



Combined effect of thermal and mechanical activation on the combustion and phase formation laws in the Cr–Si–C system

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ABSTRACT

In this work combustion and phase formation laws for mechanically and thermally activated Cr–Si–C system were studied. For thermal stimulation in the combustion reaction $\text{Mg}-(\text{C}_2\text{F}_4)_n$ high caloric mixture was used. It was shown that in the system under study, combustion takes place by two sequential stages. The first stage is interaction between Si and $(\text{C}_2\text{F}_4)_n$ or Mg with $(\text{C}_2\text{F}_4)_n$ (temperature can rise up to 1200 °C), which are responsible for combustion front propagation. In the first stage, formation of small amount of CrSi_2 takes place. The second stage is Si + C reaction which is responsible for high-temperature combustion. In the second stage, formation of CrSi_2 completes. The influence of mechanical treatment on combustion laws for $(\text{Cr-Si}) + (\text{Si-C}) + (\text{Mg}-(\text{C}_2\text{F}_4)_n)$ system was investigated. It was shown that mechanical activation (MA) is effective for systems where amount of chromium is high, while for systems where Si–C part is appreciable MA does not have any affect.

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1. Introduction

Structural materials possessing high electrical conductivity, erosion and corrosion resistance, and strength at elevated temperature are widely used in modern technologies [1,2]. Particularly, silicon based composites (e.g. $\text{WSi}_2\text{-MoSi}_2$, $\text{WSi}_2\text{-ZrO}_2$, $\text{Si}_3\text{N}_4\text{-SiC}$, $\text{WSi}_2\text{-SiC}$, and $\text{CrSi}_2\text{-SiC}$) are promising [3–8].

In the use of materials at elevated temperatures in harsh environments, it is apparent that in most instances ceramics is the best choice to provide corrosion resistance [9]. Particularly, significant attention is focused on continuous carbon fiber-reinforced carbon matrix composites (C/C) due to its high specific mechanical strength, resistance to the thermal shock and the retention of mechanical properties to temperatures above 2000 °C. C/C composites are stable up to 3000 °C and more in inert or vacuum environments, but have the serious drawback of reaction with oxidizing atmosphere at a temperature as low as 500 °C [10]. Fu et al. showed that the $\text{CrSi}_2\text{-SiC}$ composite has excellent oxidation resistance and that its thermal expansion coefficient matches with that of C/C composites [11,12]. The $\text{CrSi}_2\text{-SiC}$ composite with excellent oxidation resistance and a high melting point is widely used as an oxidation protective coating for heating elements, C/C composites, and materials for space shuttles. However, in the literature

there is very limited information on the preparation of $\text{CrSi}_2\text{-SiC}$ composites. The described fabrication methods are generally multi-stage. Schiavon and Yoshida reported a new fabrication method for $\text{CrSi}_2\text{-SiC}$ composite by the active-filler-controlled polymer pyrolysis, using a siloxane polycyclic network filled with CrSi_2 [13]. The synthesis process described by Vlasova et al. [14] is based on mechanical mixing of reactant powders, SiC, Cr and Si, followed by heat treatment. However, at present it is inherently lack of simple methodology for synthesis of this composite and hence the developments of new synthesizing approaches are interesting from both scientific and practical viewpoints.

The main challenge of this paper is to study the formation laws of $\text{CrSi}_2\text{-SiC}$ composite using Cr, C and Si reactant powders in a self-propagating high-temperature synthesis mode (SHS). SHS technique is an effective method for producing a wide variety of single-phase ceramics as well as composites and solid solutions [15–17].

It is well known that the size of reactants' particles (d) plays an important role in heterogeneous solid-state reactions. This fact becomes more prominent in the case of self-sustaining reactions. In order to promote a mass transfer without involving liquid phase, either a sharp decrease in d or participation of gaseous compounds is necessary. In the latter case, reagents should form gaseous compound(s) which will accelerate the reaction via gas-phase transportation. This may be achieved using certain halogen-containing organic and/or oxygen-containing inorganic compounds. These compounds may react with reactant(s) generating huge amount heat which in turn promotes solid-state reaction.

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This is the basic principle of thermal and chemical activation [18–22].

Currently mechanical activation (MA) is being widely used for controlling solid-state reactions [23]. Depending on the amount of energy accumulated in the system subjected to mechanical treatment, (i) an increase of the reactivity of grinded particles may occur or (ii) an initiation of chemical reaction (mechanochemical activation, MCA) may take place. As a result, MA allows to control and promote the process and to obtain fine-grained products, including nano-scale ones. The efficiency of MA strongly depends on the ductile/brittle properties of reagents. MA is efficient in the case of ductile reagents; while at the use of brittle compounds the effectiveness decreases [24–26].

The basic philosophy of this research is to combine different activation methods with SHS and investigate combustion and phase formation laws.

The objective of this research is threefold: (i) utilization of mechanical and thermal activation methods to investigate the combined effect of these methods on a self-sustaining character of the reaction among Cr, Si, and C elemental powders; (ii) investigation of the combustion characteristics and product microstructure of a combustion-synthesized CrSi_2 -SiC composite; (iii) determination of optimal synthesis conditions for the formation of CrSi_2 -SiC composites with different compositions ranging from 20 to 80 wt% of CrSi_2 phase.

