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Synthesis of tungsten monocarbide by self-propagating high-temperature synthesis in the presence of an activative additive

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Tungsten monocarbide was synthesized by Self-Propagating High-Temperature Synthesis. A SHS technique was developed in this work for W-C system characterized by a low adiabatic combustion temperature of 1000 K. Samples were synthesized by in combustion wave propagating along compacts of elemental tungsten, carbon and a highly exothermal mixture [Mg + $(\text{-}C_2F_4\text{-})n$] as an activative additive under argon atomsphere of 1 atm. A quite high conversion rate was achieved at a combustion temperature of 2109 K. It is shown that in the presence of a small amount of (about 10 wt.%) the additive mixture acquires the capacity to burn and sustain the combustion front wave propagating. The lattic of tungsten monocarbide obtained was hexagonal and its particle size was 1 ∼ 2 μm. In the final product, MgF_2 and a small amount of W_2C, both byproducts, were completely removed by acidic leaching. The purity of the tungsten monocarbide was 99% after leaching.

1. Introduction

Tungsten carbides are hard materials and very stable at high temperature. Tungsten carbide plates, known as widia, have been widely used in the cutting or drilling of hard materials. Tungsten carbide is more highly valued than other carbides because of its high hardness and low thermal expension coefficient [1–3]. It also has a certain amount of plasticity [2, 4], and good wettability by molten metals, particularly Cobalt [2]. However, tungsten carbide has a high melting point ($T_M = 3168$ K) and thus is difficult to prepare by metallurgical techniques in which heating at a high temperature for a long period is generally necessary [4]. From this point of view, the main objective is to develop energy-saving technologies for the synthesis of WC.

Self-propagating high temperature synthesis has been employed to prepare various high-temperature materials including ceramics, intermetallics, and composites [5], using their high exothermic reactions. The heat released during these reactions is adequate to sustain the combustion wave propagation without further addition of energy to the system. It has many potential advantages such as a low-processing cost, energy efficiency, and high production rate [6].

Currently in SHS research considerable attention is devoted to chemical activation of combustion processes, particularly in those cases when due to some reason or other self-propagation of the front is made difficult of a high yield of useful product is not guaranteed. Various carbides such as niobium, tantalum and titanium carbide [7–9] were synthesized by the SHS in the presence of some gas transport agents, such as polyethylene, polyvinyl chloride, polytetrafluorethylene, halides, as activated additive for those systems, in which the adiabatic temperature was lower than the critical adiabatic temperature of 1800 K and the combustion wave propagation was controlled by the mass transport of reactants enhanced by gas transport additives. However, the synthesis of tungsten carbide from elements by the SHS process can't be realized under normal combustion conditions due to a low adiabatic combustion temperature of W-C system, it is calculated as 1000 K [10] which considerably lacks the empirically established minimum of 1800 K for SHS reaction. Therefore, for W-C system, simple enhancement of the mass transfer rate is not sufficient to establish SHS reaction, Hence, an additional energy source needs to be introduced into the system.

In this work, a process was newly developed for the synthesis of tungsten monocarbide. In order to offer the energy source, a high-caloric mixture of Mg + $(\text{-}C_2F_4\text{-})n$ was added to the reactants, since magnesium has a greater affinity towards fluorine than most metal elements and gas transport additive $(\text{-}C_2F_4\text{-})n$ can improve the mass transfort of reactants. The feasibility of synthesis WC by the SHS approach was considered. The effects of the Mg + $(\text{-}C_2F_4\text{-})n$ and various experimental conditions on the product conversion were investigated.

