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Synthesis of high-purity ultrafine tungsten and tungsten carbide powders

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Abstract: High-purity ultrafine W or WC powder was prepared via a two-step process composed of the carbothermic pre-reduction of $WO_{2.9}$ and the following deep reduction with H_2 or carbonization with CH_4+H_2 mixed gases. The effects of $C/WO_{2.9}$ molar ratio and temperature on phase composition, morphology, particle size, and impurity content of products were investigated. The results revealed that when the $C/WO_{2.9}$ ratio was in the range from 2.1:1 to 2.5:1, the carbothermic pre-reduction products consisted of W and a small amount of WO_2 . With changing $C/WO_{2.9}$ ratio from 2.1:1 to 2.5:1, the particle sizes were gradually decreased. In order to prepare ultrafine W or WC powder, a relatively high $C/WO_{2.9}$ ratio and a lower reaction temperature at this stage were preferred. After the second reaction, the final products of ultrafine W and WC powders with a high purity could be obtained, respectively. **Key words:** carbothermic pre-reduction; carbonization; tungsten; tungsten carbide

1 Introduction

Tungsten and tungsten carbide have many unique properties, such as high melting point, high thermal stability, superior hardness, high oxidation resistance and corrosion resistance, and good electrical conductivity [1–6]. Due to these excellent properties, W and WC have been widely used in the fields of aerospace, military, metallurgy, cutting, mining tools and drilling tools etc [7–14].

Ultrafine tungsten and tungsten carbide powders have many potential applications compared to traditional tungsten and tungsten carbide, which could greatly improve the physical, chemical and mechanical properties of W alloys and WC-Co hard metals [12,13]. Therefore, the preparation of them becomes the current research focus. Table 1 gives the methods for preparation of W and WC in the last twenty years [8–17]. Among them, the widely used methods for industrial preparations of W and WC are hydrogen reduction of tungsten oxide (WO₃, WO_{2.9}) to prepare W powder, and further carbonization of W to produce WC [16,18]. It has been reported that owing to the generation of gaseous hydroxides (WO₂(OH)₂) during the hydrogen reduction process of tungsten oxide, the transport of W is enhanced by chemical vapor transport (CVT) mechanism [12–14,16,18], which could lead to the formation of W particle with a large size. Meanwhile, long reaction time and high temperature during the carburization stage were also needed due to slow kinetics of solid–solid reaction between W and C to generate WC. Therefore, it was very difficult to produce the ultrafine W and WC powders.

In order to weaken the influence of CVT mechanism and high temperature on the particle size of products, we have reported a new carbothermic reduction method to remove the oxygen from metal oxides (WO₃, MoO₃) by reacting with nano carbon black in order to prepare ultrafine Mo, W and WC [12,16,18]. Compared with the hydrogen reduction, the carbothermic

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Target product	Method	Raw material	Particle size of product/nm
Tungsten	Wire explosion process [8]	Tungsten wire	16.27-21.02
	Selective precipitation and reduction [9]	Tungsten scrap	45
	Plasma expansion [10]	WO ₃ , H ₂	300
	In-situ hydrogen reduction [11]	Nano-needle violet tungsten oxide, H ₂	<500
	Carbothermic reduction and hydrogen reduction [12]	WO ₃ , carbon black, H ₂	20-80
In-s Carbothermic Chemica Reducir Tungsten	Chemical vapor condensation (CVC) [13]	W(CO) ₆ , CO	28-53
	Reducing and carbonizing with CO [14]	WO ₂ , CO	37.1-202.4
Carbide	Mechanical alloying [15]	W, amorphous carbon	_
carolae	Carbothermic reduction-carburization [16]	WO ₃ , carbon black	200-350
	Calcining mechanically activated mixture [17]	WO ₃ , graphite	104.7

Table 1 Methods for preparations of W and WC

reduction has many advantages, such as low requirement for the equipment, simple operation, and low price of reductant. However, it is widely recognized that carbothermic reduction always leads to a high content of residual free carbon in the product [18,19]. In this study, the high-purity ultrafine W and WC powders are prepared based the carbothermic reduction process, on as approximately described in Fig. 1. First, the commercial blue tungsten oxide (WO_{2.9}), as the tungsten source, reacted with insufficient carbon black to remove most of oxygen from WO_{2.9}. After that, the deep reduction or carburization process was conducted to prepare tungsten and tungsten carbide at a low temperature. The phase transition, morphology evolution, particle size, carbon and oxygen contents of product at different stages are investigated in details.



