

Chapter 7

Ceramic Foam Composite using Industrial Solid Waste (Coal Overburden) via Sucrose Dehydration process-2

7.1 Introduction

Traditionally, porous structures have relied on ceramics like alumina, silica, zirconia, silicon nitride, and anorthite as matrices. However, the remarkable physicochemical properties of Silicon Carbide (SiC) have garnered significant attention, leading to its utilization in various industrial applications including molten metal filters, water filters, gas clean-up filters, combustion burners, catalyst supports, and sensors [173–175]. Nevertheless, the production of SiC foam utilizing pure SiC at reduced sintering temperatures has presented an obstacle due to the robust covalent characteristic of the Si-C linkage. Consequently, the demand for sintering temperatures surpassing 1800°C has led to heightened energy expenditure and increased manufacturing expenses [176]. To address this, silicon-containing polymers have been employed to fabricate SiC ceramics, acting as sintering aids. Although this approach reduces sintering temperatures, the elevated cost of these polymers and the requirement for oxygen-free environment during sintering have increased manufacturing costs, consequently limiting its industrial viability [177]. Another alternative involves the fabrication of SiC ceramics through oxidation-bonding techniques, utilizing inorganic sintering aids or catalysts such as Al₂O₃, CaO, MgO, and MoO₃. These substances interact with SiC particles, leading to the formation of newer SiC phases. This approach enhances the mechanical strength and permeability of SiC ceramics, enabling synthesis at relatively lower temperatures. Consequently, there has been a growing interest in the utilization of cost-effective raw materials that incorporate sintering aids to produce SiC foam [178–181].

Mullite, the most thermodynamically stable mineral in the Al₂O₃-SiO₂ system, possesses exceptional thermal shock resistance, low linear expansion coefficient, outstanding chemical stability, and acid-alkali corrosion resistance, and is also used for making porous structures [182]. Thermal expansion coefficient of both SiC and Mullite are comparable which makes mullite suitable candidate to be used as bonding phase [183]. This helps in reducing the sintering temperature. Moreover, mullite provides a bridge connection between SiC particles, addressing the issue of low connectivity among them [184]. Consequently, mullite-bonded SiC ceramics are anticipated to exhibit exceptional mechanical characteristics under elevated temperatures and demonstrate outstanding resistance to thermal shock.

MW has been reutilized in various ways, such as a filler in hot mix asphalt, underground mine filling material, bricks and refractories, cement, concrete, raw geomaterials in construction, and lightweight aggregates as discussed in earlier chapters. However, the potential benefits of utilizing the rich aluminosilicate minerals and other oxides, such as MgO and CaO content, as

an effective additive for producing SiC-based porous structures have not been previously explored.

Considering the beneficial characteristics of functionally graded foams and the widespread applicability of porous SiC structures in various applications, the present study aims to develop functionally graded SiC foams with gradient microstructures. A one-step thermo-foaming process is utilized to achieve the desired microstructure gradient, based on the dehydration of sucrose with sulphuric acid [153]. The foam's pore morphology is adjusted by controlling the amount of sucrose and sintering temperature, while coal mine waste is employed as an additive to enhance the economic and sustainable aspects of the fabrication process. The addition of coal mine waste reduces the material cost and lowers the sintering temperature required for consolidating SiC particles, which further reduces the sintering cost. Additionally, alumina is incorporated to observe the formation behavior of bonding phases such as cordierite and mullite. The effects of sintering temperature, coal mine waste, and alumina content on the density, porosity, and mechanical strength of the SiC foams are systematically investigated and correlated.

7.2 Materials and Methods

7.2.1 Raw materials

SiC powders (α -SiC) is used as primary ingredient and obtained from LOBA CHEMIE PVT. LTD, India. MW is collected from the open-cast mine of Bina site, Northern Coalfield Limited (NCL) Singrauli, India. Alumina powder having average particle size of 0.7 μm and surface area of 7 m^2/g (ALCOA ACC, CT 3000SG, Mumbai, Maharashtra, India) was used as additive to increase the mullitization. Both the sucrose and the concentrated H_2SO_4 (98 wt.%) used are of laboratory research quality (Loba, India).

7.2.2 Fabrication of functionally graded SiC foam

The fabrication process of functionally graded SiC foam is based on the dehydration of sucrose with sulphuric acid. In brief, the SiC powder were mixed with sieved MW powder and finer sucrose powder in a defined concentration, and the optimized amount of sulphuric acid was added to the mixture to get a slurry paste. This slurry was then cast into an appropriate cast and kept in the ambient atmosphere for 24 hours for dehydration reaction and foaming. The foamed samples were then kept in an oven at 100°C for drying. The dried green foam samples were machined to get proper shape and then kept for the sintering (1300°C-1500°C) process for final consolidation. Further to investigate the effect of Alumina addition on the phase changes of

bonding phases of SiC particles during sintering, alumina powder is mixed in different proportion in the initial SiC-MW-Sucrose mixture and the foaming process is repeated.

7.2.3 Characterization Technique

The XRD (Rigaku Miniflex 600 Desktop X-Ray Diffractometer) measurements of rawMW, SiC and sintered SiC foam are analyzed using X-ray radiation of Cu- α (1.54 Å), within 2θ range of 5-80° with 0.02°step size. SEM (EVO-MA15/18, Carl Zeiss Microscopy Ltd.) was used to understand the surface morphology and microstructure of SiC foam. Fourier-transform infrared spectroscopy (FTIR) using the Nicolet iS5 instrument from Thermo Electron Scientific Instruments LLC was employed to observe changes in functionality and bonds during both the pre- and post-dehydration process and sintering. Thermogravimetric analysis (TGA) was conducted using the TGA-50 instrument from Shimadzu (Asia Pacific) Pte Ltd to analyze the thermal decomposition behavior of the green SiC foam. The procedures for the physical and mechanical characterizations of developed SiC foam have been adopted from the previous chapter.