2. Experimental

The raw starting materials used in this work are tungsten (W) of 99% purity and 0.58–2.00 μm in size; graphite (C) particles of 99.9% purity and 3–5 μm in size; activated carbon of 99.9% purity and 3–5 μm in size; carbon black of 99.9% purity and 0.2–0.5 μm in size; magnesium powder of 99% purity and 50–80, 150, 200 mesh in size; polytetrafluroethylene (-C_2F_4-)n of 99.99% purity of chemical reagent. A predetermined amount of the reactants were mixed in an alumina ball mill for 2 ~ 3 hours and pressed into pellets of 20 mm diameter and 10 to 15 mm height under various compaction pressures. The pellet was placed in a SHS reactor under an argon atmosphere and ignited by a tungsten wire connected to a power supply. The temperature profiles were recorded by a data logger connected to the thermocouples (W-5%Re vs W-26%Re) which were inserted into the cylindrical pellets. Experimental variables investigated in the present work were (1) the amount of chemical activation [the mixture of Mg and (-C_2F_4-)n], (2) compaction pressure of the pellet, (3) molar ratio of the two elements tungsten and carbon, and (4) the carbon source. Crystal structure and phase composition of the products were obtained using an X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDX) respectively. Microstructure of the products was examined by a scanning electron microscopy (SEM). Its chemical composition was determined by ICP and carbon determinator method.

3. Results and discussion

At $T = 350$ to 450 K the polytetrafluorethylene breaks down with the formation of the fluorine [7], which enters into the reaction with magnesium and produces high heat. In this work, the formation reaction of tungsten carbide from elements is believed to involve the equations below:

$$2\text{Mg} + (\text{-CF}_2\text{CF}_2\text{-})n = 2\text{MgF}_2 + 2\text{C} \qquad (1)$$

$$\Delta G^0_{\text{f(300 K)}} = -1518.093\ kJ/mol$$

$$\text{W} + \text{C} = \text{WC} \qquad (2)$$

$$\Delta G^0_{\text{f(300 K)}} = -38.361\ kJ/mol$$

The Gibbs free energies of the relevant reactions are listed above. It is seen that Reaction 1 and Reaction 2 have the negative ΔG^{o} value, indicating that Reaction 1 and 2 are thermodynamic feasible. The calculated adiabatic temperature (T_{ad}) from reaction (1) is 1000 K [10], which is a lower value than the empirically obtained critical adiabatic temperature of 1800 K [5] need for self-sustaining combustion. This reaction can't attain a self-sustaining combustion form without the addition of energy from an exterior source [11, 12]. The mixture of pellets with the raw materials of W and C powder could not be ignited. However, after adding a certain amount of the mixture of Mg and (-C_2F_4-)n to the reactants, it could be ignited easily. It is reasonable to believe that reaction (2) starts in the early stage of reaction, consequently reaction (1) is achieved sequentially by utilizing a high heat source supplied from the reaction (2).

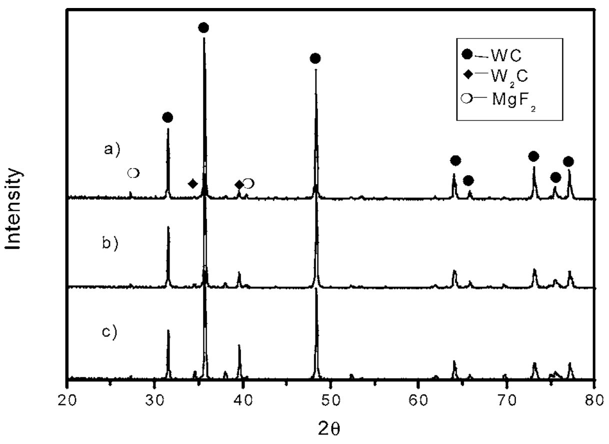

Figure 1 X-ray diffraction pattens of reaction products with different mass.% of activated additives under a compaction pressure of 710 Mpa.

