

Tungsten carbide (WC) synthesis from novel precursors

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Abstract

This paper deals with the production and properties of tungsten carbide (WC) powders from novel carbon coated precursors. The process has two steps in which the oxide powders were first coated with carbon by cracking of a hydrocarbon gas, propylene (C₃H₆), secondly mixed with a substantial amount of carbon black, and finally treated at temperatures in the range of 600–1400°C for 2 h in flowing Ar or 10% H₂-Ar atmosphere to synthesize WC. The produced powders were characterized using TEM, BET surface area analyzer, X-ray diffraction and chemical analysis (oxygen and carbon). The results obtained for various types of precursors treated in different atmospheres indicated that the coated precursors produced high quality powders. Single phase, sub-micron WC powders were synthesized at temperatures as low as 1100°C. WC powders produced at 1400°C for 2 h in flowing 10% H₂-Ar gas mixture were submicron (3–5 m²/g), single phase, and had low oxygen content (0.2–0.5 wt%). The sintering tests demonstrated that these powders can be densified to near theoretical density using 20 wt% Co binder at 1500°C for 2 h in flowing 10% H₂-Ar atmosphere. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Carbides, particularly of the transition metals, have a number of valuable properties, which make them the most promising materials for use in various new fields of technology. They possess high melting temperatures, great hardness, high chemical resistance, electrical and thermal conductivities of a metallic character, and also a number of special properties, such as, a capacity to be transformed to the superconducting state at relatively high temperatures and high emission properties.¹

The principal application for carbides is as the major constituent in “cemented carbide” cutting tools. The so-called cemented carbides (combinations of carbides such as WC, TiC, and TaC with binder metals such as cobalt and nickel) are mass-produced as tool materials and wear-resistant parts. WC is the most important carbide for this application, with a world market for the tungsten carbide-cobalt (WC-Co) composite powders estimated to be at 20 million kilograms a year.² In the early twentieth century, WC attracted the attention of the incandescent-lamp industry, not only on account of its

high melting points, but also due to its high hardness and wear-resistance, which promised to be a satisfactory substitute for the expensive diamond dies used for drawing tungsten wires.³

WC has the advantages of a high melting point (2600–2850°C)³ and high hardness (16–22 GPa 500 g load Vickers), combined with a high fracture toughness (28 MPa m^{1/2}). WC is the hardest binary carbide at elevated temperatures (~1000 kg/mm² at 1000°C).⁴ In addition to these properties, it has very high compressive strength (5 GPa @ 20°C) and it also exhibits a high resistance to both oxidation and corrosion.

WC has many applications in key high technologies from mechanical to chemical industries. It is used as cemented carbide in cutting tools, mining tools, saw blade tips, milling cutters, machine tools, cement drills and wear parts. It is the most important constituent of modern cemented carbides-widely used in abrasive, cutting tools, dies, inserts in valve stems, sand blast nozzles and other wear resistant components^{1–5} owing to its high hardness and wear resistant properties.

It is also used in the production of single carbide materials. Its solubility in other transition metals and metal carbide systems is made use of in the production of materials, in combination with carbides such as, TiC

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and TaC. Its high thermal conductivity and low thermal expansion coefficient are best suited for the manufacture of high temperature furnace crucibles, and other components. WC is also finding new applications as a substitute for noble metals like Pt, Pd and Ir in catalysis industries.^{6,7} It is also used as a catalytic electrode for anodic oxidation of hydrogen in fuel cells.⁸ WC erosion resistant coatings for aerospace components are another recent application.⁹

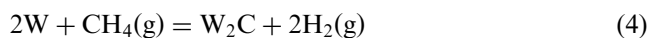
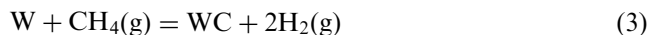
Even though the demand for WC in cutting tool industries is decreasing, its application in the field of catalysis industries is very promising. Owing to economic and technological constraints, production of high quality powders (submicron, high purity etc.) for hi-tech applications constantly impose fresh demands on further investigations of the production routes.¹⁰ In many cases, both quantity and quality of the powders, can no longer be met by conventional processes, but emphasize the use of novel technologies.

A number of processes exist for the synthesis of WC powders and each process varies in the characteristics of the powder produced. Presently, WC powders are produced by *direct carburization of tungsten powder*. The starting material for the production of W metal powder is very pure tungsten trioxide, tungstic acid (hydrated trioxide), or ammonium paratungstate (APT). The W powder is mixed dry with about 6.3 wt% of carbon black by ball-milling for an extended time. The pressed or loose mixture is passed through carbon-tube or high frequency furnaces, at temperatures of 1400–1600°C, in a flowing hydrogen atmosphere for 2–10 h.³ A similar process for producing WC based components is mentioned elsewhere.⁵ The reactions occur depending on the type of furnace, atmosphere, and the carbon content, as shown by Eqs. (1) and (2).



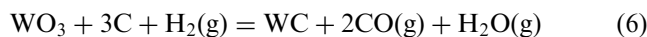
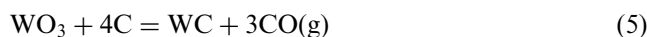
This process is an expensive process. It involves the production of pure, fine W powder in the first step. The second step is the carburization of W by carbon. The reduction conditions have a great influence on the characteristics of the metal powder and of the carbides produced. Also, the resultant powder has to be ground to a fine size and if the carbide contains too little combined carbon, the entire operation must be repeated.³ The process is cumbersome, time consuming and expensive and the powder produced by this method is not suitable for advanced applications because of its undesirable characteristics.

The carburization of metallic tungsten by carbonaceous gases occurs at a relatively low temperature. The carburization reaction of W with methane (CH₄) may proceed according to the reactions (3) and/or (4).



Carburization with CH₄–H₂ mixtures yielded WC at a temperature as low as 800°C and complete carburization of W occurred at higher temperatures.³ This process resulted in deposition of undesirable amounts of free carbon, and the formation of W₂C, along with the synthesis of WC. The reaction temperatures are very high and the reaction times vary with the composition of the carburizing atmosphere.³ In addition, the starting powder is very pure, fine W powder and altogether uneconomical to be used to produce high quality WC powder.