7.3 Results and Discussion

7.3.1 Characterization and microstructural evolution of functionally graded SiC Foam

The initial results of raw MW show that MW is the potential material to be used as a sintering additive to make mullite bonded SiC foams. The presence of Al₂O₃, SiO₂ and MgO in MW is the key content for low temperature sintering of SiC particles due to oxidation bonding phenomenon (Section 5.3, Chapter 5). The functional gradient observed in SiC Foam is a consequence of the thermo-foaming effect that arises from an exothermic reaction between sucrose and sulphuric acid. The reaction generates gases that promote foaming inside the SiC slurry. The microstructure of the foam is graded due to the viscous and gravitational effects of the slurry, leading to the formation of smaller pores at the bottom and larger pores at the top. The addition of sucrose powder acts as a blowing agent, and enables the control of the porosity of the SiC foam samples. The resulting green SiC is coated with a thin layer of carbon that is produced during the dehydration of sucrose with sulphuric acid. These coated carbons also contribute to the formation of pores during the sintering process. The detailed synthesis mechanism can be found in our previous chapter (Chapter 4). TGA analysis is carried out to study the thermal degradation of green SiC foam and to establish an appropriate heat treatment schedule (Fig. 7.1). The TGA analysis conducted reveals a weight loss pattern characterized by two distinct stages occurring between the temperature range of 50°C and 450°C. The first stage corresponds to the evaporation of water vapor, leading to a significant weight loss observed

within the temperature range of 50-210°C. In the second stage, a more gradual weight loss is observed as carbon is steadily lost due to the dehydration of sucrose, occurring between 210°C and 450°C. To eliminate organic impurities, a heat treatment schedule is employed, involving a slow and controlled heating rate of 3°C/minute up to 500°C, followed by the sintering process. Subsequently, the green SiC foam is subjected to further heating at higher temperatures ranging from 1100°C to 1400°C, employing a heating rate of 5°C/minute. This step aims to promote consolidation and enhance the overall strength of the SiC foam.

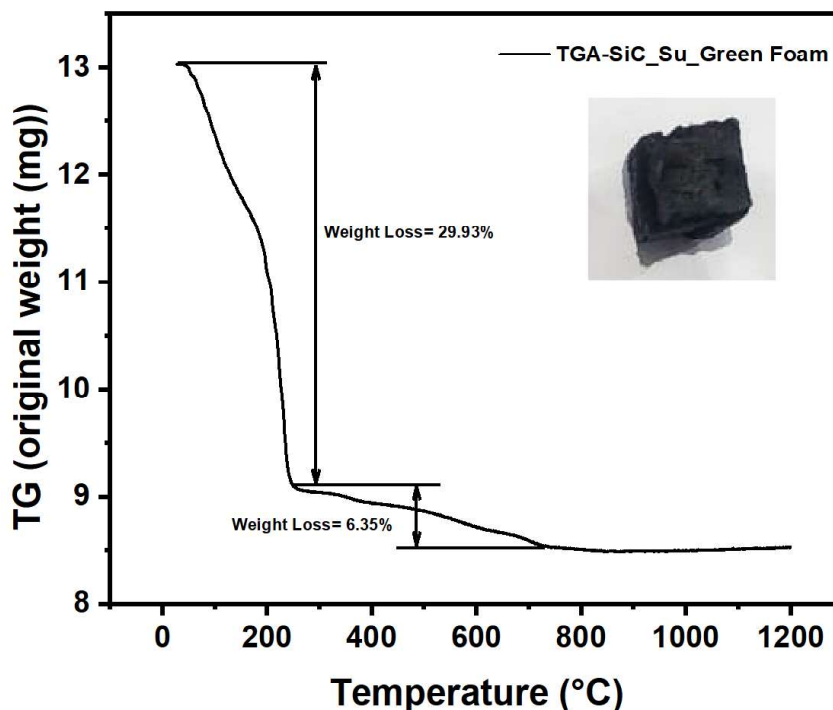
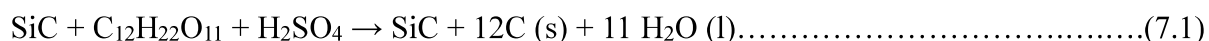


Fig. 7.1 Thermogravimetric analysis of green SiC foam

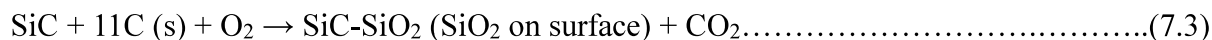
The heat treated green SiC foam provides considerable strength to the samples. Moreover, the consolidation of green SiC foam comes with chemical and phase change during high temperature heat treatment. The chemical and phase changes in heat-treated SiC foam samples are analyzed through FTIR and XRD analysis. The XRD pattern of sintered SiC foam with all variations is shown in Fig. 7.2, which is noted in the 2-theta (2θ) range from 20° to 80°. The XRD pattern for pure SiC powder shows peaks of pure SiC phase (74-1302). However, when SiC powder is foamed using 5 wt% sucrose powder and treated at 1400°C, peaks of cristobalite (76-0936) are observed in addition to SiC phase, which indicates the oxidation of SiC at higher temperatures. The appearance of cristobalite confirms the transformation of amorphous SiO₂ produced by the surface oxidation of SiC particles into cristobalite. The absence of peaks other than cristobalite and SiC confirms that there is no chemical change in the SiC structure during

