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Low-temperature combustion waves in low-energy K_2TaF_7–Si-additive systems

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ABSTRACT

This work presents the use of a thermocouple technique for measuring temperature profiles in a condensed K_2TaF_7–Si system blended with a small amount of Teflon [$(C_2F_4)_n$] or potassium chlorate ($KClO_3$). A base experiment is described in detail to demonstrate the ability of the system to react under a low-rate self-sustaining mode at ambient temperature. The ignition temperatures, temperature–time profiles, combustion parameters, and final products are presented with respect to the additive concentration. The combustion processes begin at 340 and 450 °C for the $KClO_3$ and $(C_2F_4)_n$-containing mixtures, respectively. The maximum temperatures of both $KClO_3$ and $(C_2F_4)_n$-containing mixtures range from 470 to 960 °C and the combustion self-propagates along the sample at a speed of 0.01–0.08 cm/s. The solid combustion products produced under the optimized conditions include fine powders of tantalum, tantalum carbide, and tantalum silicides. The chemical mechanism of the combustion process and reaction parameters responsible for low-speed wave propagation are presented and discussed.

1. Introduction

It is well recognized that combustion-based techniques, which are known in the literature as combustion syntheses (CS), are effective, energy-conserving methods for the synthesis of a variety of advanced functional and structural materials [1–3]. Depending upon the nature of reactants (i.e., solid, liquid, or gas) and exothermicity of the reaction (i.e., adiabatic temperature), CS can be described as self-propagating high-temperature synthesis (SHS) [4–6], low-temperature combustion synthesis in the solid phase (LCS-SP) [7,8], solution-combustion synthesis (SCS) [9–14], sol–gel combustion (SGC) synthesis [15–17], volume combustion (VC) synthesis [18–20], and smoldering [21]. Among the stated variety of the combustion processes, LCS-SP is ideal for various applications, such as the production of useful nanoscale materials (e.g., powders, fibrous and foam-like materials) and accessory devices for pyrotechnic and military applications. Additional applications include low-exothermic chemical compositions for use in therapeutic heating devices, hair-waving heater sachets, and similar items. However, most of the studies, including those cited above, emphasize the high-temperature combustion processes while little information concerning the temperature–time profiles of the combustion wave, the combustion parameters (i.e., ignition and combustion temperatures and wave velocity), and the reaction mechanisms of low-temperature combustion processes is available. Indeed, non-intense heat transfer in solid reaction media coupled with a slow chemical reaction and the formation of solid nanoparticles make the conditions for the LCS-SP wave propagation unique.

The combustion of low-exothermic compositions based on a $NaClO_3$–Sn mixture for emergency oxygen generators for aircraft was reported by Shafirovich et al. [22]. The maximum combustion temperature estimated from the temperature–time profiles was between 650 and 800 °C and the combustion wave velocity was 0.03–0.05 cm/s. Won et al. [8] reported the use of a low-energy mixture with a BaO_2–TiO_2–C composition to produce tetragonal $BaTiO_3$ nanoparticles. The ignition point of this mixture was ∼500 °C, and the as-formed combustion wave propagates at a speed of 0.2 cm/s with a maximum temperature of ∼700–900 °C. Nersisyan et al. [23] reported a combustion process of phosphor powders comprising $ZnO + SiO_2$, $Y_2O_3 + B_2O_3$, and $Y_2O_3 + Al_2O_3$ oxide systems with defined amounts of $KClO_3 + CO(NH_2)_2$ redox mixture. The optimal synthesis temperatures, as estimated from the temperature

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distributions, were found to be between 700 and 1200 °C, and the combustion velocity varied from 0.04 to 0.5 cm/s; however, at the combustion limit with highly unstable combustion waves, the propagation speed may drop to 0.03 cm/s. A similar combustion velocity (0.035 cm/s) was recorded in a $ZrCl_4$–Mg system reported by Park and co-authors [24]. Analysis of the low-temperature combustion processes reported in the literature [25,26] reveals that the lowest wave-propagation velocity in solid systems is 0.03–0.04 cm/s. Below this value, the combustion wave attenuates owing to extensive heat loss from the sample to the surroundings.

In this study, the combustion in a K_2TaF_7–Si system blended with a small amount of Teflon $[(C_2F_4)_n]$ and potassium chlorate ($KClO_3$) was investigated for the first time as a typical example of an LCS-SP process for synthesizing tantalum compounds nanoparticles. A base experiment is described in detail to demonstrate the ability of the system to react under a low-rate self-sustaining mode at ambient temperature. The ignition temperatures, temperature–time profiles, combustion parameters, and final products are presented with respect to the additive concentration. The chemical mechanism of the combustion process and reaction parameters responsible for the low-speed wave propagation are presented and discussed. These results are crucial not only from the application perspective, but also more importantly for their methodological insights, which will enable the investigation of combustion waves in new classes of LCS-SP systems.

2. Experimental

The following chemicals were used to prepare the samples: K_2TaF_7 (prepared at the Graduate School of Green Energy Technology, Chungnam National University, Korea), Si powder (99.0% purity; particle size: <50 μm; Samchun Pure Chemical Co., Ltd., Korea), Teflon powder (TF 9207Z, molecular weight $n = 100–500$, average particle size ~4 μm; Europe), and $KClO_3$ (purity 98%, particle size: <50 μm; Kanto Chemicals, Japan).

