

Proceedings of the Estonian Academy of Sciences 2025, **74**, 2, 260–265

https://doi.org/10.3176/proc.2025.2.31

www.eap.ee/proceedings Estonian Academy Publishers

ADVANCED CERAMICS, COMBUSTION SYNTHESIS

RESEARCH ARTICLE

Received 3 February 2025 Accepted 23 March 2025 Available online 20 May 2025

Keywords: silica, SHS, SiC, PTFE, microstructure

Corresponding author:

Hasmik Kirakosyan hasmik.kirakosyan@ichph.sci.am

Citation:

Kirakosyan, H., Nazaretyan, Kh., Beglaryan, H., Ivanov, R., Hussainova, I. and Aydinyan, S. 2025. Combustion synthesis of silicon carbide by magnesiocarbothermic reduction of amorphous and crystalline silica. *Proceedings of the Estonian Academy of Sciences*, **74**(2), 260–265.

https://doi.org/10.3176/proc.2025.2.31

© 2025 Authors. This is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0).

Combustion synthesis of silicon carbide by magnesio-carbothermic reduction of amorphous and crystalline silica

Hasmik Kirakosyan^a, Khachik Nazaretyan^a, Hayk Beglaryan^b, Roman Ivanov^b, Irina Hussainova^c and Sofiya Aydinyan^{a,c}

- ^a Laboratory of Macrokinetics of Solid State Reactions, A. B. Nalbandyan Institute of Chemical Physics NAS RA, P. Sevak 5/2, 0014 Yerevan, Armenia
- b Laboratory of the Synthesis of Materials Having Practical Importance from Ultrabasic Rocks and Their Investigation, M. G. Manvelyan Institute of General and Inorganic Chemistry NAS RA, H. Arghutyan 10, 0051 Yerevan, Armenia
- ^c Department of Mechanical and Industrial Engineering, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia

ABSTRACT

Amorphous silica has high potential as a precursor for synthetic applications due to its active and large specific surface area. This work aims to identify the comparative features of the self-propagating high-temperature synthesis (SHS) of silicon carbide obtained by magnesiocarbothermic reduction of amorphous and crystalline silica. It was demonstrated that the synthesis pathway and microstructure depend on the structure of silica or, in other words, on the rate of rupture of Si-O-Si bonds. Moreover, the introduction of small amounts of polytetrafluoroethylene (PTFE) significantly intensifies the combustion reaction and governs the formation of specific microstructural entities, e.g., sheets and nanoflakes. Particularly, when using amorphous silica as a precursor, it is fully reduced, resulting in a higher amount of hightemperature α -SiC compared to samples reduced from crystalline silica. This is expressed by the dominant presence of sheet-like structures in the product, the amount of which significantly increases with the introduction of PTFE into the system. In contrast, in the case of crystalline silica, the combustion is characterized by a comparatively lower temperature and lower yield. Complete reduction of the crystalline silica was possible only if PTFE was added. The fine-grained microstructure of the obtained β -SiC was preserved regardless of the amount of PTFE. According to the results of scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM/EDS) examinations, in both cases, a homogeneous distribution of the constituent elements (Si, C) was observed. The precursor morphology, combustion parameters, and PTFE were found to play a crucial role in tailoring the microstructural characteristics and degree of conversion of the combustion products.

1. Introduction

Silicon carbide (SiC) is a high-performance material known for its exceptional thermal, mechanical, and chemical properties, making it an essential component in various industries, including electronics, abrasives, and aerospace. The outstanding hardness, thermal stability, and resistance to wear and corrosion have led to its widespread use in high-temperature applications and as a semiconductor material [1]. As a result, the development of efficient and scalable methods for SiC synthesis is of great interest to both researchers and industry professionals [2].

Over the years, various methods have been developed for the synthesis of SiC, each with unique advantages and limitations. The traditional approach is the Acheson process, which involves a high-temperature reaction of silica with carbon in an electric furnace [3]. While widely used in industrial applications, this method is energy-intensive and often produces SiC with impurities. Chemical vapor deposition (CVD) offers an alternative for producing high-purity SiC, but it comes with significant cost and complexity, limiting its use to specialized applications, such as semiconductors [4]. Other methods include sol-gel processes [5], self-propagating high-temperature synthesis (SHS) [6], and plasma synthesis [7], each tailored for specific requirements in purity, morphology, or scalability.