the thermo-foaming reaction and further sintering process. The FTIR peaks of pure SiC confirm the presence of pure SiC particles in the raw powder. However, when the SiC powder is treated with sucrose and sulfuric acid, the obtained green SiC foam is covered with a fine coating of carbon. The FTIR analysis of the green SiC foam reveals several important observations (Fig. 7.3). Firstly, a less intense peak at 3450 cm⁻¹ in the O-H region suggests partial dehydration of sucrose, potentially caused by the concentrated sulfuric acid or adsorbed water vapor on the green silica foam. Additionally, a new peak at 1878 cm⁻¹ corresponding to C=O vibration is observed after carbonization, indicating the possible oxidation and esterification of the abundant O-H groups in sucrose by H₂SO₄. Sharp peaks in the range of 1000-1300 cm⁻¹, corresponding to O=S=O, -SO₃H groups, and Si-OH group, confirm the carbonization and dehydration of sucrose facilitated by H₂SO₄. Furthermore, the presence of peaks at 452 cm⁻¹, 596 cm⁻¹, 788 cm⁻¹, and 1076 cm⁻¹, as well as the disappearance of peaks in the range of 1000-2900 cm⁻¹ in the sintered sample, indicate the successful conversion of carbon-coated silicon carbide foam into SiC-SiO₂ foam. Specifically, the peaks at 452 cm⁻¹, 596 cm⁻¹, and 788 cm⁻¹ correspond to symmetric and asymmetric Si-O stretching vibrations, confirming the presence of silica in the sintered foam sample. These results confirm that carbonization occurs during the thermo-foaming process and carbon adheres to the surface of SiC, which further disappears due to high-temperature treatment. The presence of SiO₂ along with SiC as revealed by XRD and FTIR confirms the oxidation of SiC during the thermal treatment process. Based on these results, the reaction mechanism in the present thermo-foaming process by sucrose dehydration process to fabricate SiC foam with gradient microstructures can be summarized as follows.

Fabrication of Green SiC foams (Carbon coated SiC Foam):



Removal of carbon and passive oxidation reaction on the SiC surface at higher sintering temperature:



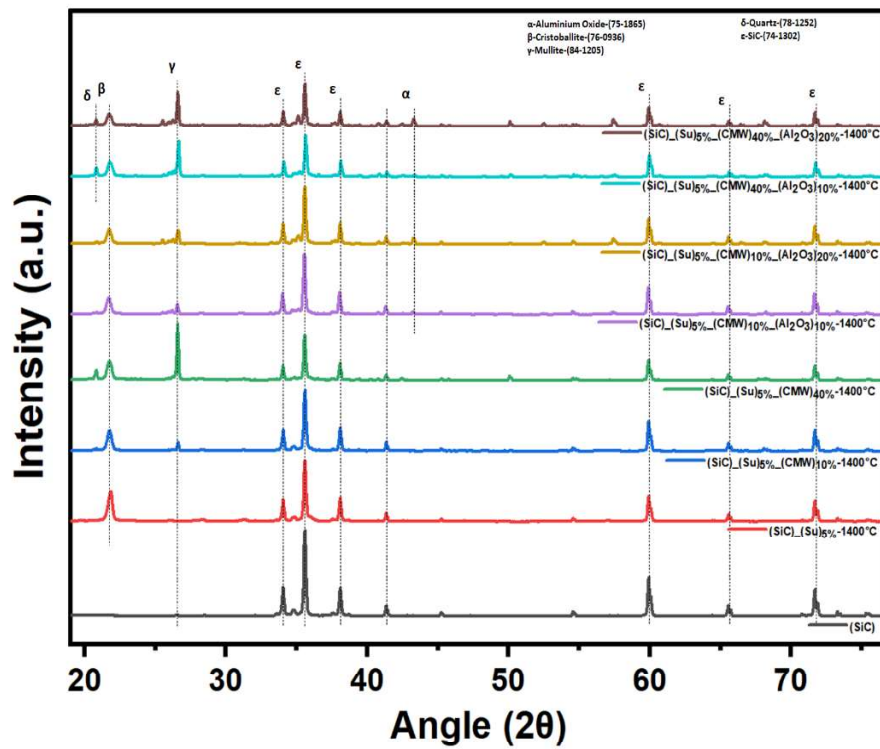


Fig. 7.2 XRD pattern of raw SiC powder and sintered SiC foam with different compositions

