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# Synthesis of $Al_2O_3$-WC composite powder by SHS process

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$Al_2O_3$-WC composite powder was synthesized by self-propagating high-temperature synthesis using Al powder as a reducing agent. WC, $W_2C$ and $Al_2O_3$ were concurrently formed in $WO_3$-Al-C system. It was found that the complete reaction was achieved with excessive addition of carbon and appropriate processing parameters such as degree of dilution, particle size of aluminum, pellet compaction pressure and carbon source. The final product which was leached by 50% 1 : 4 $HNO_3$ + HF diluted solution was consisted of $Al_2O_3$-55wt%WC having 2–3 $\mu$m of mean particle size.

## 1. Introduction

Self-propagation high-temperature synthesis (SHS) with reduction stage has drawn much attention as an effective method to produce refractory pure and composite materials [1–7]. The SHS process with reduction stage has advantageous features compared to conventional SHS processes which use expensive raw materials, because oxides or natural ore can be used as raw materials and exothermic heat during reduction can give external heat source which is applied to initiate and sustain the combustion reaction in case of low exothermic reactant mixture. With this method various high melting point materials having low exothermic energy have been successfully synthesized. Recently, considerable efforts have been generated to synthesize ceramic composites for advanced cutting tool such as $Al_2O_3$-TiC, $TiB_2$ etc. using the SHS process involving reducing stage. $Al_2O_3$-WC is the one of ceramic cutting-tool composites [8]. In carboxide which is called black hot-pressure ceramics, carbides dispersed in oxides to improve hardness. Some researchers have paid attention to the self-propagation combustion reaction mode for producing new materials in which the product powder was not pure composite powder [9, 10].

Tungsten carbide forms three intermediate phases, $W_2C$, $\alpha$-$WC_{1-x}$ and WC with $W_2C$ undergoing transformation in the W-C system. However the $W_2C$ phase is extremely brittle and has inferior tribological properties than the monocarbide. So the main purpose of this work is to promote the formation of WC from $W_2C$ phase during SHS reaction.

In this work, pure $Al_2O_3$-55%WC composite powder was prepared by SHS using Al thermic reaction with Al, $WO_3$ and C as raw materials. The overall reaction of this composite formation reaction is:

$$WO_3 + 2Al + C = WC + Al_2O_3, \quad \Delta G^0_{f(300\,K)} = -779.767\ KJ/mol \tag{1}$$

The effects of various experimental parameters on the preparing of $Al_2O_3$-WC were studied.

## 2. Experimental

The raw material, $WO_3$ and Aluminum particles used in this experiment were 99.9% purity and 325 mesh size, 99% purity and 140, 325 mesh size respectively. Activated carbon and graphite powder were aslo used as a carbon source. The predetermined amounts of the three raw material powders were mixed in an alumina ball mill and pressed into pellets of 20 mm diameter and 12–18 mm height under various compaction pressure. The pellet was placed in an SHS reactor under an argon atmosphere and ignited by a tungsten wire connected to power supply. The temperature profiles were measured by the C-type thermocouples(W-5%Re vs. W-26%Re, 0.5$\phi$) connected to data logger (DASTC). Experimental variables investigated in this work were (i) mixing ratio of the carbon, (ii) compaction pressure, (iii) Aluminum particle size and (iv) carbon source. X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Energy dispersive X-ray (EDS) were used to reveal crystal structure, microstructure and chemical composition respectively.

## 3. Results and discussion

Continuous layers which were formed during combustion reaction by a rippling effect were found on the cylindrical surface of the combusted samples, also active vaporization was observed around combustion front. It was analyzed that the vaporized products were $Al_2O_3$, $W_2C$ and amorphous carbon.

