Article ID: 1003 - 6326(2000)03 - 0421 - 03

Influence of phase components of tungsten oxide on homogeneity of ultrafine tungsten powder①

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Abstract: The influence of phase components of tungsten oxide on homogeneity of ultrafine tungsten powder by conventional hydrogen reduction techniques was studied. Results show that phase components of tungsten oxide play a crucial role on homogeneity of metal tungsten powder; ultrafine and homogeneous tungsten powder can be produced from oxides which consist of only one phase. Due to the different reduction rates (or different reduction paths) of oxide which comprises different phases, the multi-phase components tungsten oxide leads to a fine but in homogeneous metal tungsten powder.

Key words: tungsten oxide; phase components; ultrafine tungsten powder; homogeneity **Document code:** A

1 INTRODUCTION

Hydrogen reduction of tungsten oxides, subsequent mixing with carbon black and carburating is the most common way to produce tungsten carbide powders for the hardmetal industry. This technique has been practiced for decades and called "conventional hydrogen reduction process"[1]. Zeiler[1] and schubert et al[2,3] pointed out that the reduction step is very important as the final grain size of the tungsten carbide powder is determined to a great extent by the grain size of the reduced tungsten metal powder.

Therefore, the fineness and the homogeneity of tungsten powder become the key factors of manufacturing tungsten carbon powder in "conventional tungsten carbide powder manufacturing" processing. According to this opinion, the choice of reduction conditions and suitable tungsten oxides raw materials becomes more and more important.

As to the reduction conditions, Schubert[4] pointed out that the reduction temperature and humidity should be kept low to provide unfavorable condition for the formation of $WO_2(OH)_2$ and the co-current H_2 flow should be adopted during ultrafine tungsten powder production process. Kinetic and morphological studies have been performed mainly with the aim of gaining a deeper understanding of the phase boundary reactions during reduction and their interaction with the reduction parameters[5~9].

Schubert pointed out which raw materials is most convenient for ultrafine tungsten powder production is not yet clear in conventional hydrogen reduction process and the characterization of ultrafine W powders should include the use of exactly defined raw materials[2]. It is obvious that the properties of raw materials influence the reduction and thus the final properties of the reduced tungsten powder[10~12].

The purpose of this investigation is to find the influence of phase components of raw materials on the homogeneity of reduced ultrafine W powder by conventional hydrogen reduction at low temperature, low humidity and co-current hydrogen flow conditions.

2 EXPERIMENTAL

Five kinds of tungsten oxides were chosen as raw materials in this investigation, as shown in Table 1. The X-ray diffraction patterns are shown in Fig.1.

Table 1 Five kinds of oxides

Sample No.	Raw materials	Phase components
HTB	Hydrogen tungsten bronze	$H_{0.33}WO_3$
ATB	Ammonium tungsten bronze	$(NH_4)_{0.5}WO_3$
TVO	Violet tungsten oxide	$WO_{2.72}$
TBO1	Blue tungsten oxide	WO_3(≈60%), $WO_{2.9}$(≈40%)
TBO2	Blue tungsten oxide	$WO_{2.9}$(≈25%), $WO_{2.72}$(≈75%)

The reduction was carried out in an industrial pusher type furnace. Co-current H_2 flow rate is 40 $m^3/(min·m^2)$, the H_2 dew point is -40 ℃, powder layer height is 9 mm, the reduction temperatures of the three temperature zones are 600, 700, 800 ℃ respectively, and the holding time in each zone is 1 h.