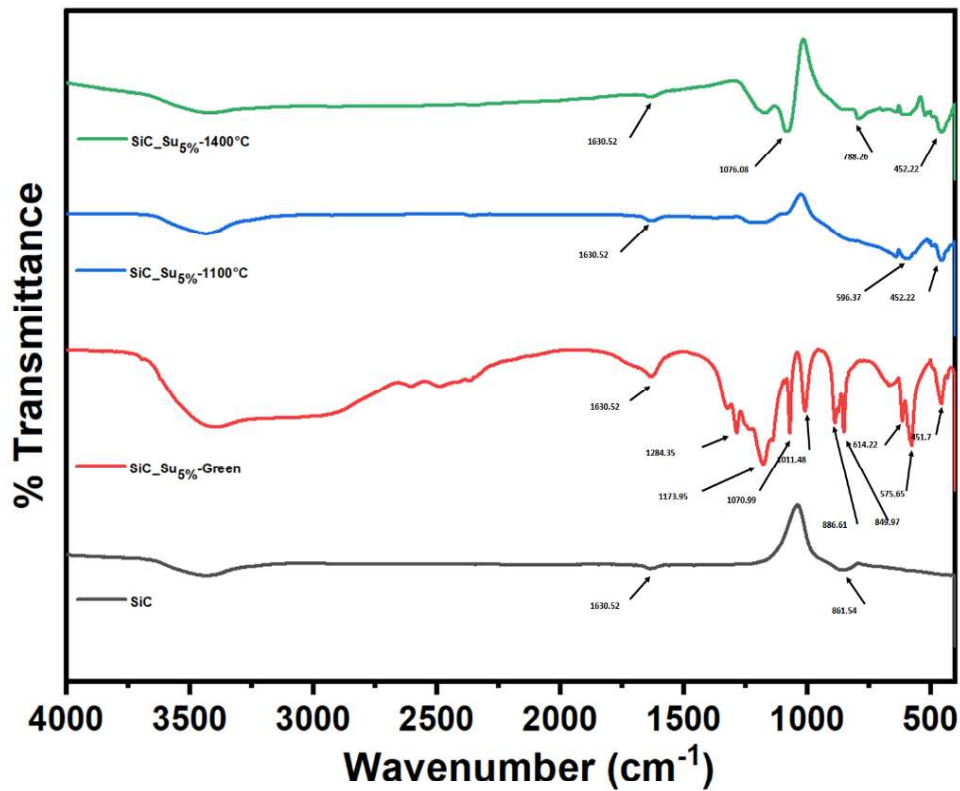


Fig. 7.3 FTIR of raw SiC powder, green SiC foam and sintered SiC foam

The optical image presented in Figure 7.4 displays a SiC foam fabricated using 10 wt % sucrose, showcasing the side, bottom, and top faces of the foam. The microstructure of the SiC foam displays a gradient in pore size, with smaller pores observed near the bottom side of the side face as compared to the top side. This gradient in pore size can be explained by the effects of viscosity and gravity on the SiC slurry during the thermo-foaming process. As gases are generated during the process, they exert pressure inside the slurry and form pores. The escaping gases experience more pressure near the bottom side due to the greater gravitational forces caused by the weight of the slurry, which results in the formation of fine pores. On the other hand, the escaping gases experience comparatively less gravitational force at the top side, resulting in larger pores. The bottom face of the SiC foam contains a greater number of small-sized pores, while the top face has fewer but larger pores. These observations are consistent with the conclusions drawn from the analysis of the side face of the SiC foam.

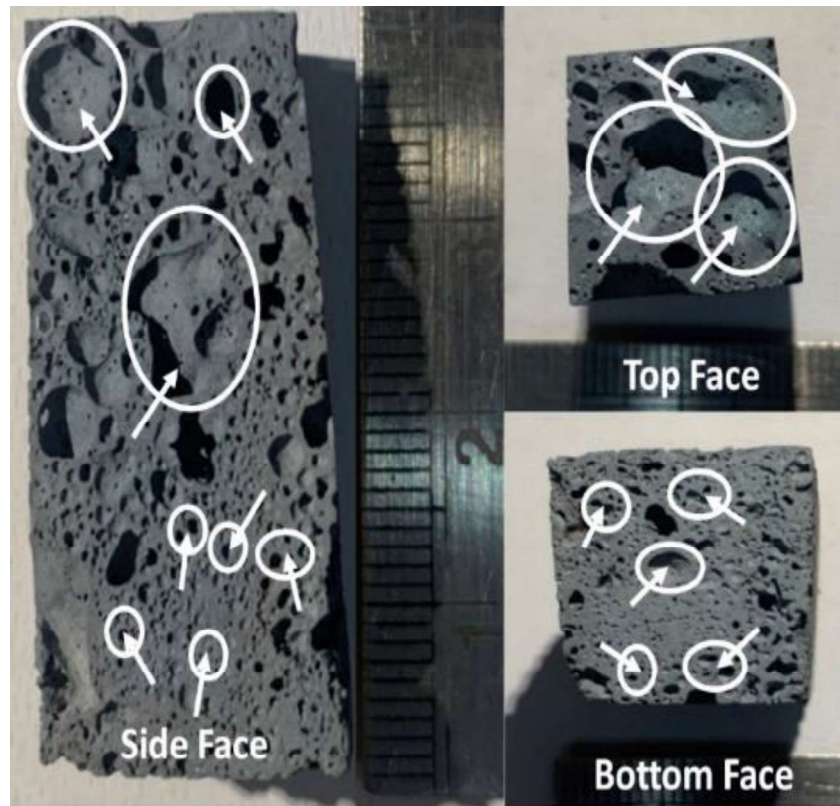


Fig. 7.4 Optical image of sintered SiC foam displaying different faces

The results of the systematic study on sucrose addition showed that increasing the sucrose content in the SiC slurry led to an increase in foaming, as shown in Fig. 7.5 (a). Specifically, a 38% increase in foam height was observed when the sucrose content was increased from 2.5 wt% to 5 wt%, and this increase further rose to 80% with the addition of 10 wt% of sucrose.