Carbothermal reduction of tungsten oxides provides a process by which WC can be produced by the direct reduction of tungstic acid with an excess of carbon at 1400°C. Metallic W is formed as an intermediary product and WC as the end product, as given by the overall reactions (5) and (6), depending upon the reaction atmosphere.³



This method is potentially advantageous for producing high quality WC powders in a single step, but conventional mixing of carbon black with tungsten trioxide has not yielded single phase powders in the past. Because the reactants exist as separate particles, the extent of this reaction is limited by the contact area between the reactants and the distribution of the carbon within the tungsten trioxide and carbon mixture. These limitations result in a product that contains unacceptable quantities of di-tungsten carbide (W₂C) and carbon. By this method the WC powder produced has a relatively wide size range, due to grain growth and agglomeration; therefore, these powders require subsequent milling. So, the powders produced by this method have to be heat-treated again to obtain desirable properties. Hence, the reaction times are very long (10–20 h), and powders produced generally have undesirable inhomogeneities due to diffusion gradients established during the reduction reaction.¹¹ Therefore, a new method based on the carbothermal reduction of novel carbon coated precursors developed for the production of submicron TiC powders¹² was investigated for the production of WC powders. This way of introducing carbon within tungstic oxide maximizes the reaction rate between the reactants by improving the contact area between the WO₃ and carbon and by providing a better distribution of carbon within WO₃. So far as the purity of products is concerned the use of a hydrocarbon gas is the ultimate carbon source. These

factors contribute to the superiority of the carbon coated precursor method, as better quality powders are produced at lower temperatures and shorter times than conventional methods.¹³

Swift et al. demonstrated the superiority of carbon coated tungstic oxide precursors.¹⁴ Combining the use of TGA, DSC, and XRD, the formation of WC by carbothermal reduction of carbon coated tungstic oxide clearly proceeds through reduction to W via the formation of lower oxides of tungsten, followed by carburization into WC.¹⁴ However, these studies were to provide information on the formation of WC powders from carbon coated precursors using a very small sample size and fast heating/cooling rates. The present work is intended to demonstrate the production of WC powders from carbon coated precursors using large sample sizes and slow heating and cooling rates, by providing industrial processing conditions. The physical, chemical, sintering and crystalline nature of the synthesized powders are also included.

2. Experimental procedure

Yellow tungsten trioxide, WO₃ (H.C. Starck, Germany) with a BET surface area of 5 m²/g was used as the starting material for this research. Carbon black (Monarch 880, Cabot, Waltham, MA) with a BET surface area of 246 m²/g and an average particle size 20 nm was used for the powdered carbon source.

The precursor powders were prepared using a split furnace (Carbolite, Watertown, WI), consisting of a 10 cm ID x 35 cm long stainless steel vessel and a heater. This furnace was used for preparing the pyrolytic carbon coated tungsten trioxide particles, utilizing polymer purity propylene (C₃H₆) (Matheson, Chicago, IL), (99.5%, liquid phase) as the coating gas. About 200 g of WO₃ powder was loaded into the vessel and placed in the furnace with its ends connected to the inlet and outlet valves of the chamber. Initially the vessel was evacuated, purged with argon, and again evacuated to a moderate vacuum level, using a rotary vacuum pump. This ensures a nearly oxygen free atmosphere inside the vessel. Then the vessel was heated to 600°C, kept at this temperature for 30 min, filled with propylene gas, and then held for 5–20 min under a pressure of 3–5 atm. Thermal cracking of propylene increases the internal vessel pressure upon initiation of the carbon coating by 0.5 atm. Then the remaining gas was released and the vessel was filled with fresh propylene. After every three such cycles the vessel was evacuated, purged with argon, and evacuated again before filling with propylene.

The coating process was continued until a substantial amount of carbon was deposited, after which the vessel was evacuated, filled with argon and allowed to cool to room temperature. The weight percentage of carbon in

the precursor was determined by burning the carbon off in air at 750°C for 6 h. Four different precursors labeled A, B, C and D were prepared with two different carbon compositions and two different mixing techniques. Precursors A and C were prepared by coating tungsten trioxide powder with carbon, deposited from pyrolytic cracking of hydrocarbons. Precursors B and D were prepared by mixing coated powder and carbon black in a Spex Mixer (Model 8000 Mixer/Mill, Metuchen, NJ). Details of these precursor preparation techniques are discussed elsewhere.¹⁵ Table 1 shows the characteristics of these precursors.

The precursors were subjected to heat treatments for the synthesis of WC powders. These experiments were performed using a tube furnace with an ID of 70 mm. The furnace was provided with an inlet and outlet to facilitate the passage of gas through the tube. A graphite crucible (ID=65 mm and length=300 mm) was used as the sample holder. Ten grams of precursor was loaded for each run. The graphite crucible holding the sample was placed in the tube furnace and the tube ends were sealed air tight. At the start of each run, the tube was evacuated and purged with the reaction gas. All of the experiments were conducted at a standard gas flow rate of one liter per minute (1LPM). The flow rate was monitored using a gas flowmeter. Gas flow was maintained until the furnace cooled to room temperature. All the runs were made according to the following standardized heating program: heat at 4°C/min to the preset temperature, hold at that temperature for 2 h and furnace cooling to room temperatures.

All precursors were subjected to 2-h isothermal heat treatment from 600°C to 1400°C (in steps of 100°C). Precursors A and B were treated in flowing argon atmosphere; whereas precursors C and D were treated similarly in flowing 10% H₂-Ar gas mixture. All the resultant powders were characterized to study the phase composition and powder morphologies.

Weight loss percentages were calculated at the end of each run to determine the degree of the reactions. From reaction (7), the percentage weight loss for the stoichiometric reaction was calculated to be 30.023% under an argon atmosphere and 27.431% under an hydrogen-argon atmosphere from reaction (8).

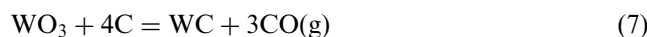
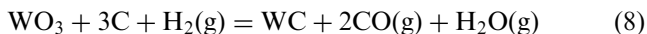


Table 1
Characteristics of precursors

Precursor	Coated carbon, wt%	Total carbon, wt%
A	18.3	18.3
B	7.6	18.3
C	13.3	13.3
D	8.9	13.5



A weight loss less than these amounts indicated an incomplete reaction, whereas a greater weight loss indicated the presence of volatile species in the powders. The resultant powders were subjected to X-ray diffraction (Model DMAX-B, Rigaku, Tokyo, Japan) using Cu K_α radiation. Phases were identified from the XRD patterns. The humps observed in the XRD patterns (between 10 and 30°) were due to the tape holding the sample in the sample holder of the instrument. Specific surface area of the powders were determined using BET Surface Area Analyzer (Gemini 2360, Micromeritics, Norcross, GA). Total carbon and oxygen content of the samples were determined by LECO (St. Joseph, MI). Powder morphology was studied using Transmission Electron Microscopy (TEM), Model (Hitachi H500 H). Scanning electron micrographs of the polished surface of sintered specimen was taken in Hitachi S570 scanning electron microscope (SEM).

