

**COMBUSTION SYNTHESIS OF SILICON CARBIDE.
ROLE OF THERMAL AND KINETIC ACTIVATION**

A. A. HAMBARTSUMYAN

A.B. Nalbandyan Institute of Chemical Physics NAS RA
5/2, P. Sevak Str., Yerevan, 0014, Armenia
E-mail: hamarmin@list.ru

Due to unique properties such as high melting point, excellent oxidation resistance, moderate density, etc. silicon carbide (SiC) is very attractive for structural applications especially if high-temperature resistance is required. In this work possibility of synthesis the SiC is explored using thermal and kinetic activation approaches. These two methods are combined to ensure steady-state combustion process and simultaneously to control phase and microstructure formation. The green mixture generally can be represented as $\text{Si} + \text{C} + k(\text{SiO}_2 + \text{Mg} + \text{C}) + m\text{PTFE}$ where k represents thermal promoter part while m is responsible for kinetic activation. So changing these variables allows to estimate influence of singular promoters or their combined affect on the combustion, phase and microstructure formation laws. It is established the optimum combustion ranges where it is possible to synthesize products with certain composition and microstructure. The final products are treated by acid solution to leach out a by-product (magnesia). The end products are examined using XRD, SEM techniques.

Fig. 7, ref. 17.

Silicon carbide is a remarkable representative of advanced structural ceramics and has a wide application in modern industry due to its extraordinary physico-mechanical properties i.e. low coefficient of thermal expansion, high chemical stability and wear resistance, high thermal shock resistance, thermal conductivity, low electrical resistance, etc. [1-4]. Moreover due to its excellent compatibility with other ceramic materials, silicon carbide considers as reinforcement for several composite and metallic matrix (e.g. $\text{MoSi}_2\text{-SiC}$, $\text{WSi}_2\text{-SiC}$, $\text{B}_4\text{C-SiC}$, etc.). Nowadays, silicon carbide is being synthesized via different methods such as CVD, plasma, laser techniques, etc. The main drawback of these methods is their high price and low productivity. Currently main production technique of the silicon carbide is carbo-thermal reduction method [5].

However this method is time and energy consuming and the obtained products commonly are contaminated.

The main goal of this work is twofold: i) to synthesize silicon carbide utilizing high effective self-propagating high-temperature synthesis (SHS) method (also so-called combustion synthesis) and ii) to control phase and microstructure formation of final products. The basic principle of the SHS is direct interaction of compounds under the combustion mode [6-9]. It is well known, that combustion synthesis of silicon carbide by direct interaction of elements (Si+C) is impossible because of insufficient energy reserve ($\Delta H_{298}^{\circ} = -17.18 \text{ kkal/mol}$, $T_{ad} \approx 1870\text{K}$). In the literature it is widely manipulated synthesis of silicon carbide under combustion mode simultaneously controlling microstructure of end-product. In this end activation approaches are used to fulfill successful synthesis. These activation approaches are applied to eliminate diffusion issues in the system under study. Below it is listed most common activation approaches:

Thermal activation [10-12] – this one has two sub-approaches 1) *Preheating approach*, when initial mixture is previously heated up to certain temperature ($\sim 700^{\circ}\text{C}$), then the combustion reaction is ignited. 2) *Using a supporting reaction* – in this case main reaction occurs due to heat released from another high exothermic reaction,

Electric field assisted combustion synthesis [13,14];

- **Chemical activation method** – in this case certain compounds, such as halogen containing organic substances (e.g. polytetrafluoroethylene: PTFE) or oxygen containing inorganic compounds (e.g. KClO_3) are used as active additives. Usually even insignificant amount of these compounds promote the combustion process allowing to perform combustion reaction even in the systems having low energetic recourses. Mainly these compound(s) are reacting with one (or more) of the main reactants releasing significant amount of heat or/and gaseous compounds. These gases promote mass-transfer processes [15] and make possible to fulfill the combustion process. For instance, in the [16] as promoter the polytetrafluoroethylene (PTFE) was explored. It was manifested that PTFE has both thermal and kinetic activation role and in order to perform steady-state combustion, the nominal amount of the PTFE should be no less than $\sim 15 \text{ wt\%}$. In this case another drawback to be emphasized is high pressure requirement (no less than 30atm) [16].

