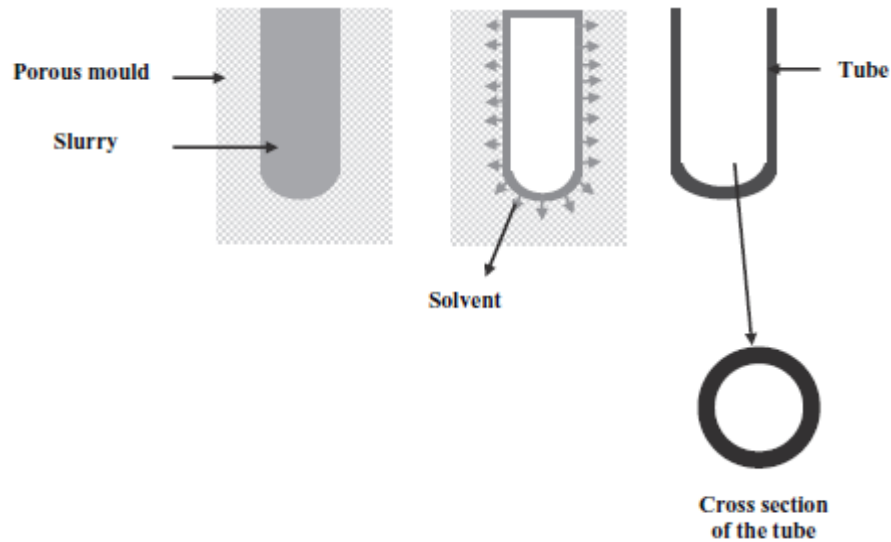
Figure 15. Slip casting process on a porous mold (Li 2007)

The slurry is characterized by its viscosity, particle diameter and concentration. A uniform thin layer can be obtained on the support depending on the induction time applied to the slurry and the drying schedule. Casting can be done under pressure or by ultrasonic frequency in order to improve the density of the layer and to avoid shrinkage that might be caused during casting (Ralf Riedel, Emanuel Ionescu et al. 2008).

6.3   Tape Casting

Tape casting is also a well-known forming method especially for flat sheet membrane preparation. Basic principles of ceramic membrane prepartion by tape casting is shown in figure 16. The prepared slurry will flow from the reservoir on a movable carrier guided by a casting knife. The thickness of the flat sheet will be determined by the distance between the tip of the knife and the carrier.
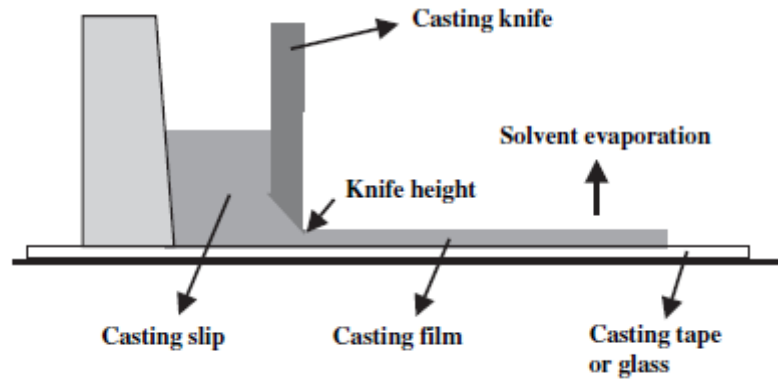
Figure 16. Tape casting process (Li 2007)

Viscosity of the slurry and carrier speed also controls the film thickness. The prepared film can be dried in the atmosphere or it can be placed in oven at a controlled temperature to avoid the degradation of the film. It is an advantageous technique for preparing large, flat and thin ceramic membranes, leading mainly to thickness between 250-1250µm (Li 2007; Ralf Riedel, Emanuel Ionescu et al. 2008).

6.4   Sintering

Sintering is the process in which the formed green ceramic is converted into a dense ceramic by heat treatment. To synthesize a ceramic that has a specific property, different processing variables such as particle size and packing, composition, temperature and sintering atmosphere have their importance. They also have an influence on the microstructure and material property of the final ceramic (Lutgard C. De Jonghe and Rahaman 2003; Ralf Riedel, Emanuel Ionescu et al. 2008).

Depending on the second phase that is formed during heating, sintering can be classified as solid state-sintering, liquid state-sintering and viscous sintering. For ceramic membrane solid sintering is the common one. In solid sintering the green ceramic is heated up to a temperature that is 0.5-0.9 of its melting point. The dominant mechanism is diffusion of atoms that results in grain growth and densification (Lutgard C. De Jonghe and Rahaman 2003).

To enhance densification of ceramic, pressurized sintering can be implemented, in which an external pressure can be applied while heating. Hot pressing (HP) and hot isostatic pressing (HIP)

are the common types of pressure sintering. HP technique combines temperature and a uniaxial external pressure while in HIP pressurized gas and high temperature enhance densification. In general, pressure sintering increases the production cost, but dense and small grain size ceramic membrane can be obtained (Lutgard C. De Jonghe and Rahaman 2003; Ralf Riedel, Emanuel Ionescu et al. 2008).

6.4.1   Sintering Phenomena

During sintering densification occurs through a process of diffusion that brings particle deformation and results in interface formation. For sintering to take place there are two conditions that must be satisfied, first free energy of the system must be lowered and second diffusion of atoms must occur. The first condition involves crystal grain boundary formation that reduces the particle surface area; as a result free energy of the system will be lowered. In the second case particle diffusion can be promoted by heating the material at high temperature (Lutgard C. De Jonghe and Rahaman 2003; Inomata 1991).

Reduction in grain boundary and increment in diffusion promotes sintering and densification of a sample. Furthermore particle size, size distribution and purity of the sample also have an influence on sintering process. Grain boundary formation is directly related to the chemical bonding and structure of the material. For instance a sample with metallic bond can be densified due to its surface energy relaxation by joining with neighbouring particles and form grain boundary easily. However in case of SiC the presence of covalent bond would not allow surface energy relaxation and render impossible the achievement of dense and strong material even if it is sintered at very high temperature and for a long period of time. SiC powders lack the driving energy required for densification that makes them fundamentally non-sinterable. Therefore addition of sintering aids is necessary to reduce grain boundary energy that enhance sintering of SiC powders, to obtain an advanced SiC ceramic with a super mechanical strength at high temperature. Silica, boron and carbon, and aluminium oxides are common sintering aids that are used for SiC sintering (refer section 5.4). Incorporation of small amount of boron lowers sintering temperature, by lowering the grain boundary energy (Lutgard C. De Jonghe and Rahaman 2003; Inomata 1991).

6.4.2   Sintering Stages

Depending on the microstructure, sintering can be divided into three idealized stages, initial stages, intermediate (thermolysis) and final stage. In initial stage, the main cause of material change is vaporisation of water that was combined chemically with the particles surface or from inorganic phases that contains water crystal. As a result of the vapour formed or due to the different thermal expansion coefficient of the phases present, stress will be caused. Therefore care must be taken as cracks might be formed. The adsorbed moisture may sustain in the membrane at temperatures exceeding 200^oC (Lutgard C. De Jonghe and Rahaman 2003; Li 2007).

Organic components such as dispersant, binders, lubricants, etc. are burnt out for further densification occurrence, this is called thermolysis. Membrane defects might be created by uncontrolled thermolysis and incomplete removal of binder. Therefore for the performance of the final synthesized membrane, it is vital to choose an appropriate binder and heating atmosphere so that the precursor can survive without being distorted, deformed or cracked (Li 2007).

If the binder in the green ceramic is small, it would open pore channels during thermolysis that are sufficient enough for the transportation of vapours and gases from internal reaction zone to the membrane surface. The internal stress caused by the decomposition and vaporisation of the organic additives depends on the permeability, precursor size, gas evolution rate. For example in dense ceramic membrane formed by fine particles, the rate of gas permeation is very slow and the stress will be high. Generally for ceramic precursors that contain large amount of organic components, the duration of the thermolysis is longer. Carbon residues are expected when thermolysis is done in an inert atmosphere (without oxygen). This carbon residue serves as sintering aid by removing the adsorbed oxygen from the particle surface (Li 2007).

