Original Research Paper

Hydrothermal synthesis of nanoplates assembled hierarchical h-WO₃ microspheres and phase evolution in preparing cubic Zr(Y)O₂-doped tungsten powders

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ABSTRACT

Three-dimensional hierarchical h-WO₃ and doping tungsten powders have recently attracted considerable attention because of their superior sensing properties and refined grains, respectively. In this article, we report a facile hydrothermal hydrogen reduction process for preparing hierarchical h-WO₃ microspheres that self-assemble with nanoplates. Meanwhile, the phase evolution process and evolution mechanisms during the conversion of h-WO₃ to W are systemically investigated. Results indicate that the highly homogeneous h-WO₃ microspheres are uniformly covered with ultrafine $ZrY_2(OH)_{10}$ micelles, which fully transform into m-WO₃ and cubic Zr(Y)O₂ after calcination at 600 °C. Microspheres possessing different pore diameters and containing nanosized particles can be obtained by adjusting the hydrogen reduction process. These phase evolution process can provide reasonable guidance for preparing tungsten oxide with high electrochemical properties and ultrafine tungsten powders. The h-WO₃ microspheres with an average size of 3 μm consist of nanoplates and the tungsten powders doped with 1.0 wt% Zr (Y)O₂ have a mean particle size of approximately 1.4 μm. Comparative test results indicate that the addition of 1.0 wt% Zr(Y)O₂ can promote the formation of low-degree particle agglomerates.

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1. Introduction

In recent years, considerable attention has been devoted to the preparation the hexagonal form of tungsten trioxide (h-WO₃) that is highly sensitive to different gases, photocatalytic splitting of water for hydrogen generation, and simple fabrication of display panels, smart windows, and mirrors. [1–3]. To date, the different morphologies of WO₃ in nanowires [4,5], nanotubes [6], nanorods [7], and nanoplates [8,9] are obtained by various reaction methods, including electrochemical techniques, hydrothermal reaction, and template-based rheological phase reaction [10–12]. However, 3D hierarchical architectures with 1D or 2D nanocrystals reportedly exhibit sensing properties superior to those of structures with low dimensions [13]. Therefore, 3D hierarchical nanomaterials assembled with 2D nanocrystals have captured a great deal of attention in current research works.

Herein, we report a facile hydrothermal route for the preparation of h-WO₃ microspheres self-assembled by 2D nanoplates. However, over the past years, oxide dispersion-strengthened tungsten has attracted a great deal of attention in current research [14,15]. The reason is that they can refine grains by promoting grain nucleation, hindering grain growth, and gathering impurities, such as O, N, and P, owing to strong rare-earth interaction, which separates on grain boundaries (GB) and decreases GB cohesion [16]. Nevertheless, the mechanical behaviors of tungsten materials are determined by the quality of tungsten powders [17–19]. Fu et al. [20] and Gamble et al. [21] found that the flowability of powders is considerably influenced by particle morphology and dimension. He [18] also reported that the properties of the tungsten products are mainly dependent on the properties of the starting tungsten reactant, namely, particle morphology, distribution, and size. Ultrafine and nanocomposite powders can significantly reduce the sintering activation energy of powders and promote

excellent sintering process, eventually forming nanostructure materials [22,23]. In addition, impurities in tungsten powders (e.g., O and N) separate at GBs that decrease the GB cohesion [24,25], resulting in weak GB and further forming low ductility of tungsten alloys. Thus, the importance of high-quality of tungsten powders in the preparation of high-performance tungsten products continues to grow.

Liquid–liquid doping methods combined with hydrogen reduction process were conducted for the synthesis of oxide dispersion-strengthened tungsten and molybdenum materials. Nanoscale oxide particles were used, and most of them were homogeneously dispersed in tungsten grain interior [26–32]. However, studies on the phase evolution and structures of tungsten powders prepared by liquid–liquid doping methods are few.

In this work, tungsten powders with uniform distribution of ZrO_2 particles were obtained by the hydrothermal in-situ hydrogen reduction process. We proposed an optimized process for preparing h-WO_3 precursor and yttrium-stabilized zirconia (Zr(Y)O_2) doped tungsten powders. The phase, morphology and microstructure of powders prepared at different stages were characterized. In addition, the phase evolution process and its evolution mechanisms were investigated.

2. Experimental procedure

2.1. Chemical composition of alloys

The raw materials used for the synthesis of the W-Zr(Y)O_2 powders were ammonium metatungstate ((NH$_4$)$_6$H$_2$W$_{12}$O$_{40}$·5H$_2$O; grade AR; 99.9% purity), zirconium nitrate ((Zr(NO$_3$)$_4$·5H$_2$O; grade AR; 99.9% purity), and yttrium nitrate ((Y(NO$_3$)$_3$·6H$_2$O; grade AR; 99.99% purity). The five types of W-Zr(Y)O_2 powders containing 0%, 0.5%, 1.0%, 1.5%, and 5.0% zirconia were denoted as Z_0, $Z_{0.5}$, $Z_{1.0}$, $Z_{1.5}$, and $Z_{5.0}$ samples, respectively, as listed in Table 1. Moreover, ZrO_2-Y_2O_3 powders containing molar ratio Zr:Y = 88:12 were denoted as ZY sample.