Fig. 1 Process flow chart of new carbothermic reduction method

2 Experimental

Commercial blue tungsten oxide (WO_{2.9}) powder from Ganzhou Huaxing Tungsten Products Co., Ltd. (China) was used as the tungsten source. Carbon black purchased from Mitsubishi Chemical Corporation was used as the main reduction agent. The characterization of carbon black, schematic diagram of experimental apparatus and the experimental procedures were shown in our previous researches [16,18]. In the carbothermic pre-reduction stage, nitrogen (N2, 99.999%) was used as protection gas under a constant gas flow rate of 300 mL/min. Hydrogen (H₂, 99.999%) and methane (CH₄, 99.999%) were used as the gaseous reducing and carburizing agent for preparing W and WC at the second stage, respectively. In this study, four groups of experiments with different C/WO2.9 molar ratios (2.1:1, 2.3:1, 2.5:1 and 2.7:1) were investigated in order to study the effect of C/WO_{2.9} ratio on the phase transition and morphology evolution of the products. The WO_{2.9} and carbon black were carefully weighed based on the specified $C/WO_{2.9}$ ratio and uniformly mixed by agate mortar. The phase compositions and morphology of the samples were characterized by X-ray diffraction (XRD; TTR III, Rigaku Corporation, Japan), field-emission scanning electron microscopy (FE-SEM; ZEISS **SUPRA** 55, Oberkochen, Germany), respectively. The infrared oxygennitrogen-hydrogen analyzer (EMIA-920V2, HORIBA, Japan) and infrared carbon-sulfur analyzer (EMIA-920V2, HORIBA, Japan) were used to measure the oxygen and carbon contents of final products, respectively.

3 Results and discussion

3.1 Carbothermic pre-reduction process

- 3.1.1 Non-isothermal experiments
 - To obtain the suitable reaction temperature of

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first carbothermic pre-reduction stage, а non-isothermal experiment with a ramping rate of 5 °C/min was performed in a thermal analysis system (HTC-2, Beijng Hengjiu Instrument Ltd. China), and the thermo-gravimetric differential thermal analysis (TG-DTA) curves of 90 mg as-milled powder (with the composition of $WO_{2.9}$ + 2.5C) are shown in Fig. 2. According to the TG curve, two turning points appeared at about 925 and 1081 °C, respectively, which indicated that the temperature required for carbothermic reduction of blue tungsten oxide began at above 925 °C, and finished at 1081 °C. From the DTA curve, three endothermic peaks were detected in the whole carbothermic pre-reduction process, indicating that three main reactions occur during this process. Therefore, to ensure a large reaction rate, the temperatures for the first stage were determined to be 1050 and 1150 °C.



Fig. 2 TG–DTA curves of as-milled powder of $WO_{2.9}$ + 2.5C at heating rate of 10 °C/min

3.1.2 Phase transition and microstructure evolution

In order to investigate the phase transition and microstructure evolution during the carbothermic pre-reduction process, the sample with C/WO_{2.9} molar ratio of 2.5:1 was reacted at 1050 °C for different time under nitrogen atmosphere. After that, the sample was cooled down to room temperature before being taken out from the quartz tube. Figure 3 presents XRD patterns of the carbothermic pre-reduction products prepared after different reaction time. When the reaction time was 10 min, it could be seen that all the diffraction peaks were assigned to WO_{2.9}. WO₂ and W, but no peak belonging to WO_{2.9} was detected. Therefore, it could be concluded that WO_{2.9} was easily reduced

to $WO_{2.72}$. When the reaction time was 20 min, the relative diffraction intensity of $WO_{2.72}$ gradually decreased, but the intensity of W and WO_2 increased. As the time was prolonged to 30 min, 1 h and 2 h, the diffraction peaks attributable to $WO_{2.72}$ disappeared, and all the peaks were identified to WO_2 and W. Furthermore, the peak intensity of W and WO_2 gradually increased and decreased, respectively. However, there was still a small amount unreacted WO_2 even if the reaction time was 2 h, since the content of carbon black was not sufficient to reduce all the tungsten oxide at low $C/WO_{2.9}$ molar ratio of 2.5:1. Therefore, the total reactions can be described as follows: $WO_{2.9} \rightarrow WO_{2.72} \rightarrow WO_2 \rightarrow W$.