Final sintering is assumed to occur in three stages as shown in figure 17: initial stage (I), intermediate stage (II) and final stage (III). When the temperature reaches the sintering temperature, mobility of atoms is achieved by diffusion and a sharp concave neck between the particles will start to form. This is the initial stage; as a result low densification will be achieved with a total porosity lowered by 12% (Lutgard C. De Jonghe and Rahaman 2003; Li 2007).
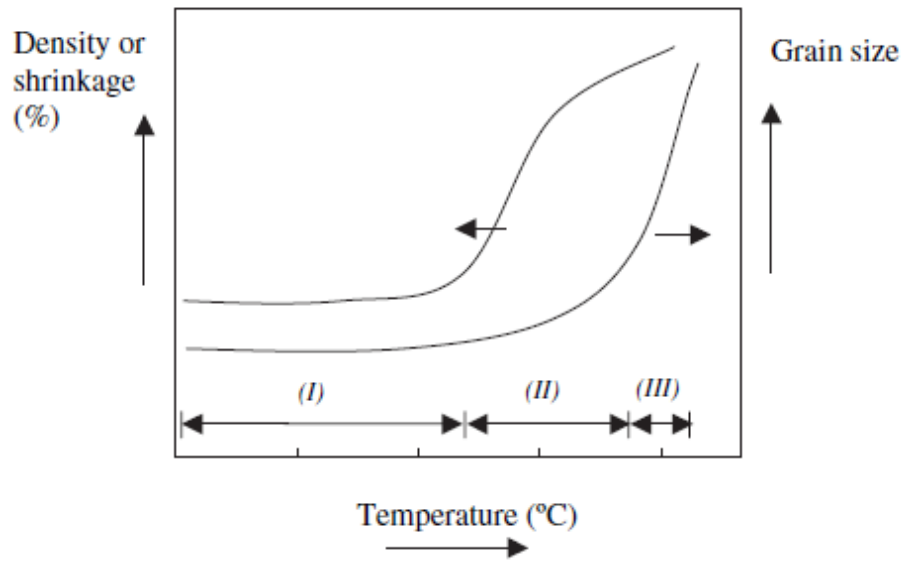
Figure 17. Grain size and density or shrinkage of a precursor as a function of sintering temperature (Li 2007)

Intermediate stage covers the highest portion of densification in sintering process as can be seen in figure 17. This stage starts when the sharp curvature developed in the initial stage becomes moderate and a three dimensional pore channel is formed (Lutgard C. De Jonghe and Rahaman 2003). Density obtained ranges between 0.65-0.90 of the theoretical value. As sintering continues grain growth become significant (Li 2007).

At the final stages, the channels will break down and isolated pores (closed voids) start to form. As a result of the closed pores grain boundaries will start to intersect with one another. Then the pores slowly shrink and large grain size starts to appear rapidly. Pore shrinkage continues and may disappear altogether (Lutgard C. De Jonghe and Rahaman 2003).

In overall at relatively low temperature slow grain growth and a rapid densification are achieved (stage II) that is followed by little densification with a rapid grain growth at a relatively higher temperature (stage III) (Li 2007).

7. CHARACTERIZATION TECHNIQUES

7.1 Mercury Porosimetry

Mercury porosimetry is a well-known membrane characterization method to determine pore size, porous volume and pore size distribution. Mercury is a non-wetting liquid, so that by applying a pressure it is forced to enter inside a pore. The relation between the applied pressure and pore size is explained by the Laplace equation (Li 2007). For this project micrometrics porosimetry equipment AutoPore IV 9500 was used.

7.2 Scanning Electron Microscopy (SEM)

Morphology of a synthesized membrane surface and cross section can be seen in details using SEM. High energy electrons beam generated in the SEM will bombard the sample surface, and electrons emitted from the interaction generate image of the sample surface. The resolution of SEM is about 5nm to 100nm and with a magnification of 10^5 (RUSTE 2014). In this project HITACHI S-4800 FEG equipment was used to analyse the synthesized membranes. The samples to be analyzed must be solid, with maximum height and thickness of 2.5 each. Also the sample must be sputtered before analysis with a conductive layer (Pt) and thus pretreated under vacuum.

7.3 Differential Scanning Calorimetry (DSC)

DSC is a thermal analysis used for characterizing the physical property of a sample when exposed to a temperature. The analysis can be isothermal for a specific time or with increasing temperature in a controlled atmosphere. Information obtained from DSC is the heat change of the sample with respect to temperature that are phase change properties such as glass transition, or decomposition (Jun Huang 2013).

7.4   ThermoGravimetry Analysis (TGA)

TGA is also used for thermal characterization of a sample, by measuring the weight loss occurring during the decomposition of sample as a function of the temperature. It is used as an optimization of the polymer to ceramic conversion, by comparing the stability at high temperature and yield of ceramic (Daudon 2014). This technique is also used to evaluate the temperature of decomposition of the organic additives incorporated in the paste to establish the final heat treatment schedule. For this project ATG Q500 High resolution (TA instrument) was used for optimizing the preceramic polymers.

7.5   Fourier Transform InfraRed Spectroscopy (FTIR)

FTIR is a characterization technique that gives information on the nature of the chemical bond present in the sample. The sample will be placed in the equipment and upon the infrared beam, interacts with it. Depending on the energy level of the chemical bonds, different vibrations bands are obtained that are characteristic of a typical function (DALIBART Michel 2000).

7.6   X-Ray Diffraction (XRD)

XRD is a very important characterisation technique for identification of phase separation and crystal structure present in crystal powders or membranes (Li 2007). For this specific project, X'pert PRO XRD equipment was used for the analysis of SiC starting powders.

7.7   Mechanical Strength

The mechanical strength of the synthesised silicon carbide membrane is analysed by a well-known three point bending test (LLOYD instrument). Test results from this analysis are Young's modulus and tensile strength that defines the bending strength of the synthesised membrane (Li 2007).

8. EXPERIMENTAL ANALYSIS

8.1 Preceramic Polymer Synthesis

8.1.1 Materials and Reactions

Polymer synthesis was carried out in a purified argon atmosphere by means of standard Schlenk manipulations and vacuum/argon-line techniques. Argon (>99.95%) was purified by passing through successive columns of phosphorous pentoxide, siccapent[TM] and BTS catalysts. The handling of the chemical products was made inside MBraun glove box (<<0.1 ppm H_2O and O_2, Germany) under argon atmosphere. Preceramic polymer containing boron, silicon and carbon (Si/B/C polymer) is synthesized through hydroboration reactions of a SiC precursor with a borane by using toluene as solvent.

8.1.2 Procedure

The whole reaction is performed under inert or oxygen free atmosphere under a fume-hood and each chemical is used under an argon flow to avoid any degradation. The vacuum/argon ramp used during the syntheses is depicted in Figure 18. A 50mL 2-neck flask is connected to the ramp with the borane holder placed at the top. To remove air, the system is allowed to stay under dynamic vacuum for 30 minutes. An ice bath is also placed under the round-bottom flask to maintain the system at 0^oC for 1-2 hours under dynamic vacuum, prior hydroboration.

Figure 18. 2-neck flask placed under dynamic vacuum and at $0^{o}C$

A total of 50mL of toluene is poured with a syringe into the 2-neck flask and the borane holder flask under argon flow. Then 3mL of SiC precursor were injected with a syringe into the flask followed by injection of required amount of borane (table 1) that finally, was added drop by drop under stirring. The mixture is left at room temperature for three days to allow completion of the hydroboration reaction.

