Research Article

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**Evolution of reduction process from tungsten oxide to ultrafine tungsten powder via hydrogen**

https://doi.org/10.1515/htmp-2021-0017
received September 11, 2020; accepted March 16, 2021

**Abstract:** Herein, the evolution of reduction process of ultrafine tungsten powder in industrial conditions was investigated. The transition process of morphology and composition was examined via SEM, XRD, and calcination experiments. The results show that the reduction sequence of \( \text{WO}_2.9 \) was \( \text{WO}_2.9 \rightarrow \text{WO}_2.72 \rightarrow \text{WO}_2 \rightarrow \text{W} \) on the surface, but \( \text{WO}_2.9 \rightarrow \text{WO}_2 \rightarrow \text{W} \) inside the oxide particles. With the aid of chemical vapor transport of \( \text{WO}_x \) (\( \text{OH} \)\(_x\)), surface morphology transformed into rod-like, star-shaped cracking, floret, irregularly fibrous structure, and finally, spherical tungsten particles.

**Keywords:** ultrafine tungsten powder, hydrogen reduction, morphology evolution, homogeneity

1 Introduction

Tungsten is widely used in products across the high density alloy [1,2], shielding material [3,4], photocatalyst [5], and cemented carbides [6].

WC-Co-cemented carbides with ultrafine or nanocrystalline grains are widely employed in the precision machining field [7–9]. The reduction step from tungsten oxide to pure tungsten powder is critical to determine the final grain size. Several factors can affect the particle size of tungsten powder, such as temperature, raw material [10], height of powder layer [11], doping [12], dew point of hydrogen [12], etc. In order to produce ultrafine tungsten powder, the temperature must be relatively low and the reaction atmosphere must be dry to prevent the evaporation of tungsten oxide, such as high flow rate of hydrogen, low material loading.

In addition to the particle size of tungsten powder, the morphology and agglomeration state of powder are crucial properties [10,13]. Ideally, all the particles of powder are spherical. However, the crystallization is inhibited by low temperature, low height powder layer, and low dew point of hydrogen, all of which are essential conditions to produce ultrafine/nanocrystalline tungsten powder. In general, pseudomorphology, coarse agglomerates, and irregular crystallization of tungsten powder are obtained from reduction of ammonium paratungstate (APT) or tungsten oxide [13]. The design of reduction conditions to avoid these issues would be useful; hence, study of the evolution process in the whole reduction process, especially in industrial conditions, is of great value. Schubert and Lassner [13] and Wilken et al. [12] have studied the morphology of tungsten powder in detail. However, the whole evolution process of morphology is still not clear due to various reduction conditions. The aim of this paper is to investigate the evolution of powder in reduction process.

2 Experimental

In this work, tungsten blue oxides (99.95%) were provided from Xiamen Tungsten Co., Ltd. (XTC). Tungsten blue oxides were used for reduction in an industrial push furnace under counter-current flow of hydrogen (provided from Linde) at the speed of one boat every 10 min. The dew point of hydrogen is ~60°C and flow rate of the incoming hydrogen was 50 \( \text{m}^3/\text{h} \).

Two temperature conditions were used for five heating zones: 700°C/700°C/700°C/700°C/700°C in condition 1 and 650°C/700°C/750°C/800°C/850°C in condition 2. In order to preserve the intermediate states of powder, nitrogen was injected into the tube immediately after all the samples were pushed in. Then, the samples were slowly pushed out and protected by \( \text{CO}_2 \) to prevent burning and reoxidation.
The reduction extent was calculated from oxygen content by measuring the increase in weight of the samples calcined at 800°C for 60 min in air. The multipoint BET-specific surface area of all samples was measured by a static volume adsorption analyzer. The phase analysis of the samples was performed using X-ray diffraction (XRD) (Panalytical X’pert PRO) with Co Kα radiation. The morphology evolution during reduction was studied under SEM (Hitachi-SU3500). Some samples were surveyed by FESEM (Hitachi S-4800II).