However, it was observed that there was only a marginal increase in foam height when the sucrose content was increased beyond 10 wt%. Additionally, it was observed that the pores in the SiC foam became more random when the sucrose content exceeded 10 wt%. Therefore, it was concluded that up to 10 wt% sucrose is sufficient for achieving a uniform gradient pore microstructure. Furthermore, the study showed that there was a linear trend in the decrease of bulk density and an increase in total porosity and apparent porosity with an increase in sucrose content. This trend can be attributed to the greater foaming effect exhibited by higher sucrose content SiC slurry, which leads to a higher amount of escaping gases.

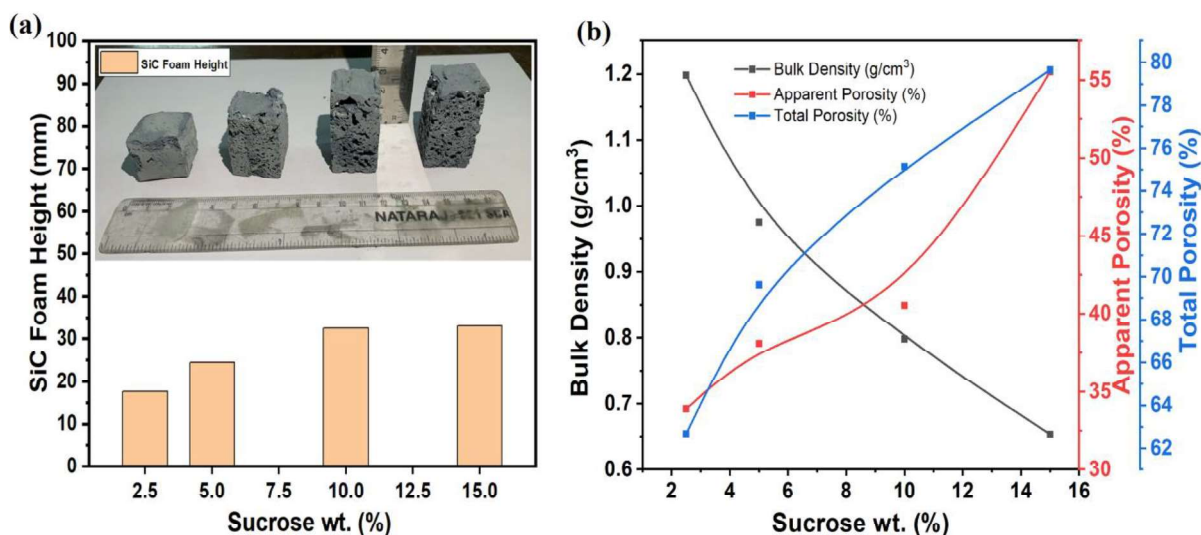


Fig. 7.5 (a) Foaming behaviour with different sucrose content, (b) Variation in physical properties of SiC foam with sucrose content. (All samples are sintered at 1400°C)

7.3.2 Effect of MW addition

The high energy consumption in the process of consolidation of SiC ceramic, leads to development of alternative approach to prepare reinforced SiC composite instead of monolith SiC body. Development of in-situ reaction bonding technique using metal oxides such as SiO₂, mullite and cordierite give a new way to achieve SiC ceramic comparatively at lower cost. Since, the major component of MW is aluminosilicate or based minerals, use of MW in making SiC based ceramic is helpful in the sense of attaining low temperature sintering due to mullite bonded SiC particles. In this context addition of different weight % of MW in foaming and physical properties of SiC foam is studied and a significant influence has been observed. The addition of MW to SiC foams has shown to have a significant impact on their properties. Fig. 7.6 (a) illustrates the foaming behavior of SiC foams due to varying proportions of MW. The addition of up to 5 wt % of MW has shown almost negligible effects on the foaming height, while the bulk density has increased, resulting in a decrease in apparent porosity. However, a

sharp increase in total porosity is observed up to 5 wt% of MW. Further addition of MW decreases bulk density, which may be attributed to the lesser density of MW powder compared to SiC powder. Foaming also increases, as seen from the foaming height graph after 5 wt% MW addition, thereby increasing the total porosity of the sample. However, foaming and bulk density values saturate after 10 wt % MW addition. Another anomaly observed in the addition of MW is that, despite the fact that foaming and total porosity are increased up to 10 wt% addition of MW, the apparent porosity value is decreased. This can be attributed to an increase in closed pores compared to open pores due to the addition of MW. However, not much significant change is observed in the physical properties of SiC-MW composite foam after 12 wt% addition. The XRD pattern shows that the addition of MW results in the formation of the mullite phase due to higher-temperature sintering of the aluminosilicate-rich content of MW. The increase in mullite intensity in the XRD pattern at higher concentrations of MW clearly demonstrates a higher rate of mullitization due to the presence of more aluminosilicate minerals. However, a higher concentration of MW leads to the appearance of the quartz phase in the foam samples, which can be attributed to a higher concentration of free silica in MW, in excess of the formation of mullite or other silicate phases. Therefore, it can be inferred from the above discussion that the addition of MW helps in the formation of the mullite phase, which further aids in the reaction bonding of SiC particles and strengthens SiC foams.

