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Synthesis of alumina–silicon carbide composites by chemically activated self-propagating reactions

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Abstract

The synthesis of alumina/silicon carbide composites by self-propagating reactions activated by Teflon is investigated. It is shown that small amounts of this material (i.e. 0.20–0.25 wt.%) guarantee the occurrence of self-propagation reactions leading to the formation of a composite. In particular, under argon atmosphere, it consists of well-formed crystals of alumina, fine grained silicon carbide and whiskers-shaped crystallites of SiC. On the other hand, aluminium nitride, silicon carbonitride/silicon cyanide, aluminum oxynitrisilicides and mullite are also found under nitrogen atmosphere. The content of SiC whiskers in the final product increases when powdered polymers (polystyrene, polyethylene, polypropylene) are added to the initial mixture together with Teflon.

Keywords: Synthesis; Alumina–SiC composites; Chemically activated SHS

1. Introduction

It is well know that composites based on corundum as well as other inorganic refractory compounds (carbides, nitrides, borides of transition metals) have generated considerable interest in the scientific as well as technological literature [1,2]. In particular, these composites possess a combination of physical and mechanical properties which make them attractive for a variety of applications.

It has been demonstrated that the above mentioned composites may be synthesized through the self-propagating high temperature synthesis (SHS) technique [3–7]. The latter one, which belongs to the more general category of combustion synthesis (CS) is characterized by the fact that once ignited, a relatively strong exothermic reaction is able to propagate as a combustion wave through the entire reacting mixture, without requiring any other energy supply, as schematically shown in Fig. 1.

An empirical criterion typically adopted for determining the feasibility of SHS is an adiabatic temperature exceeding 1800 K. For systems characterized by lower adiabatic temperatures or having a particularly high activation energy barrier, reactants can be preheated to a temperature at which a self-propagating reaction wave can be initiated and sustained. However, using such an approach, final products often include secondary phases, whose undesirable presence is the consequence of diffusional mass transport occurring during the relatively slow heating prior to the onset of the combustion reaction. To overcome these problems, promoters may be added to the initial mixture in order to guarantee self-propagation without preheating, as discussed next.

It should be noted that several ceramic powders and materials were obtained by SHS during the last two decades [3–7]. Alumina containing composites are usually synthesized following aluminothermic reactions [8,9], such as:

$$3SiO_2 + 4Al + 3C \rightarrow 3SiC + 2Al_2O_3 \quad (1)$$

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where an oxide compound (SiO_2) is reduced by a metal (Al), forming a more stable oxide compound (Al_2O_3) and a second compound (SiC).

However, the activation of self-propagating combustion reaction indicated in reaction (1) is somehow difficult due to the existence of a protective oxide film on the surface of aluminum particles.

In a recent work [10], the destruction of the protective oxide film on the aluminum particles was found to be responsible for the activation mechanism of the synthesis performed by Lee et al. [11].

As shown recently [12], the most effective promoter for the system SiO_2/Al/C was found to be the fluoropolyethylene (Teflon). In particular, small amounts of this additive (i.e. 0.20–0.25%) was able to guarantee the occurrence of self-propagation reactions leading to the formation of alumina/silicon carbide (α and β types) composites. Silicon carbide whisker-like crystals were also detected in the end products. A similar results is obtained in SiO_2/Zr/C system [13].

With the aim of optimizing the self-propagating synthesis of alumina/silicon carbide composites, in the present work we focus our attention on the analysis of the macrokinetics of reaction (1) activated by Teflon, which was scarcely investigated in previous works.