Synthesis reference	Borane volume (mL)	B/Si ratio (eq.)
SiBC9	5.10^{-3}	1.1
SiBC10	4.10^{-4}	0.08
SiBC11	7.10^{-4}	0.16
SiBC12	$1.2.10^{-3}$	0.27
SiBC13	2.10^{-4}	0.04

The synthesized Si/B/C polymer was separated from the solvent by vacuum evaporation. The solvent was collected in a trap placed in a liquid nitrogen bath. To facilitate evaporation of toluene the 2-neck flask was placed inside a heated and stirred oil bath (figure 19.a). The maximum temperature was set at 60°C through a temperature controller. After completion of this drying step, a yellow and viscous polymer was obtained that turned into a gel after a few minutes (19.b). The synthesized polymer was then collected from the flask and grinded by hand mill and sieved inside a glove box.
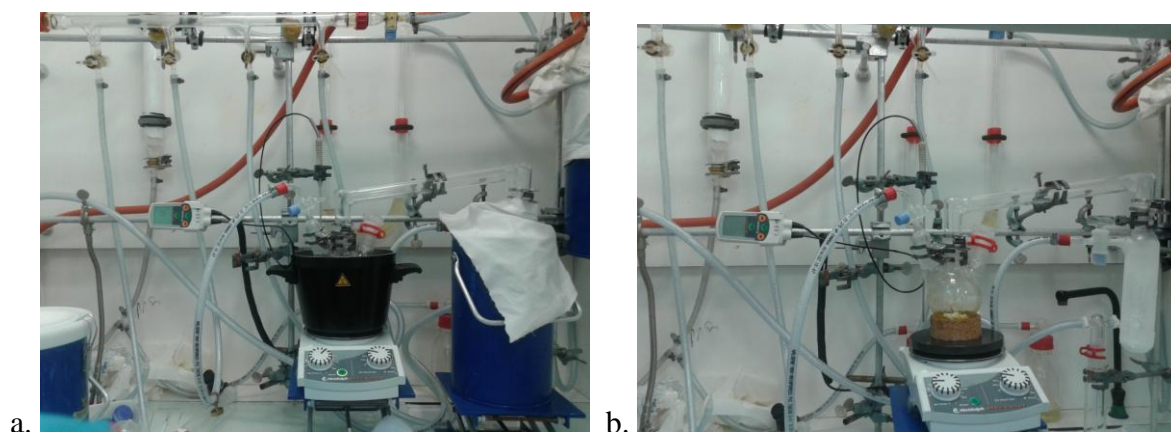

a.   b.

Figure 19. a. Solvent extraction under dynamic vacuum and at 60oC, b. After solvent extraction, yellow preceramic polymer and iced toluene are allowed to cool down and to warm up to room temperature

The pyrolysis of the Si/B/C sample was formed into a silica tube inserted in a horizontal tube furnace (Nabertherm type RS 80/500/11, Germany) connected to a glove-box. The tube was pumped under vacuum and refilled with argon (120 mL/min) to be subjected to a cycle of ramping of 5°c/min in to 100°C, dwelling there for 2 hours, and then cooling down to room temperature at 5°C/min

8.1.3 Results and discussion

To establish synthesis conditions that allow preparation of polymers with controlled properties, a series of Si/B/C polymers (SiBC9-SiBC13) have been prepared according to the B:Si ratio (table 1).

Then the collected Si/B/C polymers were characterized by FTIR to evidence the completion of the hydroboration reaction. TGA analysis was done to get the weight loss occurring upon the thermal decomposition of Si/B/C polymers.

FTIR analysis of the synthesized Si/B/C polymer was compared to pure SiC precursor as seen in figure 20. The functional group present in the polymer precursor has a double bond indicated in the figure at frequency of ~1620cm^{-1} and ~3100 cm^{-1}. From the spectra, the peak intensity of the double bond decreases with an increase in the amount of the borane added (from SiBC-13 to SiBC9). As expected, the double bonds that were present in the SiC precursor disappeared throughout the synthesis of the Si/B/C polymer due to the reaction of the allyl groups with the borane.
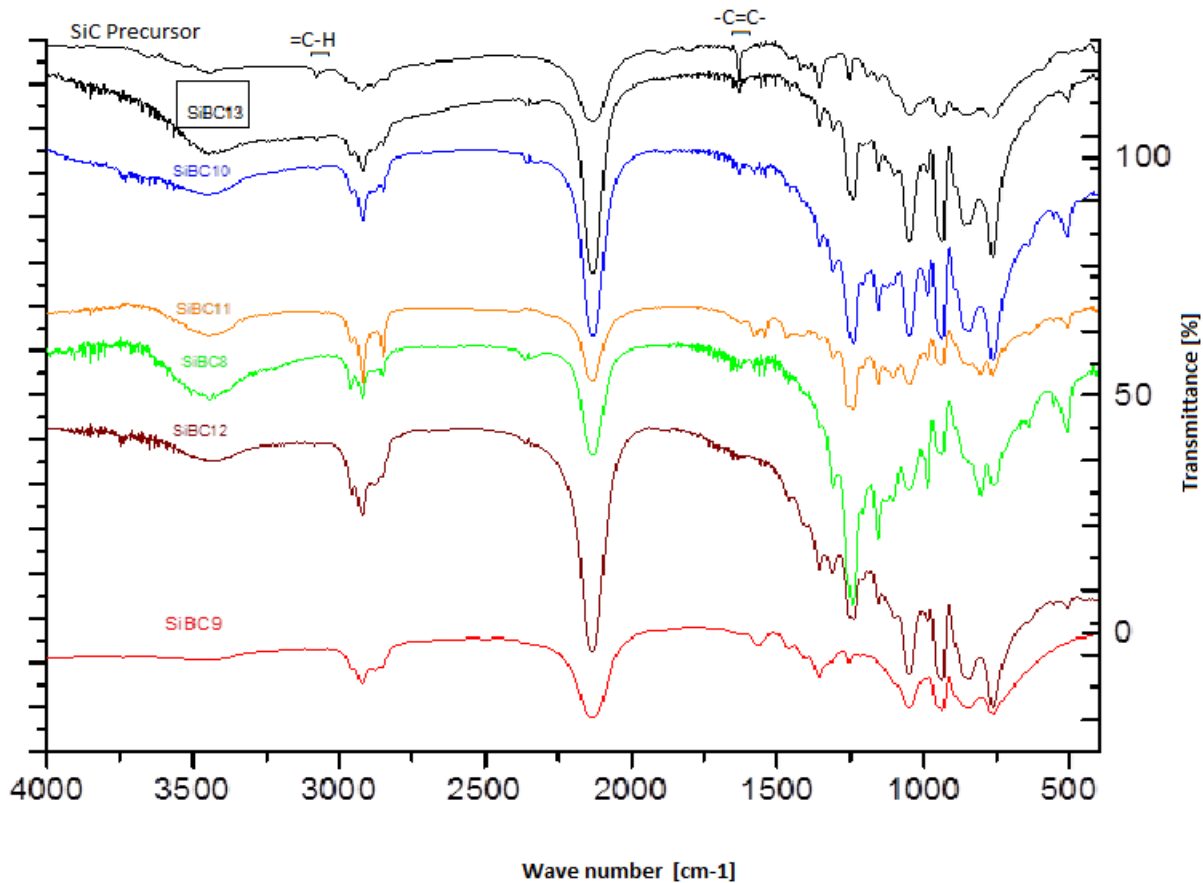
Figure 20. FTIR analysis of the five synthesized preceramic polymers Si/B/C and SiC precursor

8.2 SiC Macroporous Support Preparation

8.2.1   Materials

The raw powders used for the preparation of SiC macroporous supports were SiC-500 and SiC-800 powders (AGP Abrasifs). The additives incorporated in the paste formulation were Amijel (C*Plus 12 072, CARGILL), Methocel ((K 15 M, The Dow Chemical Company) and Darvan n ^{o}7 (RT Vanderbilt Company, Inc.) used as lubricant, plasticizer and dispersing agent, respectively. To obtain porous supports, we added corn starch (RG 03 408), CERSTAR) and maize flour starch (Maizena, Knorr) as pore forming agents. The additives were characterized by TGA analysis to

determine their temperature of degradation that began around 250°C to be completed at approximately 500°C without leaving any carbon residues in the final product.

8.2.2   Procedures

- Paste preparation

Different compositions of the mentioned chemicals were weighed separately and placed in a mixer (figure 21). After dry mixing of the powders, diluted darvan was added during the mixing. While mixing, appropriate amount of water was slowly poured in the mixer. To improve the pugging and to obtain the paste with required plasticity, the speed of the turbine was gradually increased.

