

Combustion Synthesis of Silicon Carbide

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1. Introduction

Combustion synthesis (CS) is an effective technique to produce a wide variety of advanced materials that include powders and net shape products of ceramics, intermetallics, composites and functionally graded materials. This method was discovered in the beginning of 1970's in the former Soviet Union (Merzhanov & Borovinskaya, 1972), and the development of this technique has led to the appearance of a new material science related scientific direction. There are two modes by which combustion synthesis can occur: *self-propagating high-temperature synthesis* (SHS) and *volume combustion synthesis* (VCS). A schematic diagram of these modes is shown in Figure 1. In both cases, reactants may be in the form of loose powder mixture or be pressed into a pellet. The samples are then heated by an external source (e.g. tungsten coil, laser) either locally (SHS) or uniformly (VCS) to initiate an exothermic reaction.

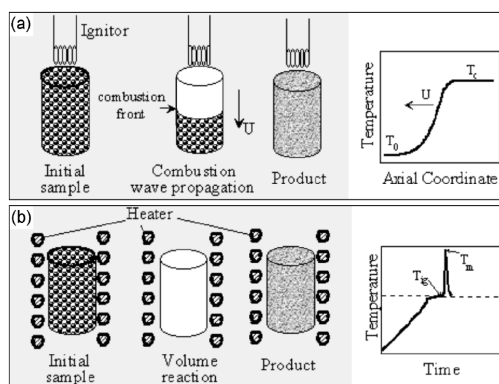


Fig. 1. Two modes for CS of materials (a) SHS; (b) VCS

The characteristic feature of the SHS mode (Fig.1a) is that locally initiated, the self-sustained reaction rapidly propagates in the form of a reaction wave through the heterogeneous mixture of reactants. The temperature of the wave front typically has quite high values (2000-4000 K). If the physico-chemical parameters of the medium, along with the chemical kinetics in the considered system are known, one may calculate the combustion velocity and

reaction rate throughout the mixture. Thus, the SHS mode can be considered as a well-organized wave-like propagation of the exothermic chemical reaction through a heterogeneous medium, which leads to synthesis of desired materials.

During volume combustion synthesis (VCS) mode (Fig.1b), the entire sample is heated uniformly in a controlled manner until the reaction occurs simultaneously throughout the volume. This mode of synthesis is more appropriate for weakly exothermic reactions that require preheating prior to ignition, and is sometimes referred to as the *thermal explosion* mode. However, the term "*explosion*" used in this context refers to the rapid rise in temperature (see insert in Fig.1b) after the reaction has been initiated, and not the destructive process usually associated with detonation or shock waves. For this reason, volume combustion synthesis is perhaps a more appropriate name for this mode of synthesis (Varma et.al, 1998).

Figure 2 represents the sequence of operations necessary for CS technology. The dried powders of required reactants (e.g. silicon and carbon) in the appropriate ratio are wet mixed for several hours to reach the highly homogeneous condition. Thus prepared green mixture is loaded inside the reactor, which is then sealed and evacuated by a vacuum pump. After this, the reactor is filled with inert or reactive gas (Ar, N₂, air). A constant flow of gas can also be supplied at a rate such that it permeates through the porous reactant mixture.

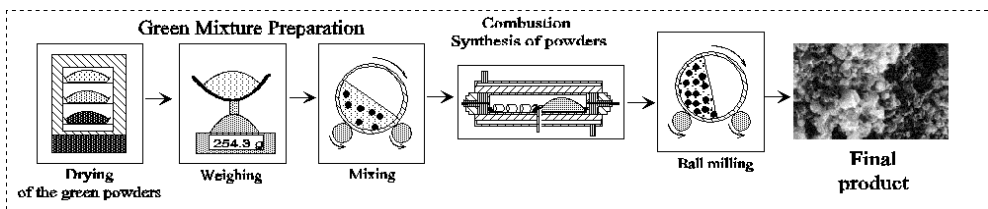


Fig. 2. The general scheme for SHS synthesis of refractory compounds

The design of a typical commercial reactor for large-scale production of materials is shown in Figure 3. Typically, it is a thick-walled stainless-steel water-cooled cylinder with volume up to 30 liters. The inner surface of the reactor is lined by graphite during SHS of carbides. Local reaction initiation is typically accomplished by hot tungsten wire. After synthesis product can be milled and sieved for desired fractions.

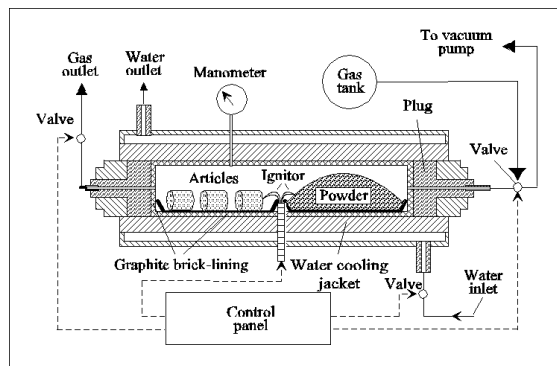


Fig. 3. Schematics of the SHS - reactor

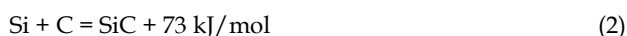
The CS method has several advantages over traditional powder metallurgical technologies (Merzhanov, 2004). These advantages include (i) short (~minutes) synthesis time; (ii) energy saving, since the internal system chemical energy is primarily used for material production; (iii) simple technological equipment; (iv) ability to produce high purity products, since the extremely high-temperature conditions (up to 4000 K), which take place in the combustion wave, burn off most of the impurities. This approach also offers the possibilities for nanomaterials production (Merzhanov et al, 2005; Aruna & Mukasyan, 2008). The number and variety of products produced by CS has increased rapidly during recent years and currently exceeds several thousands of different compounds. Specifically, these materials include carbides (TiC, ZrC, B₄C, etc.), borides (TiB₂, ZrB₂, MoB₂, etc.), silicides (Ti₅Si₃, TiSi₂, MoSi₂, etc.), nitrides (TiN, ZrN, Si₃N₄, BN, AlN), oxides (ferrites, perovskites, zirconia, etc.), intermetallics (NiAl, TiNi, TiAl, CoAl, etc.) as well as their composites. The principles and prospects of CS as a technique for advanced materials production are presented in various reviews and books (Munir & Anselmi-Tamburini, 1989; Moore & Feng, 1995; Varma et al, 1998; Merzhanov, 2004; Merzhanov & Mukasyan 2007, Mukasyan & Martirosyan, 2007). In this chapter the focus is on the combustion synthesis of silicon carbide (SiC), which due to its unique properties is an attractive material for variety of applications, including advanced high temperature ceramics, microelectronics, and abrasive industry.