Fig. 1. XRD pattern of SiO_2 obtained from serpentine (a) and quartz (b), SEM micrographs of SiO_2 obtained from serpentine (c) and quartz (d).

Among these, SHS has emerged as an effective method for the rapid and energy-efficient preparation of SiC powders [6,8]. Studies have shown that the microstructures of SiC synthesized via SHS are highly dependent on process parameters, such as the type of silicon oxide precursor, carbon source, and the use of additives such as magnesium or aluminum to enhance reactivity [9]. The combustion temperature and heating rate also play a crucial role, influencing grain size, crystallinity, and the presence of residual phases. For instance, higher combustion temperatures generally lead to larger SiC grains with improved crystallinity, while lower temperatures may result in finer particles but a greater likelihood of unreacted intermediates [10]. Additionally, the presence of some additives can enhance reaction kinetics, modify the final morphology, and improve the purity of the synthesized SiC [11]. In particular, the addition of polytetrafluoroethylene (PTFE) has been shown to enable the formation of pure SiC from silicon in both spherical and rod-like microstructures [12].

The microstructure of SiC strongly influences its properties and suitability for various applications. SiC in wire or whisker form, for example, exhibits high tensile strength, excellent thermal stability, and enhanced fracture toughness, making it ideal for reinforcing composites in aerospace and structural applications. On the other hand, SiC powders with a controlled particle size and morphology are preferred for electronic applications, where high purity and uniformity ensure optimal performance. Additionally, the crystallinity and grain size of SiC can impact its thermal conductivity, hardness, and resistance to wear, all of which are critical in industrial and cutting-edge technologies [13,14].

This research aims to explore the combustion preparation of SiC using magnesio-carbothermic reduction of silica of various origins [15]. The coupling of the endothermic reduction reaction (SiO₂ + C) with a high-caloric (SiO₂ + Mg) one allowed the execution of a moderate and controllable combustion reaction (the so-called thermal-kinetic coupling) [11]. The focus lies in understanding the influence of precursor morphology, the combustion parameters, and the role of additives such as PTFE on the degree of conversion and the process of microstructure evolution.

2. Experimental section

The synthesis was conducted using two distinct forms of silicon oxide, amorphous and crystalline-structured. The amorphous silica (99.8% purity, particle size <200 nm) (SiO₂(I)) was derived from a serpentine mineral [16], and the crystalline silica was sourced from quartz (99.8% purity, particle size <40 μ m) (SiO₂(II)). The significant structural differences between these two forms were validated through X-ray diffraction (XRD) (Fig. 1a,b) and microstructural analyses (Fig. 1c,d).

Magnesium (MPF-3, Russia, particle size 0.1-0.18 mm) and carbon (P-803, Russia, particle size $<0.1 \mu$ m, pure grade) were used as reducers. PTFE (Sigma-Aldrich Co. LLC, $(C_2F_4)_n$, FT-4, particle size $<10 \mu$ m, pure grade) was incorporated as needed to achieve microstructural modifications in the final product (wt%). Cylindrical pressed samples were prepared from powdered mixtures of the initial materials for the combustion process. The samples had a density of $1-1.5 \text{ g/cm}^3$, a diameter of 20 mm, and a height of 50–60 mm. Compression was performed under a force of ~140 MPa to achieve the desired form and density.

The combustion process was carried out in an argon atmosphere (purity 99.98%) under a pressure of 5 atm. The ignition was achieved by short-duration heating of a tungsten coil. The temperature-time history was recorded using two



Fig. 2. XRD patterns of the combustion products of the $SiO_2(I) + 2Mg + C + x$ wt% PTFE (a) and $SiO_2(I) + 2Mg + yC + 1$ wt% PTFE (b) mixtures.

tungsten-rhenium thermocouples placed 10 mm deep within the sample and spaced 15-20 mm apart.

The products contained SiC and a secondary byproduct, magnesium oxide (MgO). To remove MgO, the product was leached with a 20 wt% hydrochloric acid (HCl) solution at 150 °C, as per the reaction:

$$MgO + 2HCl \rightarrow MgCl_2 + H_2O.$$

Excess HCl (10% above stoichiometric requirements) was used, followed by washing with distilled water. Chloride ion absence was verified with silver nitrate (AgNO₃). The purified product was then dried in a vacuum oven at 110 °C and prepared for further analysis.