3 Results

3.1 Reduction progress

The reduction extent was calculated by oxygen index of the powder; therefore, the reduction content of 0 and 100% represents WO₃ and W, respectively. XRD was used to confirm the oxygen index of powder comprising W and WO₂. As shown in Figure 1, samples in condition 1 were not completely reduced because of relatively low temperature. In condition 2, samples were completely reduced in 150 min. Three stages are shown in Figure 1 for both conditions. Stage 1: in the preheating zone of the furnace, the reaction was not significant as the temperature was still low. Stage 2: a rapid reaction stage continued for about 20 min. Change in color can be easily observed from blue to violet and brown, suggesting that the reduction sequence was WO₂.₉ → WO₂.₇₂ → WO₂. The reaction velocity was relatively fast [11,14], and by the end of this stage, the reduction extent was 33%. XRD results in Figure 1(b) show that the content of WO₂ reached up to 98%. Stage 3: in the third stage, WO₂ was reduced to W directly. The reduction curves were parabolic, which are typical of a chemical reaction at the moving interface [15]. The increase of reduction velocity from 100 to 130 min in condition 2 (red line) was because of the increase in temperature. The whole sequence was WO₂.₉ → WO₂.₇₂ → WO₂ → W. In both reduction conditions, no β-W was found in XRD results.

Figure 2 shows the evolution of BET values in two reduction conditions. In the process from WO₂.₉ to WO₂, the BET values underwent increase and subsequent decrease to about 3.5 m²/g. The increase of BET values results from the formation of WO₂. However, the size of WO₂ is not the key factor in final size of tungsten powder. In the stage 3, temperature affected the evolution of BET values. In condition 1, BET values increased from 3.5 to 5.5 m²/g in the first 70 min of stage 3 and then raised to 9 m²/g rapidly in 30 min. In condition 2, with the rise in temperature, the BET values decreased to ~2 m²/g.
3.2 Morphology evolution

The reduction sequence has been investigated to be $\text{WO}_{2.9} \rightarrow \text{WO}_{2.72} \rightarrow \text{WO}_2 \rightarrow \text{W}$. The morphology shows the corresponding evolution in each stage. In the preheating zone of furnace, microstructure of powder seemed unchanged, as shown in Figure 3. The color of powder became dark blue because of the tiny differences in chemical composition and roughness of the surface. The time shown in all figures is from the boat pushed into the furnace and not the effective reduction time.

As shown in Figure 4, rod-like forest spread to the whole surface when the boat was pushed into the heating zone. The color of the powder became violet, indicating that WO$_{2.72}$ was formed. Subsequently, WO$_{2.72}$ was rapidly transformed into WO$_2$. Figure 5 shows the transformation process from WO$_{2.72}$ to WO$_2$. Small rods aggregated together and disappeared gradually, instead of the granules (~2μm) split by star-shaped cracking structure [12] at the end of stage 2. In industrial reduction conditions, WO$_2$ with star-shaped cracking structure is inevitable. As W was reduced from these granules, final morphology of tungsten powder was decided by the process from WO$_2$ to W. In dry conditions, the granular morphology would be retained after WO$_2$ reduced into tungsten.

In the long reduction process from WO$_2$ to W, the granules that were split by the star-shaped cracks dispersed gradually. Figure 6a shows the evolution process of the granules. Firstly, trigonal granules changed into a circular floret structure. The floret structure probably evolved from the star-shaped cracks morphology because residual star shape cracks can be observed in Figure 6(b). Then, the floret granules changed into irregularly fibrous, leading to the emergence of a covered microstructure.

Finally, as shown in Figure 7(b), spherical tungsten particles were formed in condition 2. Because of low temperature and dry atmosphere in producing ultrafine powder, a part of the granules was reduced in situ, resulting in a considerable number of agglomerates in condition 1 (Figure 7(a)).

4 Discussion

4.1 Mechanism of morphology evolution

The formation of WO$_2$(OH)$_2$ is one of the major reasons for the coarsening of tungsten powder during reduction [16,17].

Figure 3: Morphology of samples. (a) Initial state; (b) in preheating zone.

Figure 4: Morphology of rod-like forest at (a) low magnification and (b) high magnification.
The morphology evolution in Figures 4–7 indicates that this kind of chemical vapor transport works in all the reduction procedures. The vapor intermediary is probably $\text{WO}_x(\text{OH})_y$ because of the variation of valency of W in different reduction steps. Figure 8 presents the forepart of $\text{WO}_{2.72}$ and $\text{WO}_2$ formation. Rod-like $\text{WO}_{2.72}$ forest grew up from the rough surface by the deposition of reduced hydrated $\text{WO}_{2.72}$ vapor on the head of each rod, leaving small holes on the original surface of $\text{WO}_{2.9}$. Similarly, prior $\text{WO}_2$ formed on the head of $\text{WO}_{2.72}$ rod and then captured hydrated $\text{WO}_2$ vapor rising from the bottom of $\text{WO}_{2.72}$ forest, resulting in aggregated $\text{WO}_2$ granules.