2. Combustion Synthesis of Silicon Carbide from the Elements

From the viewpoint of chemical nature, *gasless combustion synthesis from elements* is described by the general equation:



where $X_i^{(s)}$ are elemental reactant powders (metals or nonmetals), $P_j^{(s,l)}$ are products, Q is the heat of reaction, and the superscripts (s) and (l) indicate solid and liquid states, respectively. In the case of SiC synthesis from elements the reaction can be written as follows:



The reaction (2) has a moderate enthalpy of product formation (compared to $\Delta H_{273} = -230$ kJ/mol for Ti-C system) and thus has relatively low adiabatic combustion temperature ($T_{ad}=1860$ K; compared with 3290 K for Ti-C reaction). Thus it is not easy to accomplish a self-sustained SHS process in this system. However, almost all available literature on CS of silicon carbide is related to this chemical pathway. Several approaches have been developed to enhance the reactivity of Si-C system. They can be sub-divided in five major groups:

- (a) CS with preliminary preheating of the reactive media;
- (b) CS with additional electrical field;
- (c) chemical activation of CS process;
- (d) SHS synthesis in Si-C-air/nitrogen systems;
- (e) mechanical activation of the initial mixture

The employment of one or another approach depends on the desired product properties, e.g. purity, particle size distribution and morphology, yield and cost considerations. To

understand these specifics, including advantages and disadvantages of different technologies, let us discuss them in more details.

2.1 CS with preliminary preheating of the reaction media

The obvious way to increase reaction temperature is a preliminary preheating of the reactive mixture to some initial temperature (T_0). The dependence of T_{ad} as a function of T_0 for stoichiometric (1:1 mol) mixture is shown in Figure 4. It can be seen that increase of T_0 above 900 K allows increasing T_{ad} to ~ 2300 K. The first publication on SHS of SiC from elements, describes the optimization of the preheating procedure of the reactive media to produce pure silicon carbide powder (Martynenko & Borovinskaya, 1978). It was shown that initial temperature of 900K and synthesis conducted in argon flow leads to the stable combustion wave propagation in stoichiometric Si + C mixture with formation of β -SiC powder with grain size of $\sim 3 \mu\text{m}$. Later this general approach, i.e. to increase the combustion temperature by preliminary preheating of the reaction media, has been used by many other researchers leading to the development of effective technologies for CS of SiC powder.

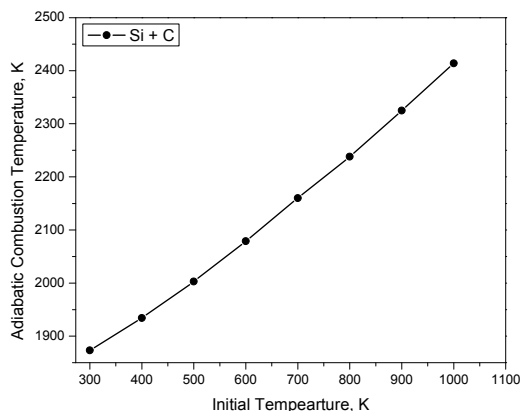


Fig. 4. Adiabatic combustion temperature in Si+C system as a function of initial temperature of the reaction mixture

For example, Pampuch, et al, 1987, showed that uniform preheating of the stoichiometric Si+C mixture in the flow of argon gas, leads to the self-ignition (VCS mode) of the heterogeneous media at temperature $\sim 1300\text{C}$ with formation of β -SiC powders, which has a morphology similar to that of initial carbon as it is demonstrated in Figure 5. Two types of carbon precursors were used: carbon black (Fig.5a) and charcoal (Fig.5c). The BET surface area of the β -SiC obtained by using carbon black and charcoal, was 5.8 and $6.2 \text{ m}^3/\text{g}$, respectively. The crystallite size, determined from the broadening of the (111) X-ray peak, was 200 nm in the former and 145 nm in the latter case.

It was further demonstrated that suggested VCS approach allows effective synthesis of pure SiC powders, containing 99.6% of β -phase, $<0.05\text{wt}\%$ of free Si; $0.1 \text{ wt}\%$ of free carbon; and $0.3 \text{ wt}\%$ oxygen. It was also outlined (Yamada et al., 1985; Pampuch et.al, 1989) that self-purification effect is a characteristic feature of SC-based methods. Indeed, it was shown that

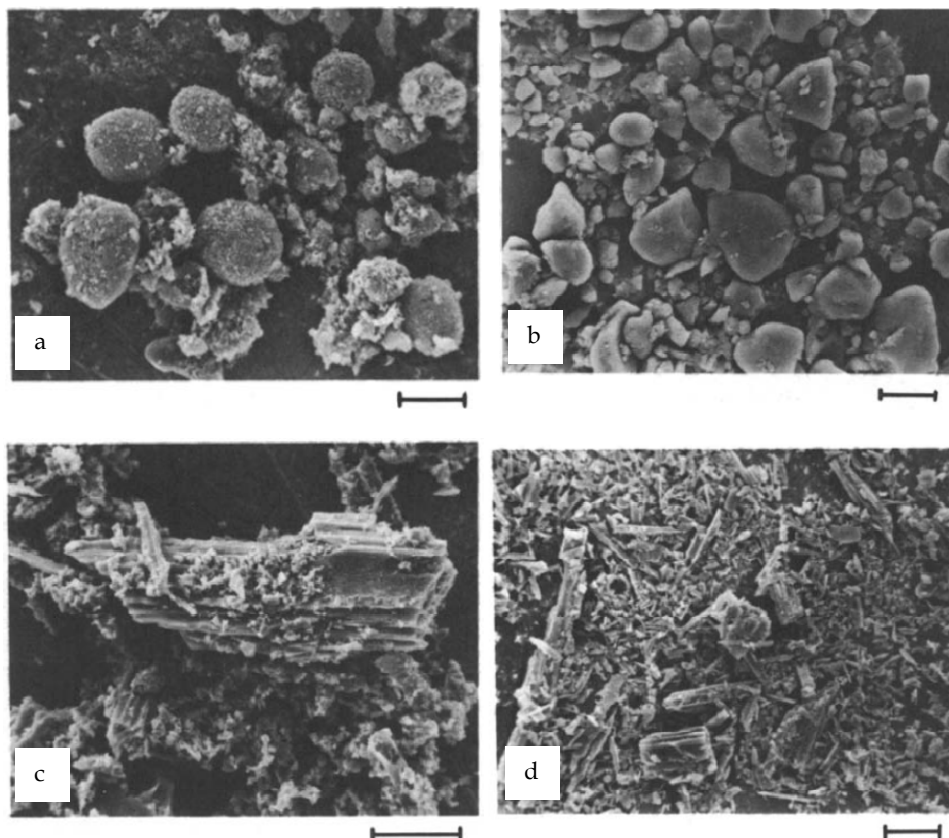


Fig. 5. Micrographs of initial carbon precursors (a) - carbon black; (c) - charcoal and corresponding products (β -SiC) (b) and (d); the bar scale = 50 μm .