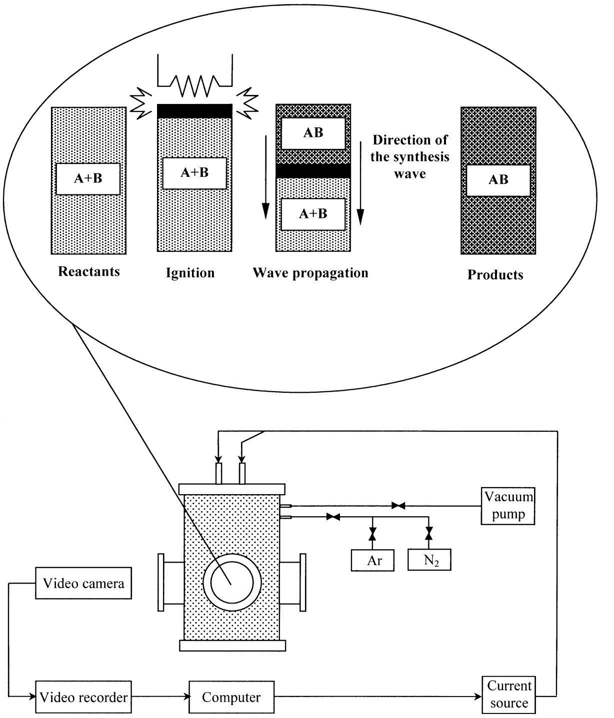


Fig. 1. Schematic representation of the experimental apparatus and the SHS process.

2. Experimental set-up and procedure

The experiments were carried out in a constant pressure reactor schematically shown in Fig. 1 using cylindrical pellets (30 mm in diameter and 30–40 mm high) obtained under a pressure of 1.2–1.3 ton/cm^2. The relative green densities of the pellets were determined from weight and geometrical measurements and resulted to be in the range 0.60–0.65. Experiments were conducted using N_2 or Ar atmosphere at pressure levels of 0.5–5.0 MPa. Aluminum powders (ASD-4, Russia) with particle size less than 10 μm, natural quartz sand (Rostov-on-Don, Russia) grinded up to particle size less than 15 μm (with 99% SiO_2 content), granulated carbon black (P803, VNIITU, Russia) with particle size less than 1 μm, powdered Teflon (PTFE, FT-4, Kuskovsk's Chemical Factory, Russia) ranging from 0.3 to 7.0% wt in the initial mixture and polystyrene (PS), polyethylene (PE) or polypropylene (PP) (Kuskovsk's Chemical Factory, Russia) with particle size less than 10 μm were used in the experiments. It should be noted that the reactant content in the starting mixture is computed according to the stoichiometry of reaction (1), where the amount of carbon is due to carbon black as well as the hydrocarbonaceous polymer used. On the other hand, teflon addition is not accounted for in the stoichiometry of reaction (1) but it provides only an excess of carbon to compensate the partial carbon losses due to evolving gases. During a typical experiment the pellet is placed into the reactor and the reaction is initiated by means of a tungsten wire ("Pobedit" Factory, Vladikavcas, Russia) connected to the power supply, which was programmed to produce an energy pulse by setting 12–15 V for about 1.0–1.5 s.

The maximum combustion temperatures (T_c) were measured with a tungsten-rhenium thermocouple of 100 μm in diameter. The average values (U_c) of combustion velocities were determined from signals of several thermocouples, embedded into the sample at prescribed distances from each other. The control of the experiments as well as the recording of thermocouples signals were carried out using a personal computer.

The burned down samples were exposed to X-ray analysis taking advantage of a DRON-3.0 or a "Rigaku Geigerflex" diffractometer and using the CuK_α Ni-filtered radiation. The study of sample microstructure (both initial, and burned down) was carried out using either a BS-300 Scanning Electron Microscope (SEM) or a Cambridge 250 MK3 one, equipped with LINK AN 10/55S Energy Dispersive X-ray System (EDS).

3. Results and discussion

The influence of the relative amount m (wt.%) of Teflon in the starting mixture on combustion temperature (T_c) and velocity (U_c) of propagation of the combustion wave was first investigated.

