# PREPARATION OF TUNGSTEN AND TUNGSTEN CARBIDE SUBMICRON POWDERS IN A CHLORINE-HYDROGEN FLAME BY THE CHEMICAL VAPOR PHASE REACTION

#### G. Y. ZHAO, V. V. S. REVANKAR and V. HLAVACEK

Ceramic and Reaction Engineering Laboratory, Department of Chemical Engineering, State University of New York at Buffalo, New York (U.S.A.)

(Received March 16, 1990)

#### Summary

A hydrogen-chlorine flame chemical vapor deposition reactor has been developed to synthesize ultrafine powders of refractory compounds (*e.g.* carbides and nitrides). At the laboratory scale, synthesis of tungsten and tungsten carbides (both  $(WC)_{1-x}$  and  $\alpha - W_2C$ ) gave encouraging results. The collected refractory powders do not have internal porosity, they exhibit spherical shape and have a very narrow size distribution. The size of the particles and the crystalline structure depends on the flame temperature, flow rate of the reactants and residence time of particles. In short, they depend on the flame characteristics. Thermochemical calculations were carried out to obtain the optimum conditions for different carbide powder synthesis. The flame is completely characterized and the temperature distribution within the reactor is obtained.

## 1. Introduction

As technology advances, the need for advanced ceramics and refractory materials for high temperature applications, such as laser nozzles, turbine engines, aerospace applications continues to increase rapidly [1]. Ultrafine ceramic powders can be synthesized by different high temperature operations involving either thermal decomposition or reducing halides and hydrides. For these operations, flame technology has proven to be the dominant technology. Different papers have been published on the flame operation [1–11]. Maude [12], in 1941, first developed a process by using hydrogen and chlorine in a (concurrent diffusion) flame to generate hydrochloric acid. The calculation showed that the adiabatic temperature of the  $H_2$ -Cl<sub>2</sub> flame is around 3000 K. Sato *et al.* [13] used a  $H_2$ -Cl<sub>2</sub> flame to synthesize silicon nitride. However there is no description of the operating conditions. We systematically performed a series of theoretical and experimental studies to utilize this process to synthesize ultrafine ceramic powders. This process has a number of advantages over others because of the low cost of chlorine and because sufficient heat is generated by these hydrogen-chlorine reac-

tions. We found that it is economically feasible to synthesize tungsten and tungsten carbide powders in a  $H_2$ - $Cl_2$  flame and this is supported by our theoretical calculations.

## 2. Experimental details

The experimental apparatus consists essentially of four parts: (1) the gas and reactant supply, (2) the burner, (3) the reaction chamber, and (4) the exhaust system and powder collector system. The complete system is shown in Fig. 1 and schematically in Fig. 2. The gas and reactant supply system consists of two separate quartz and copper tubes passing through the preheater. The copper tube is used to feed hydrogen and liquid reactants, whereas the quartz tube is used for chlorine and solid reactants. Solid and liquid reactants were fed by the evaporation method using a preheater. A separate screw feeder evaporation is used for a large-scale system. The temperature of the preheater is controlled by a temperature controller. The reactant lines meet in the burner, which consists of two coaxial quartz tubes having diameters of 1 cm and 2 cm respectively. Chlorine passes through the center tube, while hydrogen passes through the annular part between these two tubes. The reactor is a Pyrex tube of diameter 5.2 cm with a water cooling jacket. The length of the reactor varies depending on the length of the flame. The upper part of the reactor contains ports to insert (1) a pilot burner for the ignition of the



Fig. 1. Photograph of our  $H_2$ -Cl<sub>2</sub> flame reactor assembly.



Fig. 2. Schematics of the  $H_2$ -Cl<sub>2</sub> flame reactor. 1, Chlorine inlet tube; 2, hydrogen inlet tube; 3, evaporator for liquid reactants; 4, preheater; 5, ceramic boat containing solid reactant; 6, heating element; 7, pilot burner; 8, thermocouple; 9, main burner; 10, water jacket; 11, flame; 12, exit tube; 13, powder collector.

main burner and (2) a thermocouple for the measurement of the temperature of the flame which is 2.8 cm from the exit of the burner. The structure of the pilot burner is the same as the main burner and it is also made of a quartz tube but has a smaller size. The exhaust system consists of an exit tube and a filter. We modified the filter many times and finally settled upon a water-cooled solvent-filled collector containing glass beads. The waste gas goes out through an exit located on the shoulder of the collector.

