

Visualization and Investigation of Combustion of CaSi_2 /PTFE Mixtures

Waldemar A. Trzcinski, Stanislaw Cudzilo, Mateusz Szala

Military University of Technology, Faculty of Advanced Technology and Chemistry
Kaliskiego 2, 00 908 Warsaw, Poland

1 Introduction

Russian scientists leaded by A. G. Merhzanov (Ref. [1]) were the first scientific team which used a high-temperature exothermic combustion proceeding in the solid reactants to synthesize advance ceramic materials (Self-Propagating High Temperature Synthesis – SHS). Up to now, more than 500 substances of unique features have been obtained by the SHS method – Ref. [2]. It was observed at the end of the XX century that the self-sustaining combustion synthesis can also create many nanostructures, such as nanocrystallites, nanofibres and nanotubes of carbon [3-5]. For example, silicon carbide (SiC) nanofibers and nanotubes with a diameter from a few to several tenths nanometers and a length from several to more than one hundred micrometers were obtained from calcium silicide/polytetrafluoroethylene (CaSi_2 /PTFE) system using the combustion synthesis route [6]. Because of unique physical properties, such as a large energy gap, high thermal conductivity and chemical inertness, SiC nanofibres may find many applications, in which some electronic features as well as the possibility of working under high-temperature and harsh-environmental conditions are needed.

Despite of many works devoted to the synthesis of SiC nanofibres by combustion of CaSi_2 /PTFE mixtures, up to now their growth mechanism has not been fully explained. The analysis of SEM images and a composition of gaseous combustion products indicates that the growth of nanofibres of SiC proceeds according to the following mechanism: vapour – liquid – solid (VLS) – Ref [6]. In this work, an attempt is undertaken of visualisation of the growth process of SiC nanofibres by the use of a CCD camera with a Schlieren system. Moreover, overpressure histories, mass of solid combustion products and heat of combustion are measured in a closed reactor and they are compared with the results of thermochemical calculations.

2 Experimental

Fine powder of polytetrafluoroethylene was mixed with calcium silicide particles of size below 100 μm in a ratio of 57.8/42.2. The mixtures of CaSi_2 /PTFE were pressed into pellets of 20 mm diameter under a pressure of 5 MPa. The combustion process was initiated by an electrically heated resistance wire attached to the top of the pellet. Combustion synthesis was carried out in closed steel reactors (chambers) of 402 and 285 cm^3 in volume. To evaluate the influence of initial conditions, the chamber was filled with various gases at different pressure, or as well as the mass of the pellet was changed.

The combustion process of CaSi_2 /PTFE mixtures was observed in the 402 cm^3 chamber. The chamber was equipped with optical special windows and placed in the observation section of the Schlieren system. The process was recorded by the use of the Photron FASTCAM camera. To measure overpressure histories of the combustion process, a piezoelectric gauge was mounted in the wall of the chamber.

Visualization of the combustion synthesis was possible barely during the first stage of combustion. Solid products produced in the chamber covered the windows. Thus, observation of the crystallization of SiC nanofibres was difficult. Chosen pictures of pellet combustion are shown in Fig. 1.