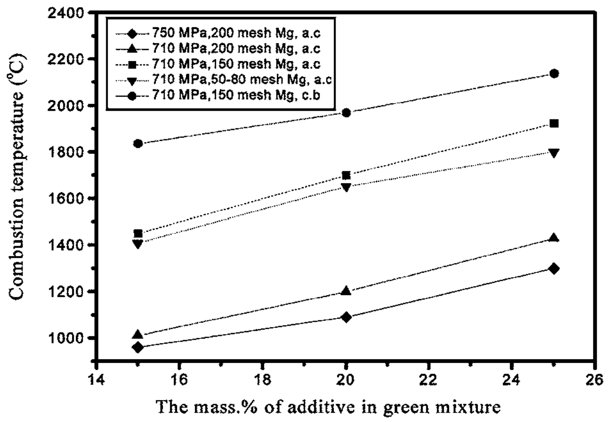

Figure 2 Effect of activated additive, mass % at various densities of pellets on the combustion temperature.

In this system, vaporization at the combustion front was observed. The products were observed to be largely expended and friable compared to the initial pellets.

Addition of 10% mass of the activated additive changes the combustion from an unsteady to a steady-state mode. Fig. 1 shows the effect of activated additive on the combustion temperature. When the activated additive is about 15, 20 and 25 mass percents, the temperature is 1400 °C, 1625 °C, and 1800 °C respectively (See Fig. 2). It can be seen that there are byproducts W_2C and unreacted W, in addition to WC, which is the main phase in the products. Increase of the amount of additive in the green mixture leads to increase of WC and decrease of the amount of byproduct W_2C and unreacted W. This was because the diffusivity of the C increased as the reaction temperature increased as shown in Fig. 2, thus the reaction rate of the WC increased.

Fig. 3 shows the X-ray diffraction patterns of the reaction products obtained with 10% of additive at various compaction pressure. At 10% of additive, WC is a minor phase, the amount of this phase increases with increase in compaction pressure. However, as the compaction pressure exceeded 612 MPa, the pellet, with 10% additive, could not be ignited. Authors reported that the permeability of the pellet influenced the reactivity in WO_3-Al-C combustion system [13].

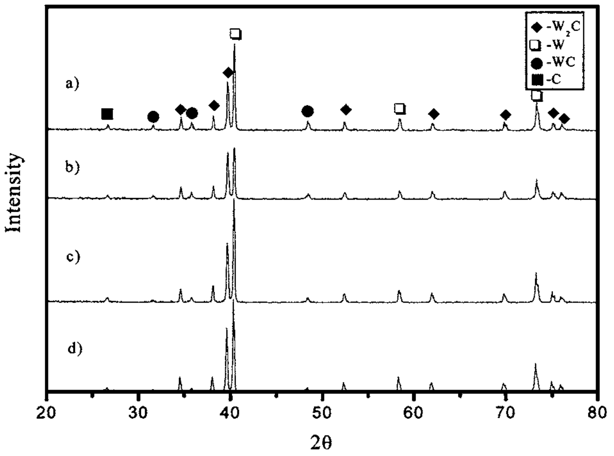

Figure 3 X-ray diffraction pattens of the reaction products varying with compaction pressure of pellets.

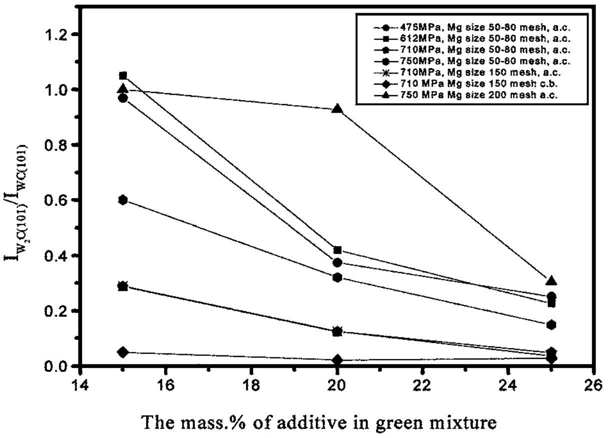

Figure 4 Effect of the mass % of additive on $I_{\mathrm{W2C(010)}}/I_{\mathrm{WC(010)}}$ at various comaction pressure.