The pilot burner was ignited in air by using hydrogen followed by chlorine injection. The colour of the pilot flame turned from golden yellow to bluish white. The system was flushed with argon. The pilot burner was then inserted into the side arm to ignite the main flame. The chlorine flow rate was slowly increased and then the hydrogen was introduced until the required length and temperature of the flame was reached. Once the flame was stabilized, the reactants were injected under controlled conditions.

#### 3. Flame characteristics

In order to obtain the characteristics of our flame, we performed numerical simulations as well as actual temperature distribution measurements by using a special kind of minute thermocouple. Figure 3 shows the temperature distribution of our flame from the pilot burner for the typical flow rates of hydrogen  $(2 \, \text{lmin}^{-1})$ and chlorine  $(1.5 \text{ I min}^{-1})$ . The pilot burner has an inner diameter of 0.4 cm and an outer diameter of 0.8 cm, similar to the main burner. From Fig. 3 it can be seen that the highest temperatures exist at the center and at the exit of the tube where the hydrogen and chlorine gases meet. The temperature decreases along the axis and at every section of the flame at positions increasingly distant from the exit. The temperature also decreases radially. In this typical operation (hydrogen flow rate of  $2 \lim_{n \to \infty} 1 \min^{-1}$  and chloring flow rate of 1.5  $\lim_{n \to \infty} 1 \min^{-1}$ ) the temperature varies from 1000 to 1600 K. However, our operating conditions are at higher flow rates of hydrogen and chlorine  $(3-6 \ 1 \ min^{-1} \ and \ 2-4 \ 1 \ min^{-1} \ respectively)$ , which generates a larger high temperature range. Depending on the flow rate, the length of the flame varied from 9 cm for this operation to 30 cm for the maximum flow rate. The radius also varied from 10 to 20 mm. However, for all these operations the temperature distribution pattern remained the same, although a slight increase in temperature at the axis of the flame was observed. Hence, depending on the residence time requirement, the flame length can be controlled. The numerical simulation (to be published elsewhere [14]) shows that the oxygen interference in measuring the above temperature distribution in air is negligible. Hence the calculation and measurements are fairly accurate for the operation.

The transverse temperature distribution measurement was carried out within the reactor from the edge of the flame by using a special thermocouple probe inserted at the upper part of the reactor as described above. The typical temperature distribution pattern for flow rates of hydrogen of  $4 \ l \ min^{-1}$  and chlorine of  $3 \ l \ min^{-1}$  is shown in Fig. 4. At this particular condition, the temperature varied from



Fig. 3. Flame shape and the temperature distribution of the flame from the pilot burner.



Fig. 4. The transverse temperature measurement in our reactor at a position 2.8 cm from the exit of the main burner.

1300 K at the center of the flame to 450 K at the edge of the reactor, *i.e.* 2.5 cm from the edge of the flame.

## 4. Thermochemical consideration

The calculation of chemical equilibrium conditions is the first step in considering specific chemical vapor deposition (CVD) processes. Hojo *et al.* [15], in 1978, calculated the equilibrium relationships for the system  $WCl_6-CH_4-H_2$  for preparing tungsten and tungsten carbides.

Our thermodynamic equilibrium compositions for  $Cl_2-H_2-WCl_6-CH_4$  system were calculated from 300 to 1700 K, the latter value is the highest temperature which can be reached in our present operation. The chemical species considered in this calculation are 35 gaseous species and seven condensed species. Thermodynamic data of all these species are found in the JANAF tables [16] and Barin *et al.* [17].