2. Experimental methods

A mixture of magnesium and polytetrafluoroethylene (PTFE), $[2\text{Mg}-(\text{C}_2\text{F}_4)_n]$ (further marked as Thermal Activator-TA) was chosen as promoter for the reacting system under study [27–29]. The reaction between magnesium and PTFE is highly exothermic and can be represented as follows:



$$\Delta H_{298}^\circ = -1123.2 \text{ kJ mol}^{-1}, \quad T_{\text{ad}} = 3240^\circ\text{C}$$

Experiments were carried out in a reactor of constant pressure with a volume of 3 L. The cylindrical samples consisting of mixed Cr, Si, C, Mg, and PTFE, with 30–40 mm in diameter and 30–40 mm in height were prepared using uniaxial press. Bulk density of these samples varied from 1.5 to 2.4 g/cm³ depending on their composition. The following powders were used as raw materials: Cr (with 5 μm average particle size), silicon powder (KR-1 mark with 10 μm average grain size), granular carbon (P-803 mark with 99.8% purity and <1 μm particle size), magnesium powder (MPF-3 mark with 99.7% purity and <200 μm particle size) and polytetrafluoroethylene (PTFE) FT-4 mark powder (with 99.6% purity and <10 μm particle size). Combustion synthesis experiments were carried out under 0.5–2 MPa argon pressure (with 99.7% purity, oxygen content less than 0.15 vol.%). Mechanical activation of initial mixture was performed in the ball mills. Stainless steel grinding medium (12–14 mm in diameter) was used. The ratio of the grinding media to milled powder was 6:1 by weight. A constant speed of 120 rpm and milling time of 1–10 h were used.

The maximum combustion temperature (T_c) and the temperature distribution in the combustion wave were measured by tungsten-rhenium thermocouples (W/Re-5, W/Re-20, 200 μm in diameter) covered with a thin layer of boron nitride. Combustion front velocity was determined by recording signals from several thermocouples embedded at different axial positions in a sample. The output signals of thermocouples were transformed by a data acquisition board at the rate of 1 kHz, and were recorded by PC. The standard error of measurements for T_c and U_c were $\pm 15^\circ\text{C}$ and 5%, respectively.

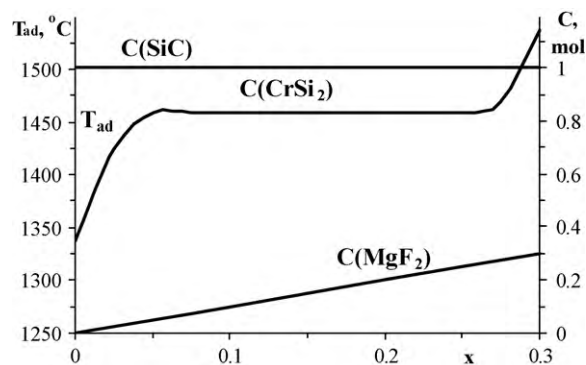


Fig. 1. Adiabatic combustion temperature (T_{ad}) and equilibrium composition of combustion products (on graphic marked as C) calculated for the $(\text{Cr}-2\text{Si}) + (\text{Si}-\text{C}) + x\text{TA}$ system vs. x value.

The products (the combustion products are powders) were milled in vibratory mills (vibration speed 20 kHz) and milling time was 10 min. The products were examined using XRD method with monochromatic $\text{CuK}\alpha$ radiation (diffractometer DRON-3.0, Burevestnik, Russia). The microstructure of the synthesized composites was evaluated using scanning electron microscope (BS-300, Tesla, CZ). Differential thermal and gravimetric analyses were conducted using DTA/DTG, Q-1000 instrument. DTG and DTA point registration at every 1 s, sample 70 or 100 mg in Al_2O_3 crucibles, Al_2O_3 powder as reference material. Measurements were conducted in argon flow. Heating rate was programmed to be $20^\circ\text{C min}^{-1}$.

3. Results and discussion

3.1. Thermodynamic analysis

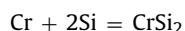
One of the primary tasks to successfully design the combustion synthesis system is to carefully consider the thermodynamics. For estimating the value of adiabatic combustion temperature (T_{ad}) and equilibrium composition of the final products, preliminary thermodynamic analyses of the $(\text{Cr}-2\text{Si}) + (\text{Si}-\text{C}) + x\text{TA}$ system, where “ x ” is molar coefficient, were performed using the “ISMAN - THERMO” software developed for multicomponent heterophase systems [30]. Calculation of equilibrium characteristics is based on the minimization of the Gibbs free energy of the system, which accounts for the contributions of Gibbs free energies for all components and their concentrations. The results were confirmed by FACT on line thermodynamic software package [31]. In all calculations carbon obtained during the decomposition of PTFE was taken into account as a part of a total carbon balance.

Results generated from the calculations show that there is no chemical interaction between CrSi_2 and SiC over a wide temperature interval (20–1800 °C). The major compositions and adiabatic temperature are summarized in Fig. 1.

It can be seen that for “ x ” values varying from 0 to 0.05, the adiabatic temperature increases from 1340 to 1457 °C. Then in the range $0.05 \leq x \leq 0.25$ the adiabatic temperature remains constant at 1460 °C due to melting of chromium silicide. With the increase of x value, the adiabatic temperature increases.