The overall reaction shown in Equation 1 is believed to take place as a combination of following sequential reactions

$$WO_3 + 2Al = W + Al_2O_3, \quad \Delta G^0_{f(300\,K)} = -818.128\ KJ/mol \tag{2}$$

$$W + C = WC, \quad \Delta G^0_{f(300\,K)} = -38.361\ KJ/mol \tag{3}$$

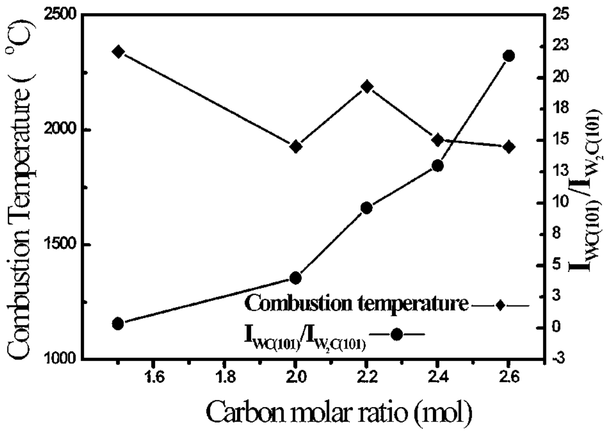

*Figure 1* Effect of carbon additive on combustion temperature and the ratio of indensity $I_{WC(101)}/I_{W_2C(101)}$.

The above reactions occur at the temperature higher than the melting point of aluminum (660 °C), aluminum reduces tungsten oxide first before the reaction of tungsten and carbon [10]. The calculated adiabatic reaction temperature of $WO_3$-2Al-C system is 4070 K [11]. It was found that the reaction was explosive when the combustion was carried out at stoichiometric molar ratio, also, it was too intense to observe the reaction, because too much gas was rapidly generated during reaction. The effects of excess adding of carbon over the stoichiometric molar ratio $WO_3 : Al : C$ of 1 : 2 : 1 on combustion temperature, and the changes of relative intensity, $Iwc(101)/Iw_2c(101)$ of the products are shown in Fig. 1. The combustion temperatures were decreased as the carbon mole ratios were increased, whereas the relative intensities $Iwc(101)/Iw_2c(101)$ were increased. This is because $W_2C$ is more stable at high temperature than WC, Fig. 2, also excess addition of carbon may act not only as a source material for the synthesis of WC but also as a diluent of the thermit reaction in the $WO_3$-Al-C system. The X-ray patterns of the products obtained with various $WO_3 : Al : C$ molar ratios with 325 mesh aluminum powder are shown in Fig. 3, and other conditions are listed in the caption. As the carbon mole ratios were increased, the amount of WC in the products was increased in the range of carbon molar ratio from 1.5 to 2.6, while $W_2C$ was decreased. The peaks of WC and $W_2C$ agree with standard data [13] very well. The lattice code of WC and $W_2C$ are hexagonal(HCP). The lattice parameters, structure type and space group of WC are $a_0 = 0.2890$ nm, $c_0 = 0.2819$ nm, D3h1 and No.187 respectively, and that of $W_2C$ are $a_0 = 0.2990$ nm, $c_0 = 0.4720$ nm, L'3 and No.194 respectively. The above results indicate that the control of the carbon concentration is most important factor in order to get hexagonal WC preferentially. This results are distinctly different from the group IV transition metal carbides like TiC which retains its cubic structure over a whole range of carbon contents. WC has been reported to be a line compound at the stoichiometric composition by Storms [14]. Particle size, pellet compaction pressure and carbon source are other factors which influence the kinetics of solid state combustion reaction are dependent on the dispersion and the effective contact area of the reactants.