Figure 21. Mixer (DITO, Electrolux)

- Shaping

The prepared paste was shaped as flat and capillary supports by using specific equipment: roll-pressing technique represented at figure 22-a and vertical extrusion using a design extrusion mold and the hydraulic press shown at figure 22- b.

a)   b)
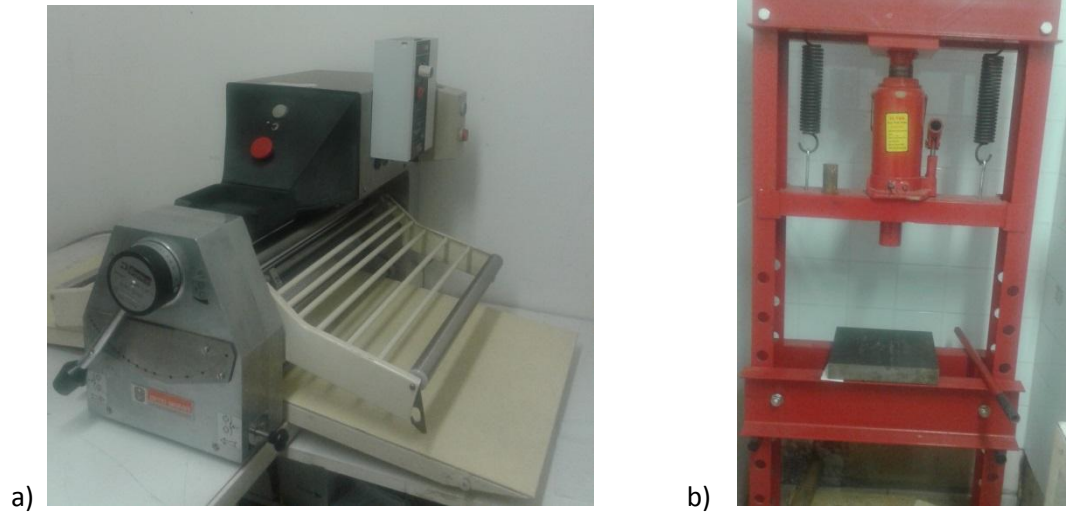
Figure 22. Photographs of shaping equipments: a) roll-pressing (DITO SAMA) and b) hydraulic press used for vertical extrusion

- Drying

The obtained green SiC supports of both geometries were dried before sintering to enhance their hardness and to improve handling. For this reason the flat supports were placed in an oven for a day at temperature of $70^{o}C$ and the capillaries inside a cylindrical paper on a roll-drier (figure 23) for a similar time.
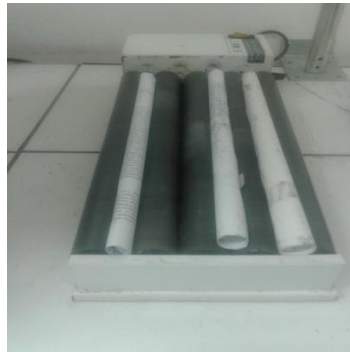
Figure 23. A photograph of a roll-drier

- Sintering

The dry green supports containing SiC were then sintered in a furnace by applying the temperature program depicted in figure 24 to form a porous supports. The first step was used for removal of the organic additives, while the last step aimed for sintering. As explained in section 6.4, to maintain the quality of the support the rate of heating was kept low at $3^oC/min$. Figure 25shows photographs of sintered porous SiC ceramics and SEM image. The flat support was roll-pressed at 3mm of thickness and the capillary tube was extruded with an internal diameter of 2mm and a wall thickness of 0.8mm.
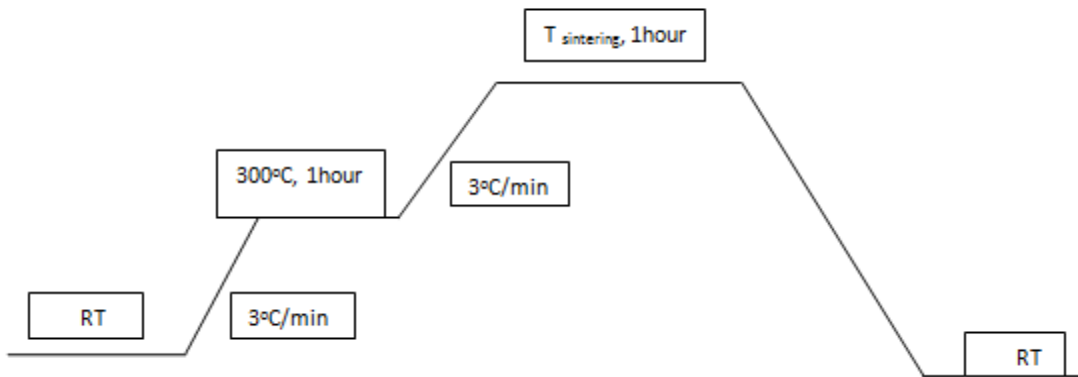
Figure 24. Temperature program used for sintering the prepared supports

c)

d)
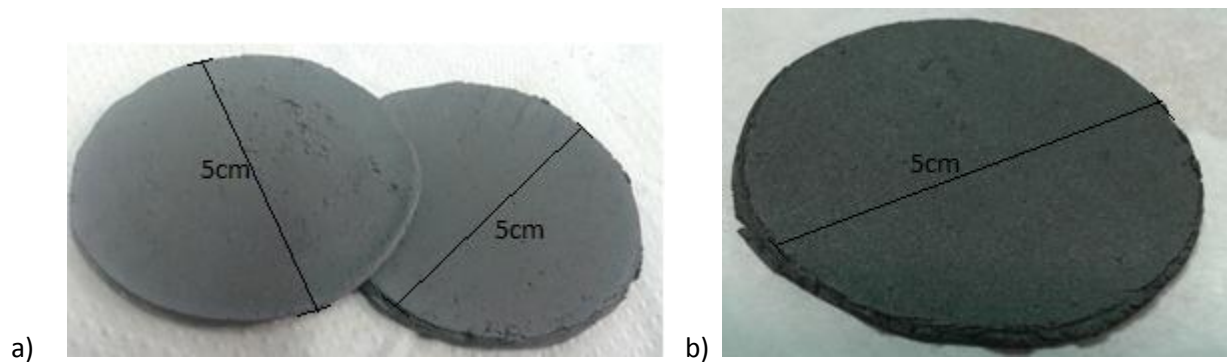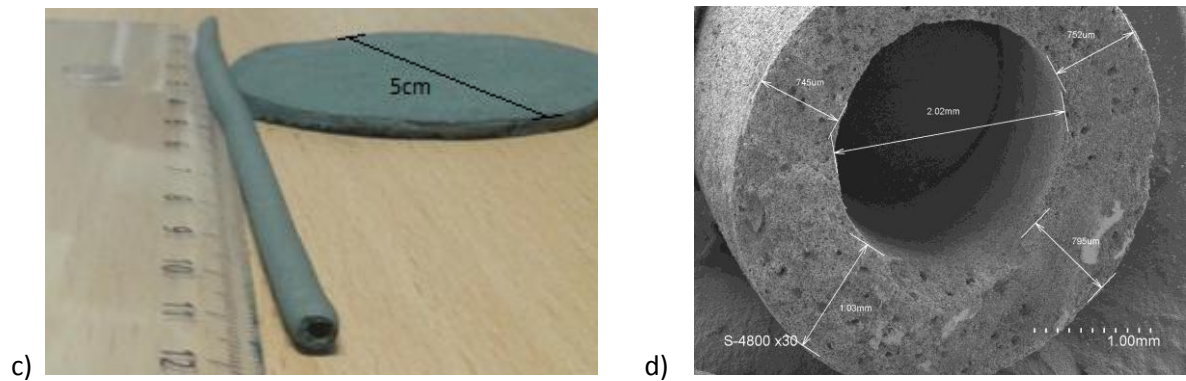
Figure 25. Photographs of sintered flat and capillary supports sintered at a) 1200°C in air, b) 1200°C in argon and c) 1600°C in argon. SEM picture d) represents the cross-section of a capillary sintered at 1200°C in air

8.2.3   Results and Discussion

Prior to paste preparation SiC-500 and SiC-800 powders were characterized by XRD. α-SiC polytype, specifically 2H and 6H types, were identified as shown in figure 26. The particle diameter of SiC-500 and SiC-800 were 11.8-13.8μm and 5.5-7.5μm, respectively.
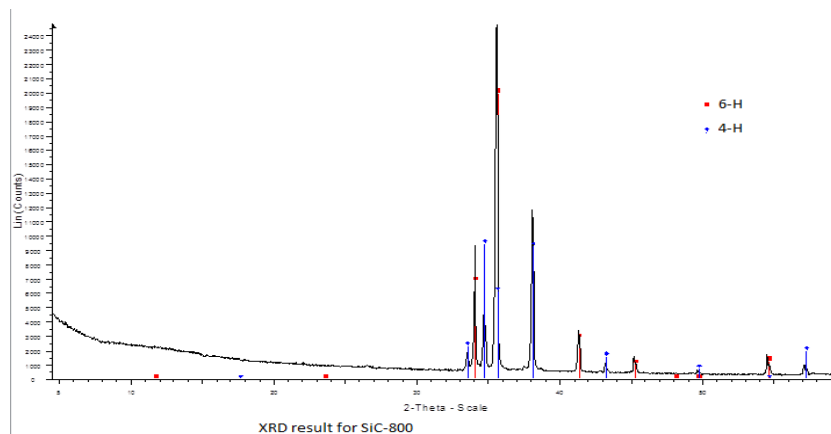
a)
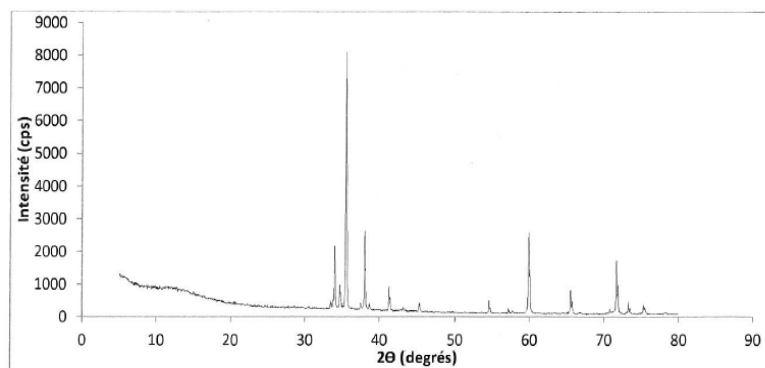
b)

