



Preparation of tungsten carbides by reducing and carbonizing WO₂ with CO

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ABSTRACT

Tungsten carbides, which can be widely used as cutting and drilling tools, chemical catalysts and aerospace coatings, have attracted widespread attentions. The present work reported a simple method to prepare tungsten carbides by using WO₂ as the raw materials and CO as the reduction and carbonization agent. It was found that at lower and moderate temperatures, all the final product was WC, while at higher temperatures, the final products were W₂C or W. The reduction and carbonization mechanism was also studied theoretically and experimentally. WO₂ was reduced and carburized to WC in one step at lower temperatures; WO₂ was first reduced and carburized to W₂C and then to WC at moderate temperatures; while at higher temperatures, WO₂ was first reduced to metallic W and then carbonized to WC or W₂C, but with the temperature increasing, the carbonization became difficult and required much higher CO content.

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1. Introduction

Tungsten carbides, which belong to the group of cemented carbides and refractory carbides, have advantages of high melting point, high hardness, low friction coefficients, high thermal stability and low thermal expansion coefficient[1]. These advantages make tungsten carbides appropriate for various engineering applications such as manufacture of cutting tools, rock drill tips and general wear parts[2–5]. Besides, tungsten carbides have been used as the Pt electro-catalyst support for various processes[6]. A wide variety of applications have been recognized for bulk nano-ceramics and nano-ceramic composites, for instance, the durable ceramic parts for automotive engines, ultrafine filters, aerospace erosion resistant coatings, flexible superconducting wire and fibre optic connector components[7].

Tungsten carbides mainly include two phases, namely, WC and W₂C. In general, higher tungsten carbide WC has one common structure, hexagonal structure. However, lower tungsten carbides W₂C have several structural modifications: β-W₂C, β'-W₂C, β''-W₂C and ε-W₂C. The presence of different types of carbon atoms distribution causes the possibility of the formation of several structural modifications of W₂C[8,9].

There are many methods for preparation of tungsten carbides. These methods include direct carburization of tungsten powder, high-energy mechanical ball milling[10], the spray conversion process[11], solid-gas reaction[12], sol-gel and in-situ carburization [13], and combustion synthesis[14]. The traditional method is to direct carburization of tungsten powders: tungsten powders are mixed with carbon black by ball-milling for an extender time, and then carbonized at 1400–1600 °C (1673–1873K)[15]. Because the tungsten powders and carbon black can not contact inadequately, the reaction proceeds slowly. The application of different sources of tungsten containing precursor and carbon-containing gas for preparation of tungsten carbides has been reported in literatures.[16,17]. These methods successfully prepared tungsten carbides. However, some of the preparation processes can be complicated. Because in these processes, a special precursor must be prepared before reduction and carbonization, such as the coating of precursor with carbon. Table 1 summarized the typical specific methods which were reported in the literatures, for preparation of WC. In all of the specific methods of preparation of tungsten carbide, the processes required either a higher temperature or a long time. Venables and Brown[22] studied the reduction of WO₃ with CO, which showed that the reaction temperature can be reduced.

The aim of this work is to prepare tungsten carbides by using WO₂ as the raw materials and CO as the reduction and carbonization agent. The reduction and carbonization mechanisms were

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studied theoretically and experimentally as well.

2. Material and experimental

WO₂ powders (larger than 100 mesh, 99.9% metals basis) from Aladdin Industrial Corporation were employed as the raw material. Co powders (40–100 mesh, 99.9% metals basis) from Chengdu Jinchun metal material Co., Ltd. were also used as raw materials.

An HCT-2 Thermo-Gravimetric Analyzer (TGA) was used to monitor the weight change of samples during reduction and the experimental apparatus was described elsewhere. [23] A sample of around 100 mg was used in each experimental run and after an alumina crucible (8 × 8mm) with samples was put into the TGA, high-purity argon was introduced to flush air out of the furnace. In isothermal reduction, the furnace was first heated from room temperature up to a desired reduction temperature at a rate of 10 °C/min while maintaining the argon atmosphere. Once the thermal balance stabilized, the argon gas was switched to reaction gas, and the weight loss was then monitored continuously by the TGA. After reacting for a certain time, the reaction gas was switched to argon again, and samples were cooled down to room temperature. In non-isothermal experiments, CO was first used to flush air from the furnace, and then the furnace was heated from room temperature to 1200 °C at heating rates of 4, 6 and 8 K/min, in different runs. In all experimental runs, a constant gas flow rate of 60 ml/min (about 0.318×10^{-2} m/s at 25 °C) was maintained. The flow rate of gas was controlled by gas flow controllers (Alicant, Model MC-500SCCM-D).