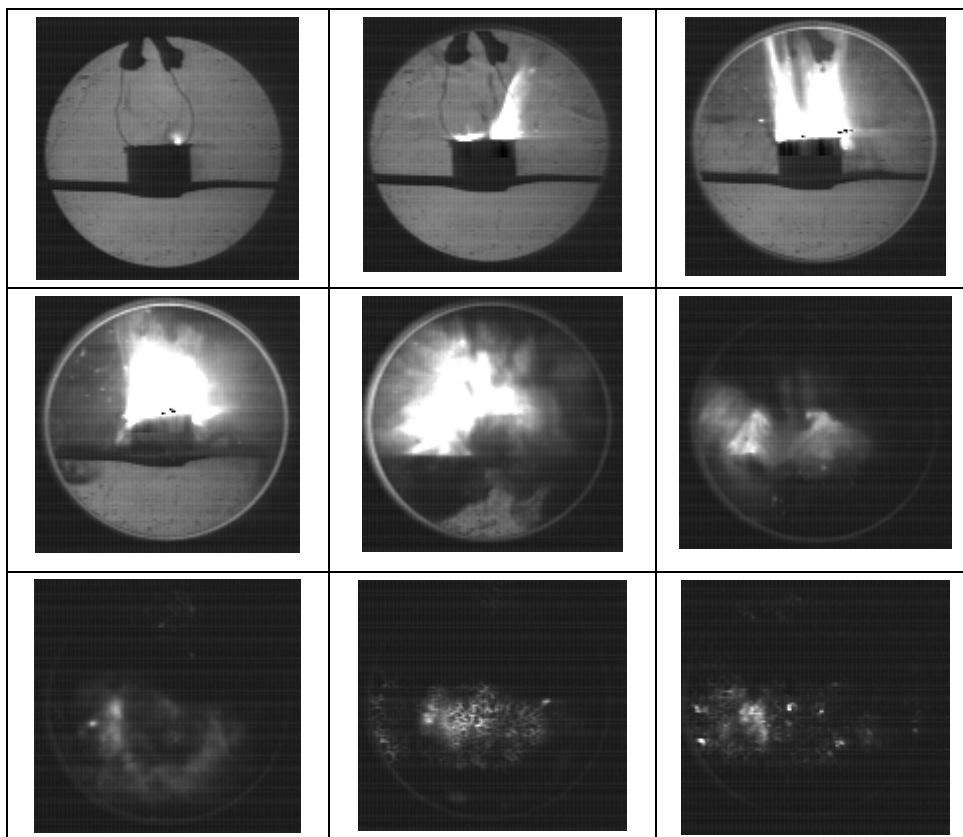


Fig. 1. Schlieren pictures of the 10 g pellet combustion in air. Time interval between pictures – 0.1 s.

After ignition of a pellet, a turbulent expansion of gaseous combustion products is visible in the first pictures. The 0.6 g pellet falls down after burnout of the resistance wire while other pellets are fastened at the centre of the chamber. During the first stage of combustion of the 10 g pellet the combustion wave propagates with a fairly plane front to the pellet bottom. Since solid products are produced during combustion, a big part of windows is not transparent to the flash light illumination. Due to this fact, the observation of the cloud's structure and creation of nanofibres for further stages of the combustion is impossible. However the fact should be noticed that the condensation of solid products proceeds during the combustion of a pellet. Thus, the results of this visualization confirm the inference given in Ref. [6] that the vapour-liquid-solid (VLS) nucleation mechanism involving gaseous species is responsible for the product formation in the $\text{CaSi}_2/\text{PTFE}$ systems.

To measure overpressure histories in the closed vessel for the combustion process of $\text{CaSi}_2/\text{PTFE}$ mixtures, a piezoelectric gauge (Kistler 601A) was used. Overpressure records from the chamber are presented in Figs. 2-3.

Two factors influence the pressure changes in the reactor. The gasses produced at the front of combustion wave causes an increase in the pressure. On the other hand, the condensation of solids behind the wave reduces the pressure value. Initially, the first process dominates and the overpressure in the chamber increases. From the photographs of the combustion process and overpressure histories it follows that the sample of CaSi_2 powder burns more rapidly than the CaSi_2 pellet. So, the influence of the crystallization process, which is relatively slow, on the pressure rise is lower in the first case. Thus the maximal overpressure produced by the 5 g powder sample in the chamber filled with air atmosphere is higher than that generated by the pellet of the same mass.

The mass of solid combustion products and heat of combustion were measured in a 285 cm^3 volume chamber filled with air or nitrogen. The results will be discussed in the next paragraph.

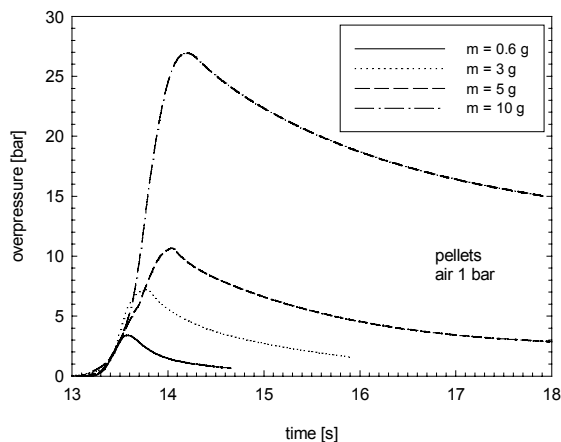


Fig. 2. Overpressure histories recorded in the chamber filled with air for $\text{CaSi}_2/\text{PTFE}$ pellets of different mass