XRD result for SiC-500 powder

Figure 26. XRD results of (a) SiC -500 and (b) SiC-800 powders

To understand the effect of temperature, sintering atmosphere, pore agent and bonding agent on the physico-chemical properties of the SiC supports, different compositions were prepared and sintered at different temperatures and under different atmospheres. The different compositions prepared in weight percentage (wt. %) are summarized in table 2.

Table 2. Paste compositions

Name	SiC-500	SiC-800	Amijel	corn starch and maize starch[*]	Darvan	Methocel	$Na_2B_4O_7,10H_2O$
MM01	---	80	5	5	5	5	---
MM02	40	40	5	5	5	5	----
MM03	32	32	5	5	5	5	16
MM04	41	41	5	2.5	5	5	----
MM05	40	40	5	5[*]	5	5	----

MM01 is a 50g of paste composition that contains 40g of SiC-800 and each 2.5g of amijel, corn starch, darvan and methocel. While MM02 is a 100g paste that contains 40g of each SiC-500 and SiC-800 and 5g of each additive that are used in MM01.

For MM03, a sodium borate bonding agent was used with a weight ratio of 2:8 with respect to the total SiC powders used that is 32g of each SiC powders and 16g of sodium borate. The additives used in MM03 were the same as in MM02 with respect to type and composition.

To see the effect of pore forming agent three analyses were done. In addition to the first three paste compositions, the corn starch was reduced by half in MM04 sample keeping the other elements similar to MM02, so that the total paste prepared was 97.5g. Finally, MM05 was prepared by using maize starch as pore forming agent instead of corn starch. 100g was prepared and the paste composition was similar to MM02.

To study the effect of temperature and firing atmosphere, sintering temperature range from 1200-1400°C under air flow and from 900-1600°C under argon flow were analyzed for the prepared paste compositions. For simplification, the paste sintered at different temperature and atmosphere is named as "paste name-temperature in ^{o}C-atmosphere".
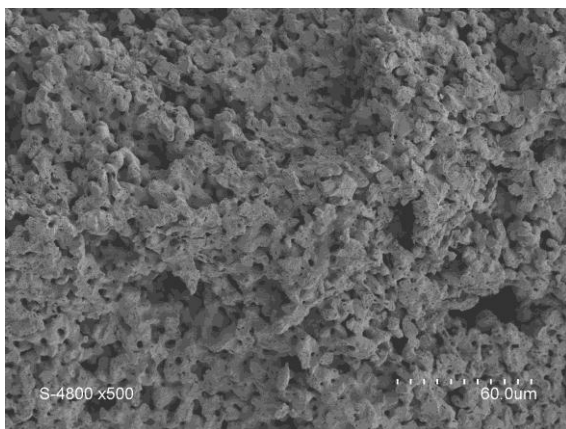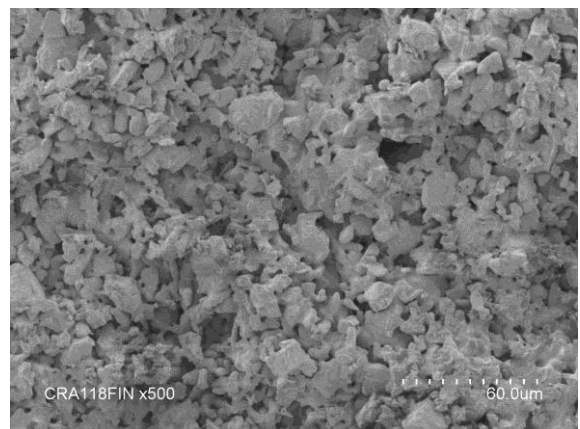
a. MM01-1400-Air   b. MM02-1200-Air
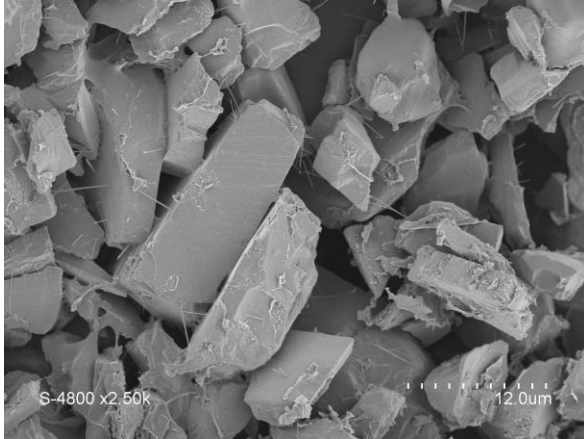
c. MM02-1600-Ar
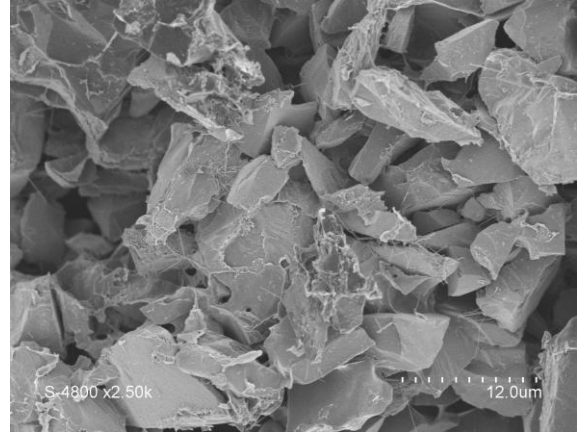
d. MM02-1200-Ar
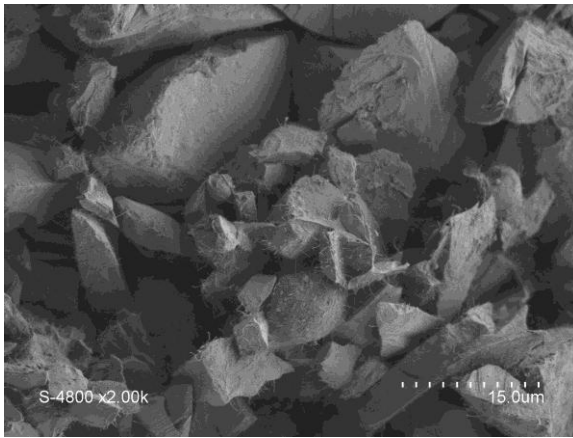
e. MM03-900-Ar
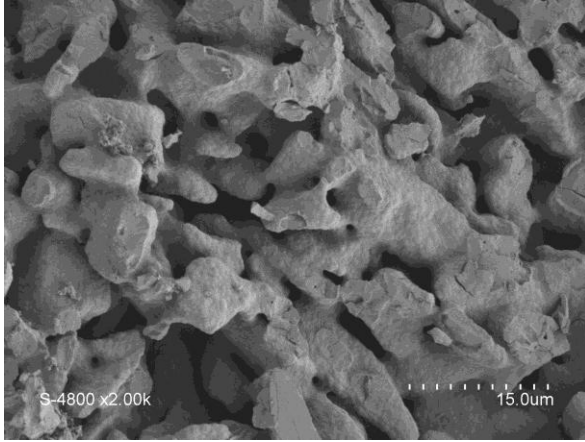
f. MM04-1200-Air
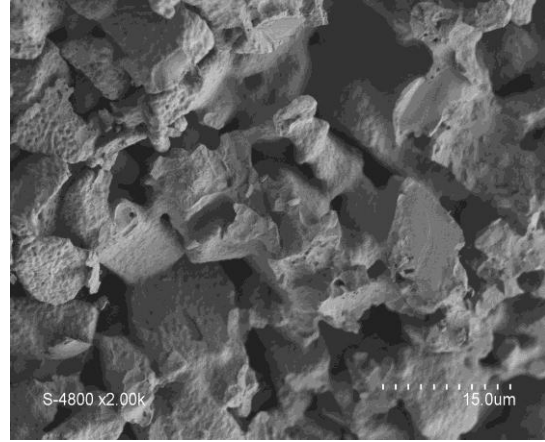
g. MM05-1200-Air
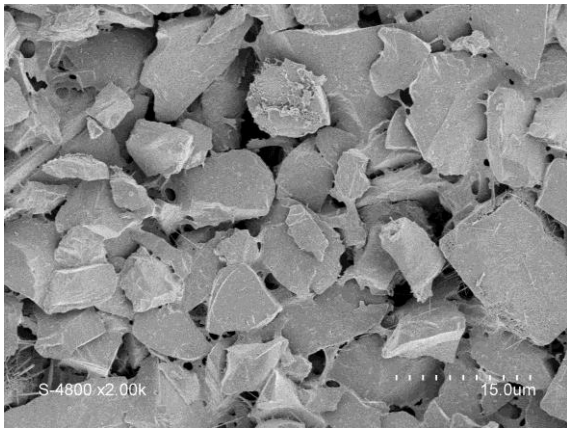
h. MM04-1600-Ar
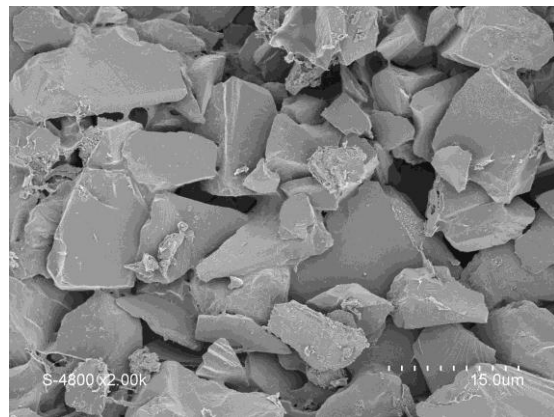
i. MM05-1600-Ar

