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Combustion synthesis of tungsten carbides under electric field I. Field activated combustion synthesis

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Abstract

The activation of self-propagating combustion reactions in the W–C system was achieved by using an electric field. Self-sustaining combustion in elemental reactants with the composition corresponding to WC can be activated only when the imposed field is above the threshold value of 1V cm^{-1}. The nature of the combustion products depended on the magnitude of the field. The product consisted of two kinds of tungsten carbides, WC and W_2C. The effects of tungsten particle sizes and the relative densities of the reactant compacts on the synthesis of tungsten carbide were also investigated. Finally, the reaction mechanism of tungsten carbide was proposed. X-ray and microscopic analysis of the quenched combustion front suggested that the synthesis of WC is a process involving the solid diffusion of carbon into a carbide layer. W_2C is the intermediate phase between WC and reactants (W and C).

Keywords: A. Powder; D. Carbides; Solid state reaction

1. Introduction

The properties of tungsten carbide (WC), such as high melting point (2600–2850 °C) [1], high hardness (16–22 GPa), high fracture toughness (28 MPa $m^{1/2}$), very high compressive strength (5 GPa, 20 °C) [2], are primary reason for its use as tool material and in wear-resistant parts. WC is also finding new applications as a substitute for noble metals like Pt, Pd and Ir in catalysis industries [3,4]. WC erosion resistant coatings for aerospace components are another applications. Carbides of tungsten have been prepared by a variety of methods. In one of the earliest reported accounts, tungsten carbide was synthesized by direct carbonization of tungsten powder, in which the reactions occur at high temperature and in a flowing hydrogen atmosphere. More recently, other methods, such as chemical processing (carbothermal reduction of tungsten oxides or carbon coated tungsten oxide precursors method [5]), fluid bed method, mechanical alloying, etc., have been used to prepare them. Some require high temperature and long reaction time.

A promising and energy-efficient technique known under the acronym of CS (combustion synthesis) or SHS (self-propagating high-temperature synthesis) for the preparation of advanced materials has been developed [6]. In a typical SHS process, compacts of powder mixtures are ignited at one end to initiate the self-sustaining reaction. However, for the case of some systems with thermodynamic limitation, i.e. a low reaction enthalpy or relatively low adiabatic combustion temperature (T_{ad}), ignition is impossible without additional activation. Taking the system of tungsten-carbon as an example, T_{ad} values of WC and W_2C are 1127 and 673 °C, respectively, which are considerably lower than the empirically established minimum of 1527 °C for SHS reactions. For these systems which are relatively less exothermic, the common approach has been the preheating of the reactants, which accomplishes the goal of raising T_{ad}, but which can suffer from the formation of extraneous phases, such as pre-combustion phases through diffusion.

Recently, a new method, referred to in the literature as field-activated combustion synthesis (FACS) [7], based on the use of an electric field to activate self-propagating

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reactions in relatively low-heat-of-formation or less-exothermic systems, was developed. Experimental results and modeling studies have lead to the conclusion that the effect of the field is to provide Joule heating at a rate of σE^2 with σ being the conductivity and E the field [8]. Depending on the electric conductivity of reactants and products, ignition results in the initiation and propagation of a combustion wave in reactant systems which heretofore could not be synthesized by SHS (without preheating), including SiC, SiC–AlN, TaC, B_4C–TiB_2, $MoSi_2$–SiC, Ti_3Al, and others [9–18].

In the first part of our work the method was used to synthesize tungsten carbide. The effects of various processing parameters on FACS of tungsten carbides were discussed and the fast formation mechanism from tungsten and carbon under electric field was proposed. No previous results on the combustion synthesis of tungsten carbides by FACS method have been reported. The aim of this study was to provide a better understanding of the role of electric field involved in the field-activated combustion synthesis of tungsten carbides.

2. Experimental procedures

Equiatomic mixtures of tungsten and activated carbon powders were used to assess the effect of electric field on SHS reactions. Two kinds of tungsten powders (both with a reported purity of 99.99%, supplied by Korea Tungsten Co.) with an average particle size of 2.09 and 0.6 μm, respectively, were used. Either of them was dry-mixed in an alumina ball mill with 99.9% pure activated carbon powders (an average particle size of 20 μm, supplied by Kojondo Chemical Co.). Tetragonally shaped pellets with dimensions of 10×10×15 mm were cold-pressed under various compaction pressures ranged from 200 to 500 MPa in a two-plunger steel die. The pellets were then placed between two spring-loaded graphite electrodes across which a voltage was applied. The spring was used to keep two electrodes in intimate contact with the flat top and bottom surface of the sample. Thus, the distance between electrodes is the thickness of the sample, 15 mm. This experimental geometry provides an electric field perpendicular to the expected direction of wave propagation. A tungsten-heating coil, placed near the edge of the sample was used to initiate the combustion and was turned off immediately after the reaction was initiated. A schematic representation of this setup is shown in Fig. 1. The activated combustion synthesis experiments were carried out inside a stainless steel pressure chamber under one atmosphere of argon.