Fig. 3 XRD patterns of carbothermic pre-reduction products obtained after reacting at 1050 °C for different time with C/WO_{2.9} molar ratio of 2.5:1

The morphologies of raw material WO_{2.9} and carbothermic pre-reduction products obtained at 1050 °C after reacting for different time for sample with $C/WO_{2.9}$ ratio of 2.5:1 were also detected by field-emission scanning electron microscopy (FE-SEM), and the images are shown in Fig. 4. From Figs. $4(a_1, a_2)$, it could be known that the large WO_{2.9} particles were irregular blocky-shaped with the average size of about 55 μ m, which were composed of many platelet-shaped grains with the size of about 70 nm. After reacting for 10 min, from Figs. $4(b_1, b_2)$, it could be seen that lots of grains were needle-shaped with the average size of above 1 μ m. According to the literatures [11,20,21], the needle-shaped product was WO_{2.72}, which coincided with the XRD results shown in Fig. 3. When the reaction time was increased to 20 and 30 min, as shown in Figs. 4(c, d), the large particle with

needle-like shape disappeared, and all particle size became smaller than 100 nm. As further prolonging the reaction time to 1 h, it could be seen that the products were composed of a large number of smaller particles with irregular shape and few larger particles with smooth surface, which had the particle size of ~70 and 500 nm, respectively. Combined with the XRD results shown in Fig. 3, it could be concluded that the two kinds of particles were WO₂ and W, respectively. Finally, the uniform and highly-dispersed powder was obtained when the reaction time was 2 h.

Based on the above experimental results, a holding time of 2 h was used for the carbothermic pre-reduction stage. 10 g mixed powders with different C/WO_{2.9} molar ratios were roasted at the target temperature in flowing N₂ gas atmosphere, and the phase compositions are shown in Fig. 5. It could be seen that regardless of the experimental conditions, the main phases of products were W and a small amount of WO₂ expect the case of C/WO_{2.9} ratio of 2.7:1. With the increase of the C/WO_{2.9} molar ratio from 2.1:1 to 2.5:1, the peak intensity of WO₂ was gradually decreased, but that of the W was increased. In addition, when the C/WO_{2.9} molar ratio was a constant, the peak intensity of WO₂ was decreased with the increase in temperature. It could be concluded that a higher C/WO_{2.9} molar ratio and a higher temperature are beneficial to the reduction of tungsten oxide to tungsten. When the C/WO_{2.9}



Fig. 4 FE-SEM images of raw materials of $WO_{2.9}$ and carbothermic pre-reduction products obtained after reacting at 1050 °C for different time with C/WO_{2.9} molar ratio of 2.5:1: (a₁, a₂) Raw material $WO_{2.9}$; (b₁, b₂) 10 min; (c) 20 min; (d) 30 min; (e) 1 h; (f) 2 h

(a) $1050 ^{\circ}\text{C}, 2.1:1$	• - WC	$\mathbf{v}_2 \mathbf{A} - \mathbf{W}$	(b)	1	•-WO ₂ •-	W ₂ C		-
• •	• •	t	.		1050 °C, 2.1:1		n. I	_
1150 °C, 2.1:1			_		1150 °C, 2.1:1		m	
1050 °C, 2.3:1	.				1050 °C, 2.3:1		m	
1150 °C, 2.3:1			<u> </u>	٨	1150 °C, 2.3:1			
1050 °C, 2.5:1				٨	1050 °C, 2.5:1			
1150 °C, 2.5:1					1150 °C, 2.5:1			
1050 °C, 2.7:1					1050 °C, 2.7:1	•	•	
1150 °C, 2.7:1					1150 °C, 2.7:1	~	الم	
10 20 30 40	50 60	70 80	90 20	25	30	35	40	
	2 <i>θ</i> /(°)				$2\theta/(^{\circ})$			

Fig. 5 XRD patterns of carbothermic reduction product prepared at 1050 and 1150 °C for 2 h with different C/WO_{2.9} ratios

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ratio was increased to 2.7:1, it was noted that no diffraction peak of tungsten oxide was detected. Besides the main phase W, a new phase W_2C appeared, which indicated that a C/WO_{2.9} ratio of 2.7:1 was enough to remove all the oxygen from the raw material WO_{2.9}.