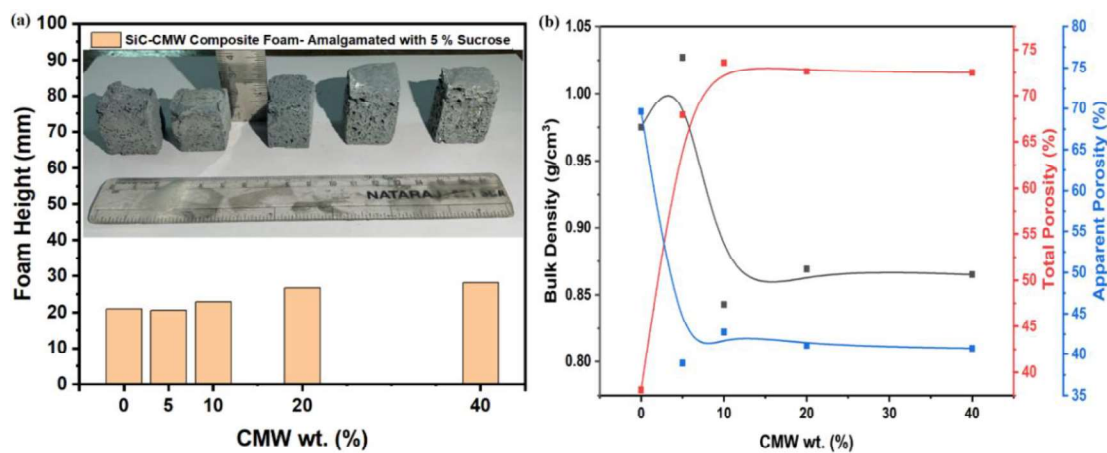


Fig. 7.6 (a) Foaming behaviour with different MW content, (b) Variation in physical properties of SiC foam with MW content. (All samples are prepared using 5 wt% sucrose and sintered at 1400°C)

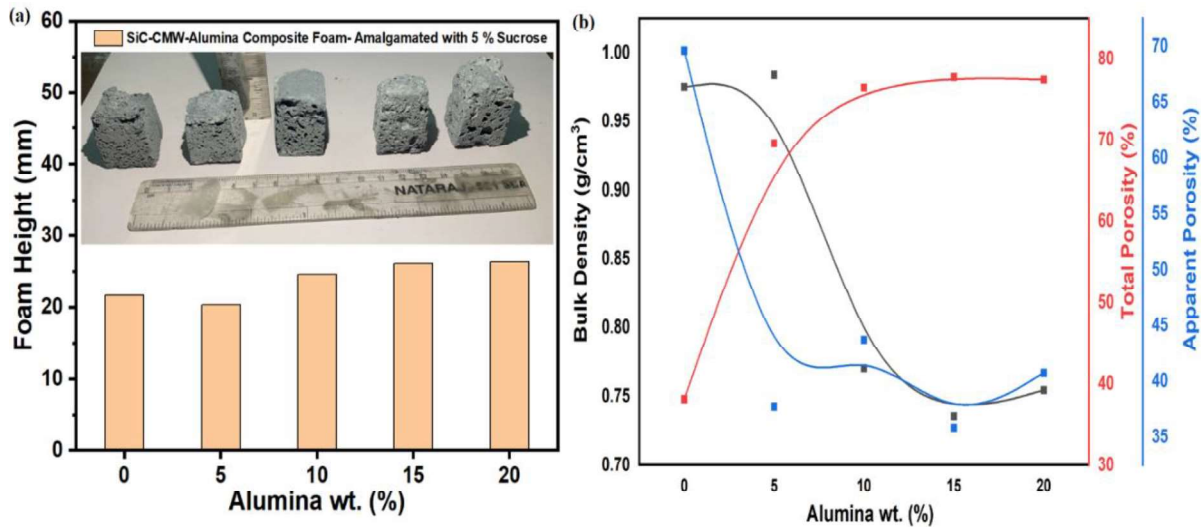


Fig. 7.7 (a) Foaming behaviour with different Alumina content, (b) Variation in physical properties of SiC foam with Alumina content. (All samples are prepared using 5 wt% sucrose, 10 wt% CMW and sintered at 1400°C)

7.3.3 Effect of Alumina addition

The addition of MW leads to the development of the mullite phase, but exceeding the MW weight percentage leads to the existence of free silica in the form of quartz, which decreases the thermal shock resistance of the foam. To counteract this, further addition of alumina is considered so that this excess reacts with free silica and transforms into the mullite phase. A systematic study on physical and chemical properties of SiC foam with the addition of alumina weight percentage is carried out, and it is found to have a positive impact. In the first attempt, the alumina content is varied with a constant content of 10 wt% of MW in SiC. The XRD data shows that alumina intensifies the mullite phase as compared to without alumina. However, when an excess of alumina is used (20 wt%), the appearance of the alumina oxide phase is also observed in the sample, suggesting non-reacted alumina. Foaming due to alumina addition is not as influential as shown by MW addition (Fig. 7.7 (a)). Up to 10 wt% of alumina addition has shown some increase in foaming height beyond which foaming is almost constant. An increase in bulk density is observed with an increase in alumina wt%, which may be attributed to the higher powder density of alumina with respect to SiC and MW. A sharp increase in total porosity of SiC foam is observed with alumina up to 10wt%, which remains steady beyond 10 wt% (Fig. 7.7 (b)). Microstructural study also corroborates a similar pattern showing more pores in the SEM image of higher alumina content samples (Fig. 7.9 (e,f)). However, a decreasing trend is observed for apparent porosity, which may be attributed to the formation of