3. Results and discussion

3.1. Precursor

Fig. 1 shows the XRD patterns of the precursor produced by the coating process. During the coating process, tungsten trioxide particles, WO_3 were reduced to a series of intermediate oxides. The diffraction peaks were determined to be $\text{W}_{25}\text{O}_{73}$, $\text{W}_{20}\text{O}_{58}$, $\text{WO}_{2.9}$, $\text{W}_{24}\text{O}_{68}$, and

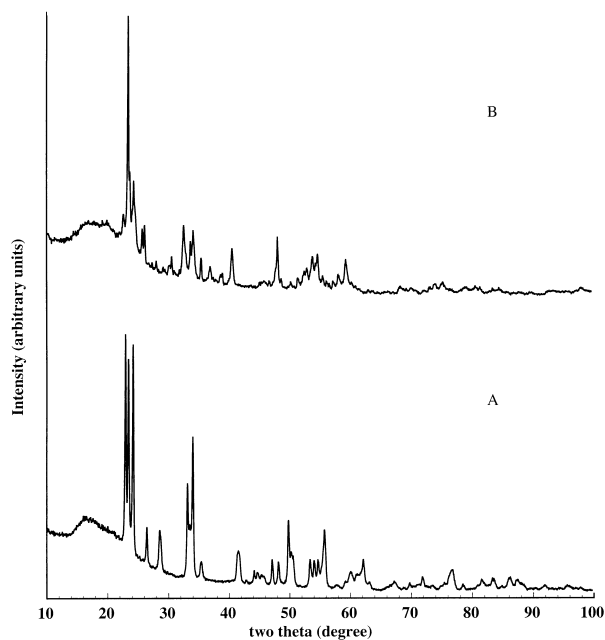


Fig. 1. XRD patterns of (A) starting WO_3 powder and (B) the carbon coated precursor produced by the new process.

$\text{W}_{18}\text{O}_{49}$. This figure shows the differences between the tungsten trioxide and the coated precursor. This was due to the starting of the reduction process during the precursor preparation step. The hydrocarbon gas used for coating, propylene (C_3H_6), and the carbon deposited, as a result of pyrolytic cracking of the gas, reduced tungsten trioxide to its lower oxide states. These lower oxides of W are also called the Magneli phases. The formation of these Magneli phases took place because of reducing ability of hydrocarbon gas at 600°C. Despite the partial reduction process, there was no indication of carbide formation during the coating process. BET specific surface area of the particles after coating was reduced from 5 m^2/g to 3–4 m^2/g depending on the amount of carbon deposited on their surfaces. These measurements indicate that carbon forms a layer over the surface of oxide particles rather than existing as a particle. If it was the later case, BET surface area of resultant precursors would have been significantly increased. Fig. 2 is a TEM micrograph of precursor A which clearly shows the carbon deposited over the oxide particles was of uniform thickness. Fig. 3 is a TEM micrograph of precursor D that consists of coated carbon on the surfaces of oxide particles and carbon black.

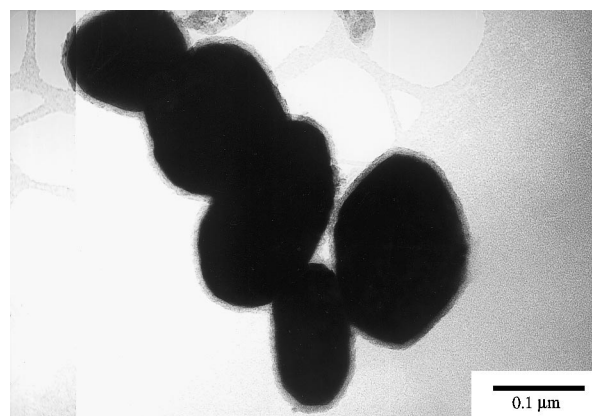


Fig. 2. TEM micrograph of precursor A.

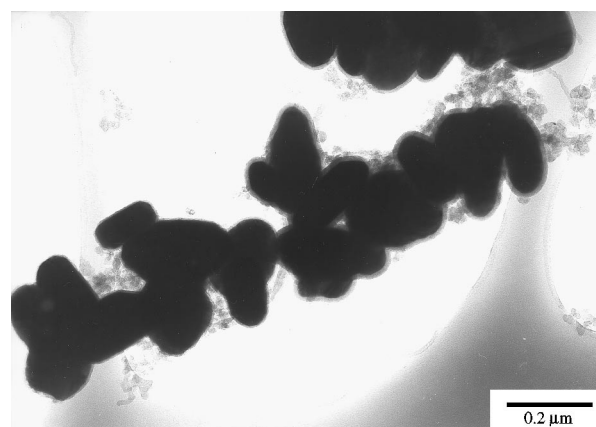


Fig. 3. TEM micrograph of precursor D.

3.2. Resultant powders

3.2.1. Precursor A treated in flowing argon atmosphere

Precursor A was prepared by depositing pyrolytic carbon on tungsten oxides. It contains a total carbon content of 18.3 wt%. Fig. 4(a) and (b) shows the XRD patterns of powder produced by treating precursor A in flowing argon atmosphere for 2 h at temperatures in the