As Fig. 1 clearly shows, in all ranges of “ x ” value, combustion products contain chromium disilicide and silicon carbide and a certain amount of MgF_2 .

In summary, overall chemical reactions may be schematically present as follows: note the reaction (2) is multiplied by “ k ” and the reaction (3) by “ x ”:



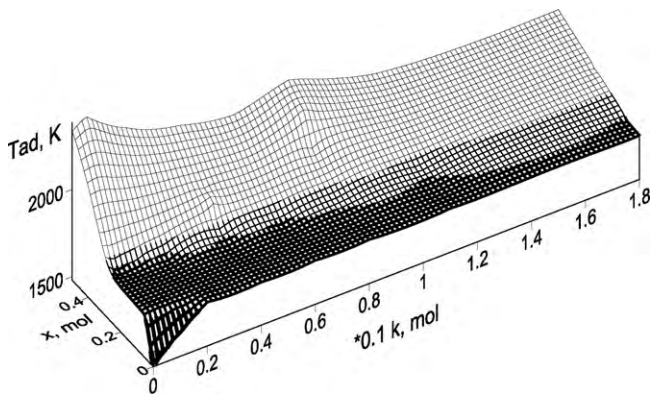
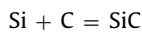
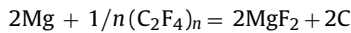


Fig. 2. Adiabatic temperature map for the $(\text{Cr} + 2\text{Si})\text{--}k(\text{Si} + \text{C})\text{--}x\text{TA}$ system vs. x and k values.

$$\Delta H_{298}^{\circ} = -97.5 \text{ kJ mol}^{-1}, \quad T_{\text{ad}} = 1210^{\circ}\text{C} \quad (1)$$

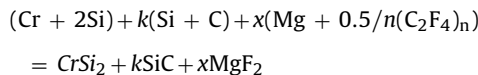


$$\Delta H_{298}^{\circ} = -71.9 \text{ kJ mol}^{-1}, \quad T_{\text{ad}} = 1670^{\circ}\text{C} \quad (2)$$

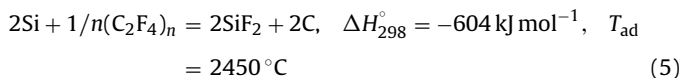
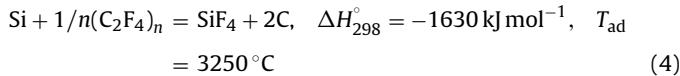


$$\Delta H_{298}^{\circ} = -1128.5 \text{ kJ mol}^{-1}, \quad T_{\text{ad}} = 3230^{\circ}\text{C} \quad (3)$$

Total



In this case fluorination of silicon may proceed as well:



The (4) and (5) reactions may also play a role in chemical activation due to the formation of gaseous fluorides [21,22].

Fig. 2 presents the results of thermodynamic calculations for $(\text{Cr} + 2\text{Si})\text{--}k(\text{Si} + \text{C})\text{--}x\text{TA}$ reacting system, where x and k are molar coefficients. In compliance with thermodynamic analysis the combustion temperatures for this system tend to grow in parallel with an increase in the x factor (indicates the portion of activated additive – $\text{Mg}\text{--}0.5(\text{C}_2\text{F}_4)_n$ mixture).

The dark marked area in Fig. 2 corresponds to the melting zone of chromium disilicide ($T_{\text{melt}} = 1457^{\circ}\text{C}$). In order to obtain $\text{CrSi}_2\text{--SiC}$ composite, the value of “ x ” has to be above 0.25 and the corresponding adiabatic temperature over 1457°C (highlighted area in Fig. 2).

3.2. Differential thermal analyses

In order to obtain better understanding of combustion characteristics in the system under study, it is essential to have a clear picture of reaction mechanism. For this purpose firstly thermogravimetric and differential thermal analyses for the (i) $(\text{Cr} + 2\text{Si})\text{--}0.7(\text{Si} + \text{C})\text{--}0.3(\text{Mg}\text{--}0.5\text{FT}\text{--}4)$, (ii) $(\text{Cr} + 2\text{Si})\text{--}0.7(\text{Si} + \text{C})\text{--}0.2(\text{Si}\text{--}\text{FT}\text{--}4)$ systems as well as for pure PTFE were conducted (Fig. 3). In this case DTA-3 curve represents PTFE's differential thermal analyses. Such a choice of initial compositions

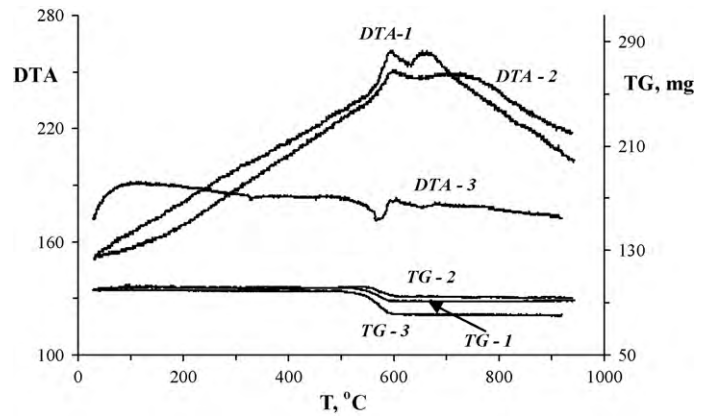


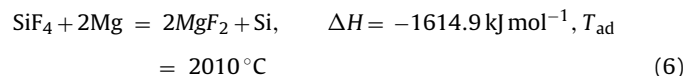
Fig. 3. DTA and TG curves for the systems: (1) $(\text{Cr} + 2\text{Si})\text{--}0.7(\text{Si} + \text{C})\text{--}0.3(\text{Mg}\text{--}0.5\text{FT}\text{--}4)$, (2) $(\text{Cr} + 2\text{Si})\text{--}0.7(\text{Si} + \text{C})\text{--}0.2(\text{Si}\text{--}\text{FT}\text{--}4)$, (3) PTFE.

has pursued a goal to figure out contribution of Si + PTFE interaction (reactions (4) and (5)) to the entire process.