Figure 27. SEM images of the various synthesized supports after firing at different temperatures and atmospheres

- *Effect of temperature*

As stated earlier to analyze the effect of sintering temperature, a similar paste composition was sintered at different temperatures under similar atmosphere. Flat support of MM01 was placed at 1400°C under air (MM01-1400-air) (Figure 27-a). The sintered support looked white and seemed resistant to handling. XRD result of MM01-1400-air can be seen in figure 28. The presence of the

diffraction peak at 22° confirms that silica phase was formed during firing in air. The white color is thus characteristic of the presence of excess silica formed by oxidation of silicon carbide.
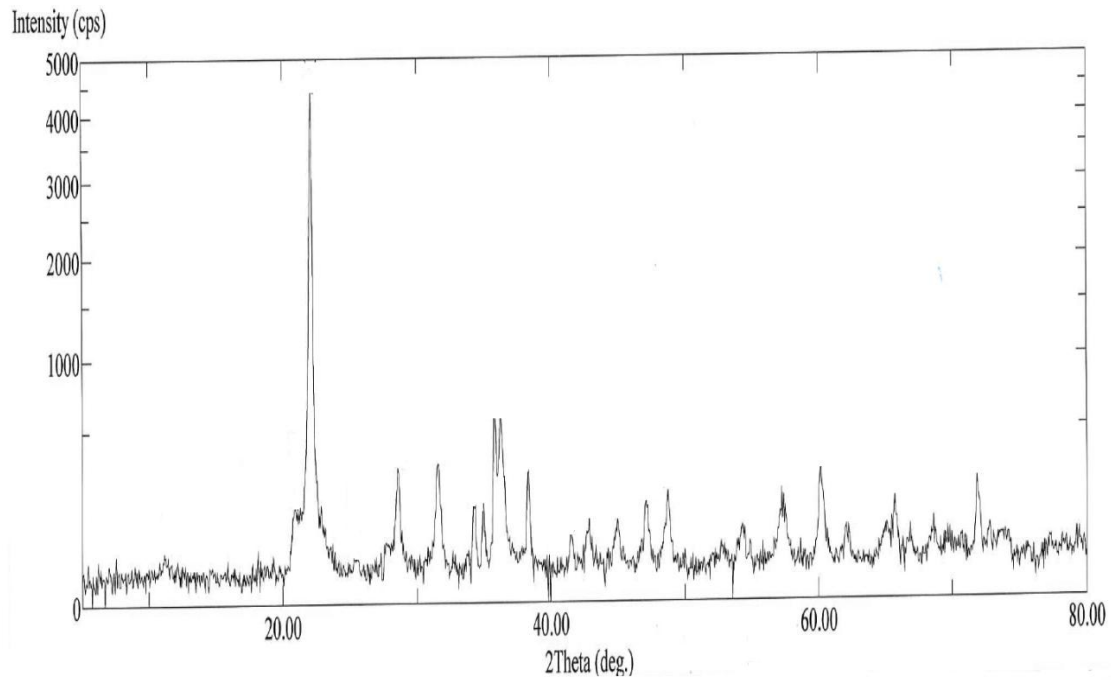
Figure 28. XRD results of MM01-1400-Air under air
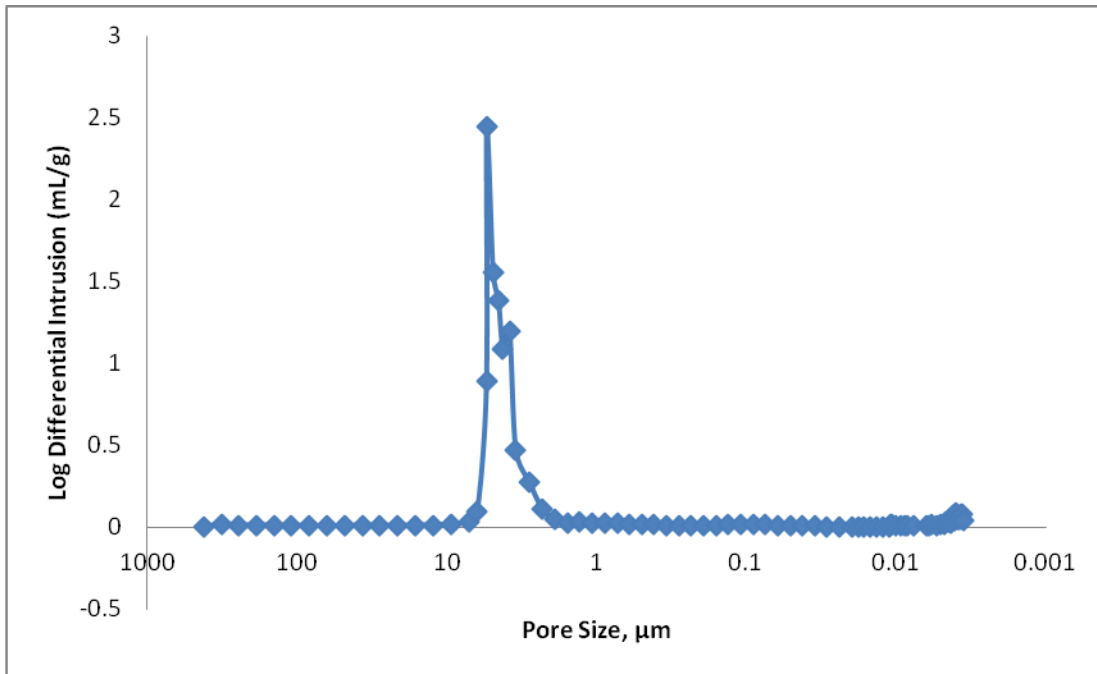
Figure 29. Pore size distribution of MM01-1400-air