3 BET SPECIFIC SURFACE AREA OF POWDERS

The multi-point BET specific surface area (BET-

① **Received date:** Sep.18, 1999; **accepted date:** Dec.12, 1999

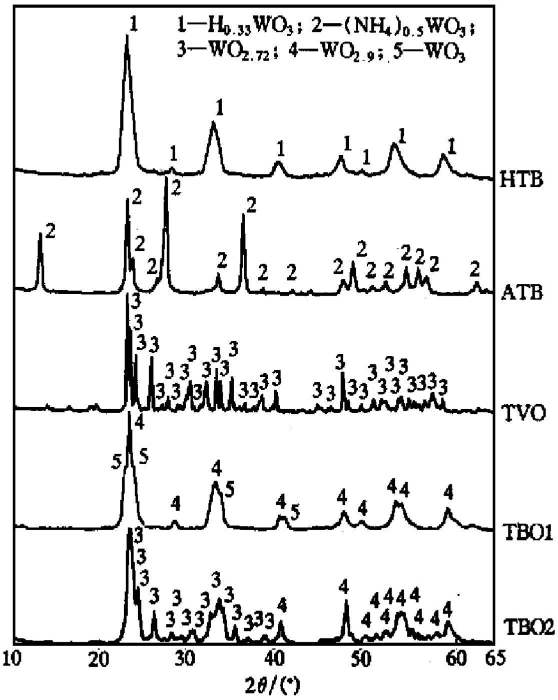

Fig.1 X-ray diffraction patterns of five oxides

s) of tungsten powders reduced from the oxides is respectively measured by static volume adsorption analyzer. The results are shown in Table 2. The BET particle size of powder (BET-*d*) is calculated by formula of 6/19.3/s.

Table 2 BET-*s* and BET-*d* of tungsten powders

Tungsten oxides No.	Tungsten powders		
	No.	BET-s/($m^2 \cdot g^{-1}$)	BET-d/μm
HTB	HTB W	2.689	0.12
ATB	ATB W	4.865	0.06
TVO	TVO W	3.122	0.10
TBO1	TBO1 W	3.952	0.08
TBO2	TBO2 W	3.944	0.08

4 DISCUSSION

4.1 BET-*d* of ultrafine tungsten powder

As shown in Table 2, the BET-*d* of five tungsten powders are all below 0.2 μm, and it can be verified through SEM graphs as Fig.2 and Fig.4. So, ultrafine tungsten powder can be obtained from different tungsten oxides chosen in this study.

4.2 Ultrafine tungsten powders derived from TBO materials comprising only one phase

Schubert has pointed out[4] the possible reduction reactions during tungsten oxide reduction (500 ℃ to 1 100 ℃), as indicated in Fig.2. Owing to the presence of one oxide phase, the reductions occur taking the same reduction path at the same reduction rate. So approximately homogenous tungsten powder was produced respectively from hydrogen tungsten bronze, ammonium tungsten bronze and violet tungsten oxide, each of which consists single phase component respectively, as Fig.3.

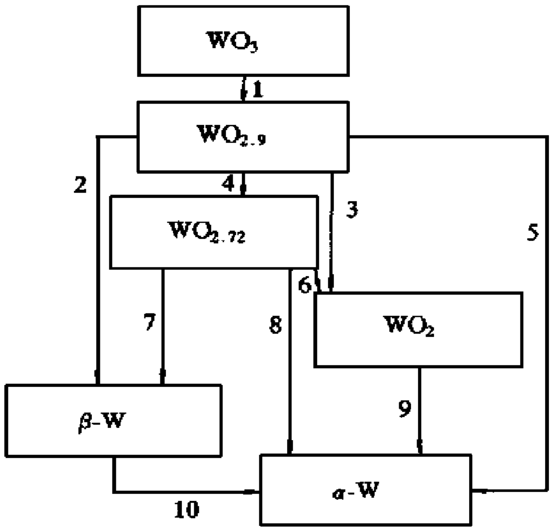

Fig.2 Reduction reactions during oxides reduction (500 ℃ to 1 100 ℃)

4.3 Tungsten powders reduced from multi-phase components TBO materials

4.3.1 TBO1 W reduced from TBO1

TBO1 consists of two phases of WO_3 (≈60 %) and $WO_{2.9}$ (≈40 %). As shown in Fig.2, the reaction of WO_3 to $WO_{2.9}$ (path 1) proceeds over the entire temperature and humidity range, and lasts about several minutes[4]. Although two different phases present, because of the approximate reduction rate, TBO1 W particles seem homogenous with a little difference in particle size, as shown in Fig.4(a).