Figures 6(a-h) show the FE-SEM images of the carbothermic pre-reduction products obtained after reacting for 2 h. The particle sizes were estimated from three FE-SEM images and the average particle sizes for sample reacting under different conditions are shown in Fig. 6(i). From Figs. 6(a-h), it could be seen that most of the particles had smooth and irregular shape in all the cases. In addition, as the C/WO_{2.9} ratio was increased from 2.1:1 to 2.5:1, the average particle size was decreased from 112 to 58 nm at 1050 °C and from 163 to 76 nm at 1150 °C, respectively. Furthermore, it could be also noted that with the increase of carbon content, the carbothermic pre-reduction products had higher dispersion and looser structure. In the previous study to prepare Mo, W and WC powders [12,16,18, 22,23], it was found that relatively high carbon content was beneficial to decreasing the particle size of product. The same conclusion was also obtained in the current study. However, when the ratio of $C/WO_{2.9}$ was further increased to 2.7:1, the particles had obviously grown up by neck-sintering and the mean particle sizes were increased to 141 nm at 1050 °C and 224 nm at 1150 °C. Combined with the phase compositions of products at C/WO_{2.9} ratio of 2.7:1, the reason for this phenomenon may be that W_2C which has a lower melting point relative to W was generated at a C/WO_{2.9} ratio of 2.7:1, which leads to a higher sintering activity of products to promote the particle growth. Moreover, when the reaction temperature was increased from 1050 to 1150 °C at a constant ratio of C/WO_{2.9}, the particle size was increased in all the cases, since a high temperature was beneficial to the sintering process. This further confirmed that the C/WO_{2.9} ratio and the reaction



Fig. 6 FE-SEM images (a–h), average particle size (i), and carbon and oxygen contents (j) of carbothermic pre-reduction products obtained at different temperatures and C/WO_{2.9} ratios: (a) 1050 °C, 2.1:1; (b) 1050 °C, 2.3:1; (c) 1050 °C, 2.5:1; (d) 1050 °C, 2.7:1; (e) 1150 °C, 2.1:1; (f) 1150 °C, 2.3:1; (g) 1150 °C, 2.5:1; (h) 1150 °C, 2.7:1

temperature had significant effects on the particle size of carbothermic pre-reduction product.

The oxygen and carbon contents of the carbothermic pre-reduction products obtained at 1050 °C were measured, and the results are shown in Fig. 6(j). It could be seen that with the increase of C/WO_{2.9} molar ratio, the carbon content gradually increased from 0.019% to 0.089%, but the oxygen content decreased from 4.84% to 0.098%. Combined with the XRD results (Fig. 5), owing to the presence of tungsten oxide (WO_2) , the product with C/WO_{2.9} ratio of 2.1:1 had a relatively high oxygen content and low carbon content. However, for the C/WO_{2.9} ratio of 2.5:1, the values of oxygen content and carbon content were 0.735% and 0.031%, respectively, which indicated that a molar ratio of 2.5:1 was very close to the theoretical stoichiometric ratio of preparing W. As further increasing C/WO_{2.9} ratio to 2.7:1, the carbon content in the product increased to 0.089%, while the oxygen content decreased to 0.098%. The reason for this was that the sufficient carbon could remove all the oxygen from tungsten oxide, but the excessive carbon could react with W to generate W₂C. It was pointed out that the tungsten oxide has great potential for removing W₂C and free carbon [12]. Therefore, in order to prepare high-purity ultrafine W and WC powders, a relatively low C/WO_{2.9} ratio of 2.1:1 or 2.5:1 should be adopted in the first stage.

3.2 Preparation of W powder by deep reduction with H_2

To remove the residual oxygen and prepare high purity tungsten powder, the carbothermic pre-reduction products were deeply reduced by hydrogen at a low temperature of 750 °C for 2 h. The XRD patterns of secondary reduction product are shown in Fig. 7(a), from which it could be noted that all the diffraction peaks were identified to W



Fig. 7 XRD patterns (a), average particle size (b) and FE-SEM images (c–j) of products after deep reduction at 750 °C for 2 h: (c) 1050 °C, 2.1:1; (d) 1050 °C, 2.3:1; (e) 1050 °C, 2.5:1; (f) 1050 °C, 2.7:1; (g) 1150 °C, 2.1:1; (h) 1150 °C, 2.3:1; (i) 1150 °C, 2.5:1; (j) 1150 °C, 2.7:1