50% of metallic impurities presented in the initial precursors were eliminated in the high temperature conditions of CS wave. Also it was shown that addition of Al to the initial mixture leads to the formation of ~10wt.% of α -SiC phase. It is important to outline the difference between approaches suggested by Martinenko and Pampuch. While in both cases the preheating was used as a tool to enhance the reaction rate, in the former case the mixture was preheated to ~ 900 K, followed by local mixture initiation, i.e. SHS mode was used, and in the later case, the self-ignition conditions ~1500 K was reached to promote the VCS mode. More recently another approach for preheating of the Si+C carbon mixture to produce SiC powder by SC was suggested by Chinese scientist (Wu & Chen, 1999; Chen et.al 2002). This method suggests using of a custom-built oxy-acetylene torch, which is moving along the surface of reactive mixture in air with speed (~3 mm/s) of the propagation of the combustion wave, leading to the relatively high yield (~94%) of desired product. From the view point of energy consumption this method is more affected as compared to the discussed above and allows synthesis to be accomplished in air. While the purity of thus

obtained product is not so high, the microstructure of the powder is attractive, involving high surface area agglomerates with sub-micron grains (see Figure 6).

It is important that CS +preheating approach allows one-step production of the SiC ceramics. It was for the first time demonstrated by Japanese scientists in 1985 (Yamada et al., 1985), who used a high pressure self-propagating sintering method. In this case Si+C mixture was encapsulated into the high-pressure heating cell, on which pressure of 3GPa was applied in a cubic anvil device. Reaction was initiated by preheating the cell by carbon heater. Ceramics, which was synthesized under optimum conditions, contains ~96% of β -SiC phase, has density 2.9 g/cm³ and micro hardness 23 GN/m².

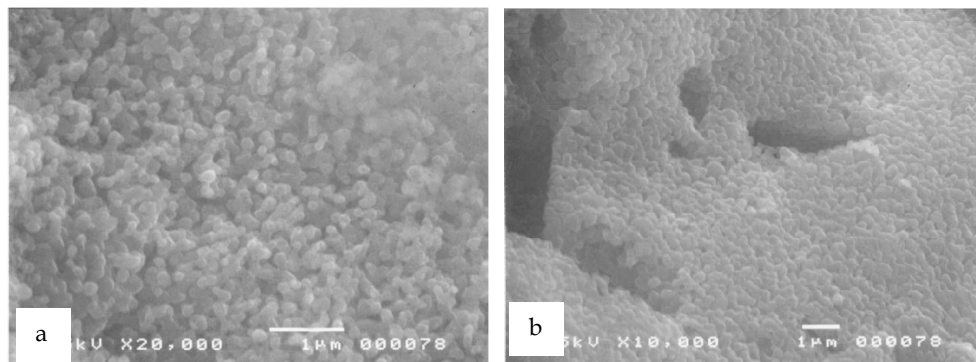


Fig. 6. Microstructure of the SiC powders synthesized by torch-related CS method under different combustion temperatures: (a) higher; (b) lower.

2.2 CS with additional electric field

The other way to use preheating to provide conditions for CS self-sustained regime is to pass the current through the initial reactive medium. This approach was for the first time suggested by Yamada et al., 1986, followed by works of Steinberg's (Gorovenko et al., 1993; Knyazik, et al., 1993) and Munir's groups (Feng & Munir, 1995; Xue & Munir, 1996; Munir, 1997; Gedevanishvili & Munir, 1998).

The direct passing of the electric current through the sample, i.e. Joule preheating (Figure 7a) reaching, self-ignition VCS mode was used by Yamada and Shteinberg. It was shown that the process involves three stages; (i) the first stage is just inert preheating of the media to excitation of the SHS reaction. Heat, generated by the resistivity of the reactant, preheats the sample and raises the temperature. If the applied electric power is cut off on this stage, SiC product is not detected; (ii) the second stage – the SHS reaction self-initiated, typically in the middle part of the sample, where the heat losses are minimal. As SiC is produced, the electric resistivity increases rapidly and the current drops suddenly, as seen in Figure 7b; (iii) the third stage – the spontaneous reaction propagates toward both ends of the sample producing stoichiometric β -SiC phase. The duration of the reaction is on the order of 0.1 s. It was shown that decreasing particle size of the initial precursor one may synthesize sub-micron SiC powders by using this method. Figure 8 shows morphology of silicon carbide powders obtained by using 5 μ m (a) and 0.1 μ m (b) silicon particles.

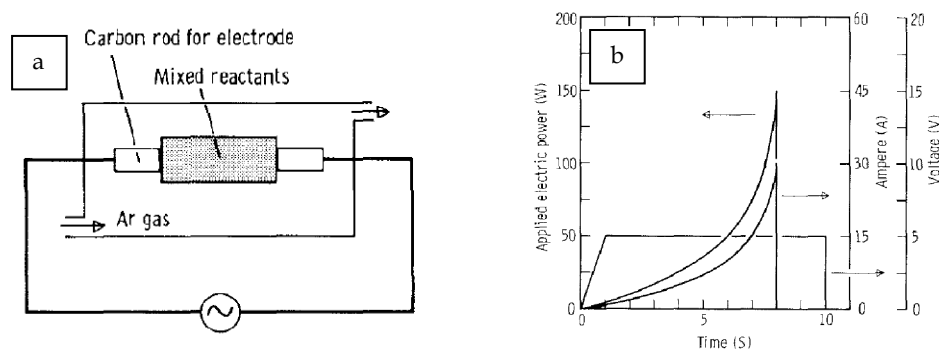


Fig. 7. Schematics of the of the set-up for CS of silicon carbide with Joule media preheating (a) and characteristic I-U diagram of the process (b)

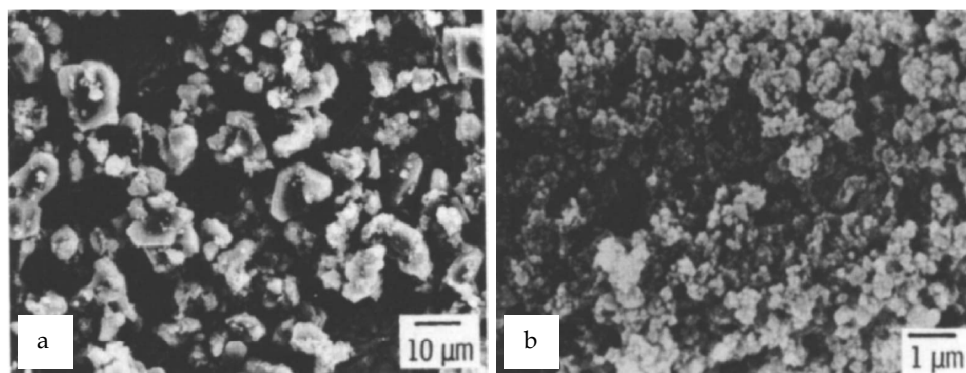


Fig. 8. Microstructure of the SiC powder obtained by CS with Joule preheating by using silicon powders of different size: (a) 5 μm ; (b) 0.1 μm .