Thermochemical computational results (using the JANAF tables [16]) at atmospheric pressure for the experimental temperature range are shown in Fig. 5. Under our operating conditions, HCl, H<sub>2</sub> and CH<sub>4</sub> are in large excess and are always the predominant species, and their molar fractions do not depend on temperature. Other products include WC (solid), W<sub>2</sub>C (solid), W (solid), C (solid), depending on the temperature range and the molar ratio of H<sub>2</sub>, Cl<sub>2</sub>, WCl<sub>6</sub> and CH<sub>4</sub>. In most cases either WC, W<sub>2</sub>C or W is the predominant product at the given temperature and condition. The alternative appearance of W<sub>2</sub>C and WC is due to their thermodynamic properties and the phase difference.

In Fig. 5(a), we varied the chlorine molar composition in the total gas stream. The gas composition is expressed in molar fraction. Here the  $H_2$ ,  $CH_4$  and  $WCl_6$ 



Fig. 5. Thermochemical calculation of our flame reactor (WCl<sub>6</sub>-CH<sub>4</sub>-Cl<sub>2</sub>-H<sub>2</sub> system). (a) Effect of Cl<sub>2</sub> mole fraction on the products (H<sub>2</sub> = 1.0 mol, CH<sub>4</sub> = 0.01 mol, WCl<sub>6</sub> = 0.001 mol). (b) Effect of CH<sub>4</sub> mol fraction on the products (H<sub>2</sub> = 1.0 mol, Cl<sub>2</sub> = 0.60 mol, WCl<sub>6</sub> = 0.001 mol). (c) Effect of WCl<sub>6</sub> mol fraction on the products (H<sub>2</sub> = 1.0 mol, Cl<sub>2</sub> = 0.60 mol, CH<sub>4</sub> = 0.01 mol).

flow rate composition is 1.0, 0.01 and 0.001 respectively, which is kept constant. As we increase the  $H_2/Cl_2$  ratio, the temperature where the free tungsten forms increased from 350 to 500 K; the formation of free carbon also shifted to higher temperatures. When the  $H_2/Cl_2$  ratio was increased from 1 to 2.5, the temperature of formation of free carbon increased from 860 to 1050 K. The formation of  $W_2C$ and WC also shifted to the higher temperature region. At very high  $H_2/Cl_2$  ratios the formation of WC slowly disappears. Hence the operating conditions, such as the H<sub>2</sub>/Cl<sub>2</sub> ratio, play an important role in obtaining the required product. Figure 5(b) shows the effect of CH<sub>4</sub> on the product at different flow rates. When there is no CH<sub>4</sub> flow rate, the WCl<sub>6</sub> completely reduces to pure tungsten powder. As the CH<sub>4</sub> flow rate increased, pure tungsten forms only at lower temperatures, and W<sub>2</sub>C and WC start appearing and also the temperature of formation and the temperature range of appearance of these two species starts to shift to the lower region. The free carbon appears only when  $CH_4$  flow rate exceeds the  $WCl_6$  flow rate. Figure 5(c) shows the effect of WCl<sub>6</sub> on the system. Obviously the amount of WCl<sub>6</sub> does not affect the temperature region of tungsten, W2C and WC formation. Only when the mole number of WCl<sub>6</sub> reaches that of CH<sub>4</sub> does a very small amount of WC exist. If we feed higher amounts of WCl<sub>6</sub>, the WC will not appear in our chemical equilibrium calculation. From the above results, we can conclude that the key factor in obtaining tungsten or tungsten carbide is the flame temperature (optimum range) for an assumed mole ratio between WCl<sub>6</sub> and CH<sub>4</sub>. From our calculation, the optimum mole ratio between chlorine and hydrogen was 0.6 with the flow rate of  $Q_{\rm H_2} = 6.0 \ \rm l \ min^{-1}$ . The other two conclusions which can be drawn from our calculation are: (1) by controlling the flow rate and the ratio of CH<sub>4</sub> to WCl<sub>6</sub> we can obtain pure tungsten, W<sub>2</sub>C, WC<sub>1-x</sub> or the mixture of these and (2) free carbon can be avoided by decreasing the flow rate of CH<sub>4</sub> and Cl<sub>2</sub> and increasing WCl<sub>6</sub>, *i.e.* by controlling the flame temperature.