The combustion process evolution was recorded from video camera equipped with a time-code generator. The propagation velocity of combustion wave was determined by timing of the propagation from one end of the sample to the other. The surface temperature profiles of the sample during combustion were measured with a two-color optical pyrometer with a response time of 10 ms focused on the middle portion of the sample. The combustion products were identified by X-ray diffraction analysis and their microstructures were determined from scanning electron microscopy (SEM).

3. Results and discussion

In general, the imposition of either the field (except at very high) or the ignition source alone does not produce self-propagating waves. In the absence of electric field, the exposure of one end of the sample to an ignition for several minutes does not result in the initiation of a combustion wave or evidence of any reaction beyond the heat-affected zone. Experiments on the W–C system showed that a self-sustaining combustion wave cannot be established unless the field strength exceeds a minimum (threshold) value of 1 V cm^{-1}. At this strength, a combustion wave could be initiated but it only propagated to approximately 80% of the sample length before it stopped. With the increase of the field strength, the activation of the ignition source causes the propagation of a combustion wave throughout the sample. The influence of the applied electric field on the propagation wave velocity is shown in Fig. 2. The figure shows three regions, relative to the strength of the applied field. At low fields, $\leqslant 1$ V cm^{-1}, no SHS reaction takes place, but above this threshold value the rate of self-sustaining reactions increases approximately linearly with field strength as the applied field was increased in the interval between fields of 1 and 15 V cm^{-1}. When the field is about 15 V cm^{-1} or higher, no ignition source is required, in other words, the reaction is initiated by the Joule heating of the field itself. The phenomena of Fig. 2 are referred to as simultaneous or volume combustion with the implication that the reaction is taking place over the entire sample with no wave propagation.

The effect of the electric field on the maximum combustion temperature for the synthesis of WC from the

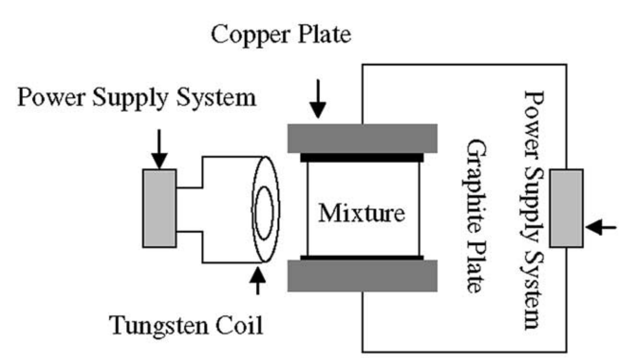

Fig. 1. Schematic representation of field-activated combustion synthesis, FACS.

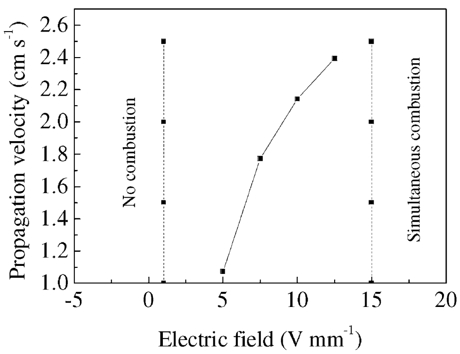

Fig. 2. The dependence of wave velocity on field strength in the synthesis of WC.

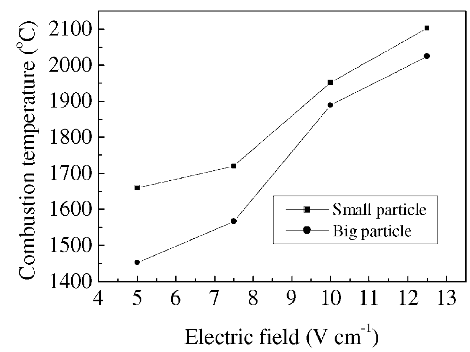

Fig. 3. The effect of the particle size of tungsten on the combustion temperature for the synthesis of WC at different field strength.