It was also confirmed that CS method leads to the self-cleaning of the powders during combustion process. For example, it was shown that oxygen content in the final products (0.2-0.3wt.%) was much less than that (0.5-0.7 wt.%) in the corresponding initial mixtures. Different scheme for using of electrical field for synthesis of materials was suggested by Munir (cf. Munir 1997). The approach involves the imposition of a voltage across (not along) the reactant compact and the reaction is initiated by a heating coil as it is shown in Figure 9a. With the imposition of an ignition source and a field, it is possible to accomplish the self-sustaining reaction wave propagation in the powder mixtures of Si and C in inert atmosphere. Dynamics of the electric voltage and current during field-assisted SHS of silicon carbide, is shown in Figure 9b. It can be seen that as the reaction front starts to propagate (indicated by 'S' in the figure), the voltage drops and then remains relatively constant until the wave reaches the end of the sample (indicated by 'E' in the figure). The behavior of the current is consistent with that of the voltage, so is the behavior of the calculated resistance. The steadiness of the electrical parameters during SHS may indicate

that the current is primarily confined to the narrow reaction zone. Such localization of the current to the reaction zone is a typical phenomenon for all reaction systems with resistivity of products much higher than that for initial mixture. It was shown that the critical value for the applied electrical field ($E \sim 6$ V/cm) exist, below which the reaction front cannot propagate in self-sustained manner. Increase of E above critical leads to almost

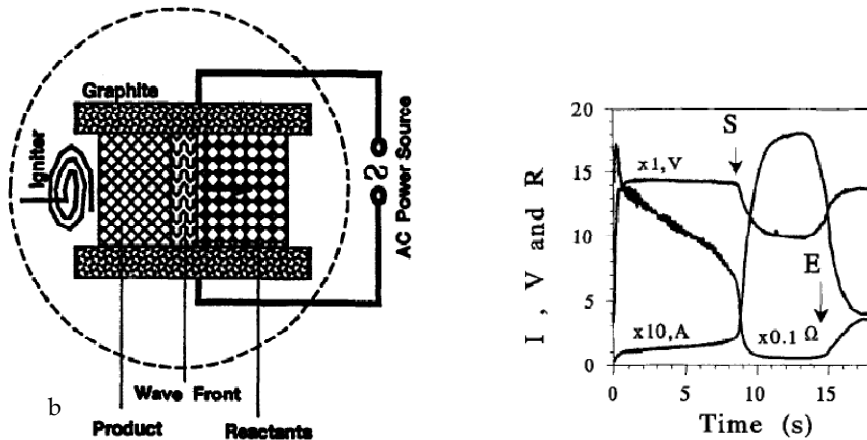


Fig. 9. Schematics of field-assisted SHS process (a) and typical current (I), voltage (V) and resistivity (R) behaviour during field-assisted SHS in Si+C system (b)

linear increase of combustion front velocity in the range 0.1-0.8 cm/s followed by the thermal explosion conditions that take place at $E \sim 20$ V/cm. As a result of field-assisted self-propagating high-temperature synthesis β -SiC powder (Feng & Munir, 1995) is produced with well crystallized morphology in the form of plates having thickness ~ 2 μm and size of ~ 20 μm (Figure 10). This approach was widely used for synthesis of different complex ceramics (AlN-SiC; MoSi₂-SiC etc), which cannot be produced by conventional means (Xue & Munir, 1996; Munir, 1997; Gedevanishvili & Munir, 1998).

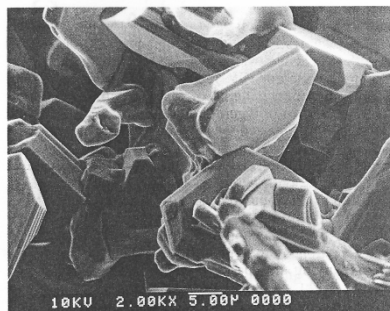
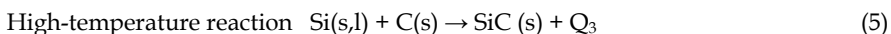
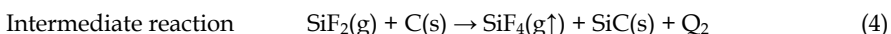


Fig. 10. Microstructure of SiC powder produced by field-assisted SHS method

2.3 Chemically activated SHS

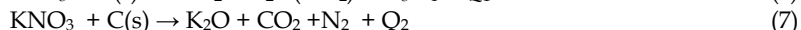
Another universal approach to enhance reactivity of the low exothermic Si-C system is, so-called, chemically activated SHS, which was for the first time suggested by Nersisyan et al., in 1991. It was proposed to use $(-\text{CF}_2-\text{CF}_2)_n$ polytetrafluoroethylene (PTFE) as an additive for the Si+C powder mixture. The following set of equations represents the main chemical reactions take place in the combustion front:



It was proved that in Si + C + PTFE system combustion wave consists of two main zones. The first one involves mainly reaction (3) between silicon and PTFE which on one hand leads to the preheating of the Si+C reaction media and on the other hand to the formation of gaseous silicon containing species (SiF_2 , SiF_4). The second, carbidization stage proceeds owing to reactions (4) and (5). Reaction (5) may occur in self-sustain manner partially owing to preheating of the media by heat of reaction (3) and additional heat released in reaction (4). Note, that gas phase reaction (4) and condensed phase reaction (5) should lead to different morphologies of the SiC product. Indeed it was shown that two different types of particles can be synthesized (Nersisyan et al., 1991). With the certain amount of PTFE additive the cube-shape particles with size on the order of 10 μm can be produced, while for the other composition the formation of the long ~ 1 mm thin (0.5 μm) fibers were observed.

Next, the set of additives including KNO_3 , NaNO_3 , NH_4NO_3 and BaNO_3 was investigated (Kharatuan & Nersisyan, 1994). It was demonstrated that among these promoters ($\text{KNO}_3 - \text{Si}$) is the best one leading to effective synthesis of relatively small (~ 1 μm) SiC particles with the amount of free carbon less than 0.5 ew.% as a major impurity. Also it was shown that SHS process consists of two main stages:

Stage I - oxidation



Stage II - carbidization



With importance of the additional reactions



As in the case of PTFE additive the reactions (6) and (7) provide enough additional heat to support the main reaction (8), which in this case may self-propagate in the inert atmosphere. It was also shown that because the involvement of gas phase reactions the argon gas pressure is a critical parameter to control the process. The typical temperature time profiles obtained under different synthesis conditions are shown in Figure 11 and illustrate the mentioned above important conclusions. It can be seen, that two stage combustion front may propagate only if argon pressure is above some critical value.