In this work it is pursuing the goal to reduce the required amount of PTFE and ambient gas pressure. In this end it is suggested to explore combined effect of two activation methods on the combustion and phase formation laws. Moreover it is explored possibility to control microstructure of synthesized products.

The main composition of green mixture is $\text{Si-C-}k(\text{SiO}_2\text{-}2\text{Mg-C})\text{-mPTFE}$ where *k* part is responsible for thermal activation while *m* part is kinetic one. It is assumed that in the Si-C-PTFE system amount of promoter can be reduced if some additional high exothermic reaction would be take place. As additional source of heat the $\text{SiO}_2\text{-}2\text{Mg-C}$ system is chosen because it is highly exothermic ($T_{ad}=2060^{\circ}\text{C}$) reaction and in this case silicon carbide and magnesia are formed. The magnesia can be easily removed by acid treatment while silicon carbide is the target product. Moreover some part of silicon can be replaced by silicon oxide which can significantly decrease price of end-product.

In this work influence of these factors on the combustion, phase and microstructure formation laws are explored.

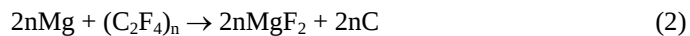
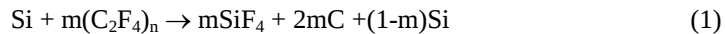
Experimental

The experiments were performed in a constant pressure reactor (with working volume 3 l) in the argon (99.5% purity) atmosphere at gas pressure from 1 to 50 atm. A silicon powder of the KR-1 trademark (98% purity, Fe <0.7%, Al<0.7, Ca<0.6; 90% $\mu<14 \mu m$, specific surface area $3.9 m^2/g$), carbon black of the P-803 trademark (specific surface area $36 m^2/g$), grinded silica (99% purity, $\mu<15 \mu m$), MPF-3 trademark powdered magnesium (99.7 % purity) and as an active additive powdered PTFE (FT-4 trademark, with particle size less than $15 \mu m$) were used. Cylindrical pellets were prepared (30 mm in diameter, 40-50 mm height, with $0.9-1 g/cm^3$ density) from the mixture of initial reagents (**k** and **m** factors are changed in the range 0-60 and 0-15%, respectively). Then they were placed into the reactor which is evacuated, purged and pressurized with argon prior to the ignition. The combustion is initiated from the top of the pellet by an electrically incandescent tungsten spiral. The combustion temperature (T_c) is registered by tungsten-rhenium (W-5%Re/W-20%Re) thermocouples $200 \mu m$ in diameter. The average velocity of combustion wave propagation (U_c) was determined from the signals of thermocouples embedded in different heights of the sample. The product subjected to grinding and was washed from MgO, with a 5-10% solution of hydrochloric acid under mixing condition at room temperature. And then washing was continued with distilled water until all chlorine ions had disappeared. The phase composition of products was determined by X-ray analyses (diffractometer DRON-3.0), and chemical examinations are performed to determine the amount of remained silicon. A scanning electron microscope (BS-300) is used to examine the microstructure of initial reagents and products obtained.

Results and discussion

Thermodynamic analysis. For estimating the value of adiabatic combustion temperature (T_{ad}) and equilibrium composition of the final products, preliminary thermodynamic analyses of the Si-C-**k**(SiO₂-2Mg-C)-**m**PTFE system where **k** and **m** are molar coefficients, are performed using the ISMAN-THERMO software developed for multicomponent heterophase systems [17]. Generated results are plotted in the figure 1 where adiabatic temperatures vs. **m** and **k** factors are illustrated.

The calculations showed that in the Si-C-PTFE-SiO₂-2Mg system varying amount of promoters the combustion undergoes in difference pathways. Thus, depending on **k** and **m** values, Si reacts with PTFE according to reaction (1), simultaneously the reactions (2) and (3) may take place as well. It is worth noting that increasing amount of **k** leads to increasing the contribution of reaction (3).