closed pores due to the addition of alumina. When the weight percentage of MW is increased from 10% to 40%, and further alumina is added, intensified peaks of mullite are observed, suggesting better mullitization in the presence of a higher content of MW and alumina. Quartz phase is still evident, but comparatively at a lower intensity than without the addition of alumina. Further, in the 40 wt% of MW, when the alumina content is increased from 10 to 20 wt%, the quartz phase is found to be decreased, and the mullite phase is increased, showing better mullitization in the presence of a higher concentration of MW and alumina. This increase in mullitization can be easily visualized through SEM images (Fig. 7.10) showing the formation of mullite rods along the grains of SiC. Foaming height is increased when 40 wt% MW with alumina addition is used as compared to 10 wt% MW with alumina (Fig. 7.8 (a)). However, the foaming effect is less evident with an increase in alumina content when 40 wt% MW samples are used. The total porosity of the foam samples is increased with the addition of alumina (Fig. 7.8 (b)). The microstructural image also corroborates a similar pattern of an increase in porosity, as seen in the SEM images, showing more intracrystalline pores in the higher content of alumina (Fig. 7.9 (h)) compared to the lesser content of alumina (Fig. 7.9 (g)).

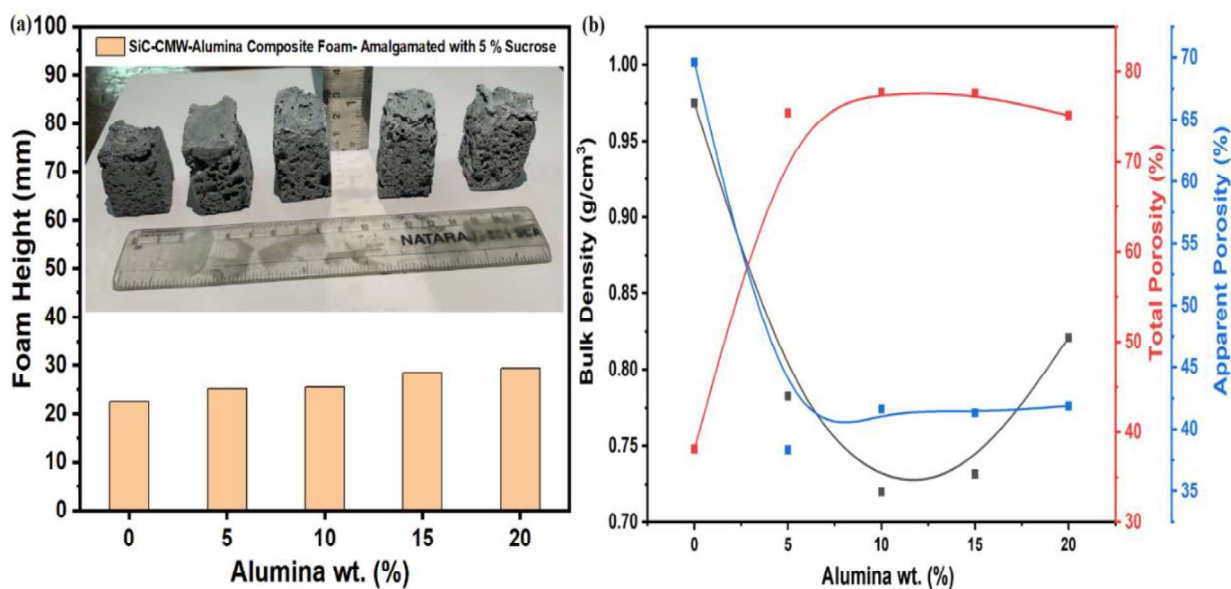


Fig. 7.8 (a) Foaming behaviour with different Alumina content, (b) Variation in physical properties of SiC foam with Alumina content. (All samples are prepared using 5 wt% sucrose, 40 wt% CMW and sintered at 1400°C)