The results of these experiments are shown in Fig. 2 where the curve related to the adiabatic combustion temperature (T_{ad}) obtained by thermodynamic calculation is also reported. As can be seen from Fig. 2, in the absence of Teflon ($m=0$) the $3SiO_2/4Al/3C$ system has rather high theoretical adiabatic combustion temperature ($T_{ad}=2320$ K), in spite of which the activation of the combustion process is not possible. Addition of Teflon (0.20–0.25 wt%) promotes the formation and propagation of combustion wave. Correspondingly, the combustion wave propagates through the sample at a velocity of 0.1 cm/s and $T_c=2000$ K, which is about 300–350 K lower than T_{ad}. By increasing the Teflon amount in the starting mixture T_c firstly increases, thus reaching a maximum at $m=2.0$–3.0 wt.%, and then decreases at larger values of m. The increase of T_c in the first part of the curve can be explained by intensification of aluminum oxide film destruction process and consequent increasing of the degree of reaction completeness. At $m=2.0$–3.0 wt.% the maximum activation effect is achieved, and the combustion temperature reaches a value of 2130 K. On the other hand, the decrease of T_c observed at $m \geqslant 3.0$ wt% is caused by heat consumption due to Teflon decomposition. The monotonous increasing of U_c with m demonstrates the leading role of Teflon to guarantee the self-propagating character of the reaction.

From XRD analysis reported in Fig. 3 the phase composition of endproducts includes silicon carbide (β-SiC moissanite-3/ITC/RG, α-SiC moissanite-2/ITH/RG) and alumina (α-Al_2O_3). Under nitrogen atmosphere other species, such as aluminum nitride, silicon carbide nitride, aluminum silicon nitride oxide (SiAlON), $Al_6Si_6N_8O_9$, are also detected.

In order to study the morphology of reaction products and to identify the corresponding chemical composition, SEM and EDS analyses were carried out also for the initial mixture as shown in Fig. 4a and b. As may be seen from Fig. 4a the individual reactants in the initial mixture differ in shape and particle size. Aluminum particles are round, with size within the range of 1–5 μm, while the quartz sand particles display a size of 2–15 μm. Carbon and Teflon particles are on the other hand rather fine. The morphology of end products sharply differs from the initial one, as it may be seen from Fig. 4b.

Here two type of particles are seen: the first ones are almost perfect hexagonal crystallites with size 5–30 μm while the others are fine particles with size less than 1 μm.

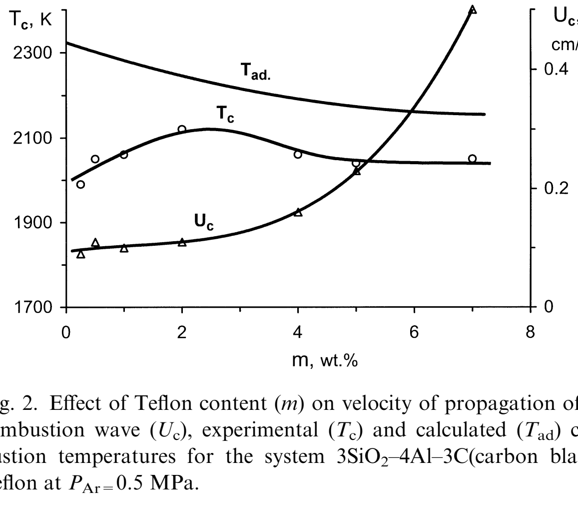


Fig. 2. Effect of Teflon content (m) on velocity of propagation of the combustion wave (U_c), experimental (T_c) and calculated (T_{ad}) combustion temperatures for the system $3SiO_2$–4Al–3C(carbon black)–Teflon at $P_{Ar}=0.5$ MPa.