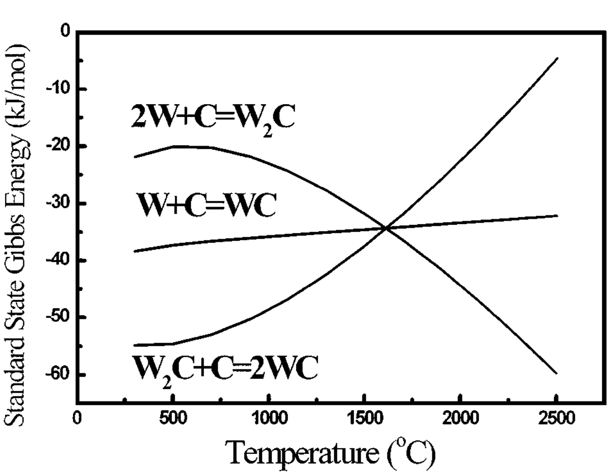

*Figure 2* Standard state Gibbs energies for potential reactions which may occur in W-C system. These plots are based on tabulated data [12].

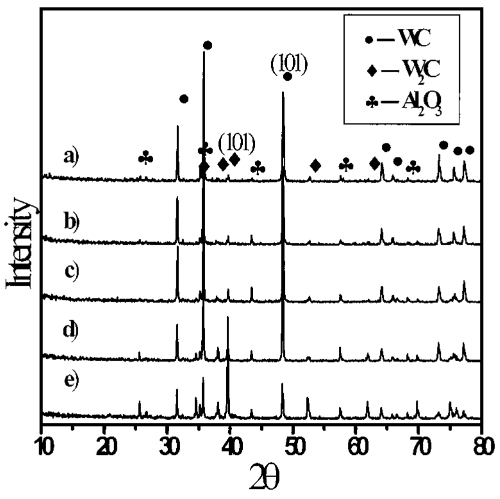

*Figure 3* X-ray patterns of reaction products varying with carbon molar ratio ($WO_3 : Al = 1 : 2$, graphite, Al size 325 mesh). a) 2.6, b) 2.4, c) 2.2, d) 2.0, e) 1.5.

Fig. 4 shows the XRD patterns of reaction products varying with carbon mole ratio and 140 mesh size

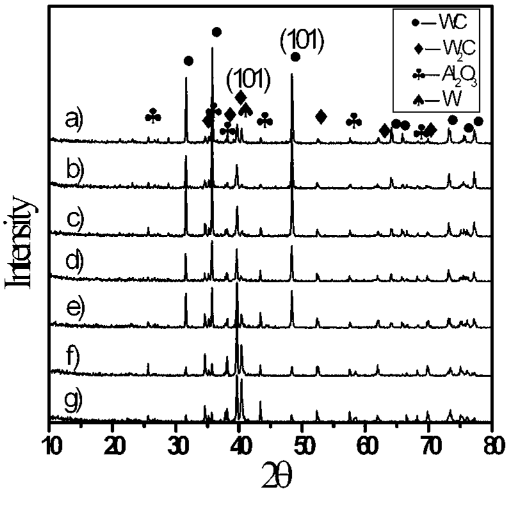

*Figure 4* X-ray patterns of reaction products varying with carbon molar ratio ($WO_3 : Al = 1 : 2$, graphite, Al size 140 mesh). a) 2.6, b) 2.4, c) 2.2, d) 2.0, e) 1.8, f) 1.3, g) 1.0.