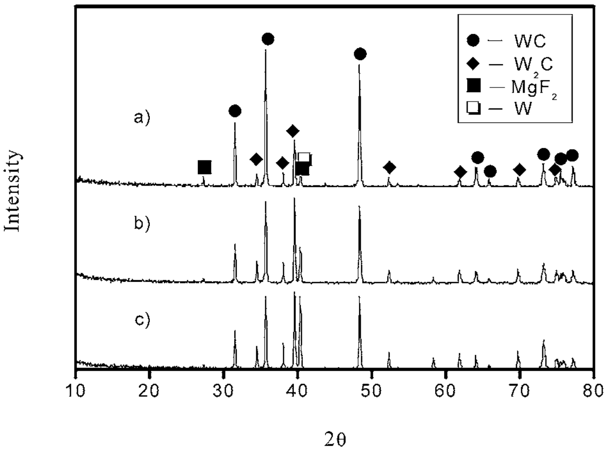

Figure 5 X-ray diffraction pattens of reaction products with different mass.% of activated additive under a compaction pressure of 750 MPa.

In this case, the pre-heating zone becomes extremely short over 612 MPa of compaction pressure because the permeability of the Mg vapor to the green pellet decreased as the relative density increased. In gaseous reaction, combustion front propagation is controlled by the amount of the vapor phase and permeability [14]. Also, the effect of permeability of a specimen on the combustion velocity was described in the previous research; detailed derivation procedure is in ref. [15].

$$\Delta h = \frac{h_\mathrm{i} - h_\mathrm{f}}{h_\mathrm{i}} \approx \frac{\rho A V_\mathrm{T}}{\pi r^2} - \frac{kA}{\mu} \cdot \frac{\mathrm{d}P}{\mathrm{d}x} \cdot \frac{1}{U\pi r^2} \approx \rho V_\mathrm{T} - \frac{k}{\mu} \cdot \frac{\mathrm{d}P}{\mathrm{d}x} \cdot \frac{1}{U} \tag{3}$$

where r: radius of the specimen, h_i and h_f: initial and final height of the specimen respectively, ρ: density (kg/m^3), A: area of the specimen(m^2), V_T: volume of Mg vapor per unit mass at the combustion temperature and pressure(m^3/kg), U: combustion velocity(m/sec), k: coefficient of the gas permeability(m^2), μ: dynamic viscosity of the gas(kg·sec/m^2), dP/dx: pressure gradient(kg·m^{-2}/m). When the density of the pellet increased, the permeability, k decreased and then the combustion velocity, U decreased. Hence, the extinguishment of the combustion flame in the sample with over 612 MPa of compaction pressure can be explained with the combustion velocity decrease as described in Equation 3.

Fig. 4 shows the effect of mass of additive in the green mixture with various compaction pressure and Mg particle size on the ratio of relative intensities $I_{\mathrm{W2C(101)}}/I_{\mathrm{WC(101)}}$ in the case when more then 10% of the additive was added to the mixture. It obviously demonstrates when the compaction pressure is higher than 710 MPa, while the green density is 78% TD, the amount of WC in the product sharply decreases, but W_2C increases. Comparing Figs 1 and 5, it was found that the formation of even a greater amount of WC and a complete elimination of W_2C are caused by the decreasing compaction pressure from 750 to 710 MPa, moreover, there practically is no reactant W remained in Fig. 1. The combustion temperatures of the samples in Figs 1 and 5 are shown in Fig. 2, the former is higher than the latter. In Fig. 4, it is shown that Mg particle size practically does not affect the content of the product at 710 MPa, which can be considered a critical value of compaction pressure on the green pellet, being favorable for the formation of WC phase in this system.