## 5. Results and discussion

The basic reaction of the flame is  $H_2 + Cl_2 = 2HCl$ ,  $\Delta H = 184$  kJ mol<sup>-1</sup>. The adiabatic temperature under the assumed condition should be around 3000 K. However, this temperature may exist in a very small region in the flame which is impossible to detect. If we want to express this in terms of power, assuming the reactants go to completion, it is about 500 W.

In our experiment, one important problem for the production of tungsten or tungsten carbide is the feed rate of  $WCl_6$ . Figure 6 shows the temperature effect on the evaporation rate of  $WCl_6$  by assuming  $WCl_6$  is evaporated from the part of the side wall of an isothermal tube with the same area as the exposed surface of the ceramic boat using the following equation [18]:

$$W_{\rm A}^{(m)} = k_{xm} \frac{(x_{\rm A0} - x_{\rm A\infty})}{1 - x_{\rm A0}} S$$

where  $W_A^{(m)}$  is the molar flow of species A through the exposed surface of the ceramic boat, S is the exposed surface area of the ceramic boat,  $x_{A0}$  is the vapor



Fig. 6. Theoretical evaporation rate of  $WCl_6$  and experimental result. The theoretical calculation assumes the evaporation is from the wall of a section of the tube where the boat of  $WCl_6$  is kept.

pressure of the solid reactant (*e.g.* WCl<sub>6</sub>) divided by the static pressure of the gas flow in the tube where the boat is located.  $x_{A\infty}$  is the molar fraction of gas species A at the upstream of the boat and in the center of the tube.  $k_{xm}$  is the mass transfer coefficient in a binary system, which can be calculated by the Chilton–Colburn analogies using the equation given in ref. 19, and it is a function of Reynolds number and Schmidt number. Hence we were able to control the flow rate of WCl<sub>6</sub> accurately. This calculation was matched by our experimental observations (see Fig. 6).

The WCl<sub>6</sub> vapor which enters the flame carried by chlorine was reduced in the presence of hydrogen. We introduced halide vapor from the chlorine side to maintain the flame stability. The residence time of the active species in the flame is very important in controlling the size. It should be slightly greater than the reaction time so that the morphology and particle size are controlled by the temperature of the flame, concentration of the precursors and residence time. We synthesized a wide variety of materials with varying particle size in our flame reactor. We obtained bluish-gray pure tungsten, grayish-blue WC<sub>2</sub> carbide and black pure tungsten or mixture of all three. Figures 6(a)-6(c) show the typical scanning electron micrographs of our tungsten, WC<sub>2</sub> and WC<sub>1-x</sub> respectively. From the micrographs, we can clearly see the perfect spherical shape of all three materials. Figure 7 shows the typical particle size distribution of our tungsten and W<sub>2</sub>C powders. This shows that we can obtain submicron powders with a controlled



Fig. 7. Size distribution of the powder. (a) Tungsten, (b)  $W_2C$  and (c)  $WC_{1-x}$ .





Fig. 8. Scanning electron micrographs of our submicron powders.



Fig. 9. Powder energy-dispersive X-ray analysis picture.

particle size in our flame reactor. Our typical size range is 200-600 Å. We can increase the particle size by decreasing the total flow rate, *i.e.* by effectively increasing the residence time. However, the bigger the particle size, the wider the size distribution and the sphericity of the particle is lost. Experiments showed that a high flow rate of the primary gases (chlorine and hydrogen) can shrink the resistance time of the particles formed, producing smaller sized particle. Again, if we increase the reactant flow rate (*i.e.* the flow rate of CH<sub>4</sub> and WCl<sub>6</sub>), the homogeneous nucleation rate increases and thus a large amount of smaller sized particles form. Here, the standard deviation of size distribution becomes larger because of coagulation. Figures 8 and 9(a)-9(c) are X-ray diffraction pictures of our powders; the standard lines for W (solid), WC<sub>1-x</sub>(solid) and  $\alpha$ -W<sub>2</sub>C (solid) are also shown. In Fig. 9(c) we can see several small peaks at the right side of the main peak of tungsten, which may be due to the oxidation of tungsten by oxygen from various sources used in our system or due to the pyrophoric nature of the powder. A series of steps has been taken to avoid this contamination.