4.2 Heterogeneity in reduction process

To produce homogeneous tungsten powder, it might be expected that raw oxide has a single component. However, the reduction process on each reduction stage
was heterogeneous. As shown in Figure 9, rod-like WO$_{2.72}$ could be observed on the surface but the fracture surface was still flat. Only a small amount of WO$_{2.72}$ was detected by XRD. The fracture surface in Figure 9(a) was formed after the samples were removed from the furnace. It suggests that the reduction path inside the particle was different from that on the surface; as intermediate WO$_{2.72}$ would not have formed inside. As predicted by Donoso et al. [14], only 20% of WO$_{2.72}$ form in the whole reduction process at 750–900°C.

As presented in Figure 10, in the process of aggregation of rods, some regions reacted preferentially, leaving rod-like residues. Star-shaped cracks observed in Figure 10 are supposed to result from the evaporation of residual WO$_{2.72}$ or the internal stress originating from the shrinkage of aggregated WO$_2$. When the star-shaped
cracking structure was spread to the whole surface, a different internal structure with nanocrystalline WO2 particles could be observed (see Figure 11). In addition to the observed inhomogeneity in one oxide particle, the difference in reduction content between oxide particles was great, leading to a wide distribution of particle size.

4.3 Agglomeration in ultrafine tungsten powder

In industrial conditions, undesirable agglomerates are difficult to avoid in order to produce submicron powder. As presented in Figure 12, these agglomerates cause the powders to maintain the original morphology of raw material. The coarse agglomerates may lead to formation of inhomogeneous mixture with carbon, even to coarse WC particles, which induces abnormal grain growth in production of cemented carbide.

As discussed above, the agglomeration is due to lack of chemical vapor transport in the step 3. To avoid agglomeration, the key factor is the promotion of aggregate transformation into spherical particles. The paradox is that the factors promoting chemical vapor transport also lead to coarsening of the powder. One possible method to address the issue is the design of a suitable boat structure and hydrogen flux to suppress the coarsen mechanism of repeated oxidization and reduction of powder by rapidly discharging the water vapor, enhancing the contribution of chemical vapor transport mechanism.

5 Conclusion

Herein, the evolution of reduction from tungsten oxide to tungsten powder by hydrogen was investigated in industrial conditions. The intermediate states of powders were preserved via abrupt introduction of nitrogen. In the two experimental conditions employed in this work, the reduction sequence was observed to be $\text{WO}_2.9 \rightarrow \text{WO}_2.72 \rightarrow \text{WO}_2 \rightarrow \text{W}$ on the surface, but $\text{WO}_2.9 \rightarrow \text{WO}_2 \rightarrow \text{W}$ inside the oxide particles. The morphology changed along with the transformation of phases during reduction, including rod-like $\text{WO}_2.72$ forest, $\text{WO}_2$ granules with star-shaped cracks, floret pattern, irregularly fibrous structure, and spherical W particles. The multiple morphologies were attributed to the chemical vapor transport mechanism by the production of $\text{WO}_4$(OH)$_y$ with different valencies of W ions in different reduction steps. Also, as there was difference in evolution process between surface and interior, only observation of surface morphology may lead to misunderstanding of the reduction process.

Acknowledgments: The authors are grateful for the support from the National S&T Major Projects (2018ZX04042001) and the Science and Technology Commission of Fujian Province of China (2017H0008).
Funding information: This study was funded by the National S&T Major Projects (2018ZX04042001) and the Science and Technology Commission of Fujian Province of China (2017H0008).

Author contributions: Yue Wang: experiment design and data analysis. Ben Fu Long: sample testing and data analysis. Chun Yu Liu: experiment performance. Gao An Lin: guidance for the experiment scheme.

Conflict of interest: Authors state no conflict of interest.

Data availability statement: The data used to support the findings of this study are available from the corresponding author upon request.