According to this result, it can be considered that compaction pressure on the green pellet is one of the most important factors strongly affecting the self-sustaining combustion and quality of the products. In the case of heterogeneous combustion the rate of heat release depends on the specific surface contact. Compression of a pellet prior to SHS enlarges the surface contact and increases reactivity of the system and, thus, the speed of combustion wave propagation. However, compression to a high density can also substantially change a scale of heterogeneity when a network consisting of metal particles forms. This network causes an increase in conduction thermal conductivity but a decrease convection thermal conductivity in the pellet, thus leads to unstable modes of combustion. In summary, it is considered that the optimum density of the pellet is favorable for both the exothermal reaction (2) and the diffusion of carbon to tungsten.

As shown in Fig. 6, the transformation rate of WC is the highest in using carbon black as carbon source among the three. Fig. 7 is the SEM morphology of

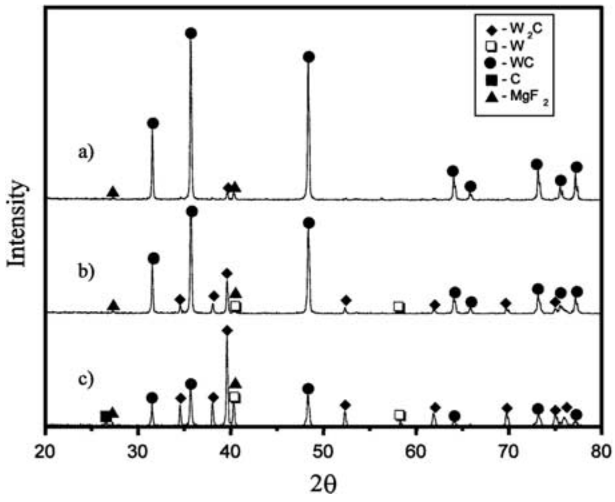

Figure 6 X-ray diffraction pattens of reaction products varying with carbon source.

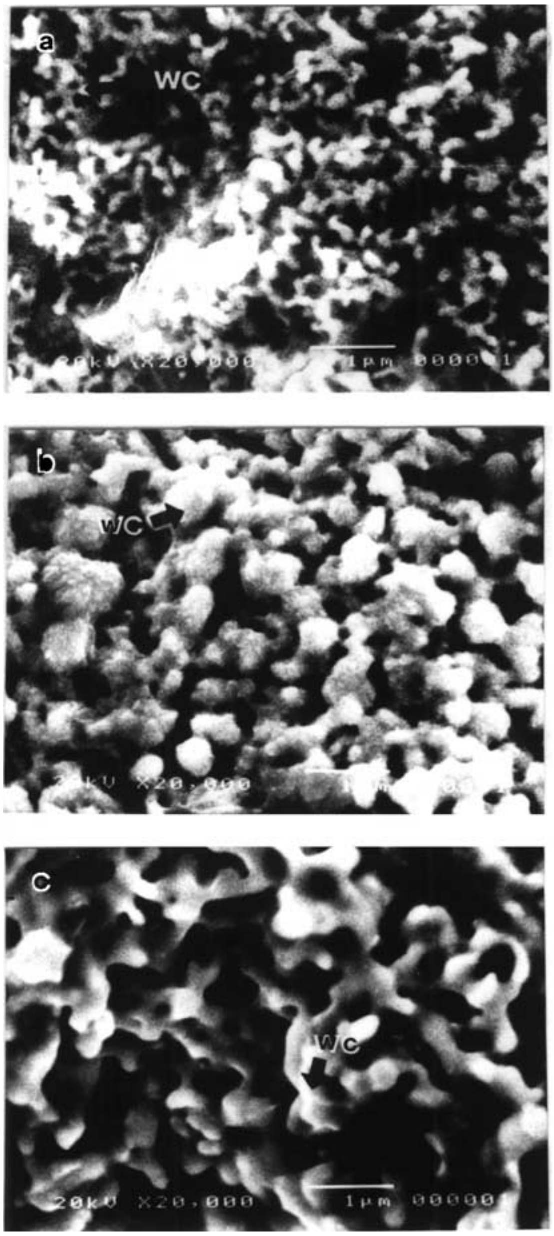

Figure 7 SEM photogragh of reaction products with varying carbon sources.