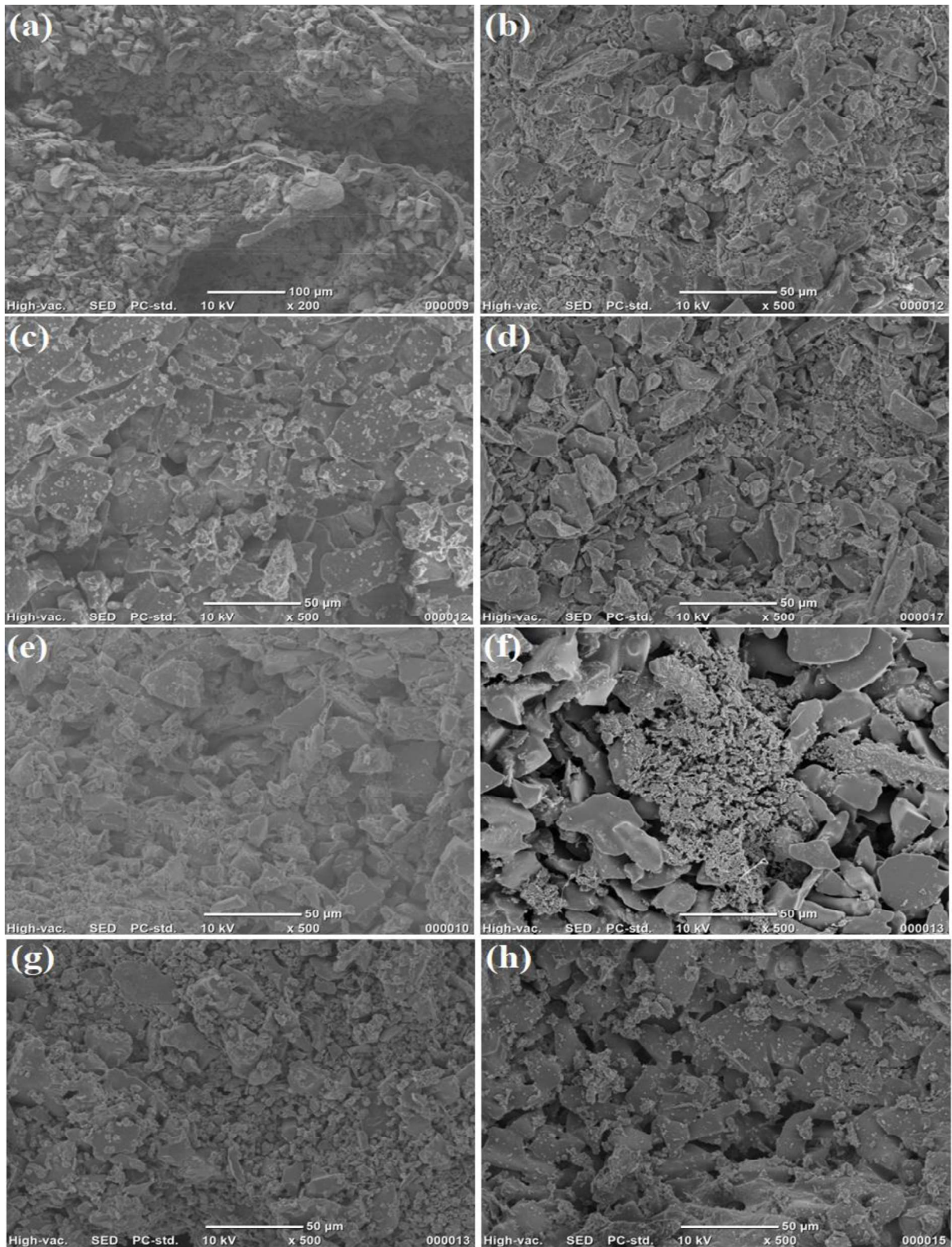


Fig. 7.9 SEM microstructure of SiC foam (a) 5 wt% sucrose, (b) 10 wt% sucrose, (c) 5 wt% MW-5 wt% sucrose, (d) 20 wt% MW-5 wt% sucrose, (e) 5 wt% alumina-10 wt% MW-5 wt% sucrose, (f) 10 wt% alumina-10 wt% MW-5 wt% sucrose, (e) 5 wt% alumina-40 wt% MW-5 wt% sucrose, (f) 10 wt% alumina-40 wt% MW-5 wt% sucrose

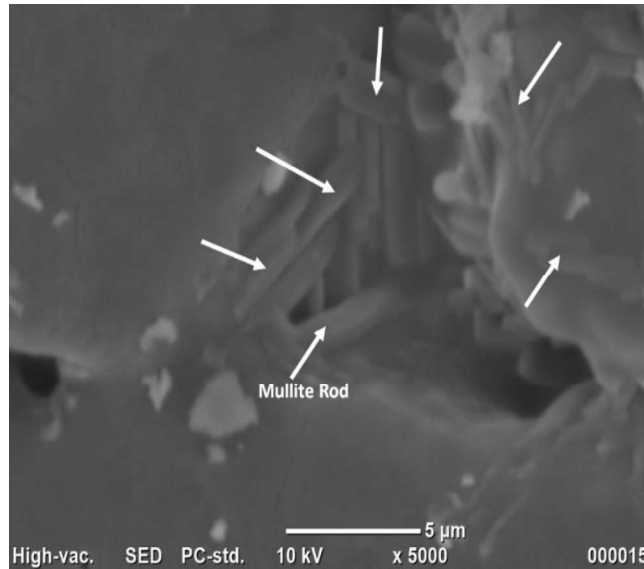


Fig. 7.10 SEM image of SiC foam treated with 5 wt% sucrose, 10 wt% MW, 10 wt% Alumina and sintered at 1400°C, showing development of mullite rods

7.4 Conclusion

The present work is an effort to produce high porosity SiC foams having gradient microstructure comparatively at lower cost using reaction bonding technique. The foaming effect and gradient in pore size are obtained due to thermo-foaming technique by the dehydration of sucrose. Exothermic reaction between sucrose and sulphuric acid generates gases which ultimately helps in foaming. Gradient in pore size is obtained due to the gravitational and viscous effect of SiC slurry. Mullite has been used as a reaction bonding material which is subsequently in-situ obtained during the sintering process. Formation of silica and mullite has comparatively lowered the sintering temperature of silicon carbide, which ultimately lowers the fabrication cost. The in-situ developed mullite phase is obtained due to the reaction between alumina and silica, a major component of coal mine waste. MW is used as a cheap source of aluminosilicate minerals, thereby reducing the material cost in making SiC foams. Further, the addition of alumina helps in better mullitization and hence better bonding of SiC particles. Alumina addition compensates for the extra alumina needed for stoichiometric mullite formation, which was not possible due to the low concentration of alumina in MW. The fabricated functionally graded SiC foams are found to have bulk densities and porosities in the range of 0.6–1.2 g/cm³ and 60–80% respectively. Results demonstrate that the use of MW as a cheap source of aluminosilicate mineral is a promising source for the in-situ development of the mullite phase, which further helps in the bonding of SiC particles comparatively at lower sintering temperatures, thus deliberately reducing high energy consumption and cost.