According to DTA trace, the endothermic effect is recorded (DTA-3 curve) at 550°C which corresponds to the decomposition temperature of PTFE (this may be proven by mass loss recorded by TG-3 curve).

The exothermic peak corresponding to 610°C is observed on DTA trace for the $(\text{Cr} + 2\text{Si})\text{--}0.7(\text{Si} + \text{C})\text{--}0.2(\text{Si}\text{--}\text{FT}\text{--}4)$ mixture (DTA-2 curve). This effect is accompanied by mass loss (please refer to TG-2 curve in Fig. 3). One can state that in this case reaction occurs between the silicon and compounds obtained from decomposition of PTFE. Schematically these interactions are presented in the reactions (4) and (5). Comparing the data of DTA-3 and DTA-2 curves one can state that reaction starts immediately after decomposition of PTFE. DTA-1 and DTG-1 curves correspond to the $(\text{Cr} + 2\text{Si})\text{--}0.7(\text{Si} + \text{C})\text{--}0.3(\text{Mg}\text{--}0.5\text{FT}\text{--}4)$ system.

Based on the results of thermogravimetric and differential thermal analyses one can conclude that decomposition of PTFE takes place at 550°C then immediately follows fluorination of silicon. In the case of Mg-containing mixture, at $630\text{--}640^{\circ}\text{C}$ magnesium melts and then fluorination of magnesium takes place according to the reaction:



3.3. Combustion laws for the Cr–Si–C–TA system

The investigations were carried out mainly for the green mixtures where after combustion 40% $\text{CrSi}_2\text{--}60\%\text{SiC}$, 80% $\text{CrSi}_2\text{--}20\%\text{SiC}$ and 20% $\text{CrSi}_2\text{--}80\%\text{SiC}$ composites were expected. The corresponding compositions of initial mixtures were: (i) $(\text{Cr} + 2\text{Si})\text{--}4(\text{Si} + \text{C})\text{--}x\text{TA}$ (mixture I), (ii) $(\text{Cr} + 2\text{Si})\text{--}0.7(\text{Si} + \text{C})\text{--}x\text{TA}$ (mixture II) and (iii) $0.1(\text{Cr} + 2\text{Si})\text{--}(\text{Si} + \text{C})\text{--}x\text{TA}$ (mixture III). Such choice of mixtures is based on the following argumentations: in this case it is possible to obtain composites where the amounts of compounds are varied in a wide range: from 20 to 80 wt%:

- (1) Because of containing ductile (Cr) and brittle (Si, C) reagents, the efficiency of MA in experiments can be regulated by varying the relative amount of reagents.
- (2) Changing the ratio of components makes possible to change whole energy resource which will allow finding out contribution of thermal activation in the total process.
- (3) Variation in the type/amount of additive and duration of MA may be used to influence the combustion characteristics and

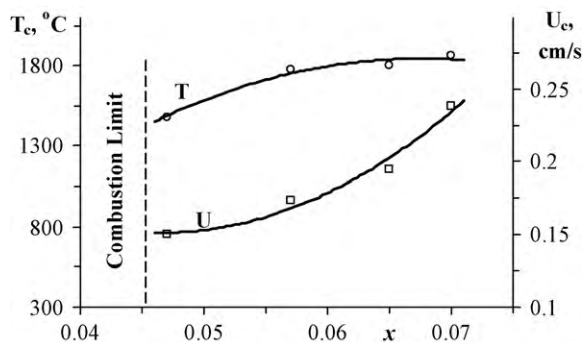


Fig. 4. Combustion parameters for the $(Cr+2Si)-4(Si+C)-xTA$ system vs. x value at $P_{Ar} = 0.5$ MPa.

thus to evaluate the contribution of MA and TA to the entire process.

3.3.1. Combustion laws for the $(Cr+2Si)-4(Si+C)-xTA$ system (mixture I)

3.3.1.1. Effect of thermal activation. The effect of thermal activation was firstly explored for the mixture I, and the x values varying between 0.04 and 0.07 combustion laws were studied. The combustion parameters vs. promoter's amount (x value) can be visualized as shown graphically in Fig. 4. It can be clearly seen in Fig. 4 that for " x " values varying from 0.047 to 0.055 combustion temperature increases from 1500 °C to 1800 °C.

In the range 0.055–0.07 the combustion temperature remains constant at ~1800 °C, while combustion velocity continuously grows. It is believed that at high content of TA contribution of the gas-phase reactions increases. According to obtained data combustion does not proceed when amount of TA is below 0.045.