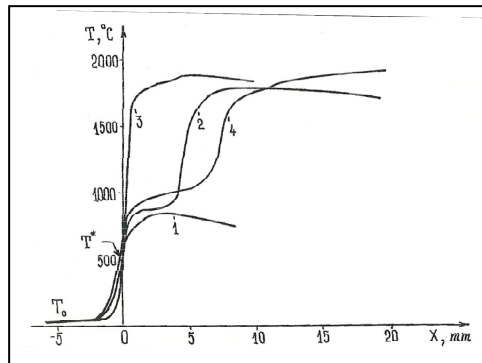
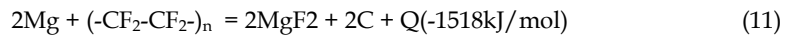


Fig. 11. Typical temperature profiles in SHS wave for Si+C+15% (KNO₃+Si) mixture at different argon pressure (MPa): (1) 0.1; (2) 0.2; (3) 1.5; (4) 5.5

Later more complex [Mg + (-CF₂-CF₂)_n] additive was used to synthesize SiC powder in SHS mode (Zhang et al., 2002). The following reaction scheme takes place in the combustion front:



The pure β-SiC powder was obtained after leaching of the as-synthesized product in 10% vol. % (HNO₃ + HF) solution for 4 h. The characteristic microstructure is shown in Figure 12. It can be seen that this approach allows production of powders with average particle size of ~ 5 μm.

Chemical activation method was also widely used in combination with other approaches to enhance reactivity of Si-C system, i.e. reaction in the atmosphere of the reactive gases (e.g. nitrogen and air)

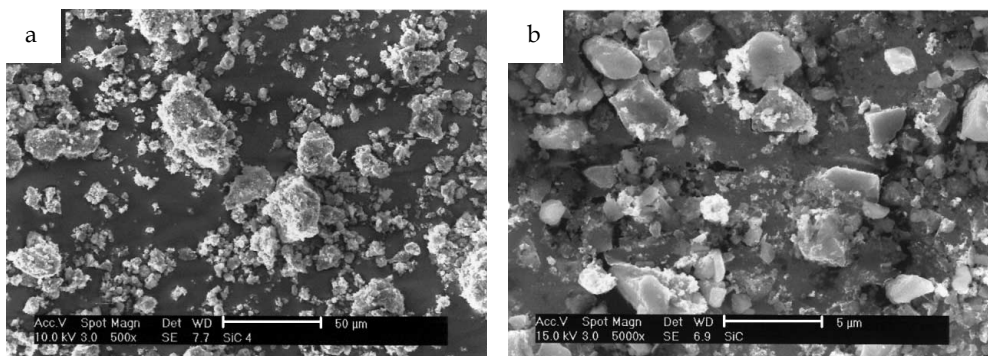


Fig. 12. Typical microstructure of as-synthesized product (a) and after leaching (b)

2.4 SHS in Si C-nitrogen/air system

SHS reaction between silicon and nitrogen (Mukasyan et al., 1986), as well as carbon burning in air are much more exothermic as compared to Si+C reaction. First, it was suggested to use air as an atmosphere to carry CS of silicon carbide (Martynenko, 1982). It was shown that optimization of synthesis conditions, which include the usage of initial Si-C mixture with slight excess of carbon, air pressure above critical (~3PMa) and clever change of the air content in the reactor, allows production of silicon carbide powder with 5-7 wt.% of silicon nitride and relatively high specific surface area up to 10 m²/g. Microstructure of this powder is shown in Figure 13. Later conducting experiments in pure nitrogen (Yamada et al., 1989) it was shown that combustion wave consists of two stages (see Figure 14). First is reaction of nitrogen with silicon to produce some amount of silicon nitride which leads to preheating of the rest of the media, followed by carbidization reaction with maximum temperature around 2100 K.

This approach was further widely used for synthesis of silicon carbide - based powders (Agrafiotis, et al., 1990; Kata et al., 1997; Puszynski & Miao, 1998; Kata & Liz, 2005; Kharatyan et al., 2006; Yang et al., 2009, etc). First, it is worth noting the idea of possible reduction and decomposition of the silicon nitride in the combustion front, which may lead to the synthesis of silicon carbide powder with minimum (<1wt%) amount of silicon nitride. Indeed, as it was suggested by Kata, the following reactions may occur under certain conditions:



leading to the complete elimination of the undesired silicon nitride phase in the synthesized product.

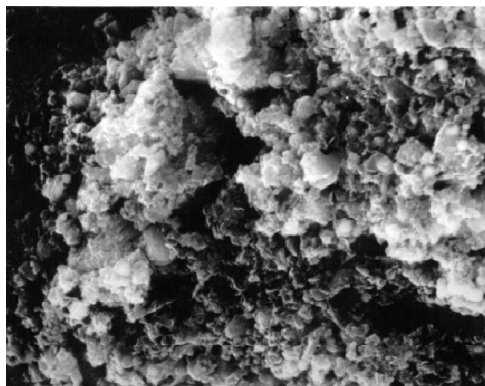


Fig. 13. Microstructure of SiC powder obtained By SHS in Si-C-air system

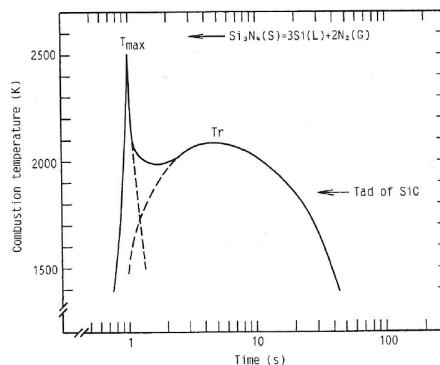


Fig. 14. Typical temperature profile of SHS wave in Si-C-N₂ system

Method for combustion synthesis of SiC/Si₃N₄ powders in Si-C-(CF₂-CF₂)_n system was also developed (Kharatyan et al., 2006). It was shown that the use of fluoroplastic as an activating component allows a single-stage synthesis of Si₃N₄-SiC composite with contents

of individual components varying from 0 to 100%. More important, that using chemical activation plus combustion in reactive atmosphere allows one to produce SiC whiskers and fibers (cf. Puszynski & Miao, 1999; Chen et al., 2001). For example, long (3mm) thin (0.2-1 μ m) SiC fibers were synthesized by using carbamide (urea) as a promoter, while combustion process took place in nitrogen atmosphere. Microstructure and results of XRD analysis of these fibers are shown in Figure 15, correspondingly.

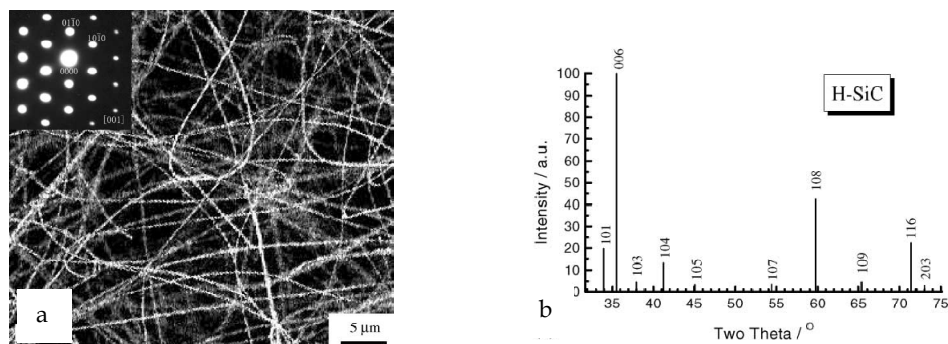


Fig. 15. Typical microstructure (a) and XRD data (b) of silicon carbide fibers synthesized in Si-C-urea-N₂ system

Combination of different activation approaches to enhance reaction in silicon-carbon system is currently widely used for developing of novel effective CS methods. The most recent ones are related to the so-called mechanical activation approach.