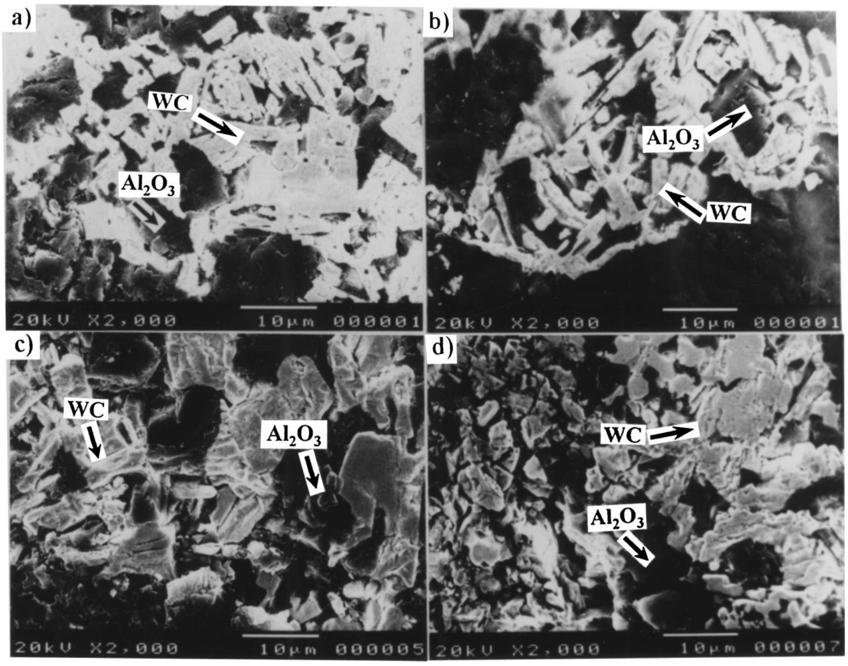

*Figure 5* SEM photomicrographs of combustion synthesized WC-$Al_2O_3$ with varying particle size of Al powder. ($WO_3$ : Al : C = 1 : 2 : 2, 58–63%TD); a) 140 mesh, b) 325 mesh, and with varying carbon source. ($WO_3$ : Al : C = 1 : 2 : 2.4, 58–63%TD, Al powder particle size 325 mesh), c) activated carbon, d) graphite.

aluminum powder. WC, $Al_2O_3$ and $W_2C$ phases were dominant products, however small amount of unreacted W phase was detected in the product. The maximum combustion temperature of the sample containing aluminum particle of 325 mesh size was 1907 °C, slightly higher value compared to 1853 °C in case of 140 mesh size. This may due to the active reaction occurred by the better contacts among the reactants. Fig. 5a–d show SEM photomicroghaphs of cross-section of combustion synthesized $Al_2O_3$-WC with varying particle size of aluminum and carbon source respectively. It has been found that particle size influences not only the reaction rate, but also the microstructure of the products formed, the average grain size of the product synthesized with 325 mesh size aluminum powder is finer and denser than that of 140 mesh. Also, the WC and $Al_2O_3$ grain size were finer with activated carbon than that of graphite.

Fig. 6 shows the effect of compaction pressure on the combustion temperature and Iwc(101)/Iw$_2$c(101) of reaction products, as the compaction pressure is increased, the ratio of Iwc(101)/Iw$_2$c(101) is seen to be increased up to a compaction pressure of 3000–4000 psi, whereas both the ratio of Iwc(101)/Iw$_2$c(101) and combustion temperature were decreased at the above 4000 psi. It is certain that there are critical compaction pressure, because the critical density is necessary to ignite the specimen in solid-solid reaction, however it is believed that the diffusion of elements, combustion reaction was hindered by the increased density above the critical value, because permeability of the green pellet is decreased by the applied pressure.

Fig. 7 shows the X-ray diffraction patterns of the products with various carbon source, where the rate of Iwc(101)/Iw$_2$c(101) is seen to increase with activated carbon compared to graphite, and Fig. 8 shows the leaching effect on the product. It can be seen that $W_2C$ is completely removed by leaching approximately 10 g of

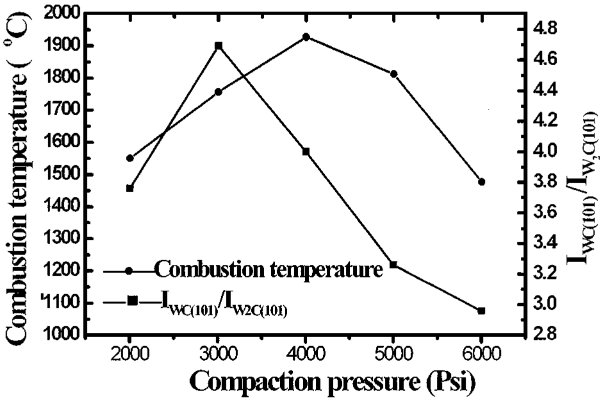

*Figure 6* Effect of compaction pressure on the combustion temperature and $I_{WC(101)}/I_{W_2C(101)}$ of reaction products.