3. Results and discussion

3.1. SiO₂(I)-Mg-C system

Combustion of a stoichiometric mixture $\text{SiO}_2(\text{I}) + 2\text{Mg} + \text{C}$ resulted in a favorable combustion temperature (1550 °C) for the formation of SiC. However, a small amount of silicon was also observed as a byproduct (Fig. 2a, x = 0), caused by magnesium evaporation at a higher temperature ($\text{T}_{b} = 1090$ °C). The addition of 1 wt% PTFE to this mixture did not significantly affect the combustion temperature (1560 °C) but increased the combustion velocity (from 0.45 to 0.6 cm/s) and led to the formation of almost pure SiC (Fig. 2a, x = 1). Further increase in the PTFE content again resulted in the appearance of silicon (Fig. 2a, x = 2). Considering the combustion temperature, velocity, and product composition, the optimal PTFE content was chosen to be 1 wt%, ensuring efficient SiC formation without silicon byproducts.

The increase in combustion velocity and temperature stability with PTFE addition is linked to kinetic coupling. Fluorine generated during PTFE decomposition reacts with silicon to form gaseous silicon fluoride (SiF_4) [11]. The transport of this gaseous phase accelerates the interaction between silicon and carbon.

In all cases, the XRD patterns revealed a broad, lowintensity band in the 2θ range of 20° to 30° , which indicates an excess of carbon in the product. To address this, the free carbon content was reduced in the SiO₂(I) + 2Mg + yC + 1 wt% PTFE mixture by the amount of carbon contained in PTFE (y = 1- Δ x). As a result, while the intensity of the carbonrelated band decreased, the formation of residual silicon was still observed in the product (Fig. 2b). The mixture of α - and β -SiC was obtained, with the dominance of the beta phase. The Rietveld refinement of the sample, when x = 1 and y = 1- Δ x, shows that the material consists of slightly more β -SiC (53.3%) than α -SiC (46.7%). However, the amount of α -SiC increases with increasing the PTFE amount in the initial mixture.

The effect of PTFE addition was obvious also on the microstructure of the product (Fig. 3), expressed by the presence of sheet-like structures in the product, the amounts of which significantly increase with the introduction of PTFE into the system.

3.2. SiO₂(II)-Mg-C system

In the SiO₂(II)–Mg–C system, utilizing quartz sand as the raw material, the combustion of the stoichiometric mixture resulted in a comparatively lower combustion temperature of 1430 °C (Fig. 4a, x = 0, y = 1). Consequently, partial carbothermic reduction of silicon dioxide is observed, and the product contains unreacted silicon dioxide as a byproduct (Fig. 4b, x = 0, y = 1, without PTFE).

The addition of 1 wt% PTFE to the mixture (Fig. 4a, x = 1) resulted in a significant increase in the combustion parameters ($T_c = 1570$ °C, $U_c = 1.7$ cm/s) and complete magnesio-carbothermic conversion. The product contains trace amounts of unreacted silicon (Fig. 4b, x = 1, y = 1). The progressive increase in reaction rate upon the addition of PTFE can be attributed to the kinetic coupling.

Decreasing the amount of carbon in the initial mixture $(y = 1-\Delta x)$ or, in other words, maintaining stoichiometry at the expense of carbon contained in 1 wt% PTFE (Fig. 4b, $x = 1, y = 1-\Delta x$), pure SiC was produced. Moreover, in this case, the Rietveld refinement reveals that the sample (x = 1, $y = 1-\Delta x$) contains a much higher amount of β -SiC (71%) compared to α -SiC (29%).

The quartz-derived product mainly contains β -SiC with fine-grained, nanoparticle-sized features (Fig. 5a) and an



Fig. 3. Microstructure of the combustion products of the SiO₂(I) + 2Mg + yC + x wt% PTFE system after acid treatment, depending on the PTFE content: x = 0, y = 1 (a), x = 1, y = 1 (b), x = 1, $y = 1-\Delta x$ (c), and the EDS analysis result when x = 1, $y = 1-\Delta x$ (d).



Fig. 4. Thermograms of the combustion process and XRD patterns of the products obtained from the SiO₂(II) + Mg + yC + x wt% PTFE mixtures (x = 0, y = 1; x = 1, y = 1; x = 1, y = 1- Δ x), depending on the amount of carbon and PTFE.

almost even distribution of the component elements (Si, C) (Fig. 5b).