In order to estimate the influence of reactants' nature on MA and TA a series of experiments were conducted for the mixtures II and III.

3.3.2. Combustion laws for the $(Cr+2Si)-0.7(Si+C)-xTA$ (mixture II)

3.3.2.1. Effect of thermal activation. Like previous cases combustion parameters are increased with increasing TA amount. As shown in Fig. 5 varying TA amount from 0.27 to 0.5 leads to the rise in the combustion temperature from 1170 °C to 1720 °C and combustion wave propagation velocity increases by about 20 times. When the amount of TA is below 0.25 it is impossible to initiate the combustion reaction.

As it was expected mechanical activation (MA) would influence effectively in the mixture II because it contains high amount of plas-

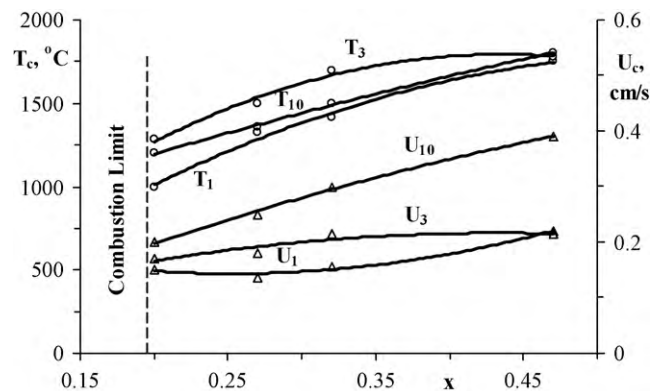


Fig. 6. Combustion temperature T_c (T_1 , T_3 , T_{10}) and combustion velocity U_c (U_1 , U_3 , U_{10}) as a function of x value for the $[(Cr+2Si)-0.7(Si+C)-xTA]$ mixtures mechanically activated for: 1 (T_1 , U_1), 3 (T_3 , U_3) and 10 h (T_{10} , U_{10}). $P_{Ar} = 0.5$ MPa.

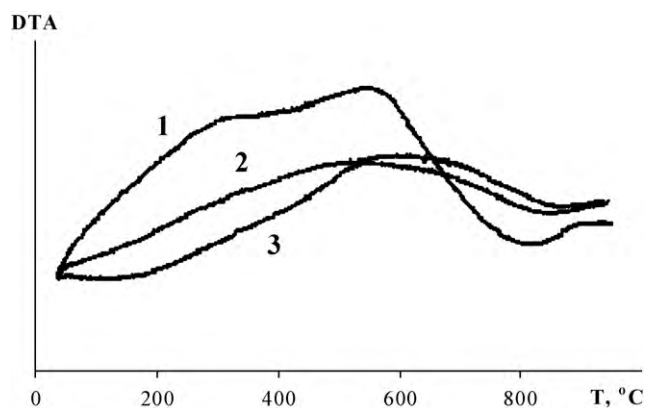


Fig. 7. DTA curves for the $(Cr+2Si)-0.7(Si+C)-xTA$ system. Duration of MA treatment: (1) 0 h; (2) 10 h; (3) 3 h: argon environment.

tic component (i.e. Cr). Coming from this assumption the mixture II was subjected to mechanical treatment (1, 3, and 10 h with the mixture/ball ratio 1/6).

3.3.2.2. Effect of mechanical activation. The combined influence of MA and TA on the combustion parameters (values of T_c and U_c) for the mixture II is illustrated in Fig. 6.

As it is shown in Fig. 6, combustion parameters T_c and U_c for the $(Cr+2Si)-0.7(Si+C)-xTA$ mixture grow with increasing MA time. It should be play the feature up that with increasing the MA dura-

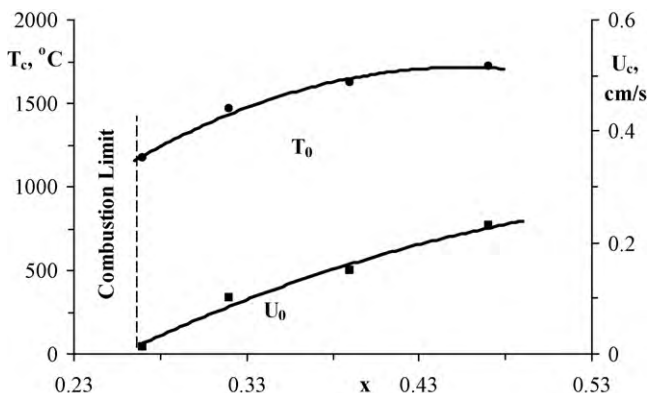


Fig. 5. Combustion parameters for the $(Cr+2Si)-0.7(Si+C)-xTA$ system vs. x value at $P_{Ar} = 0.5$ MPa.

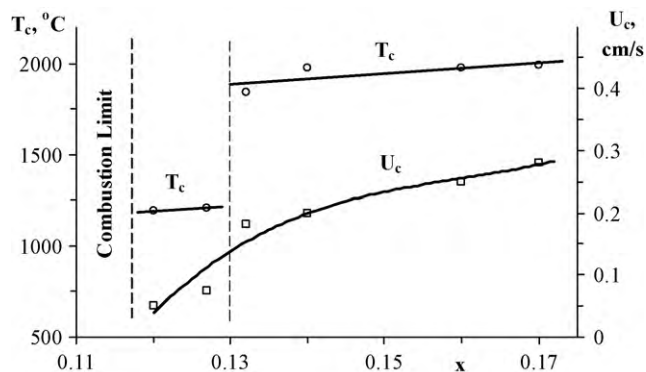


Fig. 8. Combustion parameters for the $0.1(Cr+2Si)-(Si+C)-xTA$ system vs. x value. $P_{Ar} = 0.5$ MPa.