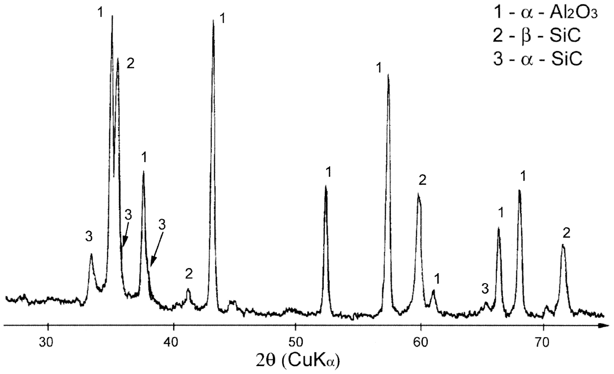
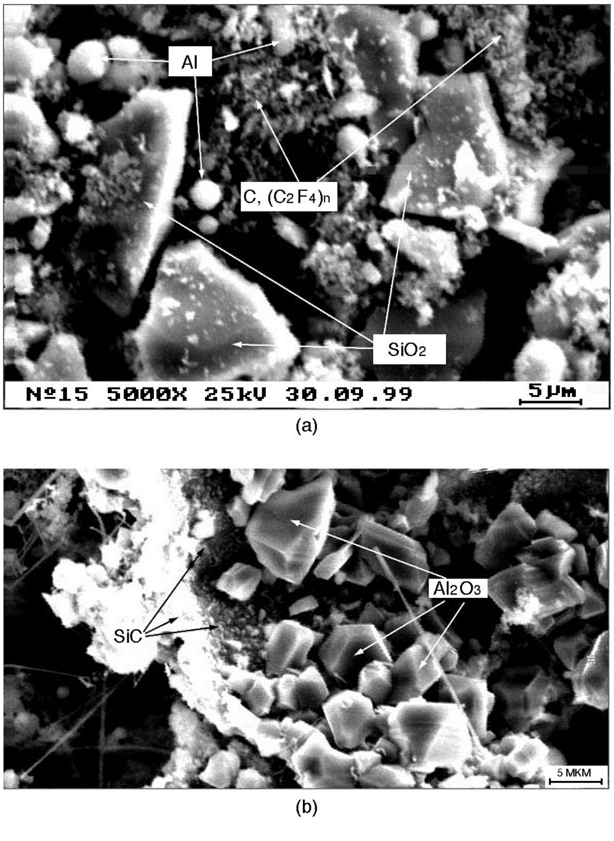


Fig. 3. XRD pattern of reaction products corresponding to the system $3SiO_2$–4Al–3C–5%Teflon at $P_{Ar}=5$ MPa.



(a)

(b)

Fig. 4. Microstructure of initial mixture (a) and reaction product (b) for the system $3SiO_2$–4Al–3C(carbon black)–4% Teflon.

From EDS analysis, these crystallites contain aluminum as a basic element, while the matrix structure is constituted by silicon.

Apart from the above-mentioned particles, whiskers are seen also in Fig. 4b. In the majority of cases EDS analysis identified them as α-silicon carbide. According to the microscopic observations, the amount of these whiskers appreciably increases if the content of Teflon in the initial mixture is augmented. It was also found that whiskers are observed mainly in large pores and cracks of the burned samples. The average whiskers thickness and length are 0.1–0.5 and 10–50 μm, respectively.

The influence of polystyrene content in the starting mixture on combustion temperature and propagation velocity is shown in Fig. 5, where K indicates the weight percentage of polystyrene added as partial substituent of carbon black so that the stoichiometric carbon requirement of reaction (1) is fulfilled. It seems that T_c and U_c do not vary appreciably with changing of K value, while displaying a relatively small maximum at $K = 5$ wt.%. The latter one is most likely connected to polystyrene decomposition. The presence of polystyrene in the starting mixture results in high brittleness of the obtained products, whose composition on the other hand, does not change with respect to the case when no polystyrene is added. The formation of hydrogen due to polymer decomposition may be responsible of the behavior of this material, since hydrogen is expulsed from the reacting mixture [14].

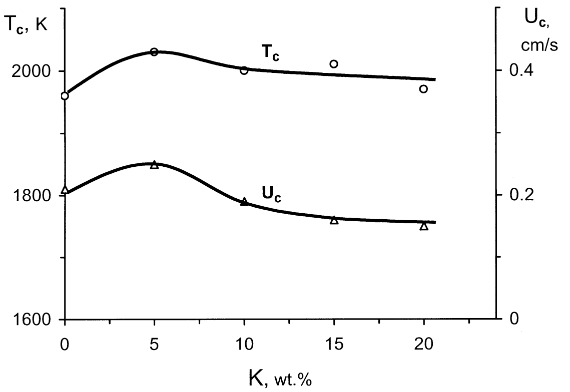


Fig. 5. Combustion temperature (T_c) and velocity (U_c) for the system $3SiO_2$–4Al–3C–4% Teflon as a function of polystyrene content (K) in the initial mixture at $P_{Ar} = 0.5$ MPa.