Figure 29 shows mercury porosimetry analysis for MM01-1400-air characterized by a narrow pores size distribution centered at 5µm. The average total porosity was 45% with an average pore diameter of 4.6µm. The SiC powder used for MM01 had relatively smaller size (~6.5µm) (refer section 8.2.3), thus results in a smaller pore diameter. On the other hand as discussed in literature review, silica formation occurs from $1100^{o}C$ when SiC is sintered under air, and is often used as a binding agent. The small pore diameter obtained could be due to this excess of silica formed around the pores that covers the SiC particle surface. The presence of oxygen in SiC ceramic reduces its future application under high temperature and steam conditions.
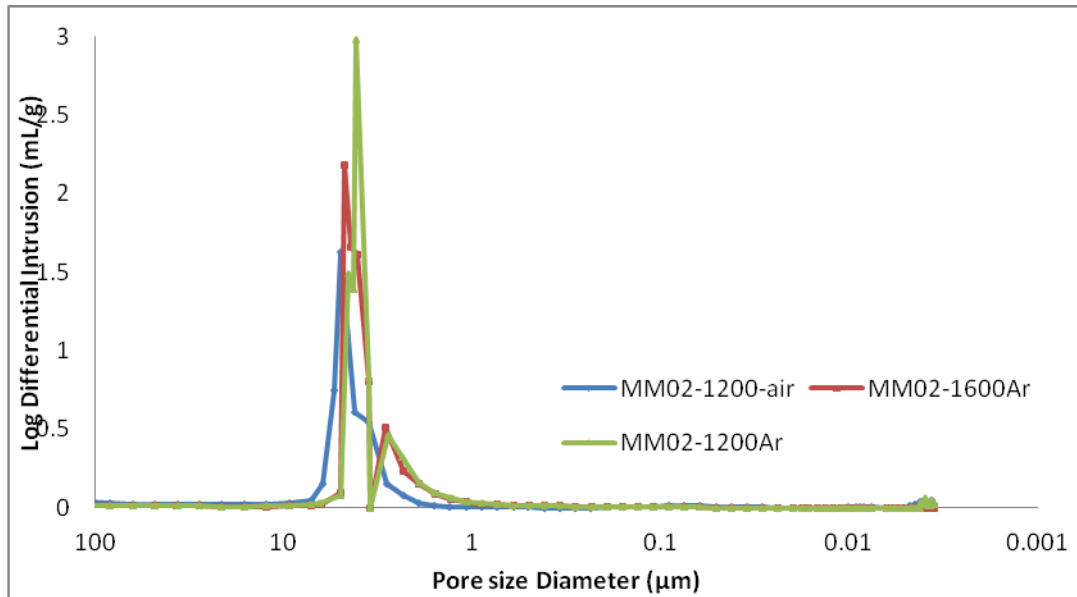
Pore size distributions of MM02 sintered under argon at 1200°C and 1600°C can be seen in figure 30. The porosity of MM02-1200-Ar and MM02-1600-Ar was almost similar around 50% with an average pore diameter of 4.1µm and 4.2µm, respectively. Though the difference in porosity and pore diameter is negligible, it can be noticed that a higher temperature under similar conditions results in low porosity and high pore diameter. Thus, higher temperature enhances sintering by accelerating diffusion of particles. From SEM image shown in figure 27 c and d, microstructure of MM02-1200-Ar and MM02-1600-Ar looks similar. In these two cases neck growth between the particles is not enough to be identified. Thus the sample was fragile and can be broken easily. A similar result is obtained for MM04 and MM05 that were sintered at different temperatures under inert. Thus adding a sintering additive is very important for SiC macroporous synthesis, for harsh industrial condition application.

- *Effect of pore forming agent*

MM02, MM04, and MM05 sintered at 1200°C under air were analyzed to see the effect of pore forming agent in the microstructure and porosity of SiC ceramics. The SEM images (figure 27- b, f

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and g) give evidence of a better particle growth occurrence in these three compositions compared to samples fired at similar temperature under argon. However from the SEM image alone it is difficult to see the difference that this paste compositions have.
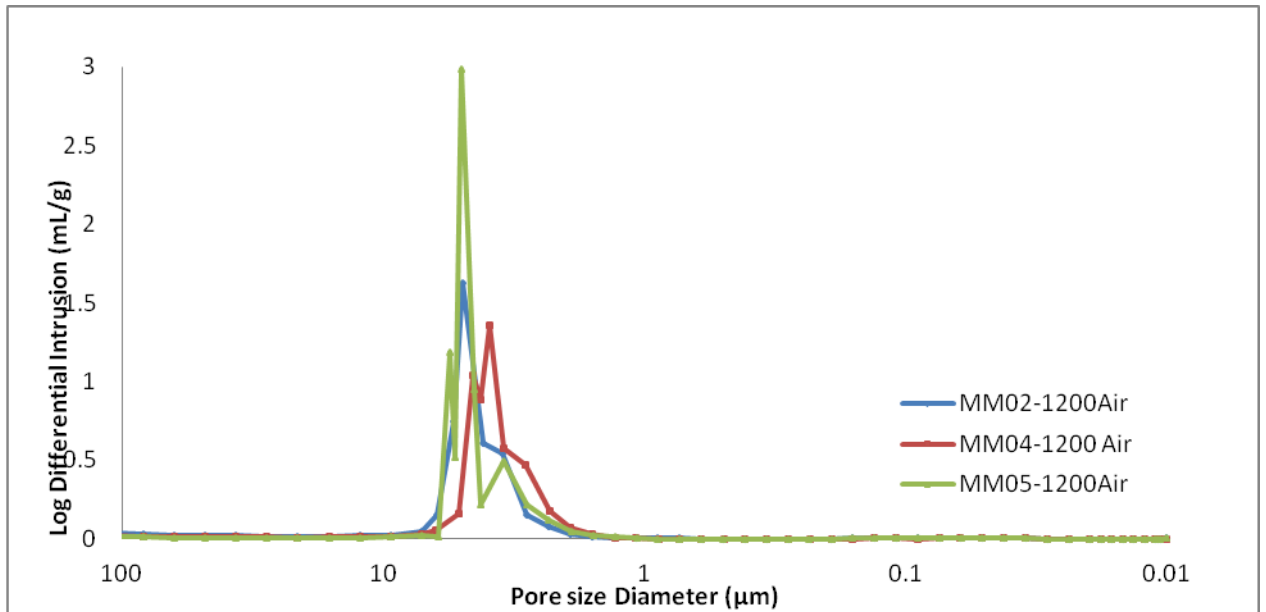
Figure 31. Pores size distributions of different compositions samples fired under Air at 1200°C

Pore size distributions from mercury porosimetry are shown in figures 31. All the three compositions sintered at the mentioned temperature have a narrow pore size distribution centered at approximately 5μm for both MM02-1200-Air and MM05-1200-Air and 4μm for MM04-1200-Air.

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The porosity and average pore size diameter are shown in figure 32. MM02 and MM05 containing 5wt.% of corn and maize starch, respectively (refer table 2), are characterized by a similar average pore size diameter. On the other hand, MM04 that contains only 2.5wt.% of corn starch is characterized by less porosity and smaller average pore diameter. This shows the significant effect of pore forming agent and that a higher content results in a larger pore diameters of porous SiC ceramics support keeping the other factors similar.

- *Effect of sintering atmosphere*

To understand the effect of atmosphere, MM02-1200-air and MM02-1200-Ar were compared. Comparing the two SiC ceramics, the one sintered under argon is fragile and can be broken easily, and also it has dust formed on its surface which might be the result of carbon ashes remaining after additives are burnt and decomposed during sintering. On the other hand, the one sintered under air is strong and is white in color (figures 25.a and b). The white color indicates the presence of silica, that is formed by oxidation of silicon at 1100-1400°C under oxygen (air). The amorphous silica helps the SiC particles to bind each other so that the overall macroporous material attains high mechanical strength. Consequently the SEM images seen in figures 27-b and d, showed a better

microstructure and grain growth for MM02-1200-air compared to MM02-1200-Ar in which the particles are isolated from one another. Even though the temperature was increased to 1600°C and sintered under argon, SEM image (figure 27-d, h, i) shows that the particles intergrowth was not high enough when compared to the one sintered at lower temperature (1200°C) under air.
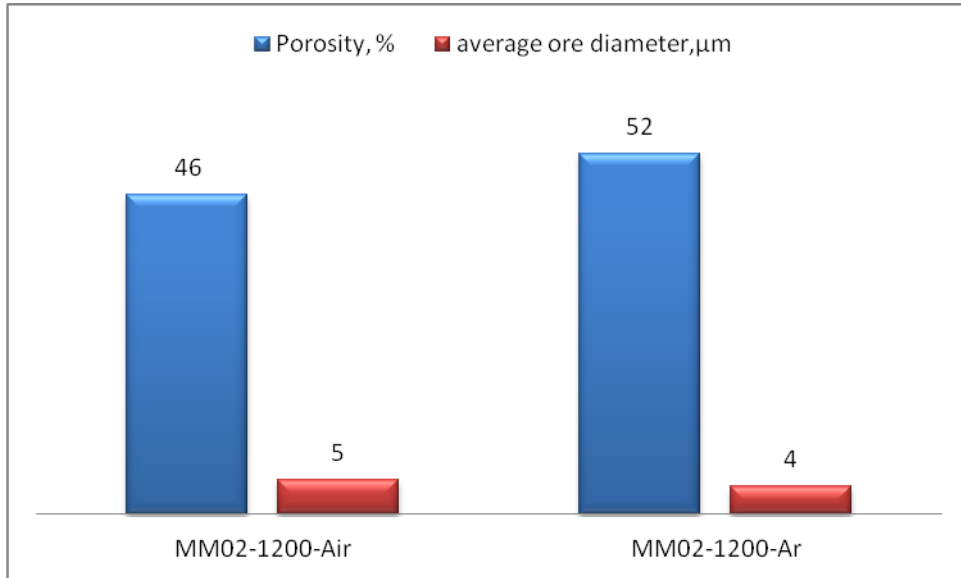
Figure 33. Porosity and average pore diameter of MM02 fired at 1200°C under air and argon