2.2. Preparation of W-Zr(Y)O_2 powders

The procedure employed for the preparation of W-Zr(Y)O_2 powders were as follows: 250 g (NH$_4$)$_6$H$_2$W$_{12}$O$_{40}$·5H$_2$O was dissolved in distilled water. The pH of the resulting was adjusted to 2.0 by adding a nitric acid solution under stirring. Next, the clear solution was transferred into a 500 ml Teflon-lined stainless-steel autoclave. Meanwhile, a certain amount of Zr(NO$_3$)$_4$·5H$_2$O and Y(NO$_3$)$_3$·6H$_2$O with [Zr^{4+}]:[Y^{3+}] molar ratio of 88:12 and stoichiometric amount of urea related to the equilibrium of the chemical reaction (Eq. (4)) were placed into another autoclave (60 ml). The filling factor was maintained at 80% by adding distilled water. The autoclaves were sealed and heated at 3.5 °C/min until the desired temperature of 170 °C was reached. After the reaction was completed, the autoclaves were naturally cooled to room temperature. Some distilled water was added into the mixture of two kinds of reaction products, followed by stirring for no less than 2 h using an electric mixer. After being filtered, the powders were dried

overnight in an oven at 90 °C, and the precursor powders were obtained. The precursor powders were calcined at 600 °C for 4 h, followed by hydrogen reduction under dry hydrogen in a tube furnace (6 L/min) at different temperature, forming the W-Zr(Y)O_2 powders.

2.3. Measurement and analysis

The internal stress was estimated using the XRD pattern in combination with the Williamson-Hall equation [33]:

$$\beta \cos \theta = 0.9(\lambda/d) + 2\varepsilon \sin \theta \qquad (1)$$

where β is the full width half maximum of the XRD peak, θ is Bragg angle, λ is the X-ray wave length, d is crystallite size and ε is internal stress.

The crystalline phases and reactions of the powders were determined through X-ray diffraction (XRD) analyses. The reflex indexation and the unit cell parameter calculation were carried out by using the JADE 5.0 software complex. Particle morphology and size were investigated with VEGA-SBH scanning electron microscope. Transmission electron microscopy (TEM) and High-resolution transmission electron microscopy (HRTEM) observations were carried out on a Phillips (Titan 80–300 FEI) operated at 200 K. The particle size distributions of the powders were measured in the aqueous phase using the Mastersizer-2000 laser diffraction particle size analyzer. The dispersion medium is the mixture of ethanol and glycerol, and the dispersing agent is sodium polyphosphate. The specific surface area was measured with a BET surface area analysis instrument (Autosorb-1, Quantachrome, USA). The average particle sizes of these doped tungsten powders were calculated based on the BET specific surface area using the following equation [33]:

$$d_{BET} = 6/(S_{BET} \cdot \rho_{Theory}) \qquad (2)$$

where d_{BET} is the average particle size, S_{BET} is the powder specific surface area, ρ_{Theory} is the theoretical density of tungsten, i.e. 19.3 g/cm^3.

3. Results and analysis

3.1. Analysis of precursor and calcined powders

Fig. 1 shows the XRD patterns of $Z_{5.0}$ and ZY samples before and after calcination at 600 °C for 4 h, respectively. As shown in Fig. 1A, intense and sharp diffraction peaks are observed, indicative of high-degree crystallinity for two types of powders. The XRD patterns of precursor powder (Fig. 1A (a)) show these diffraction peaks agree well with the standard data file (PDF#85-2460, a = b = 7.324 Å, c = 7.662 Å). Thus, these powders can be indexed to the hexagonal WO$_3$ (h-WO$_3$). Interestingly, no peaks of any other phases containing Zr elements are detected in the XRD patterns of Fig. 1A(a), indicating the formation of pure h-WO$_3$ under these experimental conditions. This is because the mixture of Zr(OH)$_4$ and Y(OH)$_3$ formed in hydrothermal reaction cannot decompose into ZrO$_2$, Y$_2$O$_3$, and H$_2$O during the drying process at 90 °C; thus, wide peaks are observed, indicating a very poor crystallinity as shown in Fig. 1B(a). However, Fig. 1A(b) shows diffraction peaks of $Z_{5.0}$ calcined powders at 23.2°, 23.7°, and 24.4° as the major intensity peaks, followed by three peaks at 33.4°, 34.0°, and 34.3°. They were assigned to the (0 0 1), (0 2 0), (2 0 0), (0 2 1), (2 0 1), and (2 2 0) crystal planes of monoclinic WO$_3$ (m-WO$_3$) (PDF#75-2072, a = 7.274 Å, b = 7.501 Å, and c = 3.824 Å), indicating that the h-WO$_3$·H$_2$O fully transformed into m-WO$_3$ after calcination at 600 °C. Detailed examination of the patterns reveals that an apparent peak at about 30°, which is the strongest one assigned to the (1 1 1) crystallographic plane of stabilized ZrO$_2$ phase. However,

Table 1
Chemical composition of the samples.

Sam.	W (wt %)	ZrO$_2$ (wt %)	Y$_2$O$_3$ (wt %)
Z_0	100	0	0
$Z_{0.5}$	99.43	0.50	0.07
$Z_{1.0}$	98.87	1.00	0.13
$Z_{1.5}$	98.31	1.50	0.19
$Z_{5.0}$	94.37	5.00	0.63
ZY	0	87.30	12.70