In Table 1, the values of combustion temperature and propagation velocity may be compared when varying the type of powder polymer added as partial substituent of carbon black to the initial mixture at a fixed percentage, i.e. 10 wt.%, while maintaining constant the amount of Teflon.

According to microscopic investigations, the content of SiC whiskers in the end product increases appreciably with increasing the polymer amount added into the initial mixture. Typical microphotographs of burned down samples indicate that SiC whiskers are mainly long and thin (cf. Fig. 6a) with melted balls on the top and display a random distribution. However, when

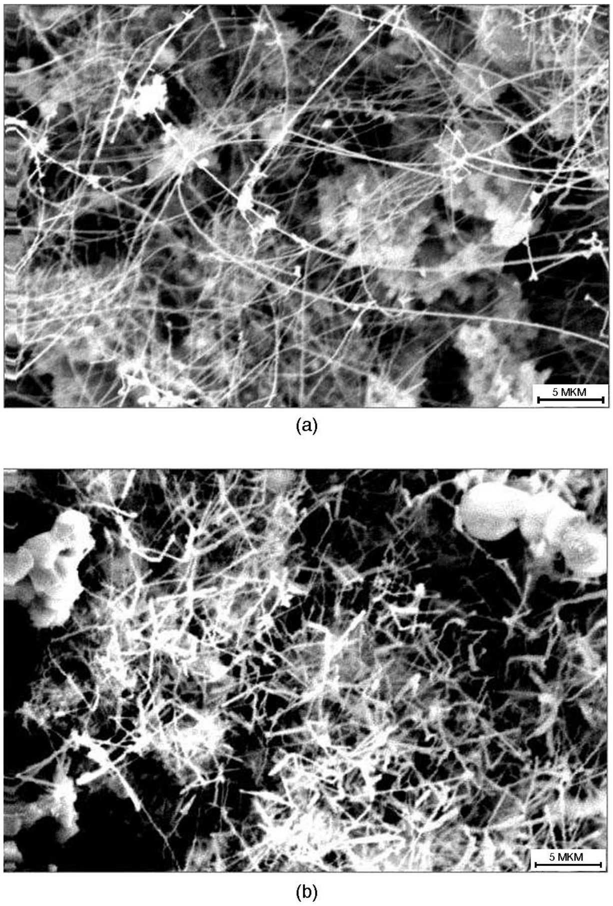


Fig. 6. SEM photographs of whiskers obtained when reacting the systems $3SiO_2/4Al/3C(90\%C+10\%\text{polystyrene})$–4%Teflon (a) and $3SiO_2/4Al/3C(80\%C+20\%\text{polystyrene})$–4% Teflon (b), respectively, at $P_{N2} = 0.5$ MPa.

Table 1
Effect of powder polymer species added to the initial mixture in addition to Teflon on combustion temperature, front velocity and product composition

Initial mixture	T_c (K)	U_c (cm/s)	Phase composition
$3SiO_2+4Al+3C(90\%C+10\%(C_8H_8)_n)+\ 4\%(C_2F_4)_n$	2000	0.19	α-Al_2O_3, β-SiC, α-SiC(2H), traces of SiO_2
$3SiO_2+4Al+3C(90\%C+10\%(C_2H_4)_n)+\ 4\%(C_2F_4)_n$	1950	0.17	α-Al_2O_3, β-SiC, α-SiC(2H), traces of SiO_2
$3SiO_2+4Al+3C(90\%C+10\%(C_3H_6)_n)+\ 4\%(C_2F_4)_n$	2020	0.16	α-Al_2O_3, β-SiC, α-SiC(2H), traces of SiO_2

increasing polystyrene content, sometimes short and thick crystals are also observed (cf. Fig. 6b). Different concentration levels of gases along sample cross section may be responsible of the morphological characteristics of these whiskers.