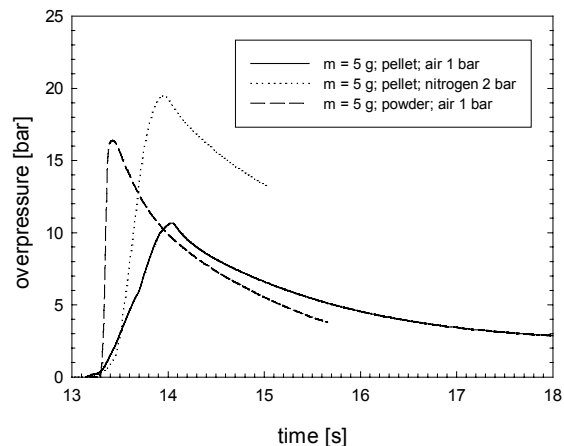


Fig. 3. Overpressure histories recorded in the chamber filled with air for $\text{CaSi}_2/\text{PTFE}$ pellets of different mass

3 Thermochemical calculations

Thermochemical calculations in this work were performed by the use of the CHEETAH code [7]. The BKWS set of parameters for the BKW equation of state and covolumens factors for gaseous species were applied. A chemical equilibrium of the combustion products was assumed in the calculations.

In the first step, the maximal overpressure inside the 402 cm^3 chamber was estimated by assuming a constant volume explosion. The results obtained for different $\text{CaSi}_2/\text{PTFE}$ sample mass are compared with the measured overpressure values. This comparison shows that the process of combustion of $\text{CaSi}_2/\text{PTFE}$ mixtures differs substantially from the explosion process. Condensation and crystallization of solids during the combustion decreases extremely the overpressure in a closed vessel.

The heat of combustion and final composition of combustion products were calculated for the state corresponding to a chamber volume and temperature of 300 K. Calculated heat of combustion of the tested mixture is higher than the calorimetric heat. Predicted total mass of solid products is also higher in comparison with that measured in the 285 cm^3 chamber. Main calculated solid products of combustion are SiC , CaF_2 and Si for the both gaseous fillers. Carbon appears only in calculated products of the 0.6 g pellet in air. There is single gaseous products (SiF_4) in the predicted final composition.

As it is shown in Ref. [8], elemental, XRD, EDS, and Raman analyses prove that the solid products of $\text{CaSi}_2/\text{PTFE}$ system burned in an air atmosphere contain $\text{SiC}(s)$, $\text{C}(w)$, $\text{Si}(s)$, $\text{CaF}_2(m)$ and $\text{SiO}_2(w)$, while the combustion in argon provides $\text{SiC}(s)$, $\text{C}(m)$, $\text{Si}(s)$, and $\text{CaF}_2(s)$. Symbols s , m and w denote strong; medium and weak fraction in the solid products, respectively. The main difference between the set of solids estimated from thermochemical calculations and that measured in Ref. [8] is the quantity of carbon. It must be added that after combustion considerable amount of soot was observed inside the 285 cm^3 chamber filled with nitrogen.

From the analysis of the experimental data given in Ref. [8] and the results of thermochemical calculations, measured and calculated total mass of solid products and combustion heat it follows that the final composition of combustion products for the $\text{CaSi}_2/\text{PTFE}$ mixture fixes at the temperature higher than 300 K assumed for calculations. However, this temperature must be also significantly lower than the adiabatic combustion temperature because the set of products calculated for the adiabatic temperature includes a great number of gaseous and solid species which are not present in the final combustion products [8]. Thus, the final composition of combustion products corresponds to certain nonequilibrium states.

4 Inferences

The results of visualization of the $\text{CaSi}_2/\text{PTFE}$ 57.8/42.2 mixture confirms that the vapour-liquid-solid (VLS) nucleation mechanism involving gaseous species is responsible for the product formation. However, the observation of the gaseous cloud's structure and creation of SiC nanofibres during further stages of the combustion process was impossible since solid products caused that a big part of windows was not transparent to the flash light.

Calculated heat of combustion of the $\text{CaSi}_2/\text{PTFE}$ mixture is higher than the calorimetric heat measured in air or nitrogen atmospheres. Predicted total mass of solid products is also higher in comparison with that measured in the chamber. Main calculated products of combustion are solid SiC, CaF_2 , Si and gaseous SiF_4 . However, significant amount of carbon is observed in the chamber. This means that the final composition of combustion products corresponds to certain nonequilibrium states.

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