The final products obtained from silica of various origins contain different amounts of alfa-beta phases and exhibit significantly different microstructures. Sheet-like structures were predominantly present in the SiC obtained from amorphous serpentine, while flake-like nanostructures were observed in the quartz-derived SiC during the comparatively fast combustion reaction. These insights underscore the importance of precursor selection and additive incorporation in optimizing the combustion synthesis of SiC with a specific microstructure.



Fig. 5. Microstructure of the combustion products from the SiO₂(II) + 2Mg + $(1-\Delta x)C + 1$ wt% PTFE mixture: after acid treatment (a) and EDS analysis results (b).

4. Conclusions

- 1. The structure of the initial silicon oxide precursor, whether amorphous (SiO₂(I)) or crystalline (SiO₂(II)), significantly influences the combustion parameters and reaction yield.
- 2. The introduction of small amounts of polytetrafluoroethylene (PTFE) accelerates the combustion process and contributes to complete reduction.
- 3. The ratio of the alfa-beta phases is sensitive to the silica precursor type, the initial mixture composition, and the combustion parameters.
- 4. The microstructure of silicon carbide (SiC) can be tuned using silica of various origins. The amorphous silica precursor leads to the formation of sheet-like SiC structures, while the crystalline silica precursor produces a finegrained SiC.

Data availability statement

All research data are contained within the article and can be shared upon request from the authors.

Acknowledgments

This work was supported by the Committee of Science of the Ministry of Education, Science, Culture and Sports of the Republic of Armenia (grant No. 23LCG-2F001), the Hovnanyan Family Foundation, and the Estonian Research Council (grants No. PSG220 and No. PRG643). The publication costs of this article were partially covered by the Estonian Academy of Sciences.

References

- Sun, K., Wang, T., Gong, W., Lu, W., He, X., Eddings, E. G. et al. Synthesis and potential applications of silicon carbide nanomaterials/nanocomposites. *Ceram. Int.*, 2022, 48(22), 32571– 32587. https://doi.org/10.1016/j.ceramint.2022.07.204
- Maboudian, R., Carraro, C., Senesky, D. G. and Roper, C. S. Advances in silicon carbide science and technology at the microand nanoscales. *J. Vac. Sci. Technol. A*, 2013, **31**(5), 050805. https://doi.org/10.1116/1.4807902
- Kumar, P. V., Gupta, G. S. Study of formation of silicon carbide in the Acheson process. *Steel Res.*, 2002, 73(2), 31–38. https:// doi.org/10.1002/srin.200200170
- Xu, Y., Cheng, L. and Zhang, L. Composition, microstructure, and thermal stability of silicon carbide chemical vapor deposited

at low temperatures. *J. Mater. Process. Technol.*, 2000, **101**(1–3), 47–51. https://doi.org/10.1016/S0924-0136(00)00428-3

