Research Article

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

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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 $\text{WO}_x(\text{OH})_y$, 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: $700^\circ\text{C}/700^\circ\text{C}/700^\circ\text{C}/700^\circ\text{C}/700^\circ\text{C}$ in condition 1 and $650^\circ\text{C}/700^\circ\text{C}/750^\circ\text{C}/800^\circ\text{C}/850^\circ\text{C}$ 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 CO_2 to prevent burning and reoxidation.

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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 K_{α} 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 WO_3 and W, respectively. XRD was used to confirm the oxygen index of powder comprising W and WO_2 . 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 $WO_{2.9} \rightarrow WO_{2.72} \rightarrow WO_2$. 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 WO_2

Figure 2: BET measurements in two reduction conditions.

reached up to 98%. Stage 3: in the third stage, WO_2 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 $WO_{2.9} \rightarrow WO_{2.72} \rightarrow WO_2 \rightarrow W$. 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 $WO_{2.9}$ to WO_2 , the BET values underwent increase and subsequent decrease to about $3.5 \text{ m}^2/\text{g}$. The increase of BET values results from the formation of WO_2 . However, the size of WO_2 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 $5.5 \text{ m}^2/\text{g}$ in the first 70 min of stage 3 and then raised to $9 \text{ m}^2/\text{g}$ rapidly in 30 min. In condition 2, with the rise in temperature, the BET values decreased to $\sim 2 \text{ m}^2/\text{g}$.

Figure 1: (a) Reduction extent in two reduction conditions; (b) XRD curve at the end of stage 2.

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

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 $\text{WO}_{2.72}$ was formed. Subsequently, $\text{WO}_{2.72}$ was rapidly transformed into WO_2 . Figure 5 shows the transformation process from $\text{WO}_{2.72}$ to WO_2 . Small rods aggregated together and disappeared gradually, instead of the granules ($\sim 2\mu\text{m}$) 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(a). 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 $\text{WO}_2(\text{OH})_2$ is one of the major reasons for the coarsening of tungsten powder during reduction [16,17].

Figure 4: Morphology of rod-like forest at (a) low magnification and (b) high magnification.

Figure 5: Transformation process from $\text{WO}_{2.72}$ to WO_2 . (a) Aggregation at the top of $\text{WO}_{2.72}$ forest; (b) WO_2 with star-shaped cracks.

Figure 6: Morphology evolution of WO_2 on the surface. (a) Floret structure; (b) irregularly fibrous.

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 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 WO_2 formed on the head of $\text{WO}_{2.72}$ rod and then captured hydrated WO_2 vapor rising

from the bottom of $\text{WO}_{2.72}$ forest, resulting in aggregated 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

Figure 7: Morphology of tungsten powder. (a) With agglomerates; (b) spherical particles.

Figure 8: Morphology change by chemical vapor transport. (a) $\text{WO}_{2.9} \rightarrow \text{WO}_{2.72}$; (b) $\text{WO}_{2.72} \rightarrow \text{WO}_2$.

was heterogeneous. As shown in Figure 9, rod-like $\text{WO}_{2.72}$ could be observed on the surface but the fracture surface was still flat. Only a small amount of $\text{WO}_{2.72}$ 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 $\text{WO}_{2.72}$ would not have formed inside. As predicted by

Donoso et al. [14], only 20% of $\text{WO}_{2.72}$ 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 $\text{WO}_{2.72}$ or the internal stress originating from the shrinkage of aggregated WO_2 . When the star-shaped

Figure 9: Fracture surface of the samples reduced for 35 min in condition 1. (a) Low magnification; (b) high magnification.

Figure 10: Morphology of residual rod-like $\text{WO}_{2.72}$. (a) Low magnification; (b) high magnification.

Figure 11: Morphology of nanocrystalline particles on the back of WO_2 granules. (a) Low magnification; (b) high magnification.

Figure 12: Ultrafine tungsten powder with coarse agglomerates.

cracking structure was spread to the whole surface, a different internal structure with nanocrystalline WO_2 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, 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 $\text{WO}_x(\text{OH})_y$ 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.

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