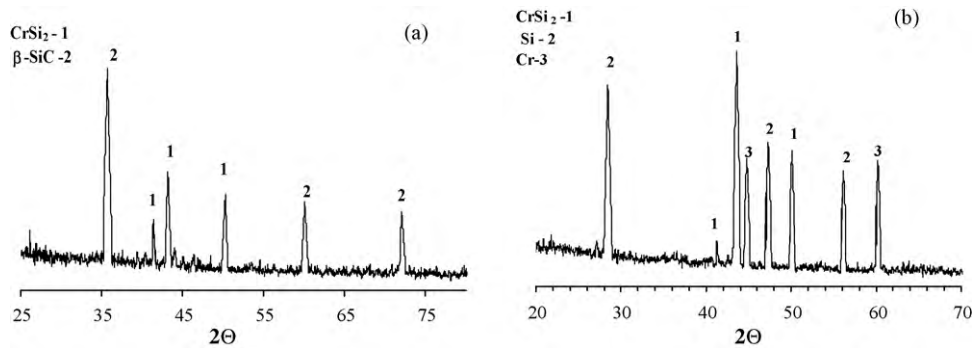


Fig. 9. XRD patterns of combustion products for the $0.1(\text{Cr}+2\text{Si})-(\text{Si}+\text{C})-x\text{TA}$ system: (a) $x=0.25$ and (b) $x=0.12$; $P_{\text{Ar}}=0.5$ MPa.

tion, the combustion limit is shifted toward lower values of x . Thus, combustion limit for mechanically non-treated mixture appears at $x=0.27$ (please refer to Fig. 5), while after MA combustion limit appears at $x=0.2$ (Fig. 6). This fact proves the assumption that MA has certain contribution in the entire process. The results obtained for the combustion temperature must be underlined. Thus, as seen from Fig. 6 combustion temperature slowly grows for the mixtures subjected to 1 and 3 h MA, while when MA = 10 h, combustion temperature takes intermediate place in comparison with T_1 and T_3 . It must be draw attention on fact that the combustion velocity of 10 h MA mixture is the highest. In order to get the phenomena over, a series of experiments were conducted by thermogravimetric and differential thermal analyses (Fig. 7).

Fig. 7 shows there is an endothermic effect on the DTA curves for $(\text{Cr}+2\text{Si})-0.7(\text{Si}+\text{C})-x\text{TA}$ system at 800°C . It can be clearly seen that for the non-activated mixture the highest endothermic effect is recorded. The endothermic effect for the mixture treated 10 h is less than for 3 h activated mixture. It is believed that this effect is caused by energy accumulated in the system subjected to mechanical treatment. Thus at 3 h MA an increase of reactivity of grinded particles takes place while at 10 h MA probably formation of solid solution occurs.

It seems also interesting to explore the effect of MA duration on the amount of iron contamination in final products. The data of chemical analysis show that, upon MA for 10 h,

the initial Fe content in green mixture (0.5 wt%) grows only to 0.65 wt%.

3.3.3. Combustion laws for the $0.1(\text{Cr}+2\text{Si})-(\text{Si}+\text{C})-x\text{TA}$ (mixture III)

3.3.3.1. *Effect of thermal activation.* In order to determine the influence of TA on combustion laws, the effect of TA amount on combustion parameters was studied. The dependencies of T_c and U_c vs. x , are illustrated in Fig. 8.

In this case two regimes of combustion were observed: low-temperature regime at $x < 0.127$ and high-temperature one at $x > 0.127$ (Fig. 8). Therewith, transfer from one regime to another took place within a narrow interval of TA content (critical concentration value), followed by a temperature jump. The maximum combustion temperature for low-temperature regime averaged from 1100°C to 1250°C , while for high-temperature one it raised up to 1900°C . The results have testified that the jump of temperature value does not affect the monotonous growth of the combustion velocity (it contentiously increases from 0.05 cm/s to ~ 0.275 cm/s). In accordance with XRD analyses the high-temperature regime leads to required products ($\beta\text{-SiC}$ (JCPDS No. 02-1050) and chromium disilicide (JCPDS No. 35-0781), Fig. 9a) while at low-temperature regime formation of silicon carbide does not take place: chromium disilicide, free silicon and chromium were detected (Fig. 9b).