2.5 Mechanical activation of CS reaction in Si - C system

High energy ball milling (HEBM) is the processing of powder mixture in high-speed planetary ball mills and other devices, where the particles of the mixture are subjected to significant mechanical impacts with a force sufficient to break the brittle and plastically deform the ductile components (Suryanarayana, 2005). Brittle particles are milled to finer grains, whereas ductile particles (usually, metals) are subjected to multiple deformations, all together forming layered composite particles with the layer thickness decreasing as the milling time is increased. Thus such mechanical treatment not only decreases the particle size of reactants, but also increases their contact surface area, which is typically free from oxide films. Moreover, the defects of the crystalline structure are accumulated in the media during HEBM. All these factors enhance the chemical activity of the combustible mixture and thus, are called mechanical activation (MA). The MA may include partial or complete dissolution of one reactant in the other (mechanical doping or mechanical fusion); otherwise, the components of the mixture can be involved into a chemical reaction with formation of a new compound during HEBM (mechanical synthesis). The analysis of literature allows one to conclude that mechanical activation (i) decreases the self-ignition temperature of various combustible systems, (ii) expands the flammability limits, (iii) favors a more complete reaction, and (iv) typically increases the combustion wave front velocity (cf. Rogachev & Mukasyan, 2010). In the above context, it looks logical to apply this approach for reaction enhancement in low exothermic carbon-silicon systems.

Recently the process was developed (Yang et al., 2007a), which involves the following steps: (i) adding a small amount (1-3wt.%) of NH_4Cl and PVC into the Si-C powder mixture; (ii) mechanically activating of the mixtures through HEBM (2-12 h); mixture preheating to temperature (950-1200°C) and keeping it at this temperature until the reaction self-initiates. It was demonstrated, that MA allows one to initiate reaction at relatively low temperature 1050°C and reach full conversion by using small amounts of additives. Fine $\beta\text{-SiC}$ powders with specific surface area 4.4 m^2/g , and the particle size $< 5 \mu\text{m}$ was synthesized. However, it was shown that optimum MA time should be applied, because long HEBM leads to synthesis of larger SiC particles (compare Fig. 16 a and b).

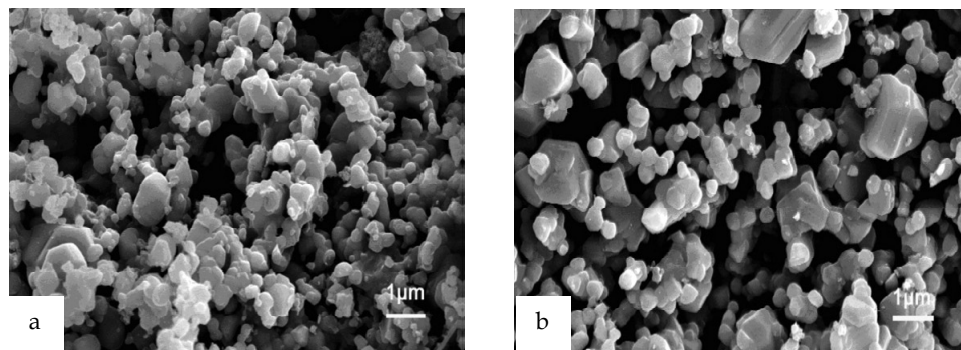


Fig. 16. Microstructure of SiC powders after different time of MA: (a) 2 h; (b) 12 h.

Similar approach but with synthesis in SHS mode was also developed (Yang et al., 2007b). While slightly larger amount (~6wt.%) of PTFE should be used as compared to VCS mode, but still it is almost three times less than critical promoter concentration for not activated mixture. It is also important that much finer particles (Figure 17a) can be synthesized in this mode which also has narrow particle size distribution (Figure 17b).

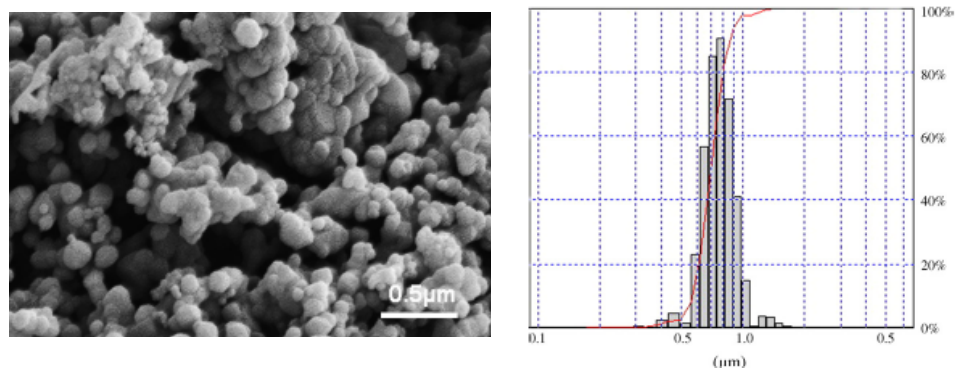


Fig. 17. Microstructure (a) and particle size distribution (b) for SiC powder synthesized in SHS mode after MA of the initial mixture

Both mechanical and chemical activations (PTFE) with synthesis in nitrogen atmosphere were used for large scale synthesis of nanopowder of β -SiC (Liu, et al., 2008). It was shown that if MA takes place with 1:16 ball to mixture mass ratio during 2 h than under 4 MPa of nitrogen only 1.5 wt.% of PTFE is required to reach full conversion of mixture to SiC phase with amount of other impurities less than 1 %.

Mechanically activated pure (without any additives) Si+C mixture was burned in air to synthesized SiC powder in SHS mode (Yang et al., 2009). It was demonstrated that after 4 h of HEBM the mixture can be ignited in air at 1 atm. First surface reaction between oxygen and mainly silicon leads to the formation of the relatively thin (~ 0.5 mm) layer of SiO₂ phase, simultaneously preheating bulk media. Second combustion wave due to reaction between silicon and carbide results in synthesis of β -SiC with small amount of Si₂N₂O phase. Typical microstructure of the SiC powder is shown in Figure 18. It can be seen that about 100 nm particles can be produced by this approach.