It is well known that the majority of SHS reactions are considered "gasless" arbitrarily, since the combustion process is usually accompanied by the evolution of gaseous impurities [15]. The combustion velocity of most SHS systems usually increases when increasing the external pressure and remains constant once certain pressure level are reached. As it was shown in previous studies [12,16], the augmentation of combustion velocity is concerned with the suppression of expansion processes during sample burning and the improvement of thermal contact between particles. From this point of view the system $3SiO_2/4Al/3C$-m wt.% PTFE is not an exception as it may be seen from Fig. 7 where the combustion temperature and front velocity are reported as a function of the working pressure and the gaseous atmosphere. In fact, as the pressure is increased the combustion velocity does the same, reaching a constant value, i.e. 0.28 cm/s in nitrogen and 0.2 cm/s in argon media, respectively. It follows from Fig. 7 that at $P \geqslant 0.5$ MPa the combustion velocity in nitrogen is appreciably higher than in argon, while the combustion temperature is practically the same. This finding demonstrates that at high pressure levels the gaseous nitrogen certainly participates to the reaction.

From the XRD analysis results reported in Fig. 8, the reaction product obtained at $P > 1.5$ MPa under nitrogen atmosphere contains, in addition to products shown in Fig. 3, the following compounds: aluminium nitride (AlN), silicon carbonitride/silicon cyanide (SiCN), aluminum oxynitrisilicide ($Al_6Si_6N_8O_9$) and mullite ($Al_6Si_2O_{13}$).

The typical microstructure of end products obtained under three levels of nitrogen pressure is shown in Fig. 9a–c. Fig. 9a shows crystallites of Al_2O_3 almost regularly distributed in a SiC matrix phase which displays a fine structure. However, in some places not fully formed Al_2O_3 crystals are found also (Fig. 9b). Since at the combustion temperature levels reached both aluminum and silicon oxide can be present as liquids, it is possible to assume that the formation of Al_2O_3 crystals occurs by crystallization from a liquid melt.

Notice that accumulation of sticks-needle shape crystals was detected both in nitrogen and argon medium. As an example, Fig. 9c shows a micrograph related to the first case. According to EDS analysis data the Si/Al ratio for these crystals is equal to 1/3 which is consistent with mullite revealed by XRD.

The influence of the initial sample density (ρ), size of aluminium particles (μ_{Al}), excess of aluminum (g_{Al}) and carbon (as soot, g_C) in the initial mixture with respect to the stoichiometry given by reaction (1) on combustion temperature and velocity, has been also investigated. It is shown that by changing ρ, μ_{Al} and g_C in the range 1.3–1.7 g/cm^3, 5–150 μm and 0–20 wt.%, respectively, the values of T_c and U_c are practically not affected.

Appreciable changes of combustion temperature and phase composition of end products occur when burning samples with superstoichiometric content of aluminum, as shown in Fig. 10. It is seen that while the value of the combustion velocity remains practically constant (U_c= 0.23 cm/s) regardless of the value of the excess of aluminum in the starting mixture with respect to the stoichiometric amount, T_c displays a maximum (2130 K) between 10 and 20 wt% aluminum excess. According to XRD analyses instead of expected free aluminum, the end product contains AlN that may be responsible of the increase of T_c value. At $g_{Al} > 30\%$, the aluminum oxide is present in the final product in two forms:α-Al_2O_3 and γ-Al_2O_3.

It was found that the thickness of whiskers increases when increasing the aluminum excess, reaching 1 μm (cf. Fig. 11) at $g_{Al} = 30\%$. EDS analyses show that in