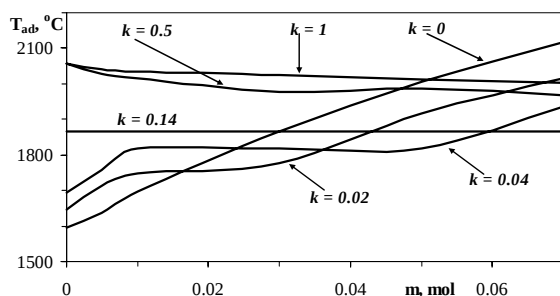


Fig. 1. Adiabatic combustion temperatures for the Si-C- $k(\text{SiO}_2\text{-}2\text{Mg-C})$ - m PFTE system vs. m and k values.

All of these reactions are highly exothermic and released heat supports to the Si-C reaction. The T_{ad} reaches up to 1800°C and mainly silicon carbide is formed. However certain amount of MgO and MgF_2 phases are formed as well. It must be underlined that in this case formed magnesia and silica also may react each with other yielding silicate. This reaction is strongly undesired and it should be eliminated. It means that there is certain restriction for usage of the $(\text{SiO}_2\text{-}2\text{Mg-C})$ mixture as promoter.

Combustion and phase formation laws of the Si-C- $k(\text{SiO}_2\text{-}2\text{Mg-C})$ system. In order to obtain better understanding of combustion characteristics in the system under study firstly it is explored combustion laws for thermally activated mixture presented as Si-C- $k(\text{SiO}_2\text{-}2\text{Mg-C})$ system. It is shown (fig. 2) that the combustion limit is appeared when amount of activator is less than $k < 0.5$ (60 %). Increasing the k value on the curves of the combustion parameters the maxima is appeared. The maximum values were registered when $k=1.2$. Further increasing k results in decreasing the combustion parameters. One can assume that firstly k acts as thermal activator while at high amount of k formed magnesia reacts with silica yielding silicate. Based on data obtained further investigations are performed in the systems where amount of k does not exceed 1.

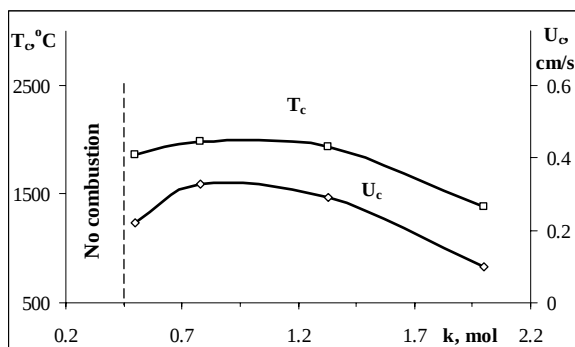


Fig. 2. Combustion parameters vs. k factor for the Si-C- $k(\text{SiO}_2\text{-}2\text{Mg-C})$ system; $P_{\text{Ar}}=5 \text{ atm}$.

According to the XRD analysis (fig. 3) pure silicon carbide is obtained when $k=0.5$ and 1 (after acid treatment).

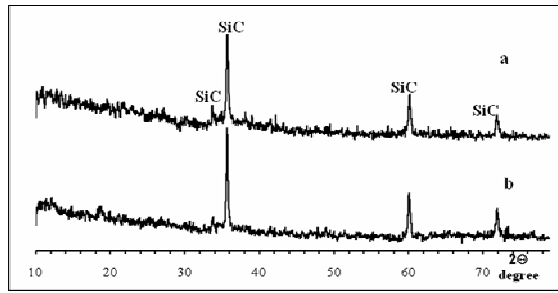


Fig. 3. XRD patterns of combustion products for a) (Si+C)-1.0(SiO₂+2Mg+C) and b) (Si+C)-0.5(SiO₂+2Mg+C) systems; $P_{Ar}=5 \text{ atm}$.

The SEM analysis shows that the products are mainly agglomerated and the size of agglomerates is varying within 20-40 μm range (fig. 4).