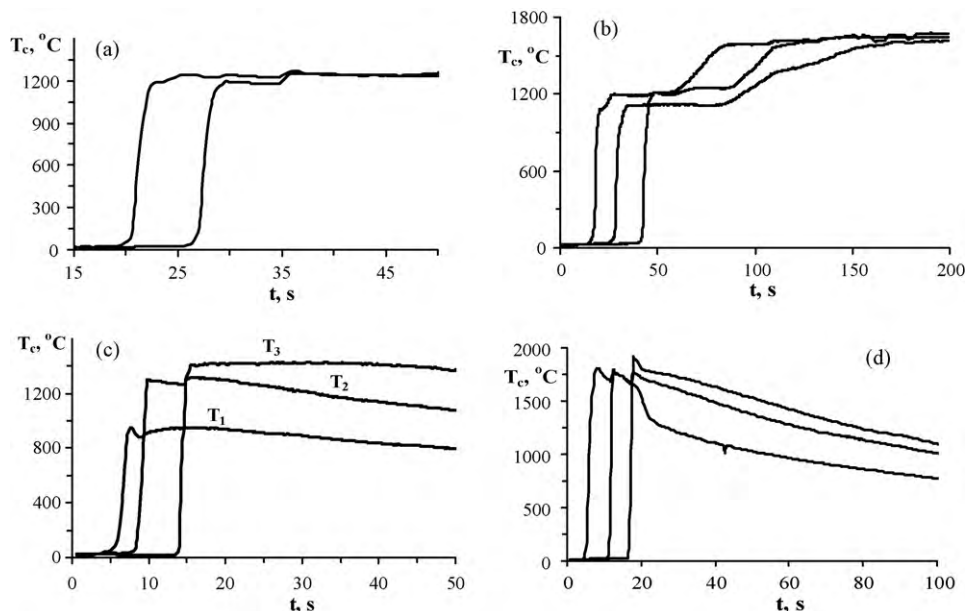


Fig. 10. Temperature distribution patterns at combustion of the $0.1(\text{Cr}+2\text{Si})-(\text{Si}+\text{C})-x\text{TA}$ system: $x=0.13$ (a); 0.133 (b); 0.137 (c); 0.15 (d).

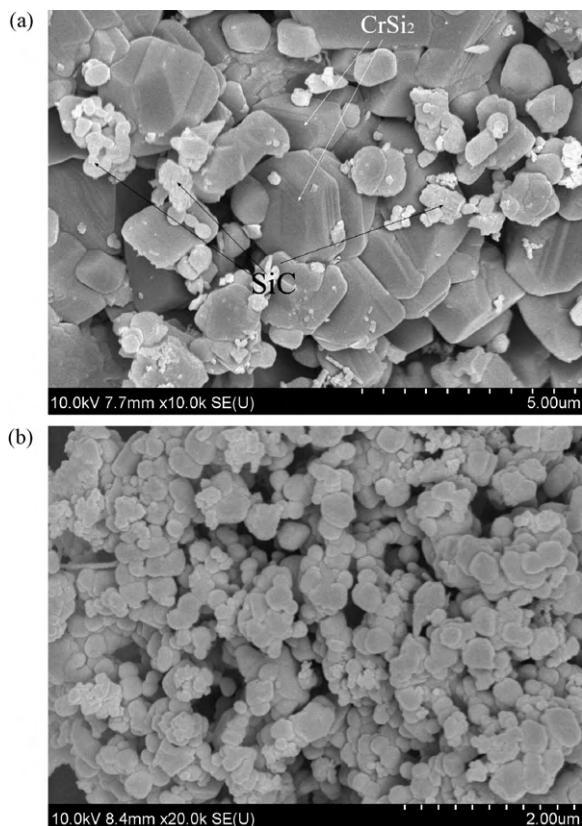
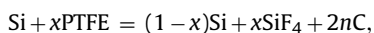
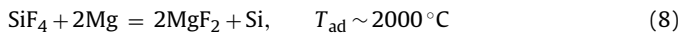
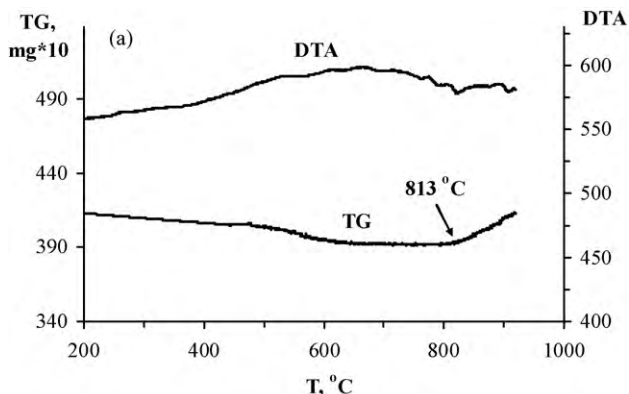


Fig. 11. Microstructure of the combustion product for the $(\text{Cr} + 2\text{Si}) - 0.7(\text{Si} + \text{C}) - x\text{TA}$ system. (a) $x = 0.15$ and (b) $x = 0.2$. MA – 3.5 h; $P_{\text{Ar}} = 0.5$ MPa.

These results lead to the conclusion that the combustion process is a multistage. Thus interaction between silicon and PTFE starts the reaction in the initial mixture and is one of the main reactions responsible for combustion wave propagation in the system under study. According to thermodynamic analysis, this exothermic reaction may raise the temperature up to 1200°C (amount of x is $0.04 < x < 0.05$) which is close to the experimentally measured data. In this stage chromium disilicide is formed as well. The next chemical stage is the interaction of magnesium with silicon fluoride by the reaction (6). Thus, the process may be schematically presented by the following reactions:



$$T_{\text{ad}} \sim 1000\text{--}1250^\circ\text{C}; \text{ for } 0.04 < x < 0.05 \quad (7)$$



The temperature generated by these reactions is essential to preheat Si–C mixture. Once the ignition of Si–C reacting system is accomplished the temperature is significantly increased and the SiC phase is formed.