- Kirakosyan, H., Nazaretyan, K., Amirkhanyan, N., Beglaryan, H. and Aydinyan, S. A novel pathway of solution combustion synthesis of silicon carbide and SiC based composite whiskers. *AIP Conf. Proc.*, 2024, **2989**(1), 040009. https://doi.org/10.10 63/5.0189204
- Mukasyan, A. S. Combustion synthesis of silicon carbide. In *Properties and Applications of Silicon Carbide* (Gerhardt, R., ed.). InTech, 2011, 389–409. https://doi.org/10.5772/15620
- Rai, P., Park, J.-S., Park, G.-G., Lee, W.-M., Yu, Y.-T., Kang, S.-K. et al. Influence of carbon precursors on thermal plasma assisted synthesis of SiC nanoparticles. *Adv. Powder Technol.*, 2014, 25(2), 640–646. https://doi.org/10.1016/j.apt.2013.10.004
- Moskovskikh, D. O., Mukasyan, A. S. and Rogachev, A. S. Selfpropagating high-temperature synthesis of silicon carbide nanopowders. *Dokl. Phys. Chem.*, 2013, 449(1), 41–43. https://doi.org/ 10.1134/S0012501613030032
- Zhang, J., Jeong, J. C., Lee, J. H., Won, C. W., Kim, D. J. and Kim, C. O. The effect of carbon sources and activative additive on the formation of SiC powder in combustion reaction. *Mater. Res. Bull.*, 2002, **37**(2), 319–329. https://doi.org/10.1016/S0025-5408(01)00770-X
- Mukasyan, A. S., Lin, Y.-C., Rogachev, A. S. and Moskovskikh, D. O. Direct combustion synthesis of silicon carbide nanopowder from the elements. *J. Am. Ceram. Soc.*, 2013, 96(1), 111–117. https://doi.org/10.1111/jace.12107
- Kharatyan, S. L. and Merzhanov, A. G. Coupled SHS reactions as a useful tool for synthesis of materials: an overview. *Int. J. Self-Propag. High-Temp. Synth.*, 2012, 21, 59–73. https://doi.org/ 10.3103/S1061386212010074
- Amirkhanyan, N., Kirakosyan, H., Zakaryan, M., Zurnachyan, A., Rodriguez, M. A., Abovyan, L. et al. Sintering of silicon carbide obtained by combustion synthesis. *Ceram. Int.*, 2023, 49(15), 26129–26134. https://doi.org/10.1016/j.ceramint.2023.04.233
- Wang, X., Gao, X., Zhang, Z., Cheng, L., Ma, H. and Yang, W. Advances in modifications and high-temperature applications of silicon carbide ceramic matrix composites in aerospace: a focused review. *J. Eur. Ceram. Soc.*, 2021, 41(9), 4671–4688. https://doi.org/10.1016/j.jeurceramsoc.2021.03.051
- Wang, Y., Dong, S., Li, X., Hong, C. and Zhang, X. Synthesis, properties, and multifarious applications of SiC nanoparticles: a review. *Ceram. Int.*, 2022, 48(7), 8882–8913. https://doi.org/ 10.1016/j.ceramint.2021.12.208
- Yermekova, Z., Mansurov, Z. and Mukasyan, A. Influence of precursor morphology on the microstructure of silicon carbide nanopowder produced by combustion syntheses. *Ceram. Int.*, 2010, 36(8), 2297–2305. https://doi.org/10.1016/j.ceramint.2010.07.032
- Zulumyan, N. O., Isaakyan, A. R., Pirumyan, P. A. and Beglaryan, A. A. The structural characteristics of amorphous silicas. *Russ. J. Phys. Chem.*, 2010, 84, 700–702. https://doi.org/ 10.1134/S003602441004031X

Ränikarbiidi põletamise süntees amorfse ja kristalse ränidioksiidi magnesiokarbotermilise redutseerimise teel

Hasmik Kirakosyan, Khachik Nazaretyan, Hayk Beglaryan, Roman Ivanov, Irina Hussainova ja Sofiya Aydinyan

Amorfse ränidioksiidi suur potentsiaal tänu selle aktiivsele ja suurele eripinnale teeb sellest sobiva lähteaine sünteetilisteks rakendusteks. Uurimistöö eesmärk on tuvastada ränikarbiidi iseleviva kõrgetemperatuurilise sünteesi võrdlevad tunnused, mis on saadud amorfse ja kristalse ränidioksiidi magnesiokarbotermilisel redutseerimisel. Uuringus näidatakse, et sünteesirada ja mikrostruktuur sõltuvad ränidioksiidi struktuurist ehk teisisõnu Si–O–Si-sidemete rebenemise kiirusest. Lisaks leitakse, et väikese koguse polütetrafluoroetüleeni (PTFE) lisamine intensiivistab oluliselt põlemisreaktsiooni ja võimaldab spetsiifiliste mikrostruktuursete üksuste, nt lehtede või nanohelveste, moodustumist. Eriti amorfse ränidioksiidi puhul toimub selle täielik redutseerimine, mistõttu on kõrgel temperatuuril moodustuv α -SiC kogus suurem kui kristalse ränidioksiidi põlemist suhteliselt madalam temperatuur ja väiksem saagis. Kristalse ränidioksiidi täielik redutseerimine on võimalik ainult PTFE lisamisel. Saadud β -SiC peeneteraline mikrostruktuur säilib sõltumata PTFE kogusest. SEM/EDS-analüüsi kohaselt täheldatakse mõlemal juhul koostisosade (Si, C) homogeenset jaotust. Leitakse, et lähteaine morfoloogia, põlemisparameetrid ja PTFE mängivad olulist rolli põlemisproduktide mikrostruktuuri omaduste ja muundumisastme kohandamisel.