As can be seen in figure 30, the pores size distribution of both SiC ceramics is relatively narrow, with a higher pore diameter for MM02-1200-Air than MM02-1200-Ar. Figure 33 compares the porosity and the average pore size values of the mentioned ceramics. Porosity of MM02-1200-Ar (52%) is higher than MM02-1200-Air (46%) while pore diameter of MM02-1200-Air (5µm) is higher than the other. This significant difference can be due to the presence of a binding agent, silica, which is present when sintering under air. The formation of amorphous silica helps the SiC particles binding and increases in density, so that low porosity and high mechanical strength are achieved. Pore growth occurs at the same time with grain growth that gives higher pore diameter for the sample sintered under air than under argon.
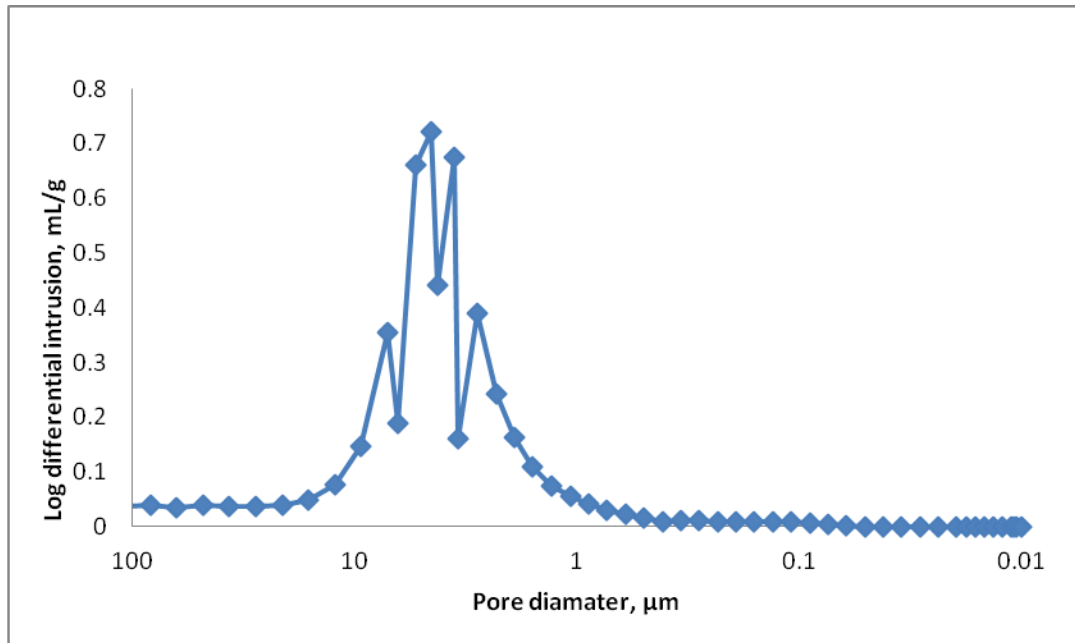
Figure 34. Pore size distribution, porosity and pore diameter of MM03-900-Ar

To see the effect of binding agent, MM03 paste was fired at relatively lower temperature (900°C) under argon atmosphere. The microstructure seen in figure 27-e shows unlike the other compositions sintered in argon atmosphere without binding agent (figures 27-c and d), neck formation between SiC particles as noticed in MM03-900-Ar. Pore size distribution (figure 34) is wider, which has a draw back in selectivity during separation. On the other hand, porosity obtained (53%) is almost similar with the other compositions sintered under argon however the pore diameter (5µm) is higher and equivalent with MM02 and MM05 sintered at 1200°C under air. This can be due to the lower particles diffusion and higher porosity at lower temperature. Sample containing the sodium borate as binding agent was characterized by a better neck growth, even though sintering was done under inert atmosphere at lower temperature. This could be due to the low melting point of sodium borate which is 743°C that enables relatively low temperature processing.

9. CONCLUSIONS and RECOMMENDATIONS

Two methods were used for SiC based non-oxide ceramic membrane synthesis. The first method was using molecular preceramic polymer precursor. Five different preceramic polymers were synthesized by hydroboration of SiC precursor. FTIR analysis of the synthesized Si/B/C polymer shows that the peak intensity indicating presence of double bond in the precursor specifically at frequency of ~1620cm^{-1} and ~3100cm^{-1} decrease with an increase in the amount of the borane added.

In the second method macroporous support from commercially available α-SiC powder together with different additives were synthesised. A total of five different compositions were prepared and sintered at different temperature and atmosphere.

MM01-1400-air macroporous support prepared from 80wt.% SiC-800 powders and 20wt.% additives has pore diameter of 4.6μm and 45% porosity. XRD analysis confirms the presence of excess silica in this macroporous support. The small pore diameter obtained could be due to the relatively small particle size of SiC powder used and/or due to the excess silica formed around the pores that covers the SiC particle surface. The presence of oxygen in SiC ceramic reduces its future application under high temperature and steam conditions.

Effect of temperature was analysed using MM02-1200-Ar and MM02-1600-Ar macroporous support (composed of 40wt,% SiC-800, 40wt,% SiC-500 and 20wt,% additives). Porosity and pore diameter obtained from the two supports were ~51% and ~4μm. This might be due to the absence of binding agent, since SiC powders are fundamentally non-sinterable materials so that increasing the temperature alone does not enhance sintering without a binding agent.

However effect of atmosphere was very significant, low porosity (46%) and bigger pore diameter (5μm) were obtained when MM02-1200-air sintered under air compared to MM02-1200-Ar. This could be due to the formation of amorphous silica binding agent that enhances grain growth by formation of neck growth between the particles. As a result a better microstructure was obtained from SEM analysis. Pore growth occurs at the same time with grain growth that gives higher pore diameter for the sample sintered under air than under argon.

Effect of pore forming agent was analysed by comparing MM02-1200-air, MM04-1200-air and MM05-1200-air which contains 5wt.% corn starch, 2.5wt.% corn starch and 5wt.% maize starch respectively. Porosity of the three compositions was relatively similar (less than 48 %), with lower porosity for MM04. In addition pore size of MM02 and MM05 were similar ~5μm while that of MM04 was 4μm. Even though the difference is not significant enough it can be concluded that a high amount of pore forming agent brings more porous substance that have relatively bigger pore diameter.

Sodium borate binding agent with SiC powders mixture with a weight ratio of 8:2 was fired at 900°C (MM03-900-Ar). The binding agent enhances neck formation even if sintering was done at relatively low temperature under argon, and this could be due to the low melting point of the binding agent (743°C). A similar porosity was obtained for this composition with the others that were sintered under argon, above 50%. It has a similar average pore diameter with compositions sintered under air. From this it can be concluded that pore growth occurs when grain growth occurs, that is binding agent promote grain growth as well as pore growth.

Preceramic polymer synthesis was done at room temperature, which has economical and environmental benefits. Also through this project it was found out that in SiC macroporous synthesis binding agent sintering atmosphere has highest effect than temperature and pore forming agent in the microstructure, porosity and pore size. As non-oxide SiC ceramic membrane has highest mechanical strength at high hydrothermal condition, it is recommended further analysis should be done on sodium borate binding agent in order to obtain a better porosity and pore size distribution.

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