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Fabrication of tungsten nanopowder by combustion-based method

Mingli Qin[a,*], Zheng Chen[a,*], Pengqi Chen[b], Shangjie Zhao[a], Rui Li[a], Jidong Ma[c], Xuanhui Qu[a]

[a] Institute for Advanced Materials and Technology, University of Science and Technology Beijing, Beijing 100083, China
[b] School of Materials Science and Engineering, Hefei University of Technology, Hefei 230009, China
[c] School of Materials Science and Engineering, Xiamen University of Technology, Xiamen 361024, China

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ABSTRACT

In this work, tungsten nanopowder was prepared by solution combustion synthesis (SCS) and hydrogen reduction. First, needle-like $W_{18}O_{49}$ as precursor was fabricated by SCS. Subsequently, hydrogen reduction of as-synthesized precursor was utilized to prepare tungsten nanopowder. The precursor synthesized by SCS exhibits high reduction reactivity and can be completely reduced to pure tungsten nanopowder at as low as 700 °C for 2 h. The tungsten particles reduced at 700 °C are spherical or elliptical and the particle size is 20–30 nm. The sintering behavior of the as-prepared tungsten nanopowder was investigated by analyzing the sintered compacts obtained at different sintering temperatures. 93.3% of relative density of the compact could be obtained at sintering temperature of 1200 °C. The microhardness of the compact sintered at 1500 °C reached the highest point of 587.14 $Hv_{0.2}$.

1. Introduction

Owing to its high melting point, excellent thermal conductivity, low thermal expansion and superior mechanical properties at elevated temperature, tungsten (W) is suitable for many engineering applications, such as military, high temperature technology, aerospace and nuclear industry. However, the fabrication of full dense W bulk materials is difficult because of its high melting point and hardness. Conventional sintering of W is commonly carried out at over 2000 °C [1–3]. Adding transition metals and using novel sintering methods are two effective ways to reduce the sintering temperature and obtain near-full dense compacts. Small additions of transition metals (Ni, Pd, Pt et al.) can enhance grain boundary diffusion, which further reduces the activated energy of sintering process and decreases the sintering temperature [4–6]. But the additions of transition metals diminish the properties of pure W such as density and erosion resistance [7]. The novel sintering methods such as spark plasma sintering, microwave sintering and hot isostatic pressing are often used to fabricate refractory metals, due to their fast heating rate and short soaking time [8–14]. However, the specialized equipment requirement of novel sintering methods limits their widespread application.

Refining the grain size of W powders to nanoscale is another way to lower the sintering temperature due to the ultrahigh specific surface area and instability of their free surface [15–20]. Wang et al. showed that nanocrystalline W powders can be pressureless sintered to near-full density at a temperature as low as 1100 °C under a hydrogen atmosphere [16]. Li et al. reported that 91.3% of theoretical density could be obtained when sintered at 1500 °C for 2 h with quasi-spherical W nanopowders synthesized by RF induction thermal process [19]. Nanoscale W powders have been fabricated by various techniques including mechanical alloying [11,21], co-precipitation [22,23], sol-gel [24,25], molten salt [26], Radio-Frequency (RF) induction thermal plasma [6,19]. Xia et al. presented that La_2O_3 doped La_2O_3/W nanoparticles with high-purity and uniform diameters of about 50 nm was prepared by a co-precipitation process and the following hydrogen reduction [22]. Liu et al. reported that nano-sized W-Y_2O_3 and W-La_2O_3 powders were synthesized by sol-gel method followed by hydrogen reduction. The average particle size of the powders was smaller than 50 nm [24]. Nevertheless, these techniques have been somehow faced with some limitations such as sophisticated apparatuses, expensive raw materials, lengthy process, low productivity, etc. Thus, a facile, low-cost, time-saving and scalable route to fabricate W nanopowder remains a practically pressing and technologically challenging task.

Solution combustion synthesis (SCS) is a wet chemical method introduced by Patil in 1988 [27]. It's an exothermal redox reaction between an oxidizer (usually nitrates) and a fuel (e.g. glycine, urea, citric acid, etc.) derived from a homogenous aqueous solution, essentially. In addition to the advantage of wet chemical method, SCS has several particular superiority. Firstly, the exothermal reaction provides the energy required for sustaining the combustion reaction without adding external energy. Secondly, the release of large quantities of gases and the very short reaction duration (in dozens of seconds) lead to

* Corresponding authors.
E-mail addresses: qinml@mater.ustb.edu.cn (M. Qin), zheng_chen1008@163.com (Z. Chen).

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generation of nano-sized powders with high specific surface area. Lastly, simple apparatuses, inexpensive raw materials and high productivity make SCS facile, low-cost and suitable for mass production. SCS has achieved great success in the preparation of nanomaterials, such as metal oxides [28–31], non-oxide ceramics [32,33], etc. However, to our best knowledge, there are few reports on the fabrication of W nanopowder via SCS.

In present study, we used a facile method to prepare W nanopowder by combining SCS and hydrogen reduction. First, by using ammonium metatungstate as tungsten source, ammonium nitrate as oxidizer, glycine as fuel, a fluffy violet precursor has been fabricated by SCS. Subsequently, hydrogen reduction of as-synthesized precursor was utilized to prepare W nanopowder. The as-prepared W nanopowder exhibited high sintering activity.

2. Experimental section

2.1. Raw materials

All the raw materials, e.g. ammonium metatungstate ($(NH_4)_6H_2W_{12}O_{40}\cdot nH_2O$), glycine ($C_2H_5NO_2$) and ammonium nitrate ($NH_4NO_3$), were commercially purchased and of analytical reagent grade.