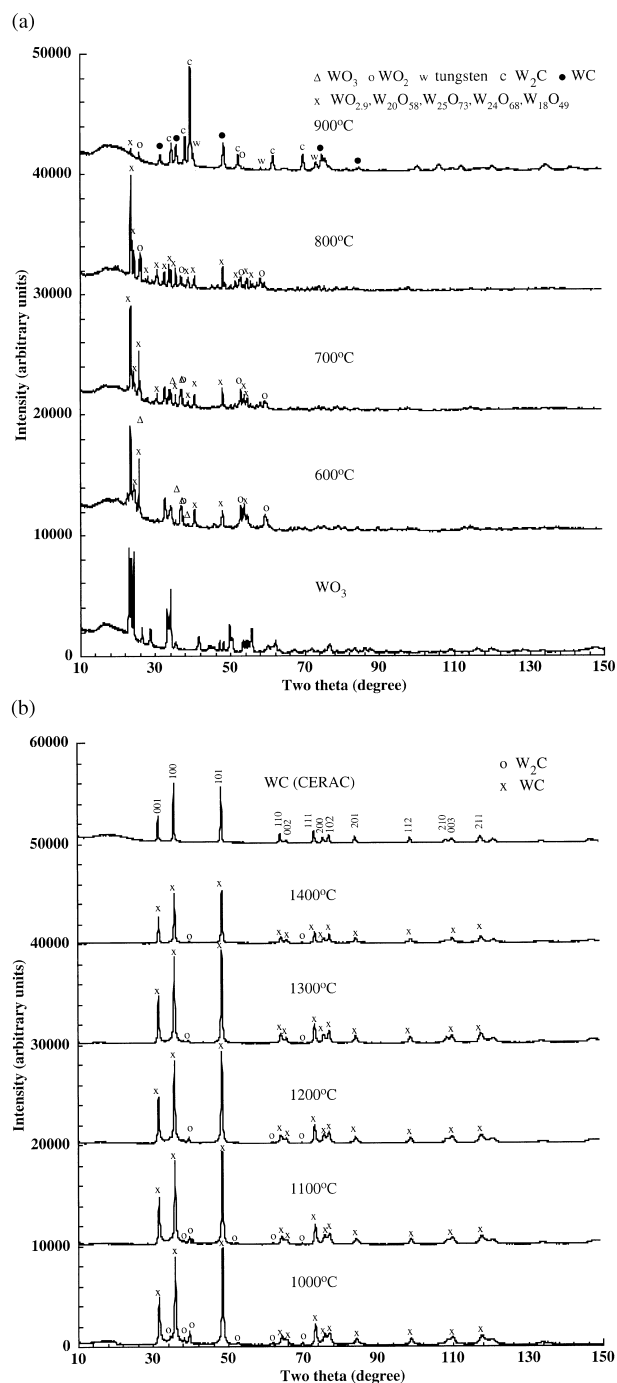


Fig. 4. XRD patterns of powders produced from precursor A in flowing argon atmospheres in the temperature range (a) 600–900°C, (b) 1000–1400°C.

range 600–1400°C, with an interval of 100°C. Fig. 4(a) shows the XRD patterns from 600 to 900°C. Reduction proceeded via the formation of tungsten dioxide (WO_2), tungsten (W), di-tungsten carbide (W_2C) and tungsten carbide (WC). Traces of WO_2 were noticed at temperatures as low as 600°C. This shows the extent of reduction that has occurred during the carbon coating step. In the figure most of the peaks marked 'x' at 800°C correspond to the oxide $W_{18}O_{49}$. This was the only precursor to form carbides of W at a temperature of 900°C.

Fig. 4(b) shows the XRD patterns obtained at temperatures in the range 1000–1400°C. By 1000°C, carburization has started, resulting in the formation of W_2C and WC. WC was the predominant phase observed at 1000°C. In this temperature range, there were no changes in the phases observed, but the intensity of the peaks corresponding to W_2C decreased with increase in temperature. XRD patterns show the evolution of phases from precursor A as a function of temperature. These results are in agreement with the published literature, even if the investigations presented in this paper do not use the same carburizing procedure. The sequence of formation of tungsten carbide is more or less the same as that observed by Leclercq et al.¹⁶

Fig. 5 shows the calculated weight loss percentages as a function of temperature for all resultant powders produced from the precursors (A, B, C and D). Significant weight loss results were obtained only at temperatures above 800°C. Between 800 and 900°C there was a steep increase in the weight loss corresponding to the formation of metallic W. At temperatures above 1000°C, weight loss percentages were practically constant indicating that the carburization process was in progress.

Fig. 6 shows the BET specific surface area of the resultant powders as a function of temperature. Initial surface area of precursor A was measured to be 3 m²/g.

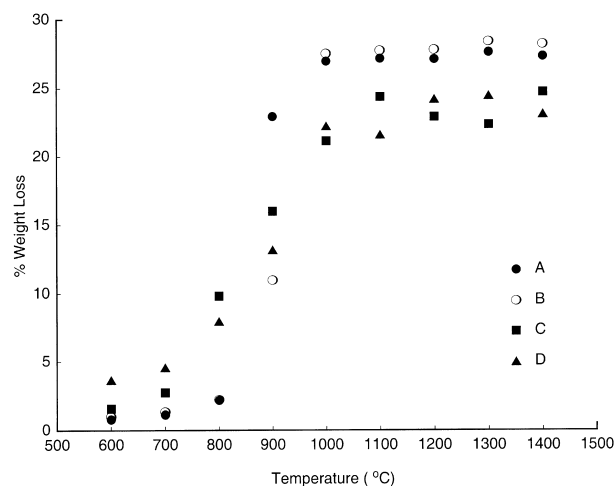


Fig. 5. Weight loss as a function of temperature for precursors A, B, C and D.

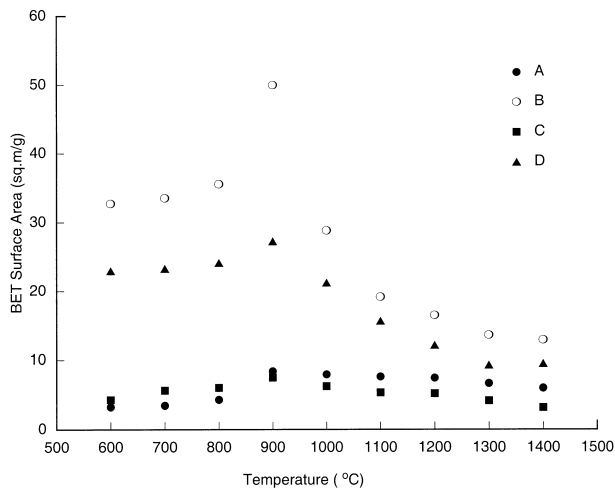


Fig. 6. BET specific surface area of powders produced from precursors A,B,C, and D as a function of temperature.

Surface area increases with temperature to a maximum at 900°C and then linearly decreases as the temperature increases. During the reduction process, oxide particles were reduced to tungsten and oxygen was removed in the form of CO or CO₂. The increase in surface area is due to the reduction of the oxides, formation of fine W particles. At temperatures above 1000°C, the decrease in the surface area can be explained by the carburization of tungsten and the formation of necks among some of the particles (sintering).

Tables 2 and 3 show the total carbon and oxygen contents of the powders as a function of temperature for the precursors. Total oxygen and carbon contents decreased tremendously in the temperature range 800–900°C and above this temperature there were no significant changes for all the resultant powders. These results confirm the completion of reduction reactions by this temperature. At temperatures above 1000°C no significant changes were observed corresponding to the carburization of W. Based on these results, reaction path for the formation of WC from the precursor A is proposed as shown in Eq. (9):

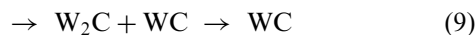
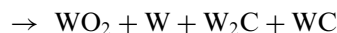
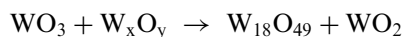
Table 3
Oxygen contents (wt%) of the powders produced from precursors as a function of temperature

Temperature (°C)	Precursor A	Precursor B	Precursor C	Precursor D
600	14.5	16.5	15.36	15.0
700	14.1	16.5	11.56	14.2
900	8.1	12.8	3.56	7.08
1000	0.6	6.29	0.42	2.1
1100	0.4	3.16	0.4	0.7
1200	0.3	2.1	0.26	0.5
1300	0.2	1.68	0.24	na
1400	0.18	1.09	0.169	0.24

Table 2

Total carbon contents (wt%) of the powders produced from precursors as a function of temperature

Temperature (°C)	Precursor A	Precursor B	Precursor C	Precursor D
700	19.2	17.9	15.7	14.4
800	18.7	18.0	15.9	14.7
1000	11.1	9.2	13.1	11.7
1100	11.1	9.8	10.5	12.3
1200	11.7	9.4	10.2	10.9
1300	10.9	9.5	12.2	9.1
1400	11.3	9.5	9.7	10.9



The powder produced at 1400°C has a BET surface area of 6 m²/g and it contains 11.33 wt% total carbon, combined and free, and 0.184 wt% oxygen.