To study the mechanical performance of the prepared WC, WC-6 wt% Co composites were prepared using the hot-press sintering technique. Around 10 g WC powders and Co powders (with mass fraction of 6%) were mixed first and then pressed into cylinder under an axial mechanical pressure of 11 MPa. The hot pressing was processed in high strength graphite die, high purity argon gas under an axial mechanical pressure of 13 MPa at 1500 °C for 3 h.

X-Ray Diffraction (XRD) (PANalytical X'Pert Powder, Panalytical B.V.) measurements were conducted for samples. Morphologies of these samples were observed using SEM (TESCAN VEGA 3 LMH, Czech Republic) technique. The Brunauer–Emmett–Teller (BET) method was employed to determine the surface areas of samples at 77 K (Micromeritics ASAP 2020, American). The hardness of WC-6 wt% Co composites sample was determined using hardness (Hengyi MH-6, China). The thermodynamics calculations were performed by using FactSage 6.2 with pure substances database.

3. Expected reactions

Equilibrium calculations were carried out for an indication of the expected reactions during the reduction and carburization. Fig. 1 gives the equilibrium diagram of CO and WO₂ system, which clearly shows the reaction products at different temperatures and CO/(CO + WO₂) ratios. It can be obtained that at low temperatures, WC is the most stable phase, but W₂C and W would be formed with increasing the temperature, and the ratio of CO/(CO + WO₂) must be rather close to 1 to form W₂C and WC at high temperatures. Figs. 2 and 3 give the calculated results for three typical experimentally used temperatures: 813 °C (1086 K), 908 °C (1181 K) and 1179 °C (1452 K). Fig. 2 shows the W–O–C predominance diagrams (for the three temperatures). The line of crosses in Fig. 2 represents a total gas pressure of 1 atm; equilibrium gas compositions (consisting largely of CO and CO₂) would lie along this line if WO₂ was to react with pure CO in different molar ratios, for a total pressure of 1 atm. The formation of WC would require a more CO-rich gas, corresponding to gas compositions towards the lower right in the predominance diagrams (along the lines of crosses). Fig. 2 indicates

Table 1
Different methods for preparation of WC in literatures.

Preparation methods	Reaction temperature	Time	Tungsten contain precursor	Carbon source
Direct carburization[15]	$W + C \xrightarrow{\text{ball milling}} W + C \xrightarrow{H_2/1400-1600^\circ C} WC$	Ball milling: 20 h Reaction: 2–10 h Mixing Ball milling: 90 h	Tungsten powder	Carbon black
High energy mechanical ball milling[18]	$W + C \xrightarrow{\text{ball milling}} W + C \xrightarrow{H_2/1000^\circ C} WC$	Reaction: 1 h	Tungsten powder	Activated granular carbon
Spray conversion process[11,19]	$WO_3 \xrightarrow{\text{spray drying at } 250-350^\circ C, 2.5-3.5 \text{ MPa}} WO_3 \xrightarrow{420-500^\circ C} WO_{2.9} \xrightarrow{700-740^\circ C} W \text{ powder} \xrightarrow{980-1000^\circ C} WC$	(WO ₃ → WO _{2.9}) Reaction: 1.2 h (WO _{2.9} → W) Reaction: 1.5 h (W → WC) Reaction: 1.5 h Carburization: over 2 h	Ammonium tungstate(APT)	Carbon black; Phenolic resin; Industrial alcohol CH ₄ +H ₂
The vapor phase reaction[20]	$WCl_6 + H_2 \xrightarrow{400^\circ C} W + CH_4 \xrightarrow{H_2/1400^\circ C} WC$		Tungsten hexachloride (WCl ₆)	Ammonium polyacrylate; CO ₂
Sol-Gel preparation method[21]	Ammonium polyacrylic + water + Na ₂ WO ₄ $\xrightarrow{\text{Saturation hexanol+HCl}}$ precipitation of tungstic acid drying at 120 °C $\xrightarrow{\text{the dry gel}}$ (1) Ar/900 °C; (2) CO ₂ /900 °C $\xrightarrow{\hspace{1cm}}$ WC	Drying: 12 h Calcine: 4 h	Sodium tungstate HCl Hexanol	

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