



Combustion synthesis of silicon carbide assisted by a magnesium plus polytetrafluoroethylene mixture

R.M. Ayral^a, F. Rouessac^{a,*}, N. Massoni^b

^a Institut Charles Gerhardt Montpellier, PMOF-UM2-CNRS Pl. E. Bataillon, 34095 Montpellier Cedex 5, France

^b CEA, DEN, DTCD, 30207 Bagnols-sur-Cèze, France

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ABSTRACT

In this study, the use of SiC combustion synthesis for immobilization of ^{14}C was considered. Due to the low exothermicity of the reaction between silicon and graphite, a highly exothermic mixture (magnesium and polytetrafluoroethylene) was used both as a chemical oven and activate additive in the mixture. With this configuration the reaction between graphite and silicon was initiated and propagated on the whole sample. The self-propagating high temperature synthesis samples were characterized by using scanning electron microscopy and X-ray diffraction.

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1. Introduction

Silicon carbide could be a promising matrix for immobilization of ^{14}C due to its high thermal stability, good resistance and corrosion [1]. This material can be synthesized through many methods; most of it is produced by the Acheson process where thermal reduction of silicon dioxide by carbon is carried out at temperatures ranging from 2400 °C to 3000 °C. This process is quite expensive and now other synthesis methods are investigated. Among the variety of methods, self-propagating high temperature synthesis (SHS) has become interesting because of energy savings and shorter processing times [2–4].

An empirical criterion typically adopted for determining the feasibility of combustion synthesis is an adiabatic temperature exceeding 1800 K [5]. For the Si–C system, the calculated adiabatic temperature is 1860 K which is too low to enable the combustion synthesis reaction. Hence, an additional energy source must be introduced into the system like preheating temperature [6,7], field assisted synthesis [8,9] or chemical oven for instance [10]. One other possible way is to use active gas like nitrogen [11] to form nitrides whose adiabatic temperatures can reach 5000 K.

Previous studies were undertaken using a powder mixture containing titanium, graphite and silicon powders [12]. We have shown that when percentage of silicon increases in the mixture

(Ti + Si + C), the temperature and the rate of propagation of the combustion reaction decrease giving rise at least to an extinction of the reaction when 80 at% of silicon is added. In this case, silicon acts as a diluent and high percentages of this element extinguishes the reaction.

Another way to enhance the reactivity of the powders is to use a high caloric mixture like (Mg + polytetrafluoroethylene (PTFE)) for example. Several papers referring to the use of Teflon in exothermic reactions exist in the literature [13–16]. Studies made by Zhang et al. [17] concern the use of this mixture as an activate additive in the reaction Si + C with different types of carbon (black carbon, activated carbon and graphite). In that paper, the authors show that the reaction between silicon and graphite is very difficult to ignite even with the mixture Mg + PTFE.

To investigate the reaction with graphite, which has been thoroughly used for nuclear applications in the past, we tried to change the conditions established by Zhang and to use both activate additive and chemical oven protected by a thermal insulator in order to reduce heat losses. This paper will describe the experimental procedure and the influence of composition of mixture on temperatures and compositions of the product. The characterizations will essentially be made by X-ray diffraction and scanning electron microscopy.

2. Experimental procedure

Silicon (Alfa Aesar 1–5 μm), graphite (Alfa Aesar, 44 μm), polytetrafluoroethylene (PTFE) (Acros Organics) and magnesium

* Corresponding author. Tel.: +33 0 467143355; fax: +33 0 467144290.
E-mail address: florence.rouessac@univ-montp2.fr (F. Rouessac).

powders (Fisher Scientific) were used as reactants. They were mechanically milled in a jar closed under argon during 12 h. Si, C reactants were weighed with different molar ratios of 1:2 and 1:1 and Mg and PTFE powders at a ratio of 23 wt.%. In the following, the mixtures will be labelled as Si:C = 1:2 (molar ratio) – Mg:PTFE = 23:23 (wt.%) and Si:C = 1:1 – Mg:PTFE = 23:23. Then, these mixed powders were pressed into pellets of 13 mm diameter under various compaction pressures (from 0 to 375 MPa).

The pellet was placed in a SHS reactor under an argon atmosphere and ignited by a tungsten wire connected to a power supply. The device used in this study was composed of a steel cylindrical reactor whose volume is 1 L. The pressure inside the reactor must not exceed 7 MPa and the temperatures of the walls cannot be higher than 50 °C. Any overheating problem was prevented by a water cooling device. The lower part of the device, constituted by ceramic support made in pyrophyllite is removable. Fig. 1 presents the experimental system: the compacted mixture made of silicon, graphite, magnesium and PTFE was covered by the highly exothermic mixture made of Mg and PTFE (chemical oven).

In order to study the evolution of temperatures during combustion synthesis, thermocouples are positioned in the upper and down side of the sample. The temperature control is realized thanks to an acquisition card “Hi-speed USB Carrier National Instruments”, with Labview software. Then, the whole is maintained in a Papyex confinement in order to avoid heat losses.

The composition of the products is determined by X-ray diffraction, with a Philips Expert device. In order to make accurate measurements, patterns are collected using capillary and following conditions (Cu $K_{\alpha 1}$ radiation, $2\theta = 20\text{--}80^\circ$, angle pitch 0.017°). A semi-quantitative analysis in X-Pert High score works on basis of the RIR (reference intensity ratio) values. It determines the estimated mass fractions of the identified phases. The normalization used in this method assumes that the sum of all identified phases is 100%. The morphology of the fractured surface of the pellet is analysed by observation with a scanning electron microscope (SEM).