3.2.2. Precursor B treated in flowing argon atmosphere

Precursor B was prepared by depositing 7.6 wt% pyrolytic carbon on tungsten oxides and mixing these composite particles with carbon black. It contains a total carbon content of 18.3 wt%. Fig. 7(a) and (b) shows the XRD patterns of powder produced by heat treating precursor B at temperatures of 600–1400°C in flowing argon gas. The reduction of tungsten trioxide proceeds via the formation of WO₂, W_xO_y and results in metallic W. The formation of WC was from the carburization of metallic W and W₂C.

Fig. 7(a) shows the XRD patterns of the powder produced at temperatures 600–900°C. W₁₈O₄₉ was the lowest intermediate oxide formed along with WO₂ at 800°C. The resultant powder at 900°C consists of mostly metallic W with traces of lower oxides of W. At temperatures between 900 and 1000°C reduction process was complete (peaks corresponding to tungsten oxides were diminished) and the carburization of metallic W had started. Metallic W was carburized into W₂C and WC at temperatures 1000°C and above. Elimination of W₂C peaks observed at higher temperatures was due to the further carburization of W₂C, which was formed at lower temperatures, into WC by carbon as represented by reaction (10):



The sequence of carburization reaction was in these steps W → W₂C → WC with an agreement in the literature.¹⁶ The reason for the difference in the temperature of the WC apparition for precursors A and B was that the temperature of carburization of precursor A was lower

than that of precursor B, since precursor A was already more reduced than B at the beginning of the carburizing process.

The weight loss percentages of the produced powders from precursor B as a function of temperature were also included in Fig. 5. The results were nearly identical to that of precursor A at temperatures below 800°C. There was sharp increase in the weight loss percentage

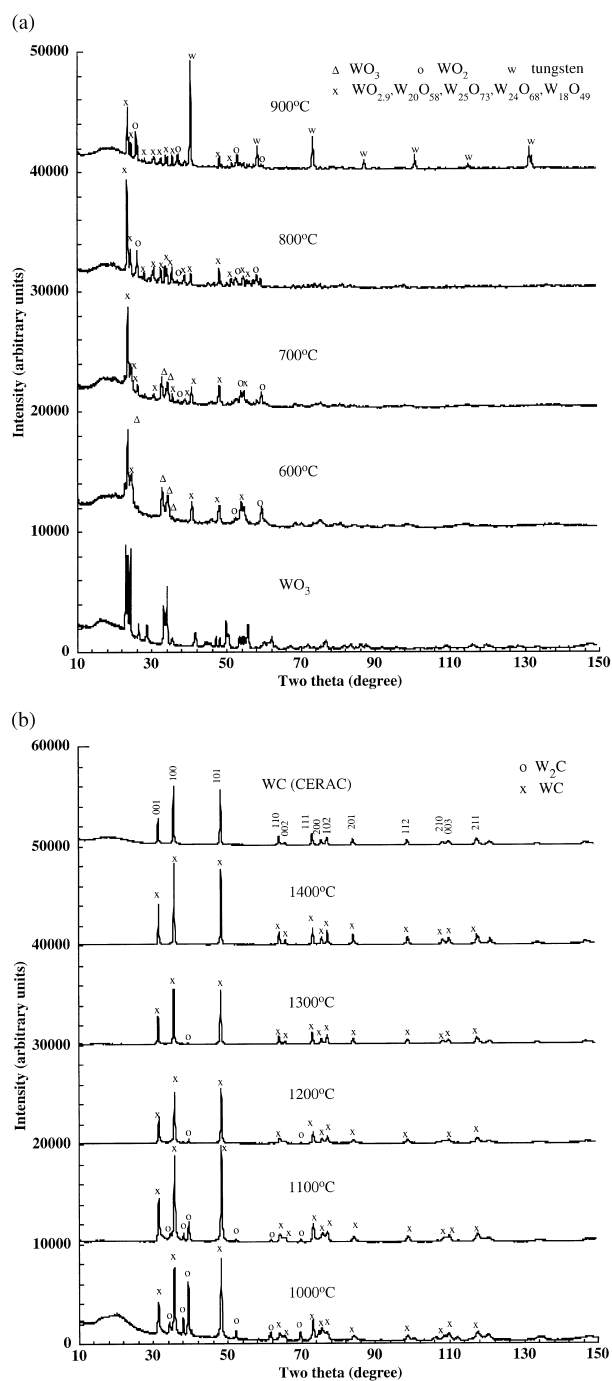


Fig. 7. XRD patterns of powders produced from precursor B in flowing argon atmospheres in the temperature range (a) 600–900°C, (b) 1000–1400°C.

between temperatures 800 and 1000°C corresponding to the complete reduction of tungsten oxides to W. At temperatures above 1000°C weight loss percentages were nearly constant. Weight loss percentages for B were relatively higher than that of A. This is because of the difference in the precursor preparation routes. Precursor B is a mixture of 7.6 wt% coated carbon and carbon black (total carbon is 18.3 wt) whereas precursor A is totally coated with 18.3 wt% carbon. Since coating and reduction occur simultaneously in the coating step, amount of coating is directly proportional to the degree of reduction. Hence, precursor A contains more amount of lower oxides than precursor B does. Comparing the oxygen contents of the powders produced at 600°C under identical conditions for the precursors A and B, from Table 3 it is evident that the amount of oxygen present in A is less than that in B. Consequently, the amount of oxide to be reduced is less in case of precursor A and hence lesser observed weight loss results. Nevertheless, the weight loss profile observed for both these precursors were identical.

Fig. 6 also shows the BET specific surface area of the resultant powders as a function of temperature. These powders had relatively high surface areas and it is due to the presence of free carbon in the powders. Surface area increased with temperature and was maximum at 900°C after which it decreased. The results correspond to the formation of metallic fine W particles at 900°C (completion of the reduction process) and subsequent carburization into WC at temperatures above 900°C. The oxygen and carbon contents of the powders are also listed in Tables 2 and 3, and the results confirm the above findings.