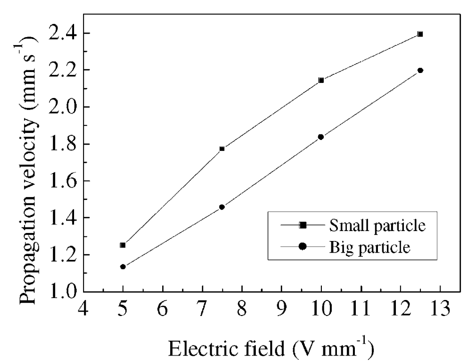

Fig. 4. The effect of the particle size of tungsten on the measured wave velocity for the synthesis of WC at different field strength.

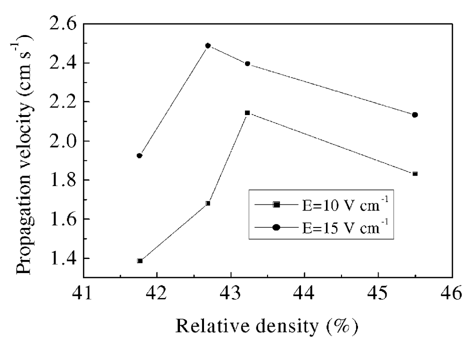

Fig. 5. The effect of the relative density on the measured wave velocity for the synthesis of WC at different field strength.

elements is shown in Fig. 3. The combustion temperature increased with the field in the range, from 1660 °C at the lowest applied field of 5 to 2103 °C at the field of 12.5 V cm^{-1}. During the FACS process, the externally applied electric field provides a Joule heat contribution which together with the heat released by chemical reaction is able to facilitate the initiation and propagation of self-sustained combustion waves. The effect of tungsten particle size on the field-activated combustion process was also examined. The dependence of the maximum combustion temperature on the particle sizes of tungsten is also shown in Fig. 3. Decreasing the size of tungsten particle from 2.09–0.6 μm causes a dramatic increase in combustion temperature from ~1452 to ~1660 °C at the electric field of 5 V cm^{-1}. In addition, the effect of the particle size of tungsten on the propagation velocity is shown in Fig. 4. The velocity increases in a qualitatively similar way to that of the temperature from 1.13 to 1.25 mm s^{-1} at the field of 5 V cm^{-1}. In the case of fine particles (0.6 μm), the velocity is about 1.1 times higher than that for the case of the coarse particles samples (2.09 μm).

The present work also included investigations on the influence of the relative densities of reactants' compacts on the synthesis process. The effect of sample densities on the propagation velocity is shown in Fig. 5. At the same applied voltage, the velocities began at low values and then increased with the relative density until maximum value. At last the velocities decreased with more relative density. The dependence of wave velocity in FACS process on the relative densities of reactant compacts is consistent with some experimental results of other research systems reported in several investigations [19]. The tentative qualitative interpretation of the observations has focused on the role of thermal conductivity in the FACS process and its relationship with the relative density. Reactants' compacts with low relative densities have correspondingly low thermal conductivities leading to a limited heat transfer from the combustion wave to the adjacent layer ahead. Thus, heat is not conducted at a sufficiently high rate to raise the temperature of the layer ahead of the wave to the ignition temperature. On the other hand, if relative density is too high, then heat is conducted far ahead of the wave and dissipated in the entire unreacted sample with the result that the ignition temperature is not reached and thus leads to lower propagation velocity. Moreover, compared with the propagation velocity at the field of 10 and 12.5 V cm^{-1}, the maximum value moves towards lower relative densities end. At the field of 10 V cm^{-1}, the velocity attains the maximum value of 2.14 mm s^{-1} for the sample with the relative density of 43.2%, while at the field of 12.5 V cm^{-1}, 2.48 mm s^{-1}

for the relative density of 42.6%. With the increase of electric field, the function of electric field on the heat transfer becomes evidence, thus the maximum value of the propagation velocity will situate at lower relative density. The combustion temperature increased in a qualitatively similar way (as shown in Fig. 6) to the increase in the propagation velocity at the field of 10 and 12.5 V cm^{-1}, respectively. At the optimum relative density, the combustion temperature attains the maximum value. The similar results on combustion temperatures can be explained by above interpretation.