3. Results and discussion

The product SiC which is involved in combustion synthesis presents an adiabatic temperature of 1860 K and an enthalpy of formation of -69 kJ mol^{-1} [18]. This value is a little higher than the empirically obtained critical adiabatic temperature of 1800 K. This reaction cannot attain a self-sustaining combustion form without the addition of energy from an exterior source.

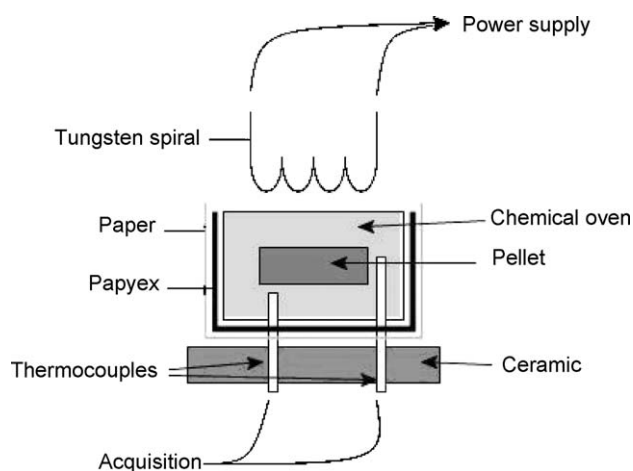
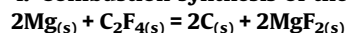


Fig. 1. Combustion synthesis device.

The reaction of formation of silicon carbide can be assisted by using the heat liberated by the reaction between magnesium and PTFE whose enthalpy of formation is $\Delta_f H^\circ (300 \text{ K}) = -1518 \text{ kJ mol}^{-1}$. This reaction is very exothermic due to the great affinity of fluorine with magnesium. The literature [17] for this system shows the influence of three parameters: (a) The ratio Si:C, it is equal to 1:2 or to 1:1. Indeed, Zhang et al. [17] have shown that the stoichiometry 1:1 did not allow to obtain a complete reaction. They attributed this result to the fact that stoichiometric amount of carbon was not sufficient for the complete reaction due to the evaporation of this component. Hence, excess carbon was added to the reactant for the compensation of the carbon loss and they worked with the ratio Si:C equal to 1:2. (b) The percentage of the mixture Mg + PTFE: it varies between 20% and 25 wt.%. For graphite, the percentage is fixed to 25%. Below this value the reaction is not complete. (c) The nature of carbon used. These authors show that with the carbon black the results are the best. In our application, the nature of the carbon is imposed with graphite. So, in order to get initiation and propagation of the reaction in the entire sample, the idea was to use (Mg + PTFE) mixture according two ways: As a chemical oven: in this case, the mixture surrounds the compact, the high exothermic reaction between magnesium and PTFE allows to add some amount of heat to the compact to ignite the reaction and to propagate it all along the sample. –Mixed to the mixture silicon + graphite: It helps for the complete propagation of the combustion wave. After processing, magnesium fluoride by-product is removed with a chemical treatment with diluted fluorhydric acid (10%HF). The efficiency of this method is evidenced in Table 1 where the percentage of MgF_2 in the product after washing is reduced to 0%.

4. Combustion synthesis of the chemical oven: the reaction



In a first step, combustion synthesis of the mixture (Mg, PTFE) was studied. The reactants are introduced in the reactor and ignited with a tungsten coil. When the reaction between Mg and PTFE starts, an abrupt increase in temperature occurs giving rise to the thermal profile shown in Fig. 2(a). The temperature reached in this case is 1933 K. As this temperature is not high enough, we investigate a way to lower heat losses during the reaction. Due to its very specific properties, Papyex[®] material can be used in furnaces as a shield. At high temperatures, it reduces heat losses due to its reflective capacity. In this case, the temperature of the reaction was growing up to 2373 K (400 K) (Fig. 2(b)) higher than previously without Papyex[®].

Fig. 3(a) shows X-ray pattern of the product. The major phase is MgF_2 and only trace amounts of graphite appear. Indeed, the reaction between magnesium and PTFE is so exothermic that graphite vaporizes and then condensates into the walls of the reactor leaving only in the crucible the phase MgF_2 .

5. Combustion synthesis in the system Si:C = 1:2 (molar ratio) – Mg:PTFE = 23:23 (wt.%)

The reactive system surrounded by Papyex[®] was composed of different pellets with the following ratios Si:C = 1:2 (molar ratio)

Table 1

Semi-quantitative analysis of Si:C – Mg:PTFE samples for different molar ratio.

| Sample molar ratio (Si:C/Mg:PTFE) | A.S.: as synthesized (HF: HF treatment) | % C | % Si | % MgF_2 | % $\beta\text{-SiC}$ | % $\alpha\text{-SiC}$ |
|-----------------------------------|---|-----|------|------------------|----------------------|-----------------------|
| 1:2/23:23 | A.S. | 10 | 8 | 20 | 43 | 19 |
| 1:1/23:23 | A.S. | 6 | 12 | 12 | 70 | 0 |
| 1:1/23:23 | HF | 8 | 0 | 0 | 92 | |

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