The samples were prepared according to the following equations: $K_2TaF_7 + (1.25 + 1.5k)Si + kKClO_3$ and $K_2TaF_7 + (1.25 + m)Si + m(C_2F_4)_n$, where k equals 0.125, 0.2, or 0.3 and m equals 0.15, 0.2, or 0.25. To prepare the reaction mixture, controlled amounts of K_2TaF_7, Si, and $KClO_3$ (or $(C_2F_4)_n$) were weighed and homogenized by mechanical mixing prior to being packed in the reaction cup. For the combustion experiment, approximately 80–100 g of the mixture was hand-compacted into a paper cup (diameter: 3.0 cm, height: 8–9 cm). During compaction, two Λ-shaped tungsten-rhenium thermocouples (WR-26/WR-5) with 50 μm diameters were placed inside the sample near the center. The thermocouples were preliminarily coated with a thin layer of Al_2O_3 (~5–10 μm) to increase the resistance to oxidation and to avoid reactions between the thermocouples and powder bed at elevated temperatures. The upper thermocouple was placed ~2.0 cm from the top of the specimen and the thermocouples were fixed at a distance of 2.5–3.0 cm from each other. Approximately 2–3 g of an exothermic mixture composed of Ti + 0.9C (black soot) + $0.1[(C_2F_4)_n]$ was placed on top of the reaction sample as an easy ignition agent. The cup containing the reaction mixture and thermocouples was subsequently placed under a nickel/chromium coil in a combustion chamber. The experimental set-up is illustrated in Fig. 1, and can be separated into three sections: (1) the argon-gas section, (2) the high-pressure combustion chamber, and (3) the temperature data logging system equipped with personal computers. Initially, the combustion chamber was evacuated and purged several times with argon to remove all oxygen from the chamber. The chamber was then filled with 1.0 MPa of argon. Local ignition of the reaction sample was achieved within 1–2 s using a nickel–chromium filament that was electrically heated to 900–1000 °C. Note that the igniter was turned off immediately after reaction initiation. A computer-assisted data logger (GL100A, Graphtec Co., Japan) continuously recorded the temperature–time history of the process at a rate of 10 Hz.

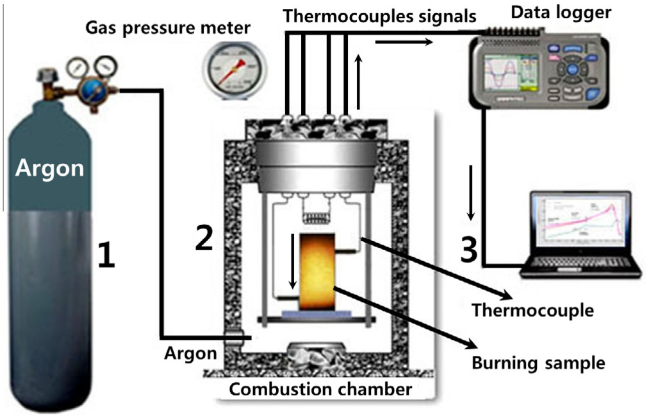

Fig. 1. Schematic of the experimental apparatus and setup.

The signals from the thermocouples in the burning sample of $K_2TaF_7 + (1.25 + 1.5k)$ Si + $kKClO_3$ ($k = 0.15$) are shown in Fig. 2. The combustion velocity was calculated using $U_c = x/t$, where x is the distance between the thermocouples, and t is the time between the arrival of the front at each thermocouple. Three experiments were performed at each concentration point. The locations of the thermocouples along the sample were also changed to assess the stability of the combustion wave along the sample. The uncertainty of the location of the thermocouples was ~10%, which resulted in an identical uncertainty for the combustion velocities that were calculated from the thermocouple signals. The uncertainty for the temperature measured by thermocouples was ±10–15 °C or 2–5% of the measurement.

After completion of the combustion process, the burnt sample was cooled to room temperature, mechanically cleaned from the surface layer (1–2 mm), and transferred to a 500 mL beaker for further purification. The reaction by-products (KF, K_2SiF_6, KCl, etc.) were removed by mixing the sample with concentrated HCl in a 300 mL glass beaker on a hot magnetic stir plate. The acid-leached powder was rinsed with distilled water and dried at 80–100 °C.

Thermodynamic calculations of the equilibrium concentrations of all reaction species were performed using a commercially available HSC Chemistry 6.0 software package (Outokumpu HSC

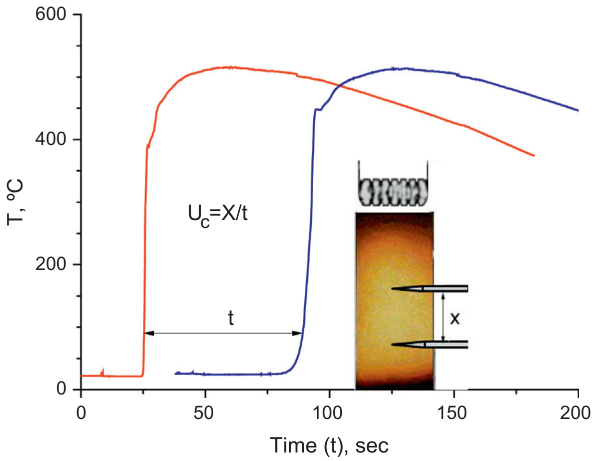

Fig. 2. Signals of the thermocouples used to calculate the wave velocity. Initial system: $K_2TaF_7 + (1.25 + 1.5k)$ Si + $kKClO_3$, $k = 0.15$.