Here reactions (7)–(9) are responsible for the low-temperature regime and combustion wave propagation, while reaction (10) causes the high-temperature regime. According to (10) reaction adiabatic temperature is 1600°C while the combustion temperature is $\sim 1900^\circ\text{C}$. This may be explained provided that reactions (7)–(9) are triggering the reaction (10) according to equation: $T_{\text{ad}} = T_0 + \Delta Q/C$; where T_{ad} is adiabatic temperature, T_0 is reactants' initial temperature, ΔQ is reaction's heat balance, C is thermal capacity of products.

Using the microthermocouple technique it was revealed for the above-mentioned system that depending on x value two types of temperature distribution may be detected in the combustion wave (Fig. 10): (i) single-stage (at $x < 0.127$) and (ii) two-stage (at $0.127 < x < 0.15$). When $x > 0.15$ again single-stage temperature distribution is registered. In Fig. 10 curves are corresponding to the data recorded for various thermocouples embedded at different axial positions in a sample.

For a single-stage process the maximum temperature accounts for $1000\text{--}1250^\circ\text{C}$ (Fig. 10a), and this is the same for the initial step of the two-stage process (Fig. 10b). Fig. 10c presents transition case when combustion starts by low-temperature regime and transfers to high-temperature one. This phenomenon may be explained by accumulation of active components gives off by PTFE's decomposition [32,33]. Most likely the same effect is responsible for the rise of combustion velocity depending on TA's amount. As follows from the temperature profiles (see Fig. 10d) further increment of active additive's amount results in merging two stages and single-stage combustion is registered.

3.3.3.2. Effect of mechanical activation. It was confirmed experimentally that MA does not have significant influence on this system. In this case combustion temperature does not change while combustion front propagates negligibly faster.

3.4. Microstructure analyses

Data on microstructure examinations indicated that combustion products contain particles with two characteristic sizes (Fig. 11). Particles with an average size of about $3\ \mu\text{m}$ are sur-

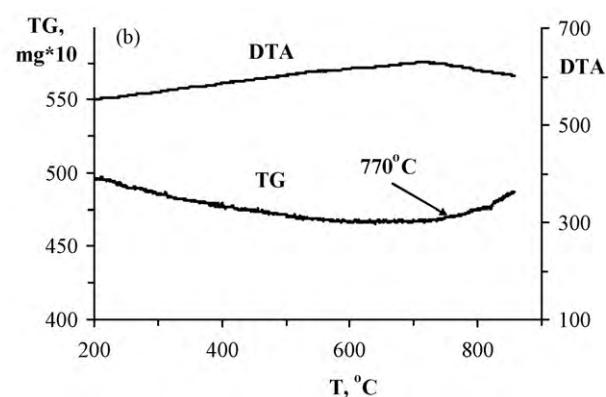


Fig. 12. TG and DTA analyses of oxidation resistances of (a) 80 wt% CrSi_2 –20 wt% SiC and (b) 20 wt% CrSi_2 –80 wt% SiC composites.

rounded with smaller ones $\leq 1 \mu\text{m}$ in diameter. Bigger particles are believed to be chromium disilicide and smaller ones, that is silicon carbide. This assumption was proven by EDX analyses.

Note that the amount of smaller particles increases with the increase of TA amount (Fig. 11b). Hence, it may be stated that phase composition and microstructure of combustion products are dependent on process conditions and the amount of the promoter. By controlling these parameters the target composite with different particle size distributions may be obtained (Fig. 12).

3.5. Resistant of SiC–CrSi₂ composites against oxidation

In order to figure out oxidation resistance of these composites they were subjected to DTA and TG analysis in the oxidizing medium (open air). According to the results obtained from CrSi₂–*n*%SiC composites, where *n* varied from 20 to 80 wt% and possessed excellent oxidation resistance up to $\sim 800^\circ\text{C}$.

4. Conclusion

Combustion laws of the thermally and mechanically activated Cr–Si–C system were studied. As a promoter (Mg–FT-4) mixture was introduced. It laid down the optimal combustion ranges for (Cr + 2Si)–(Si + C)–*x*TA system vs. amount of TA and duration of MA. It was proven that with increasing MA duration the combustion velocity grows as well as combustion limit is expanded. It was supposed that during MA the formation of solid solution takes place which promotes combustion velocity and moderates combustion temperature. It was shown that at increasing amount of *k* factor for the (Cr + 2Si)–*k*(Si + C)–*x*TA system, the effectiveness of MA decreases and when *k* = 10 the initial system practically is not subjected to MA. It was shown that depending on TA's amount two modes of combustion are realized: low-temperature and high-temperature. XRD analysis showed that the products obtained at high-temperature combustion mode consist of CrSi₂ and SiC, while at low-temperature regime non-reacted chromium and silicon were detected. According to the microstructure analysis, the end-products of high-temperature regime consist of particles with a particle size of ~ 0.5 – $3 \mu\text{m}$. It was laid down that for synthesis of composites containing less than 50%, (Si–C) mixture in the initial charge should be subjected to MA 10 h and amount of TA should be no less than 0.22. When amount of (Si–C) is higher than 50% the only TA should be used with *x* value no less than 0.33.

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