Diffraction peaks were obtained for the combustion products under electric fields ranging from 5 to 15V cm^{-1}. X-ray diffraction analyses of the synthesized products are shown in Fig. 7. The diffraction peak for the unreacted W is not evident in all combustion products. When the synthesis experiment is preformed

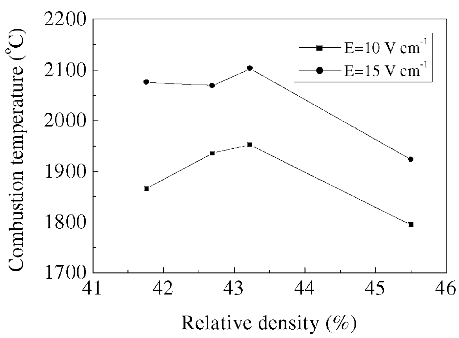

Fig. 6. The effect of the relative density on the measured combustion temperature for the synthesis of WC at different field strength.

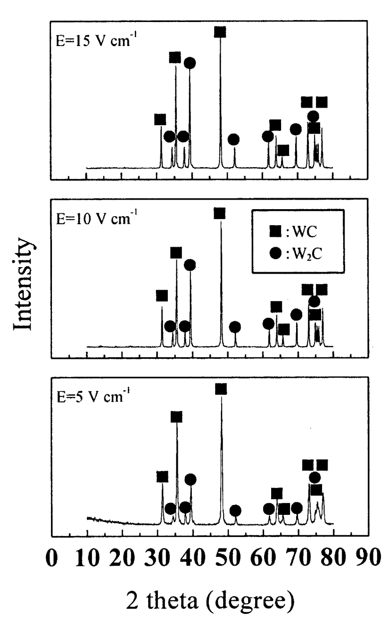

Fig. 7. X-ray diffraction patterns of W–C products synthesized at various voltages.

under progressively higher fields, the combustion reaction becomes violent and the composition of the product changes. The relative strength of W_2C in XRD diagram decreased with the increase of electric field that is to say the carbonization degree increased. Moreover, trace W_2C phase can also be detected in the combustion products. As cited in the references [20], the stoichiometric mixture of C/W resulted in an incomplete reaction between tungsten and carbon. More carbon was needed to obtain WC single phase. X-ray diffraction analysis of the present work from these systems showed the presence of W_2C along with WC, which confirms the above opinion.

At last, the mechanism of conversion from the elemental starting powders to the final material was elaborated. Five distinct zones parallel to the wave propagation direction observed in the quenched samples obtained by interrupting the applied voltage (corresponding to $E = 12.5$ V cm^{-1}) after the wave had halfway advanced through the sample. A series of SEM micrograph and corresponding X-ray diffraction analysis results on these zones are shown in Figs. 8 and 9, respectively. Zone 1 (Fig. 8a) represents the elemental reactants: the relatively larger and darker carbon particles are surrounded by the small and bright tungsten particles. In Zone 2 (Fig. 8b), the region ahead of the wave, the passage of the combustion front is indicated by the sudden appearance of product layers around the carbon grains, which suggests that an interaction between solid W and C has taken place. However, carbon grains are still clearly discernible. W and C along with minor amounts of the combustion products, W_2C and WC, are present in this zone. The latter two compounds are the major phases in Zone 3 (Fig. 8c) but W and C are still present. Zone 4 (Fig. 8d), the region behind the combustion front, contained only traces of W and C. Although the phase composition in Zones 3 and 4 is essentially the same, the relatively strength of W_2C and W is different. Finally, only W_2C and WC were observed in Zone 5 (Fig. 8e). The phenomena confirm that the carbonization degree of combustion wave-passed zone along the propagation direction increased. In addition, the applied strength of 2 V cm^{-1} was turned off during the combustion to confirm whether W_2C is intermediate phase or not. XRD pattern of the region near reactants mixtures in the quenched front is shown in Fig. 10. The fact that the region only contains W_2C together with W and C demonstrates that W_2C is intermediate phase. Since both adiabatic temperatures of W_2C and WC are less than the melting points of W (3403 °C) and C (3603 °C), a solid-solid mechanism is the only likely process. The experiment suggests that initial stage consists of the reaction between W and C to form W_2C. This step is followed by the transformation from W_2C to WC.