2.2. Synthesis procedure

Just like typical SCS experimental procedure [28,29], 100 mL pellucid solution containing 0.01 mol $(NH_4)_6H_2W_{12}O_{40}\cdot nH_2O$, 0.17 mol $C_2H_5NO_2$ and 0.40 mol NH_4NO_3 was prepared in a 1000 mL beaker. The as-prepared solution was heated in air on a temperature-controlled hot plate which could be operated up to peak temperature of 250 °C. With heating, the solution turned to gel. As the heating time extended, the mixture swelled dramatically and fierce combustion ensued. Next, the precursor was reduced by high purity hydrogen in a tube furnace. The quartz boat containing the precursor was placed in the central section of the furnace and heated to 450–850 °C with the heating rate of 5 °C/min in a gas flow of 1.2 L/min, then maintained at that temperature for 2 h. After that, the sample was cooled to room temperature, still under a hydrogen flow.

The as-obtained powder reduced at 700 °C was pressed into green compacts under a uniaxial pressure of 700 MPa and holding for 30 s without a binder. The density of green compact was about 50% theoretical density of tungsten, which was determined by calculating the weight divided by the volume of the specimens. The green compacts were sintered in a tube furnace under flowing hydrogen atmosphere. Different temperatures including 1050 °C, 1200 °C, 1350 °C, 1500 °C and 1650 °C were selected with a constant heating rate of 5 °C/min, and the holding time of each temperature was 2 h.

2.3. Characterization

Phase analysis was performed on a Rigaku UltimaIV X-ray diffractometer with a Cu-Kα source with a wavelength of 0.5406 Å. Scanning electron microscopy (SEM) pictures were collected on a FEI Quanta FEG450. Transmission electron microscopy (TEM) images were captured on a FEI G2 F20 S-TWIN instrument. The grain size of powder was calculated from XRD pattern by applying the Scherrer equation. The carbon content was determined by a Carbon/Sulfur analyzer (LECO TC-436), and the oxygen content was determined by an Oxygen/Nitrogen analyzer (LECO CS-444). The grain size of sintered samples were quantitatively measured by particle size analysis software. The densities of sintered compacts were obtained according to the Archimedes principle and relative density was calculated using a theoretical density of W (19.30 g/cm^3). The Vickers microhardness test was completed on the polished samples using microhardness tester under a 200 g·f loading and 15 s duration. At least 10 readings were obtained from sintering samples, and calculated the average results while excluded the highest and the lowest readings.

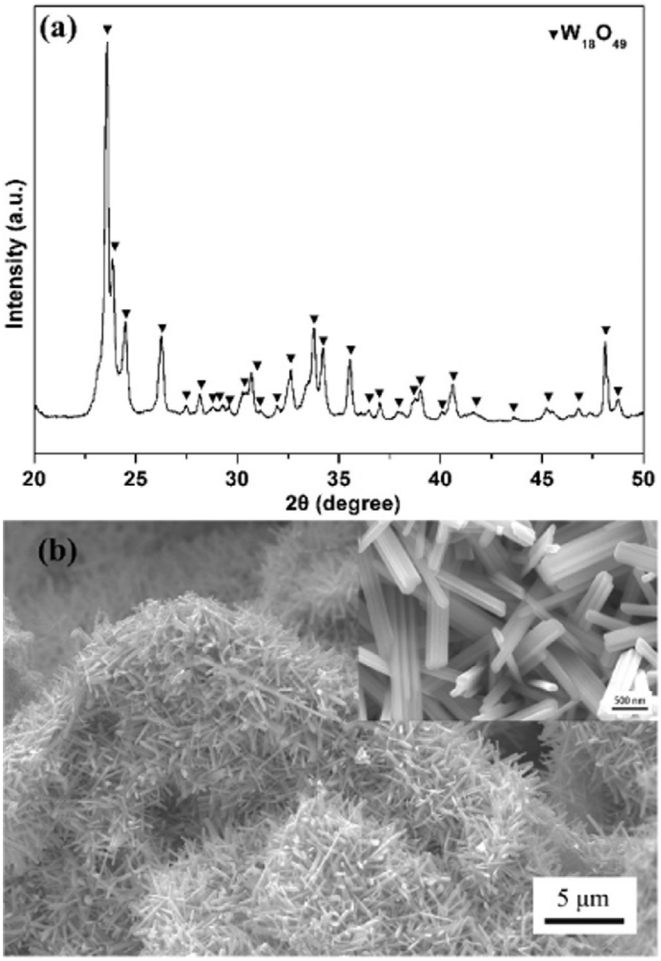

Fig. 1. (a) XRD pattern and (b) SEM image of the precursor.

3. Results and discussion

3.1. Synthesized precursor

Fig. 1 shows the XRD pattern and SEM image of the precursor synthesized by SCS. In Fig. 1a, all the peaks in the XRD pattern of the precursor can be well indexed to the monoclinic $W_{18}O_{49}$ phase (JCPDS 84-1516). It means that the SCS reaction has completely converted ammonium metatungstate to $W_{18}O_{49}$. The precursor is fluffy and composed of needles, as shown in Fig. 1b. The high magnification image gives the detailed morphology of needle-like $W_{18}O_{49}$ which consists of slenderer needles with diameter of about 100 nm. According to the literature, during the reduction process, the nucleation of tungsten crystal at certain site of the nano-needle surface is a type of in-situ nucleation. This nucleation needs the energy much lower than those in 3-D solid due to the fact that nano-needle is a 1-D solid [34]. Thus, the reduction temperature of the as-synthesized precursor will be decreased.

3.2. Hydrogen reduction process

It is well known that the hydrogen reduction process has a great effect on the morphology of the reduced tungsten particles, especially on the diameter. The as-synthesized precursor have been reduced at different temperatures to investigate the phase evolution during the reduction process and determine the most appropriate reduction