Figs. 8 and 9 are TEM micrographs of the powders produced from precursor B at 900°C. In Fig. 8 formation of W is shown. The large particle in the micrograph is tungsten oxide (W_xO_y). The smaller particles surrounding the oxide are the as formed W particles. From the micrograph it is clear that W particles formed at the

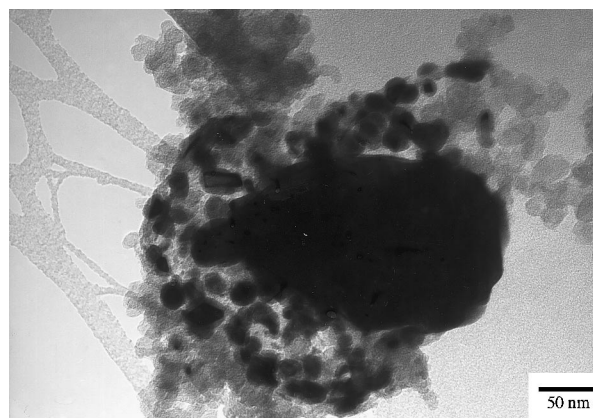


Fig. 8. TEM micrograph of the powder produced from precursor B at 900°C, apparition of tungsten particles.

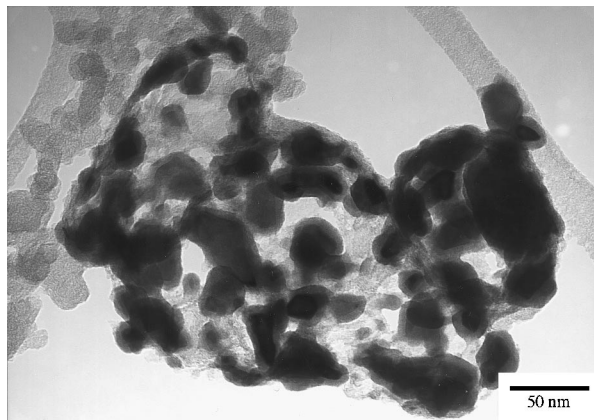
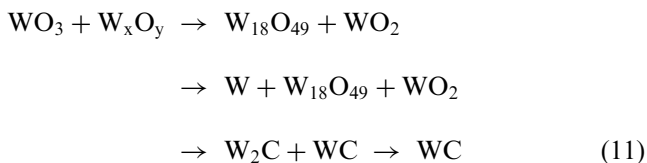


Fig. 9. TEM micrograph of the powder produced from precursor B at 900°C, formation of tungsten particles.

surface of the oxide particles. Fig. 9 shows the morphology of formed W particles.

The reaction path was similar to that of precursor A and it can be proposed as follows in Eq. (11):



Powders produced at 1400°C have a surface area of 14 m²/g, contain 9.56 wt% total carbon and 1.09 wt oxygen contents.

3.3. Precursor C treated in flowing 10% hydrogen–argon atmosphere

Precursor C was prepared by depositing 13.3 wt.% pyrolytic carbon on tungsten oxides. Fig. 10(a) and (b) show the XRD patterns of powder produced by heat treating precursor B at temperatures of 600–1400°C in flowing 10% hydrogen–argon gas mixture. Reduction and carbide formation processes were different under this reaction atmosphere.

Fig. 10(a) shows the XRD patterns of powder from 600–900°C. Peaks corresponding to WO₃ phase was absent at 600°C. Metallic W peaks were noticed at temperature as low as 700°C. At temperatures between 700 and 900°C, WO₂ was the only oxide phase present. All the oxides were reduced to metallic W in this temperature range. Reduction of all the oxides to metallic W and subsequent carburization were complete by 1000°C.

Fig. 10(b) shows the XRD patterns of powder from 1000 to 1400°C. At these temperatures, single phase WC was obtained. W₂C peaks were absent. These results indicate that reduction process was accelerated by the content of hydrogen in the flowing gas. Gaseous hydrogen reduced tungsten oxides (W_xO_y) significantly

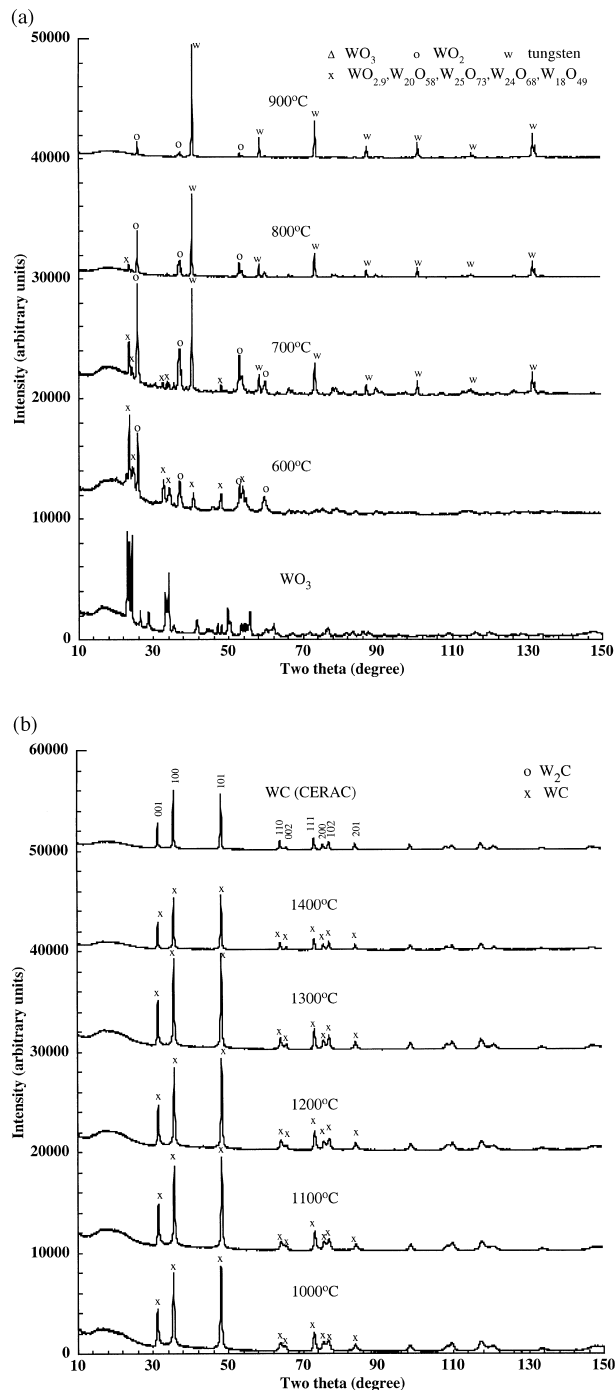


Fig. 10. XRD patterns of powders produced from precursor C in flowing argon—10% hydrogen atmospheres in the temperature range (a) 600–900°C, (b) 1000–1400°C.

at low temperatures. Carbon present in the form of coating diffused into as formed fine metallic W particles, which formed at temperatures as low as 700°C, directly producing WC without the apparition of di-tungsten carbide (W₂C).