4.3.2 TBO2 W reduced from TBO2

TBO2 comprises two different phase components of $WO_{2.9}$ and $WO_{2.72}$. Path 3 of transition of $WO_{2.9}$ to WO_2 in Fig.2 is the main path in the temperature range of about 520 ℃ to 620 ℃, and grains coarsen at 650 ℃ to 750 ℃[4]. And the reaction of WO_2 to α-W (path 9) is a rather slow one and the overall rate-controlling step for the production of tungsten powder from TBO under technical plant conditions[4], but at the same time, under "dry" reduction conditions, direct reduction from $WO_{2.72}$ to α-W (path 8) occurs, possible over the entire range of 570 ℃ to 1 050 ℃ and proceeds at a much higher reduction rate[4]. Therefore, two clear different reduction rates lead to two different particle size scales, as shown in Fig.4 (b).

5 CONCLUSIONS

1) Phase components of tungsten oxide plays a crucial role on the homogeneity of metal tungsten

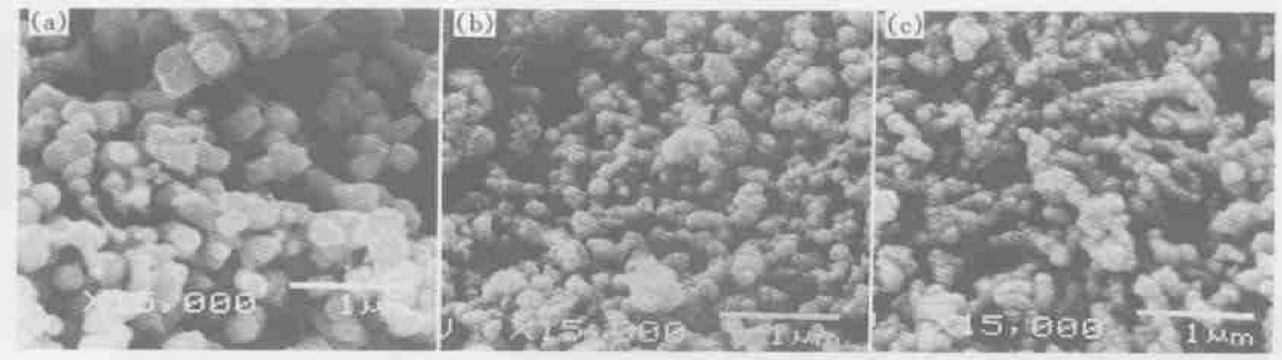

Fig.3 SEM morphologies of W powder reduced from different oxides
(a) —HTB W; (b) —ATB W; (c) —TVO W

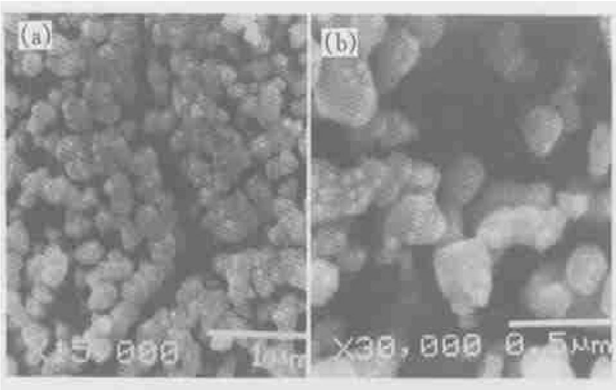

Fig.4 SEM morphologies of TBO1 W (a) and TBO2 W (b)

powder. The ultrafine and homogenous tungsten powder can be produced from oxide which consists of only one phase component in this study, the multi-phase components tungsten oxide leads to a fine but in homogeneous metal tungsten powder due to the different reduction rate (or different reduction path) of different phase.

2) Based on the phase components of oxides, the homogeneity of ultrafine tungsten powder can be predicted approximately when reduction reaction occurs in a stable hydrogen reduction processing at low temperature and high hydrogen flow. Furthermore, oxide raw material characteristic should be taken into account when micrograin hard metals are produced.

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(Edited by Zhong-guo)