(PDF Number: 4-806) except the case with a C/WO_{2.9} ratio of 2.7:1. The oxygen content of the final product was <0.2%, which indicated that the residual tungsten oxides in the carbothermic pre-reduction products could be effectively removed. Furthermore, the carbon contents of final products were also measured by the infrared carbon-sulfur analyzer, which were almost the same with the values in the carbothermic pre-reduction products after the first stage. It could be concluded that the H₂ gas could not react with W_2C to remove the carbon when the C/WO_{2.9} ratio was 2.7:1. Therefore, in order to prepare the high-purity W powder with a low carbon content, the carbothermic pre-reduction products with a low residual carbon content (C/WO_{2.9} ratio <2.7:1) should be adopted. The average particle size and morphologies of W particle after the deep reduction at 750 °C are shown in Figs. 7(b-j). It could be seen that most of the particle had a round shape and smooth surface. With the increase of $C/WO_{2.9}$ molar ratio from 2.1:1 to 2.5:1, the average particle size decreased from 121 to 61 nm at 1050 °C and from 185 to 80 nm at 1150 °C. However, as the ratio of $C/WO_{2.9}$ was further increased to 2.7:1, the average particle size of final products was increased to 151 nm at 1050 °C and 271 nm at 1150 °C. Compared with the particle sizes of carbothermic pre-reduction product (Fig. 6(i)), it could be found that the variation trend of the particle size of prepared W was similar to that of carbothermic prereduced products after the first stage. In addition, with the increase of C/WO_{2.9} ratio, the W particle became more loose and uniform. When the C/WO₃ molar ratio was 2.5:1, the particle size of the final products (after carbothermic pre-reduction at 1050 or 1150 °C for 2 h, and then hydrogen treatment at 750 °C for 2 h) could reach nanometer scale.

3.3 Preparation of WC by further carburization with CH₄-H₂ mixed gases

According to Ref. [23], micron-sized tungsten carbide powder could be prepared by reducing ammonium paratungstate and tungsten oxide with mixed gases of H_2 -CH₄. In the current study, in order to convert the residual tungsten oxide, tungsten or carbon-deficient phase (W₂C) in the carbothermic pre-reduction products (obtained at C/WO_{2.9} molar ratio range of 2.1:1–2.7:1) to WC, the products were further carburized by mixed 1703

gases of 10%CH₄+90%H₂. Based on the results of carbothermic pre-reduction stage, it could be concluded that the grain growth by CVT mechanism in the carburization process would be weakened owing to the low content of residual oxygen in carbonthermic pre-reduction product. Figure 8(a) presents the XRD patterns of products after being carburized by mixed gases of 10%CH₄+ 90%H₂ at 900 °C. It could be clearly seen that no diffraction peaks of tungsten oxide or carbondeficient phase were detected, and all the peaks were identified to be WC (PDF: 51-939). In addition, all the main peaks of WC were very strong and broad, which suggested that the WC powder obtained had high crystallinity and small particle size.

The average particle size and morphologies of WC obtained after reacting at 900 °C for 1 h are shown in Figs. 8(b-j). It could be seen that there were no obvious changes of morphology for most of the particles relative to carbothermic prereduction products. With the C/WO_{2.9} ratio increasing from 2.1:1 to 2.5:1, the average particle size decreased from 172 to 75 nm at 1050 °C and from 213 to 96 nm at 1150 °C, respectively. When the ratio of C/WO_{2.9} was further increased to 2.7:1, the average particle size of final products was also increased to 218 nm at 1050 °C and 283 nm at 1150 °C. Combined with the results of average particle sizes of carbothermic pre-reduction products and deep reduction products (W), it could be found that the variation trends of particle sizes for three different products (carbothermic reduction products, W and WC) were similar. Therefore, it could be concluded that the first stage had a crucial effect on the morphology and particle size of the finally prepared W and WC. Furthermore, from the particle sizes of three different products (Figs. 6(i), 7(b) and 8(b), under the conditions of a specific C/WO_{2.9} ratio and a specific reaction temperature at first stage, taking 2.3:1 and 1050 °C for instance, the particle sizes of carbothermic reduction product, and the finally obtained W and WC powders were 107, 109 and 150 nm, respectively. Thus, the particle size growth trend from carbothermic pre-reduction product to WC was obviously greater than that to W. This phenomenon may be caused by different reaction temperature, melting point, molar volume of final products. In the current work, the