The difference in carbide formation, passing or not through W₂C phase, is explained by the diffusion pro-

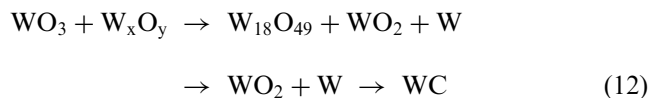
cess of C in W which can or cannot be the limiting step.^{17,18} The first step in the formation of WC is a surface reaction between the carburizing compound and the metallic W. The formation of an activated carbon atom on the surface of metallic W, C*, is generally accepted.^{17,18} If the formation of this activated carbon is slow, and the diffusion of C in metallic W is fast, W₂C will be firstly formed as bulk carbide. But if the formation of C* is fast and the limiting reaction step is the diffusion of C, the sample will appear with a shell of WC growing around a metallic W core.

In the case of precursors A and B, the diffusion of C in the metallic W is faster than the reduction of tungsten oxide. The limiting step is the reduction one, and therefore, the formation of C* cannot occur if oxide is present at the surface of the W compound. The reduction of tungsten oxide induces a limitation of the formation of C* and according to the above remarks, W₂C is firstly formed.

In the case of precursor C, due to the presence of hydrogen, the oxide is faster reduced and the formation of C* can quickly occur. The limiting step is now the diffusion of C in the metallic lattice of W and WC grows as a shell around a metallic W core (see TEM micrographs in Figs. 8 and 9). Therefore WC is the only carbide phase appearing on the XRD diagram during the carburizing process of precursor C.

Weight loss percentages calculated for this precursor are also included in Fig. 5. Weight loss percentages increased between temperatures 700 and 1000°C. The specific surface area results did not show considerable changes, but the highest surface area was recorded at 900°C and it decreased thereafter (see Fig. 6). Tables 2 and 3 show the oxygen and carbon contents of the powders produced as a function of temperature. Oxygen content decreased significantly from 600°C and stabilized at 1000°C. Total carbon content initially increased and then decreased above 900°C. Hydrogen gas picks up free carbon at low temperatures and forms hydrocarbons. The low carbon contents observed at temperatures below 800°C are due the formation of hydrocarbons, possibly CH₄.

Based on these results it can be concluded that the reaction proceeded at a faster rate in a reducing atmosphere and the reaction path can be proposed as shown in Eq. (12):



Powder produced at 1400°C has a BET surface area of 3m²/g with 9.7 wt total carbon and 0.169 wt oxygen contents. TEM studies showed the WC particles were sub-micron sized, but they appear to be highly agglomerated.

3.4. Precursor D treated in flowing argon — 10% hydrogen atmosphere

Precursor D was prepared by depositing 8.9 wt% pyrolytic carbon on tungsten oxides and mixing these composite particles with carbon black. It contains a total carbon content of 13.5 wt. Fig. 11(a) and (b) shows

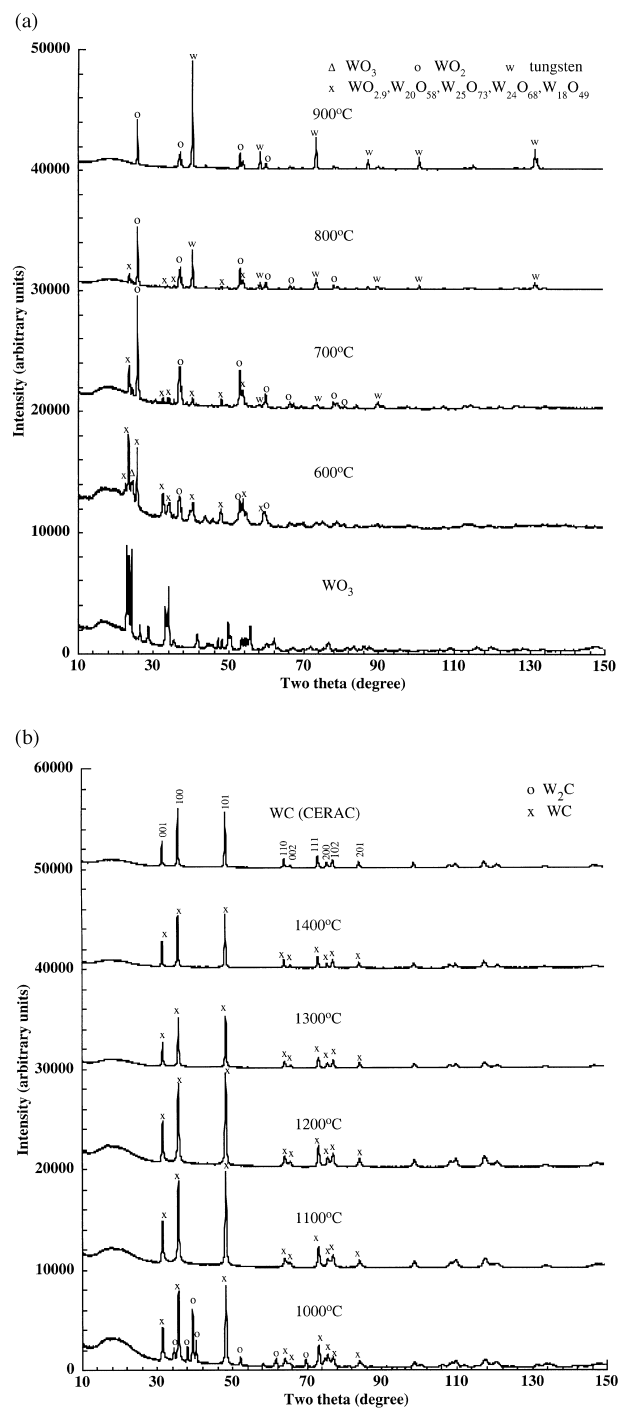


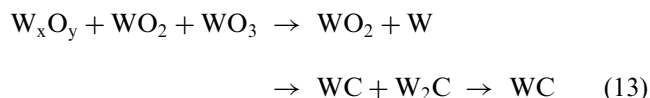
Fig. 11. XRD patterns of powders produced from precursor D in flowing argon -10% hydrogen atmospheres in the temperature range (a) 600–900°C, (b) 1000–1400°C.

the XRD patterns of the powder produced by treating the precursor D at temperatures in the range 600–1400°C in flowing 10% hydrogen–argon gas. The reduction path was similar to that of precursor C. Fig. 11(a) shows the XRD patterns for the powders produced in the temperature range 600–900°C. At 600°C only traces of WO₃ were observed. W peaks were noticed at 700°C. The predominant phase observed at temperatures of 700–900°C was W.