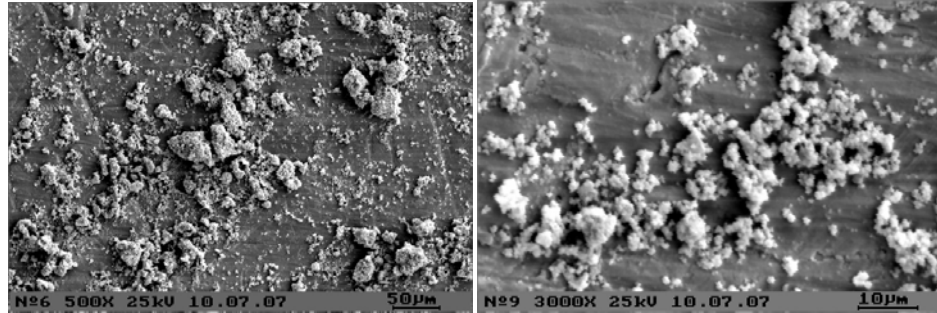


Fig. 4. The SEM images of combustion products for the (Si+C)+0.5(SiO₂+2Mg+C) system; $P_{Ar}=5 \text{ atm}$.

To control microstructure and depress formation of silicate it is investigated combined influence of thermal and kinetic promoters on the combustion, phase and microstructure formation laws. In this end it is explored the (Si+C)- k (SiO₂+2Mg+C)- m PTFE system varying amount of k and m values. As can be seen from fig. 5, increasing the k and m values lead to increasing the combustion temperature.

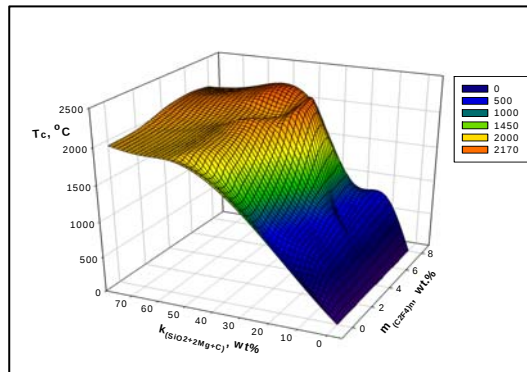


Fig. 5. Combustion temperature vs. k and m factors for the (Si+C)- k (SiO₂+2Mg+C) – m PTFE system. $P = 5 \text{ atm}$.

Based on results of thermodynamic analyses, it is plotted the temperature surface vs. k and m values and three regions are established:

First, when $T_{ad} < 500^\circ\text{C}$, there is no combustion

Low temperature combustion regime: in this case characteristic temperature varies within 500-1100°C range. In this range only Si+PTEF reaction took place according to the reaction (1).

High-temperature regimes: during this mode temperature mostly rises up to 1800-2000°C, in this case Si+C and Mg+SiO₂ primary reactions take place (fig.5).

It is worthy noting that sharp increases the velocity of the combustion front confirms evidence of gas-phase reactions (fig.6). One can expect that obtained products would have fine microstructure.

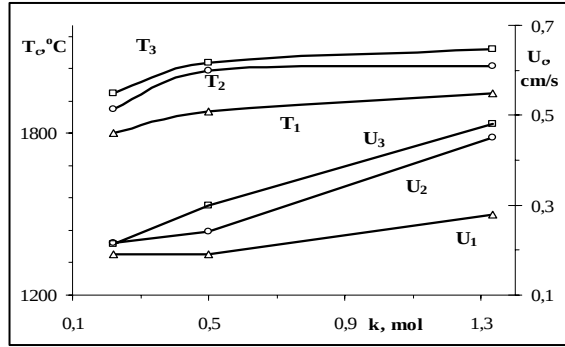


Fig. 6. Combustion parameters vs. k & m for Si+C k (SiO₂+2Mg+C)- m PTFE system. m =2 wt % (T₁,U₁), 4 wt.% (T₂,U₂), and 6 wt. % (T₃,U₃); P = 5 atm.

In general, tuning the promoters' amount and ratio it is possible to control the combustion process and govern microstructure. Thus, the microstructure analysis establishes that obtained products have relatively small grain size when combined activators were used. The large particles basically are agglomerates with 20 μ m sizes mainly consisting of small grains having ~1-5 μ m particle size (fig. 7).