References

[1] Chen, C. L. and S. H. Ma. Effects of Ni/Co ratio and mechanical alloying on characteristics and sintering behavior of W–Ni–Co tungsten heavy alloys. Journal of Alloys and Compounds, Vol. 711, 2017, pp. 488–494.

[2] Prabhu, G., A. Kumar, and T. K. Nandy. Effect of yttrium oxide dispersion on the microstructure and properties of tungsten heavy alloys. Defence Science Journal, Vol. 68, No. 4, 2018, pp. 406–411.

[3] Zhao, Q., Z. Zhang, M. Huang, X. Zhang, and X. Ouyang. Effects of H and He on the clustering behavior of transmutation elements in tungsten. Nuclear Instruments and Methods in Physics Research Section B Beam Interactions with Materials and Atoms, Vol. 470, 2020, pp. 48–55.

[4] Nguyen, B. N., C. H. Henager, N. R. Overman, and R. J. Kurtz. A multiscale microstructural approach to ductile-phase toughened tungsten for plasma-facing materials. Journal of Nuclear Materials, Vol. 508, 2018, pp. 371–384.

[5] Paik, T., M. Cargnello, T. R. Gordon, S. Zhang, and C. B. Murray. Photocatalytic hydrogen evolution from sub-stoichiometric colloidal WO 3-x nanowires. ACS Energy Letters, Vol. 3, 2018, pp. 1904–1910.

[6] José, G., C. C. Verónica, B. Andreas, and K. Bartek. Cemented carbide microstructures: A review. International Journal of Refractory Metals and Hard Materials, Vol. 80, 2018, pp. 40–68.

[7] Raihanuzzaman, R. M., Z. Xie, S. J. Hong, and R. Ghomashchi. Powder refinement, consolidation and mechanical properties of cemented carbides – An overview. Powder Technology, Vol. 261, 2014, pp. 1–13.

[8] Farag, S., I. Konyashin, and B. Ries. The influence of grain growth inhibitors on the microstructure and properties of submicron, ultrafine and nano-structured hardmetals – A review. International Journal of Refractory Metals and Hard Materials, Vol. 26, 2018, pp. 1–41.

[9] Bock, A. and B. Zeiler. Production and characterization of ultrafine WC powders. International Journal of Refractory Metals & Hard Materials, Vol. 20, 2002, pp. 23–30.

[10] Schubert, W. D. and E. Lassner. Production and characterization of hydrogen-reduced submicron tungsten powders. Part II: Controlled decomposition of APT and hydrogen reduction of the oxides. International Journal of Refractory Metals & Hard Materials, Vol. 10, 1991, pp. 171–183.

[11] Haboury, R., U. B. Pal, P. A. Zink, S. Gopalan, and S. N. Basu. Study of an energy storage and recovery concept based on the W/WO 3 redox reaction: Part I. Kinetic study and modeling of the WO 3 reduction process for energy storage. Metallurgical & Materials Transactions B, Vol. 43, 2012, pp. 1001–1010.

[12] Wilken, T. R., W. R. Morcom, C. A. Wert, and J. B. Woodhouse. Reduction of tungsten oxide to tungsten metal. Metallurgical Transactions B, Vol. 7, 1976, pp. 589–597.

[13] Schubert, W. D. and E. Lassner. Production and characterization of hydrogen-reduced submicron tungsten powders – Part I: State of the art in research, production and characterization of raw materials and tungsten powders. International Journal of Refractory Metals & Hard Materials, Vol. 10, 1991, pp. 133–141.

[14] Donoso, A. E. and B. Peters. XDEM employed to predict reduction of tungsten oxide in a dry hydrogen atmosphere. International Journal of Refractory Metals & Hard Materials, Vol. 49, 2015, pp. 88–94.

[15] Jie, D., K. Chou, X. Hu, and G. Zhang. Reduction kinetics of metal oxides by hydrogen. Steel Research International, Vol. 84, 2013, pp. 526–533.

[16] Liao, J., S. Chen, Z. Zou, H. Lu, and B. Huang. Influence of tungsten oxides’ characteristics on fineness, homogeneity and looseness of reduced ultrafine tungsten powder. International Journal of Refractory Metals & Hard Materials, Vol. 17, 1999, pp. 423–429.

[17] Venables, D. S. and M. E. Brown, Reduction of tungsten oxides with hydrogen and with hydrogen and carbon. Thermochimica Acta, Vol. 285, 1996, pp. 361–382.