Fig. 8 XRD patterns (a), average particle size (b) and FE-SEM images (c-j) of carburized products obtained after reacting at 900 °C for 1 h: (c) 1050 °C, 2.1:1; (d) 1050 °C, 2.3:1; (e) 1050 °C, 2.5:1; (f) 1050 °C, 2.7:1; (g) 1150 °C, 2.1:1; (h) 1150 °C, 2.3:1; (i) 1150 °C, 2.5:1; (j) 1150 °C, 2.7:1

reaction temperatures of preparing W and WC at the second stage were 750 and 900 °C, respectively. It was known that a high temperature promoted the grain growth, while a low temperature was beneficial to preparing products with a relatively small particle size. Meanwhile, W has a much higher melting point than WC (the melting points of W and WC are 3430 and 2850 °C, respectively), which leads to a higher sintering activity of WC powder. Furthermore, WC has a larger molar volume than W, which are 12.53 and 9.52 cm³/mol, respectively [16,18]. Consequently, the prepared WC has a much larger particle size than W. Finally, the carbon contents of those prepared WC were measured, which were in the range of 6.09%-6.17%, which were very close to the theoretical carbon content of WC (6.13%).

Therefore, it could be concluded that the high-purity ultrafine WC powder was successfully prepared by two-step process of carbothermic pre-reduction and carburization by CH_4 - H_2 mixed gas.

3.4 Preparation of W and WC by direct reaction between WO_{2.9} and H₂ or 10%CH₄+90%H₂ mixed gases

W and WC could also be prepared by directly reacting $WO_{2.9}$ with H_2 and $10\%CH_4+90\%H_2$ mixed gases. The XRD patterns and FE-SEM images of products after the hydrogen reduction at 750 °C and reduction-carburization at 900 °C by CH_4+H_2 are shown in Fig. 9, from which it could be found that the all the diffraction peaks were identified to be W and WC, and the products always had a larger



Fig. 9 XRD patterns and FE-SEM images of W (a_1 , a_2 , a_3) and WC (b_1 , b_2 , b_3) obtained by direct reduction of WO_{2.9} by H₂ or 10%CH₄+90%H₂ mixed gases

particle size (average particle sizes were about 517 nm and 1.43 µm, respectively), relative to these prepared by the current two-stage route. The season for this was that during the reduction process by H_2 and CH_4+H_2 mixed gases, the gaseous hydroxides (WO₂(OH)₂) were generated, which could significantly accelerate the growth of W particles by chemical vapor transport (CVT) mechanism [12-14,16,18]. Therefore, it could be concluded that the ultrafine W and WC powders are difficult to be prepared by directly using H₂ and CH₄+H₂ mixed gases as the reducing agent. In the current study, the carbothermic pre-reduction process was used for pre-treatment to remove most of oxygen from WO_{2.9}, and then the products further reacted with H₂ and CH₄+H₂ mixed gases to prepare ultrafine W and WC. According the experimental results, it could be concluded that the ultrafine even nano-scale W and WC powders were successfully prepared by this two-step way.

4 Conclusions

(1) The C/WO_{2.9} molar ratio and temperature at the carbothermic reduction stage had a great effect on the particle size of the products. With the increase of C/WO_{2.9} ratio from 2.1:1 to 2.5:1 and the decrease of reaction temperature, the particle size of carbothermic pre-reduction product gradually decreased.

(2) The reaction sequence of blue tungsten oxide and carbon black at 1050 °C was $WO_{2.9} \rightarrow WO_{2.72} \rightarrow WO_2 \rightarrow W$.

(3) The carbothermic pre-reduction step was crucial for the control of particle size and impurity of the final product.

(4) The ultrafine or even nano-sized W and WC powders with low contents of impurities were successfully prepared by the two-step process of carbothermic pre-reduction and carburization by CH_4+H_2 mixed gas.

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高纯超细钨和碳化钨粉体的制备

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摘 要:提出一种两步法制备高纯度 W 或 WC 粉体的工艺,该工艺包括碳热预还原 WO_{2.9},以及后续的对还原产物进行 H₂还原或 CH₄+H₂混合气体碳化。研究 C/WO_{2.9}摩尔比和反应温度对不同阶段产物的相组成、形貌、粒径 及杂质含量的影响。结果表明,当 C/WO_{2.9}摩尔比为 2.1:1-2.5:1 时,碳热预还原产物的物相由 W 和少量 WO₂组成。随着 C/WO_{2.9}摩尔比从 2.1:1 增加到 2.5:1,碳热预还原产物的粒径逐渐减小。因此,采用相对较高的 C/WO_{2.9}摩尔比和较低的反应温度有利于获得超细 W 或 WC 粉体。经过第二阶段的反应,可以制备高纯度 W 粉和 WC 粉。**关键词:**碳热预还原;渗碳反应;钨;碳化钨

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