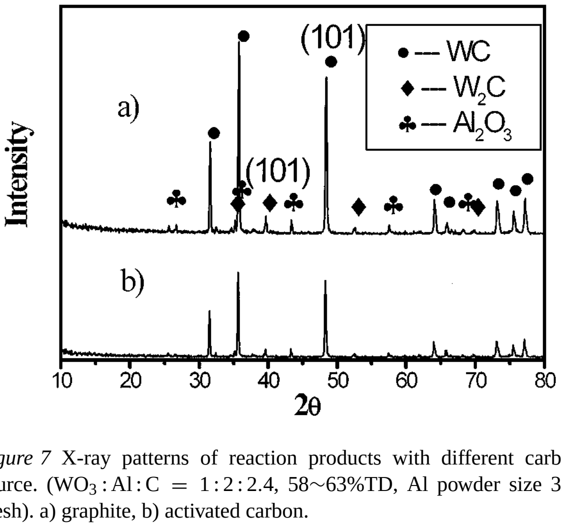

*Figure 7* X-ray patterns of reaction products with different carbon source. ($WO_3$ : Al : C = 1 : 2 : 2.4, 58~63%TD, Al powder size 325 mesh). a) graphite, b) activated carbon.

TABLE I Phase contents of $Al_2O_3$-WC prepared by SHS process

| Phase | WC | $Al_2O_3$ |
|---|---|---|
| Mass % | 55–60 | 45–40 |

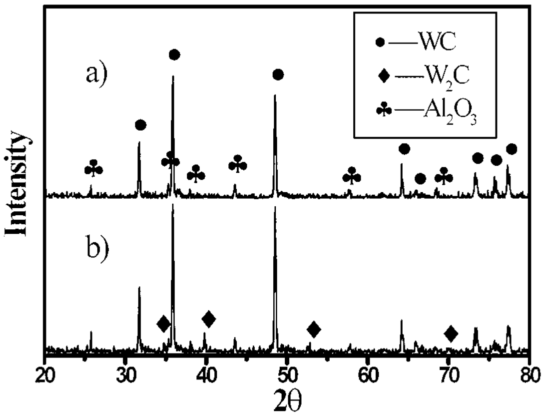

*Figure 8* Effects of leaching at 50% 1 : 4 $HNO_3$ + HF solution, (temp.: room, time: 30 min), a) after leaching, b) before leaching.

the product mixture in 100 ml of 50% 1 : 4 $HNO_3$ + HF diluted solution at room temperature for 30 min.

The $Al_2O_3$-WC final powder was analyzed by X-ray quantitative analysis (internal standard or $K$-values method), as shown in Table I. The mean particle size of produced WC-$Al_2O_3$ powder is 2–3 $\mu$m, and the WC is uniformly dispersed in $Al_2O_3$.

## 4. Conclusions

The most important variables affecting the reaction of $WO_3 + 2Al + C = WC + Al_2O_3$ were reactant molar ratio and Al particle size. Compaction pressure and carbon source were also important processing parameters affecting the final crystal structure. The optimum condition for the synthesis of $Al_2O_3$-WC is a mole ratio from 1 : 2 : 2.4 to 1 : 2 : 2.6, and 325 mesh of Al particle size. Compaction pressure from 3000 psi to 4000 psi (pellet density 58%TD, 63%TD. respectively) is the optimum range which is advantageous to either the dispersion of melting Al to reduce $WO_3$ completely or the effective contact of reduced W and C. Activated carbon is advantageous to form monotungsten carbide and aluminum oxide composite powder compared to graphite. The average grain size of the final composite powder was 2–3 $\mu$m. The small amount of $W_2C$ which was concurrently formed in the product was removed by leaching 10 g of product mixture in 100 ml of 50% 1 : 4 $HNO_3$+HF diluted solution at room temperature for 30 min.

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