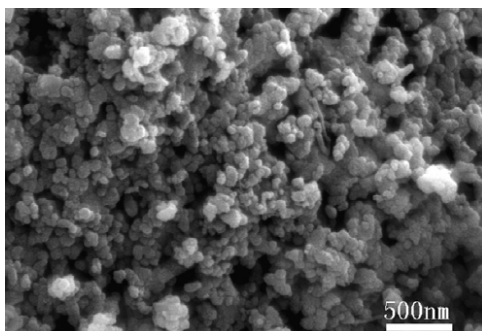


Fig. 18. Microstructure of SiC powder synthesized in air after 4h of HEBM of Si+C mixture

The most widely used method in conventional powder metallurgy is based on the Acheson idea on thermal reduction of silica by carbon, where different types of the silicon containing precursors are used (cf. Choyke & Matsun, 2004). Similar approach, but taking place in SHS mode has also been developed.

3. Combustion Synthesis of Silicon Carbide by Reduction Reactions

The other way to produce SiC powder by using SHS method involves sequence of two reactions that take place in the combustion front: reduction of silica by a metal to make pure silicon, followed by silicon reaction with carbon. The SiO₂ + Me(Mg, Al) + C system is much more exothermic, as compared to binary Si + C composition (see below). Thus, it is relatively easy to initiate the SHS mode in such reduction-type mixture without using any special enhancing means. However, only few patents (Merzhanov et al., 1992; Merzhanov et al., 1994) and scientific publications (cf. Yermekova et al., 2010) may be found that are related to the combustion synthesis of silicon carbon through the reduction of silica. Let us discuss this approach in detail.

3.1 Thermodynamic considerations

The overall combustion reaction for reduction synthesis of SiC, when magnesium (Mg) is used as a reducing element, can be written as follows:



The thermodynamic analysis (Shirayev, 1993; Mamyán, 2002) allows calculating the adiabatic combustion temperature (T_{ad}) and equilibrium products composition for reaction (15) as a function of the inert gas (argon) pressure (P) in the reaction chamber (Fig.19). It can be seen (Fig.19a) that T_{ad} increases and the amount of gas phase products decreases, with increase of inert gas pressure. Also, the absolute value of T_{ad} is > 2000 K, which is above melting (m.p.) and boiling points of magnesium (922 K and 1363 K, correspondingly), m.p. of Si (1683 K) and SiO_2 (1923K), but well below m.p. of MgO (3073 K) and carbon (4093K). It is clear that the amount of gas phase products (which includes Mg, CO and SiO) can be decreased by increasing inert gas pressure in the reaction chamber, since higher P suppresses the gasification processes.

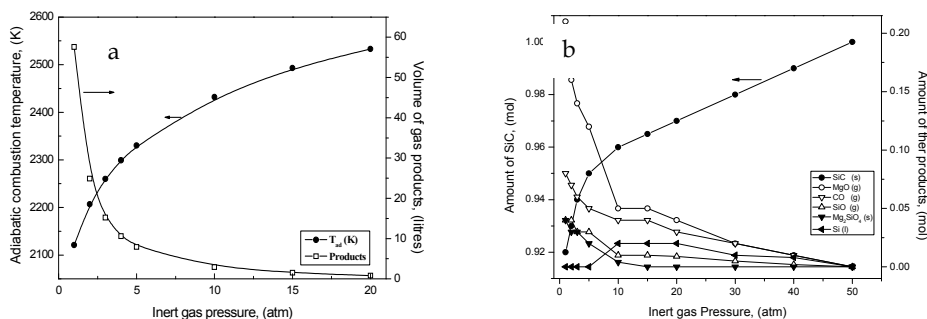


Fig. 19. Thermodynamic characteristics of the $\text{SiO}_2:\text{Mg}:\text{C}=1:2:1$ system as a function of inert gas pressure: (a) T_{ad} and Volume of gas phase products; (b) equilibrium products

In addition to main solid products, i.e. SiC and MgO, two other phases, i.e. Mg_2SiO_4 and Si, can be produced (Fig.19b). The last two phases are undesirable, because it is not easy to leach them out from the as-synthesized product. Thermodynamics suggests how one can reduce the amount of these phases. It appears that increasing of P leads to a significant decrease of the Mg_2SiO_4 and Si quantities. Moreover, at $P=50$ atm only SiC and MgO are the equilibrium combustion products in the considered system (Fig.19b). Thus 100% of SiO_2 conversion to silicon carbide for stoichiometric 1:2:1 composition can be reached under high argon pressure.

3.2 Silicon carbide powder by SHS in $\text{SiO}_2\text{-C-Mg}$ system

The thermodynamic calculation reveals that by conducting experiments under optimum gas pressure and adjusting the composition of the initial mixture one can expect the synthesis of product which involves only two solid phases SiC and MgO. The simple chemical treatment of such mixture (see details in Amosov et al., 2007) allows complete leaching of the MgO phase and obtaining pure silicon carbide powder. However, the thermodynamics cannot

suggest how one may control the microstructure of the product synthesized in the SHS. The last issue was recently investigated by Ermekova et al, 2010.

Three different types of the silicon oxide (SiO_2) powder were used: (i) from Yerken-deposit, Kazakhstan, (KZ) 98,8% purity, particle size $d \leq 100 \mu\text{m}$, (ii) Laboratory Cerac (LC), WI, USA, 99,5% purity, $d < 10 \mu\text{m}$ (iii) nano Untreated Fumed Silica (UFS), Cabot Corporation, MA, USA, 99,9% purity. The typical microstructures of these powders are shown in Figure 20. It can be seen that KZ powder has a wide range of particle size distribution with average size about $20 \mu\text{m}$ and thus low specific surface area ($1 \text{ m}^2/\text{g}$). In contrast the UFS powder possesses extremely uniform and fine microstructure, as well as high BET $\sim 390 \text{ m}^2/\text{g}$. Laboratory Cerac (LC) powder has properties which are somewhere in between KZ and UFS silica with surface area $\sim 7 \text{ m}^2/\text{g}$. Carbon black powder and Mg (Alfa Aesar, MA, USA, 99,8% purity, $d < 44 \text{ mm}$) were used as precursors for initial reactive mixture.