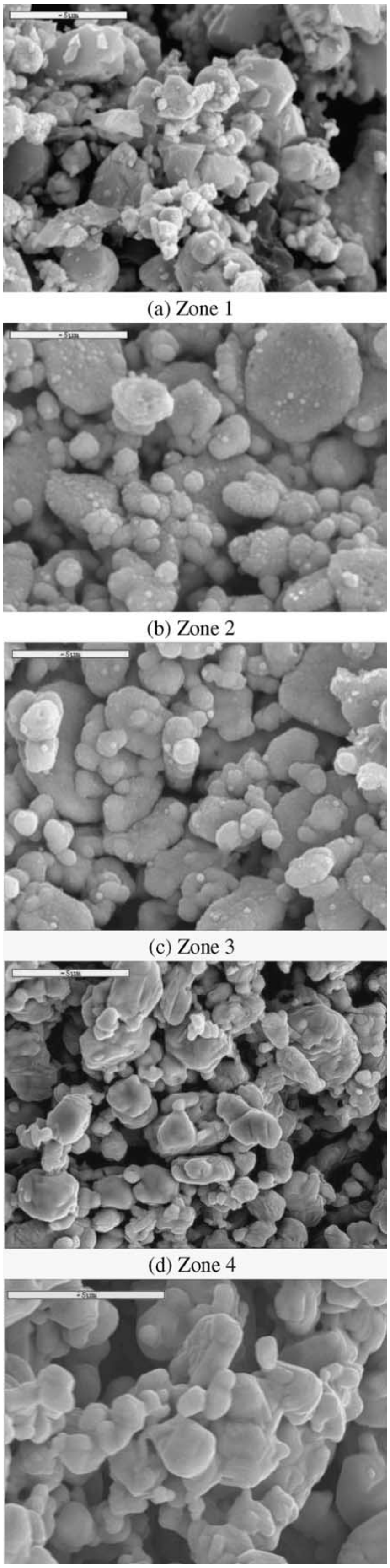

Fig. 8. SEM micrograph of the quenched sample for the FACS of WC. (a) Zone 1 (b) Zones 2 (c) Zone 3 (d) Zone 4 and (e) Zone 5.

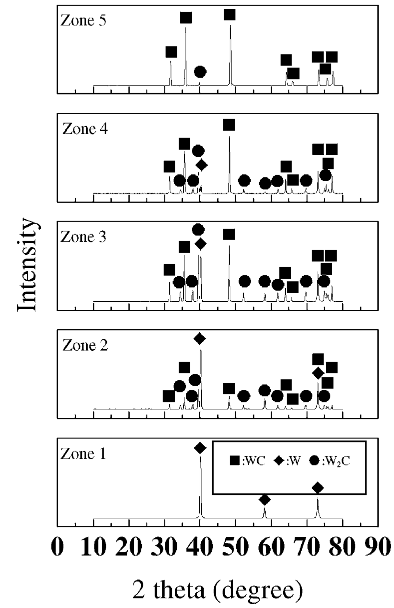

Fig. 9. XRD patterns of the corresponding zone of the quenched sample for the FACS of WC.

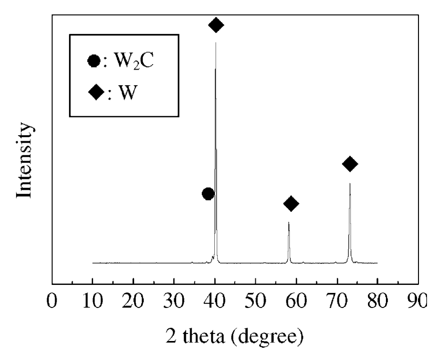

Fig. 10. X-ray diffraction patterns of W–C products synthesized at the electric field of 2 V cm^{-1}.

4. Summary and conclusions

Experimental studies were carried out to investigate the effect of electric fields on combustion synthesis reactions between W and C. The results show that the field plays a major role in these reactions. Self-sustaining combustion waves could be generated in the system of W–C only when a threshold field value was added to establish such waves. The effects of imposed electric fields on maximum combustion temperatures and propagation velocities were studied. Higher electric field leads to high combustion temperature. The velocity increase was roughly linear with the applied voltage. Similar studies were also made to investigate the role of the particle size and the relative density of the reactants' compacts in the FACS of tungsten carbide. The maximum propagation velocity and combustion temperature occur at a given normalized electric field and relative density. With the increase of the electric field, the maximum value occurs at lower relative density. X-ray analysis on an 'electrically quenched' sample revealed the sequence of the field activated reaction between W and C begins with the reaction between W and C to form W_2C, followed by the formation of WC.

Acknowledgements

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