Original Research Paper

Refining mechanisms of arsenic in the hydrogen reduction process of tungsten oxide

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ABSTRACT

Scheelite ores endolithic arsenic (As) is commonly removed as a detrimental impurity element in the process of tungsten metallurgy. However, arsenic can refine tungsten grains significantly which was found by our team. In this study, refining mechanisms of arsenic in the hydrogen reduction process of tungsten oxide were discussed in detail by X-ray diffraction, scanning electron microscope and transmission electron microscope. The results showed that the WAs_2 intermediate phases played an important role as heterogeneous nucleation core for tungsten during the nucleation process. Moreover, the process of chemical vapor transport was hampered by volatilization of arsenic, which inhibited the growth of tungsten particles. The above two effects resulted in the W–1%As composite powder with the average size of about 80 nm in diameter.

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1. Introduction

Due to possessing high melting point, high thermal conductivity, low sputtering yield and excellent mechanical strength, tungsten is commonly used in many important areas, such as filament in light bulbs, electrical contacts, rocket nozzles in space craft, as well as ultra-hard alloys for cuttings tools and anti-friction tools [1–4]. Tungsten powders are produced from wolframite or scheelite ores through the intermediate product of ammonium paratungstate (APT) or ammonium metatungstate (AMT). The existence form of As is $FeAsO_4$ in scheelite ores and its weight percentage is amounts to 0.03–0.3%. Arsenic is removed as an injurious impurity in the preparation process of AMT (or APT). However, this process is very complicated and there is still about 0.001 wt% of As remained in the AMT (or APT). Recently, we found that arsenic could refine tungsten powder grains significantly in our experiment, which provides a new idea to utilize the impurity of As in the scheelite ores to produce nanocrystalline tungsten powder by hydrogen reduction.

Ultrafine-grained W exhibits better ductility, decreased ductile brittle transition temperature and improved irradiation resistance compared with conventional coarse-grained W [5,6]. To date, such as high-energy ball milling [7], molten salt electrolysis [8], self-propagating high-temperature synthesis (SHS) [9–11], chemical vapor synthesis [12] and chemical reduction [13] method are used in the production of nanoscale tungsten powders. Unfortunately, these techniques for fabricating of tungsten nanoparticles all suffer from various disadvantages, including use of expensive raw material precursors, requirement of multi-steps high temperature process and difficulty in establishing a commercial application. In the conventional process, tungsten powders are produced by the hydrogen reduction of tungsten oxides which obtained from APT (or AMT) by calcination in an oxygen bearing atmosphere [14]. However, it is difficult to produce nanocrystalline tungsten powders with conventional evaporation and condensation methods, due to the high temperature that is needed for evaporation [15]. To overcome these drawbacks, it is necessary to improve the conventional production process of tungsten powders.

Rare earths (Sc, Y, Ce and La) are generally applied to refine tungsten powder, because they existed around tungsten particles could take the function of pinning and hampered grain growth [16,17]. However, we used arsenic to refine tungsten powder and its refining mechanisms were different from the rare earths. In this paper, the liquid–solid doping method (arsenic was added into AMT or APT) was adopted to study the refinement effect of arsenic in the hydrogen reduction process of tungsten oxide. The ultimate objective is to keep and utilize the arsenic in scheelite ores to produce nanocrystalline W powders by hydrogen reduction tungsten oxide method. Therefore the present work is concerned with the effects of arsenic on grain size, microstructure and formation of new phase during the process of calcination and reduction.

2. Experimental details

2.1. Materials and precursor synthesis

Fig. 1 shows the preparation process of W–As composite nanopowders. Commercially available ammonium metatungstate (AMT, purity >99.9%, mean particle size: 7.8 μm), ammonium para-tungstate (APT, purity >99.9%, mean particle size: 37.5 μm) and arsenic (As) were purposely used as the raw materials. As-doped AMT (or APT) precursors were synthesized by a solution chemical process through a nitric acid solution (HNO_3). The details of the precursor synthesis were described as following: firstly, arsenic was dissolved into an aqueous solution of 65–68 wt% nitric acid; then AMT (or APT) was added into the mixture solution of nitric acid and arsenic; lastly, the solution was dried at 80 °C in oven for 12 h to remove moisture and homogeneous mixture precursors were prepared. Four composite precursors of AMT, AMT–0.01%As, AMT–0.1%As, AMT–1%As (weight ratio of AMT:As equal 100:0, 99.99:0.01, 99.9:0.1 and 99:1, respectively) were synthesized by the above steps, respectively.

2.2. Calcination and reduction

Thermal processing (calcination and reduction) of the precursors was carried out in a tube furnace. The four AMT–As composite precursors were calcined at 600 °C in non-flowing air for 2 h to form As doped WO_3 composite powders, respectively. Subsequently, the As doped WO_3 composite powders (3.0–4.0 g) were filled in an alumina ceramic boat with a size of $60 \times 30 \times 14$ mm. The reduction process was carried out in a tube furnace at 800 °C for 3 h and cooled to room temperature in a flowing hydrogen (dew point: −40 °C), resulting in four samples of As doped W powders were prepared by this process and noted as W, W–0.01%As, W–0.1%As and W–1%As, respectively. All heating rate was controlled at 5 °C/min.