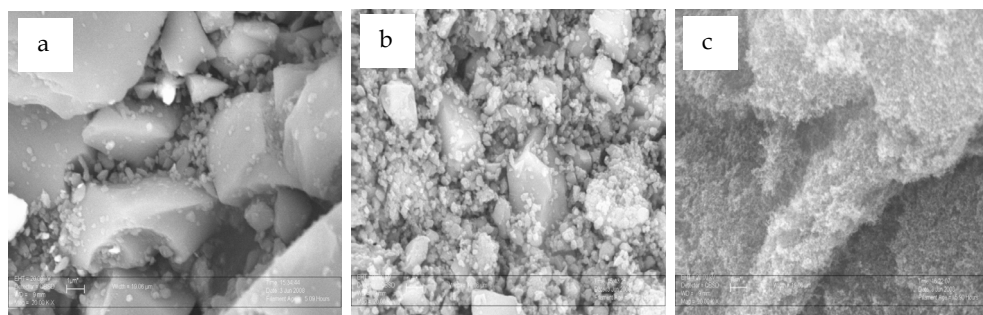


Fig. 20. Microstructure of the initial SiO_2 powders: (a) KZ; (b) Cerac; (c) UFS

2 μm

Correspondingly, three SiO_2 -Mg-C mixtures (named below KZ, LC and UFC) with different silica, but with the same optimized composition were prepared by 2 hours of dry mixing. All thus prepared mixtures were placed on graphite tray and inserted into stainless steel cylindrical reactor. The reactor was evacuated up to the 10^{-3} atm and filled with argon up to the desired pressure, in the range of 1-20 atm. The ignition was carried out by passing short electrical current impulse ($I=10\text{A}$, $U=20\text{V}$) through the coil of tungsten wire. All as-synthesized products were chemically treated for 3 hours in 36% solution of hydrochloric acid at room temperature. The acid was taken into amounts according to the predicted mass of magnesium oxide to be leached out. This process was followed by thorough powder washing in ionized water and drying at 100°C for about 2 hours.

Microstructures of as-leached powders are shown in Figure 21. It can be seen that all powders have relatively uniform particle size distribution with sub-micron average values: $d_{\text{KZ}} = 280 \text{ nm}$; $d_{\text{Cerac}} = 150 \text{ nm}$; $d_{\text{UFS}} = 90 \text{ nm}$. More close inspection (Ermekova et al., 2010) reveals that in all cases particles involve set of extremely thin hexagonal plates sintered to each other. The diagonal of the hexagon is about average particle size, while thickness is as small as 10 nm for KZ-SiC; 3-5 nm for Cerac-SiC; and 1 nm UFC-SiC

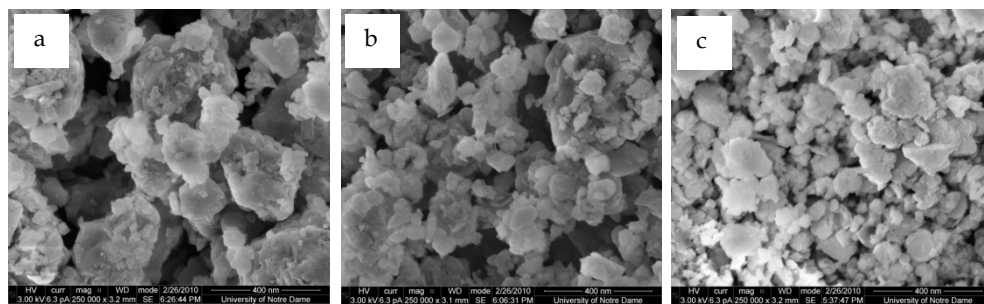


Fig. 21. Microstructure of the β -SiC powders synthesized from different SiO₂ precursors: (a) KZ; (b) Cerac; (c) UFS — 200 nm

It is shown, that silicon carbon nanopowder can be directly synthesized by combustion reaction in the silica-magnesium-carbon system. While even micro-size precursors (KZ) lead to formation of nano-particles, the scale of heterogeneity of used silica is a parameter which allows one to control the size of SiC grains. It was also demonstrated that under optimum conditions pure β -SiC powder with surface above 100 m²/g can be synthesized in SHS mode.

4. Concluding remarks

Various combustion synthesis methods, which lead to production of SiC powders, with different morphologies and particle size distributions, are discussed in this chapter. Almost all of them can be easily scaled-up to produce tons of materials per year (Merzhanov & Mukasyan, 2007). Because of the energy saving nature of combustion - based technologies, the total production cost for SHS methods primarily involves the cost of the initial precursors and milling cost (Golubjatnikov, 1993). It is important that "self-purifying" feature of the CS approaches, mentioned in this chapter (see also Bloshenko, et al, 1992), allows to use not high purity raw powders to produce high purity products. The latter contributes to the low production cost of the powders. Simple technological equipment results in relatively low cost capital investment to organize the production site. All above makes CS technology very attractive for industrial production of advanced ceramic materials.

However, it is also well recognized that world market of such advanced materials is not large enough and already distributed among well known manufacturers. Thus being attractive SHS technologies cannot compete with traditional approaches, if even slightly better and cheaper product will be suggested. The cases which may lead to success are to synthesize the materials which cannot be produced by traditional technologies or provide much cheaper product. In the author's opinion, the sub-micron silicon carbide powder is such a product. Indeed, the current conventional technologies, which are based on Acheson idea, can produce low cost silicon carbide powders in the micron range (>5 μ m) and impurity of 96-98 wt%. Production of smaller particles requires long term milling processes which typically decrease powder purity and increase cost. Not-traditional approaches

require high temperature equipment and are characterized by relatively long synthesis time, otherwise using same precursors as in SHS method and thus they have higher production costs as that for combustion-based technologies. Search of market prices for nano-sized SiC powders confirmed this conclusion.

As shown in this chapter, almost all CS-based methods lead to production of sub-micron β -SiC powders. In many cases, nano-powders (<100 nm) as well as nano-fibers can be routinely synthesized in effective energy saving way. The purity issue, i.e. amount of SiC phase, oxygen, free carbon, iron contents in the final product, is very important. Thus, selection of the specific CS-method is dictated by specific requirements on the powder properties (particle size, morphology, impurity, cost, etc.).

High pure SiC (>99 wt.%) powders can be produced by CS in Si+C system and using *preliminary preheating* approach. Note that in this case some external energy source is required to preheat the media and the typical range of synthesized particles size is 1-10 micron. Also nano-sized (average particle size 80 nm) pure product can be achieved by using *reduction reaction* in SiO₂-Mg-C system. In this case the purity will be defined not only by optimum synthesis conditions, but also by optimization of leaching stage. The latter may lead to increase of the production cost. The other aspect to be considered is the utilization of magnesium salts, which are formed during as-synthesized product leaching. However, this problem allows elegant solution. All approaches with using different *chemical activators*, including nitrogen and air environments, being very simple for technical realization and allowing synthesis of extremely fine particles, have one obstacle, which is related to the product purity. If small amount (3-7wt.%) of such refractory phases as Si₃N₄ is not the concern for the powder application then *combustion in nitrogen* is the best method to synthesized pure ceramic powder. It looks like that optimum combustion in *argon* of Si+C mixture with *PTFE additive* allows to produce nanopowders with small amount of impurities. Note, that clever evacuation of fluorides compounds from the volume of the reactor is required for this approach. *Combustion at 1atm in air* is very attractive approach. But this technology requires relatively long term high energy ball milling of initial mixtures. The estimation of the production costs is required to make conclusion regarding the effectiveness of this method.

Finally, note that CS-based methods allow direct synthesis of materials in combustion wave. Indeed, it is logical to use high temperatures formed in the reaction front not only to synthesize desired phase but also to sinter the produced powders to make pore-free materials. The list of such methods is relatively long (Merzhanov & Mukasyan, 2007) and it can be a topic for the next book.

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