#### 6. Conclusion

A hydrogen-chlorine flame CVD reactor has been developed for the preparation of ceramic materials. Using this reactor it is possible to produce submicron tungsten and tungsten carbide powders. The key problem is the control of the reactants  $CH_4$  and  $WCl_6$ , as was proved by theoretical estimations and



Fig. 10. (continued).







Fig. 10. X-ray diffraction of our products. (a)  $W_2C$ , (b)  $WC_{1-x}$  and (c) tungsten.

experimental measurements. From the practical point of view, this reactor is capable of industralization.

## References

- 1 S. K. Varshney and C. L. Beatty, Novel technique for the formation of silicon carbide, *Ceram. Eng. Sci. Proc.*, 2 (1981) 443.
- L. J. White and G. J. Duffy, Vapor-phase production of colloidal silica, *Ind. Eng. Chem.*, 51 (1959) 232.
- 3 R. Caillat, J. P. Cuer, J. Elston, F. Juillet, R. Pointud, M. Prettre and S. Teichner, Préparation d'oxydes homodisperses dans la flamme hydrogène-oxygène et quelques propriétés de ces composés, *Bull. Soc. Chim. Fr.*, 5 (1990) 152.
- 4 F. Juillet, F. Lecomte, H. Mozzanega, S. J. Teichner, A. Thevenet and P. Vergnon, *Inorganic Oxide Aerosols of Controlled Submicronic Dimensions*, personal communication, 1973.
- 5 M. Formenti, F. Juillet, P. Meriaudeau, S. J. Teichner and P. Vergnon, Preparation in a hydrogenoxygen flame of ultrafine metal oxide particles, in G. M. Hidy (ed.), *Aerosols and Atmospheric Chemistry*, Academic Press, New York, 1972, p. 45
- 6 W. Frey, Vapor phase process for the production of titanium dioxide, U.S. Patent 2,980,509, 1961.
- 7 S. H. Smiley, D. C. Brater and H. L. Kaufman, Preparation of refractory metals with unusual properties, J. Met., 17(1965) 605.
- 8 S. H. Smiley, D. C. Brater and H. L. Kaufman, Alloy powder production by flame reduction techniques, 95th AIME Annual Meeting, New York, 1966.
- 9 J. R. Merriman, S. H. Smiley and H. L. Kaufman, Preparation of unusual refractory powders by flame process, *Proc. Conf. CVD Refractory Metals, Alloys and Compounds*, 1967, p. 229.
- 10 S. H. Smiley and J. H. Pashley, Economic analysis of fluorination processes for the recovery and recycle of valuable CVD materials, *Proc. Conf. CVD Refractory Metals, Alloys and Compounds*, 1967, p. 291.
- 11 Kirk-Othmer, Encyclopedia of Chemical Technology, Vol. 12, Wiley, New York, 1982, p. 983.
- 12 A. H. Maude, Means for storing and transporting anhydrous hydrogen chloride, U.S. Patent 2,234,738, 1941.
- 13 K. Sato, K. Terase and H. Kijimuta, Synthesis of silicon nitride, U.S. Patent 4,399,115, 1983.
- 14 G. Y. Zhao, V. V. S. Revankar and V. Hlavacek, A comparison of the flow and temperature fields and the capability between flame reactors and plasma reactors for the preparation of ultrafine powders of ceramic and refractory metals (to be submitted).
- 15 J. Hojo, T. Oku and A. Kato, Tungsten carbide powders produced by the vapor phase reaction of the WCl<sub>6</sub>-CH<sub>4</sub>-H<sub>2</sub> system, J. Less-Common Met., 59(1978) 85.
- 16 D. R. Stull and H. Prophert (eds.), JANAF Thermochemical Tables, 2nd edn., NBS, U.S. Dept. of Commerce, 1971, pp. 1141.
- 17 I. Barin, O. Knacke and O. Kabaschewski, *Thermochemical Properties of Inorganic Substances*, Springer, Berlin, 1977.
- 18 R. B. Bird, W. E. Stewart and E. N. Lightfoot, Transport Phenomena, Wiley, New York, 1960.
- 19 H. Lamprey and R. L. Ripley, Ultrafine tungsten and molybdenum powders, J. Electrochem. Soc., 109 (1962) 8.