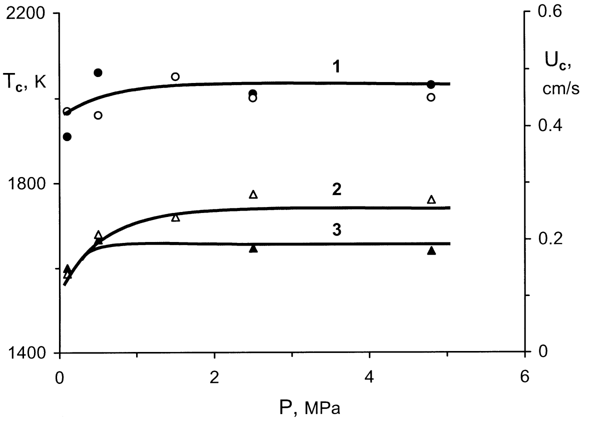


Fig. 7. Influence of gas pressure on the combustion temperature and velocity for the system $3SiO_2$–4Al–3C–4% Teflon: 1, T_c (○, in nitrogen; ●, in argon medium); 2, 3, U_c (2, in nitrogen; 3, in argon medium).

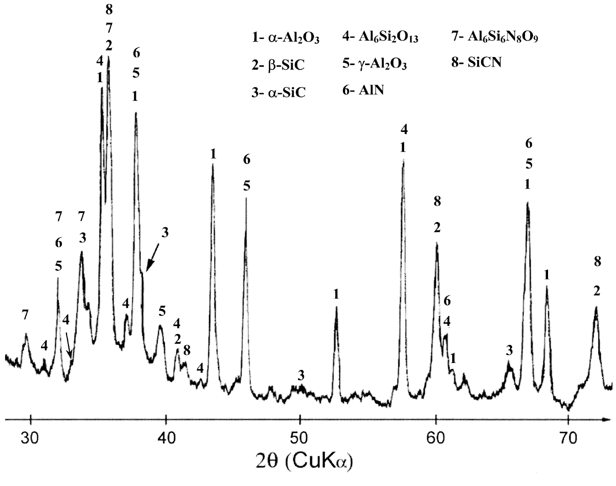
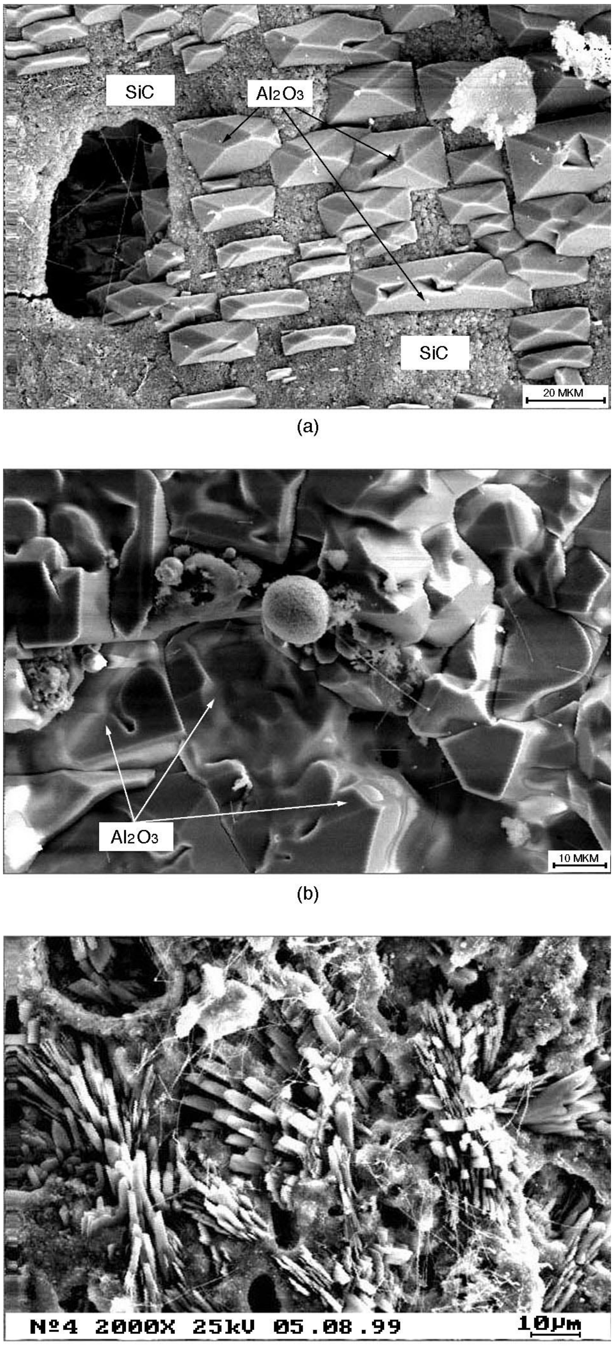


Fig. 8. XRD pattern of reaction products corresponding to the system $3SiO_2$–4Al–3C–4%Teflon at $P_{N2} = 5$ MPa.