Fig. 11(b) shows the XRD patterns at temperatures between 1000 and 1400°C. At 1000°C WC and W₂C were the only phases observed. The presence of W₂C in the XRD diagram is consistent with the difference in the limiting step of reaction between C and D. In precursor D, less coated carbon implies less reduced oxide. The reduction is slower for D than for C. So the formation of an activated carbon C* on the tungsten particles of D is slower than for C. This is why there was W₂C formation at 1000°C. At 1100°C and above, the powder produced was single phase WC. W₂C was completely absent at these temperatures.

Fig. 5 also shows the weight loss percentages as a function of temperature for precursor D. Initial weight loss percentages were relatively high for this precursor. These weight losses observed are partly due to the elimination of free carbon by the flowing hydrogen gas. Like in the case of other precursors, steep weight loss results were obtained between 800–900°C.

Fig. 6 includes the BET surface area results for the powders. The powder produced at 900°C showed maximum BET surface area results for this precursor. Above 900°C surface area decreased as temperature increased, due to the formation of WC over the surface of W and subsequent growth of these particles. Tables 2 and 3 list the total carbon and oxygen results as a function of temperature. The results were similar to those of precursor C. The reaction path can be proposed as follows in Eq. (13):



The powder produced at 1400°C has a BET surface area of 9 m²/g with 10.95 wt total carbon and 0.243 wt. oxygen contents. TEM micrograph of the powder is shown in Fig. 12. Extensive necking and particle agglomeration were noticed among the particles.

The precursor D was also subjected to heat treatment at 1400°C for 2 h in flowing argon to optimize the carbon content in the resultant WC powders. The produced WC powder contained ~6.5 wt total carbon and ~0.2 wt% oxygen with a BET surface area of 3 m²/g. The produced WC and 20 wt% Co powders were mixed in a WC container together with two WC balls and alcohol using a Spex Mixer. After 1 h of mixing, the

powder slurry was dried in a vacuum oven at 65°C. Pellets were made by single action, uni-axial pressing resulting about 55% of theoretical density. Near theoretical density obtained from the sintering of pellets at 1500°C for 2 h in flowing 10% hydrogen–argon atmosphere. Fig. 13 shows the SEM micrograph of the polished surfaces of the sintered sample. Sintering properties of WC powders from the process are underway and will be reported in an upcoming publication.

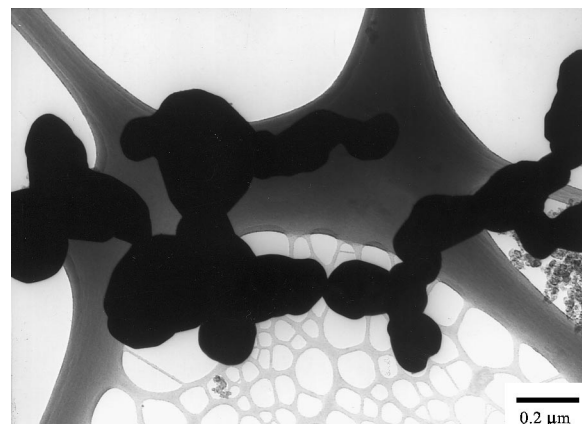


Fig. 12. TEM micrograph of the powder produced from precursor D at 1400°C in flowing argon–10% hydrogen atmospheres.

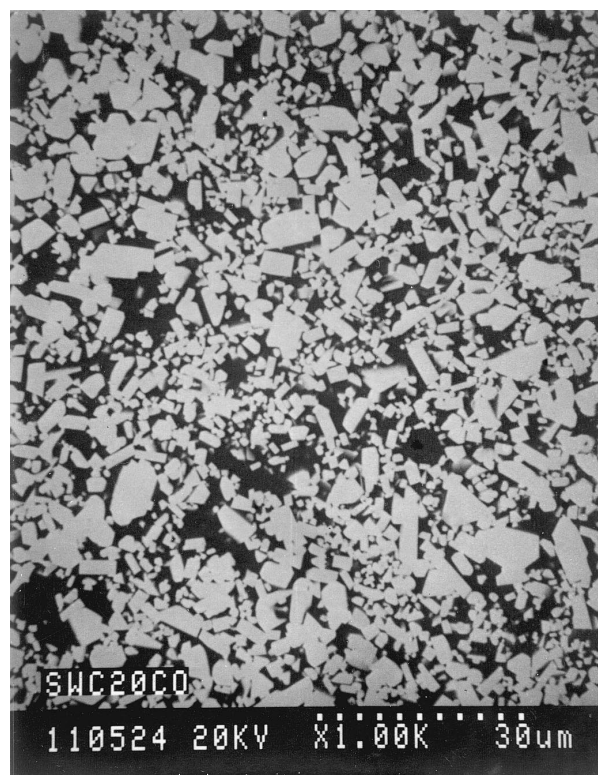


Fig. 13. SEM micrograph of the polished surfaces of WC-20 wt% Co powders sintered at 1500°C for 2 h in flowing argon–10% hydrogen atmosphere.

4. Conclusions

Precursors prepared by coating pyrolytic carbon onto the tungsten oxide powders have distinct advantage. The reactants remain in contact all the time due to which the reactions proceed at a faster rate. The reduction mechanisms were different in argon and 10% hydrogen–argon atmospheres. Reduction proceeded at a faster rate in the reducing atmosphere, in presence of hydrogen gas. Single phase WC powders can be produced at low temperatures in this atmosphere. The effect of mixing quality between the coated precursors, and the coated and mixed precursors, was not significant with regard to the final powder characteristics. In the gas phase reduction by hydrogen, the reactions proceed at a faster rate and result in the formation of nanosize W particles. WC formation is a diffusion process, occurring by the diffusion of carbon into W. Since the particle size is inversely proportional to the diffusion rates, diffusion is faster. WC is directly formed without forming W_2C which is the result of a difference in the limiting steps: formation of an activated carbon C^* on the metallic surface of a W particle, or the diffusion of carbon in the metallic lattice of W. Extensive necking was observed among the particles produced from all the precursors. Partial reduction occurs during the coating step and these lower oxides of W starts necking. This necking persists during the subsequent carburization of W. But there is a possibility to minimize the necking by controlling the thickness of carbon coating in the precursors. The sintering studies showed that these powders can be densified to 100% theoretical density using 20 wt% Co binder at 1500°C for 2 h in flowing 10% H_2 –Ar atmosphere.

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