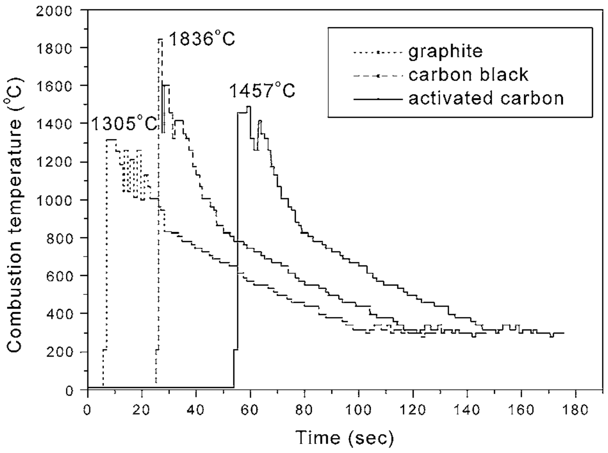

Figure 8 Temperature profiles of the combustion reaction with W : C = 0.5 : 1, compaction pressure: 710 MPa and 15% additive.

the cross section of reaction products mentioned above with various carbon sources. It can be seen that the average grain size of the products using carbon black and activated carbon as a carbon source is larger and has a narrower size distribution than graphite, the grain shape of the products using carbon black, activated carbon and graphite is short cylindrical, spherical and irregular shape, respectively. It shown that the crystalline grow completely and size become larger. Fig. 8 shows the combustion temperature profile of the sample in correspondence with Figs 6 and 7. It can be seen that the combustion temperature with carbon black as a carbon source is the highest. It is clearly indicated that ultilizing fine carbon black as a reactant is more advantageous to form WC than other carbon sources, owing to its large surface area and homogeneous distribution. The kinetics of solid state reactions are dependent on the dispersion and the effective contact area of the reactants [16]. It can be considered that the larger portion of the surface area of the powder grain causes a larger reaction interface and diffusion section between reactant grains. Therefore, the reaction on interface and the diffusivity are enhanced, making combustion temperature higher and, thus, the high combustion temperature holds more sufficient reaction time in the sample, it makes the crystalline to grow more integrated and larger.

The effect of the W : C molar ratio on the ratio of relative intensities $I_{W2C(101)}/I_{WC(101)}$ is shown in Fig. 9. As the W : C molar ratio increased from 0.5 to 1, the amount of WC decreased and unreacted W increaced due to an intriguing feature of hexagonal WC, which is the narrowness of its composition range with an insignificant deviation from stoichiometry [4, 17]. As known, during the combustion, there was a large amount of carbon in gas phase at high temperature. The composition of the green mixture should be cosseted for carbon losses during the combustion synthesis. The optimized starting composition was determined as W : C = 0.5 : 1 (or 1 : 2).

Fig. 10 shows the leaching effect on the product. It can be seen that a small amount of W_2C and MgF_2 is completely eliminated by acid leaching. The process is divided into two steps. The first step is leaching of 10 g

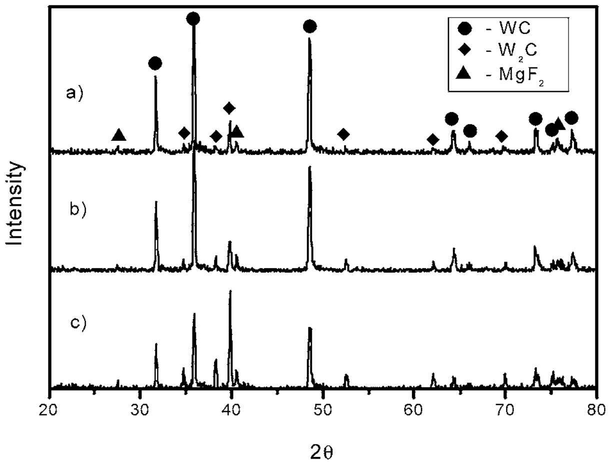

Figure 9 X-ray diffraction patterns of reaction products varying with the W and C molar ratio.