(a)

(b)

(c)

Fig. 9. Typical microstructure of endproducts obtained after combustion of $3SiO_2$–4Al–3C–4% Teflon system at various nitrogen pressures:(a) $P = 2.5$ MPa; (b) $P = 0.5$ MPa; (c) $P = 1.5$ MPa.

argon medium aluminum content in whiskers sharply grows and the ratio Si/Al becomes equal to 1/3 which corresponds to mullite. In nitrogen medium this ratio is equal to 3/5, i.e. corresponds to SiAlON.

From Fig. 11, it follows that when 30% of aluminum excess in the starting mixture was used, the formation of tape-like crystals are observed, having length up to 25–30 μm.

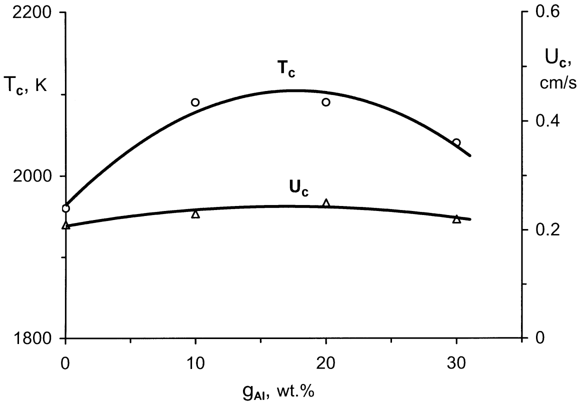


Fig. 10. Combustion temperature (T_c) and velocity (U_c) as function of aluminium excess (g_{Al}) in the initial mixture for the system $3SiO_2$–4Al–3C–4% Teflon under $P_{N2} = 0.5$ MPa.

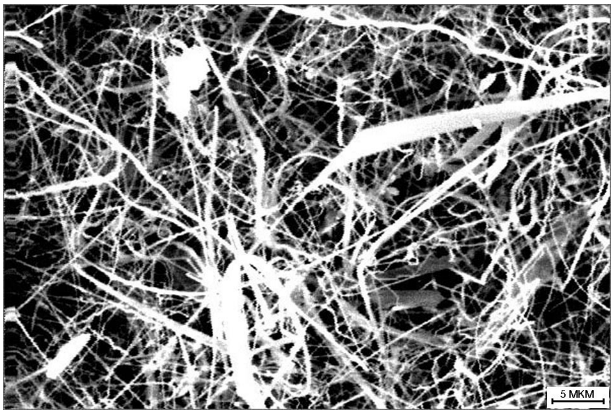


Fig. 11. Morphology of endproducts obtained after combustion of $3SiO_2$–4Al–3C–4%Teflon system with 30 wt.% aluminium excess under $P_{N2} = 0.5$ MPa.

4. Concluding remarks

The synthesis of alumina/silicon carbide composites through self-propagating reactions activated by tetrafluoroethylene polymer (Teflon) is investigated. A multifunctional role of Teflon during combustion is postulated. In particular, Teflon affects the activation of aluminum particles, gives rise to an intensification of the formation of gas-transport species and also participates in whiskers formation.

It is established that the obtained endproducts consist of well-formed crystals of alumina, fine grained silicon carbide and whiskers-shaped crystallites of SiC. Experimental results confirm that liquid phase plays a leading role during combustion and for the structure formation of endproducts.

It is also found that the addition of powdered organic polymers to the initial mixture promotes the formation of whiskers in the final product.

Acknowledgements

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