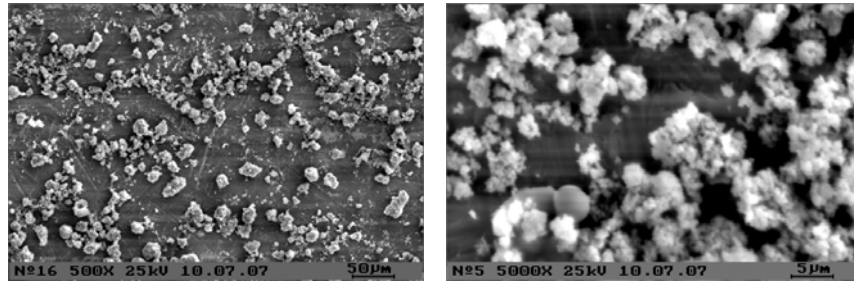


Fig. 7. Microstructure of combustion product for Si+C+0.11(SiO₂+2Mg+C)+0.034PTFE system.

As a result it is established optimal amount of active additives. Thus in order to perform steady-state combustion, the k and m values in the Si-C- k (SiO₂-2Mg-C)- m PTFE system should be: when k =0.22 mol (40 wt.%) then the m must be no less than 0.028 mol (4 wt.%). If amount of k decreases up to m =0.016 mol, then k should be no less than 0.33 mol (50 wt.%).

Conclusion

It is established that combining thermal and kinetic activation methods allows to synthesize silicon carbide with fine grain sizes (average $\sim 1-5 \mu m$). It is proven that in the $Si+C-k(SiO_2+2Mg+C)-mPTEF$ systems the $(2Mg-SiO_2-C)$ mixture acts as thermal activator while PTFE acts as kinetic promoter. Using $(2Mg-SiO_2-C)$ mixture make possible to cut off the amount of PTFE up to 3-4 time while using PTFE prevents formation the silicates.

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Պ. Սևակի փող., 5/2, 0014 Երևան, Հայաստան
E-mail: hamarmin@list.ru

Սույն աշխատանքում ուսումնասիրվել է SiC-ի ստացման հնարավորությունն այրման ռեժիմում՝ ջերմային և կինետիկական ակտիվացման եղանակների համատեղ ազդեցության պայմաններում: Համադրելով ակտիվացման երկու եղանակները, խնդիր է դրվել կարգավորել այրման պրոցեսը և ղեկավարել ստացվող վերջանյութերի միկրոկառուցվածքն ու ֆազային բաղադրությունը: Որպես հենքային ընտրվել և ուսումնասիրվել է $Si+C+k(SiO_2+Mg+C)+mPTEF$ ելային բովախառնուրդը, որտեղ k և m մեծությունները փոփոխելով հնարավոր է գնահատել նշված երկու ակտիվացման եղանակների՝ ինչպես առանձին, այնպես էլ համատեղ ազդեցությունն այրման և միկրոկառուցվածքի ձևավորման օրինաչափությունների վրա: Ստացված արդյունքների հիման վրա ընտրվել են SiC-ի ստացման օպտիմալ պայմաններն այրման ռեժիմում:

СИНТЕЗ КАРБИДА КРЕМНИЯ В РЕЖИМЕ ГОРЕНИЯ. ВЛИЯНИЕ КИНЕТИЧЕСКОЙ И ТЕРМИЧЕСКОЙ АКТИВАЦИИ

А. А. АМБАРЦУМЯН

Институт химической физики им. А.Б. Налбандяна НАН Республики Армения
Армения, Ереван, 0014, ул. П. Севака, 5/2
E-mail: hamarmin@list.ru

Благодаря уникальным свойствам карбид кремния широко применяется во многих областях современной техники. В работе исследована возможность синтеза в режиме горения SiC в условиях одновременной термической и кинетической активации. Цель подобного сочетания двух методов активации – возможность управления параметрами горения, а также регулирование микроструктуры и фазового состава получаемых продуктов. В качестве базовой выбрана смесь $Si+C+k(SiO_2+2Mg+C)+m(C_2F_4)_n$. Влияние каждого отдельного типа актива-

ции, а также их совокупное влияние на параметры горения, микроструктуру и фазовый состав полученных продуктов исследовались изменением параметров k и m . Определены оптимальные условия синтеза порошка SiC. С целью удаления окиси магния полученные продукты подвергались кислотной обработке.

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