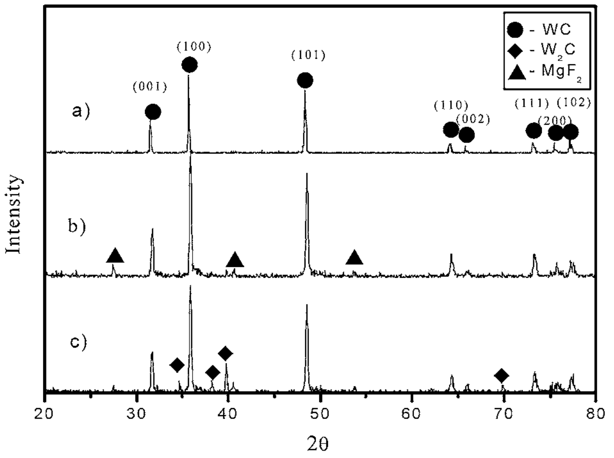

Figure 10 Effect of acidic leaching.

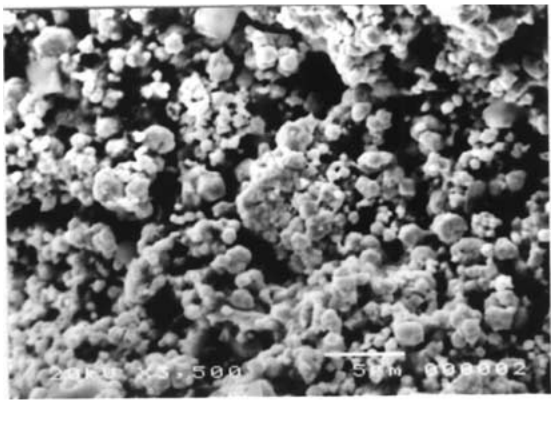

Figure 11 SEM photogragh of final powder.

of the product mixture in 100 ml of 10% $HNO_3 + HF$ diluted solution for 4 hours to remove W_2C; the second step is leaching of 10 g of the product mixture, which was treated in the first step, in 25 ml of 10% HNO_3 diluted solution for 2 hours to remove MgF_2. Fig. 11 is the SEM photograph of the final product powder. The morphology of the final product powder is found to be monodispersed, as shown in Fig. 11. Also, the chemical composition, particle size, structure type and lattice parameters of the final WC powder are shown in Table I. It is believed that the new process for stimulating a system with low adiabatic temperatures can be widely applied to other systems.

TABLE I The properties of the final powder

W (wt%)	C_{total} (wt%)	C_{free} (wt%)	Particle Size (μ m)	Structure Type	Lattic Parameters (nm)
90 ~ 93	No less than 6	No more than 0.5	1–2	Hexagonal	$a_0 = 0.2895$ $c_0 = 0.2826$

4. Conclusion

In this work, pure WC powder was prepared from elements through the SHS in the presence of a highly exothermal mixture [$Mg + (\text{-}C_2F_4\text{-})n$] as an activative additive. It has been demonstrated that the production of monophase pure carbide which has such a low adiabatic temperature as a W-C system can be achieved with the newly developed combustion system. The important factors affecting the reaction were the amount of activative additive in the mixture and the compaction pressure. The W : C molar ratio and carbon source also strongly affected the properties of the final product. The optimum economic conditions for synthesis of monophase WC are 15 mass% of additive, 710 MPa of compaction pressure, carbon black as a carbon source, and a molar ratio of W/C = 0.5. Under the above conditions, the yield of optimal product is no less than 90–95% of WC content, the small amount of W_2C which was concurrently formed in the product was completely removed by acidic leaching. The particle size of the final WC powder was 1 ~ 2 μm. The purity of WC after leaching was 99%.

Acknowledgments

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