2.3. Characterization

The constitution of the powders was examined by X-ray diffraction (XRD, D8-Focus Bruker-AXS) using Cu-Kα radiation. The morphology and microstructure of synthesized powders were characterized with a field-emission scanning electron microscopy (FESEM, Nova NanoSEM450 FEI) with energy dispersed spectroscopy (EDS, INCA Energy 250 X-max 50 Oxford Instruments) and a high resolution transmission electron microscope (HRTEM, JEM-2100F JEOL) equipped with energy dispersed spectroscopy (EDS, INCA Energy 300 mics/x-stream Oxford Instruments). Laser particle size instrument (Malvern Zetaszier Nano-ZS90) was used to measure the size distribution of the produced W particles.

3. Results

3.1. Calcined powder

Fig. 2a shows the XRD pattern of WO_3–1%As derived from AMT–1%As sample calcined at 600 °C for 2 h. All the diffraction peaks could be indexed undisputedly to be hexagonal WO_3 (JCPDS#20-1324). However, no As_2O_3 or $W_2O_3(AsO_4)_2$ peaks could be detected in the XRD patterns. The absence of detection of As_2O_3 or $W_2O_3(AsO_4)_2$ on the XRD patterns should be due to the measuring accuracy of XRD. In order to understand the existence form of As in WO_3 powder, TEM measurement has been carried out on the WO_3–1%As powders as given in Fig. 3. Fig. 3 shows TEM images of WO_3–1%As powders and the inset is selected area diffraction
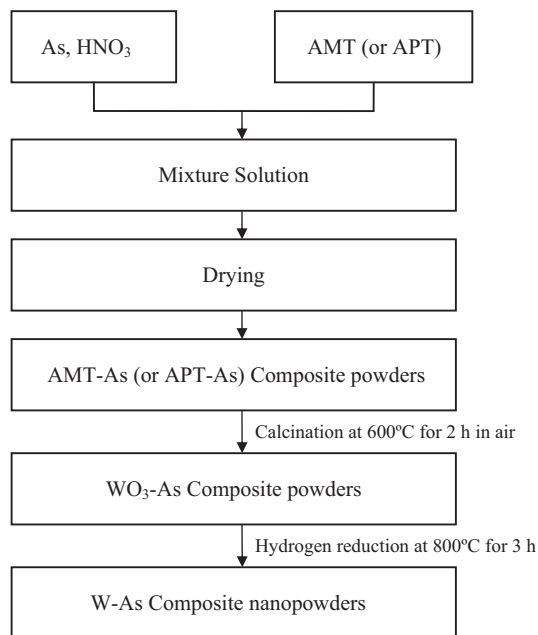

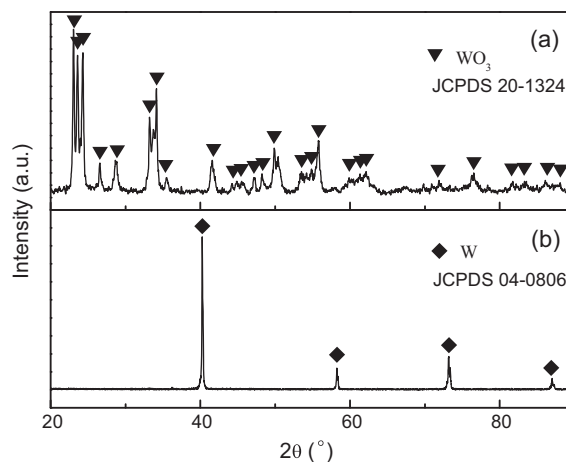**Fig. 1.** Flow-diagram of preparing the W–As composite nanopowders.

Fig. 2. XRD patterns of (a) WO_3–1%As derived from AMT–1%As calcined at 600 °C for 2 h and (b) W–1%As powders after 3 h hydrogen reduction WO_3–1%As at 800 °C.

pattern taken from the selected red[1] field. The diffraction pattern shown as inset clearly confirmed that the powders were mixture of WO_3 and As_2O_3.

The features of pure WO_3 (Fig. 4a and c) and WO_3–1%As (Fig. 4b and d) were observed by SEM. The results of SEM (Fig. 4) indicated that the loose sponge structure, which pure WO_3 and WO_3–1%As powders were composed of the many "bridges" built by crystalline rod. However, WO_3–1%As aggregate particles possessed more loose sponge structure compared with pure WO_3. These were caused by that the transformation of As_2O_3 into gas and leaving lots of pore during the process of calcination.

3.2. Reduced powder

Fig. 2b shows the XRD patterns of W–1%As powders produced by WO_3–1%As sample reduced at 800 °C for 3 h in flowing

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[1] For interpretation of color in Figs. 3, 6a and 9c, the reader is referred to the web version of this article.