

Effect of rare earth element cerium on preparation of tungsten powders

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Abstract: Tungsten powders and Ce doped powders were prepared by hydrogen reduction combined with the liquid-solid doping method. The phase composition, particle size and powder morphology of Ce doped tungsten powders were analyzed by X-ray diffraction, scanning electron microscopy and transmission electron microscopy, respectively. The results indicated that 10000 ppm Ce doped tungsten oxide powders were consisted of WO_3 phase and $Ce_4W_9O_{33}$ phase. The hydrogen reduction of Ce doped tungsten powders was basically accomplished at 800 °C for 3 h. The size of Ce doped W powders was remarkably decreased compared to the undoped W powders. The phase of $Ce_4W_9O_{33}$ was reduced to $Ce_2(WO_4)_3$ phase and $Ce_2W_2O_9$ phase during the process of hydrogen reduction. Moreover, $Ce_2(WO_4)_3$ phase and $Ce_2W_2O_9$ phase were observed from their morphologies, where the doping content of Ce was more than 100 ppm. The ternary phase embedding into W particles was assigned to $Ce_2(WO_4)_3$, while the ternary phase distributing among W particles corresponded to $Ce_2W_2O_9$. The phase of $Ce_2(WO_4)_3$ might be the nucleus of W particles and increase the number of the nucleus. And the particles of $Ce_2W_2O_9$ covered WO_2 particles and might inhibit the growth of W particles. These two reasons resulted in the decrease of the size of Ce doped W particles. Uniform fine W powders were fabricated with the doping content of Ce more than 100 ppm.

Keywords: cerium; tungsten oxide; hydrogen reduction; tungsten powders; rare earths

Due to rare earth element with a strong chemical activity, it is commonly used as a dopant to improve the properties of materials via refining grains, purifying grain boundaries, forming the secondary strengthening phase or ameliorating wettability^[1-5]. As well known, Ce is one of the most widely used dopant^[6-10]. So far, there are extensive reports about the effect of doping elements on microstructure and mechanical properties of W composites^[11-15]. The properties of the tungsten products are mainly dependent on the properties of the starting tungsten reactant, such as the morphology, distribution and size of particles. Growth of tungsten particles generally occurs during the process of hydrogen reduction, therefore reducing the value of the resulting tungsten powder^[16]. However, there are a few reports that specifically refer to the effect of trace elements on preparation of tungsten raw materials through the hydrogen reduction of WO_3 . With regard to the addition of Ce into W powders, there are only two studies reported by the same authors^[17,18]. They found that the existence form of Ce was CeO_2 , which was the nucleation core of W resulting in the reduction of particle size. Unfortunately, the main issue is lack of sufficient evidence to prove it. Thus, it is significant to ascertain the existence form of Ce.

In order to investigate the existence form of Ce and the effect of rare earth element Ce on the hydrogen reduction behavior of tungsten oxide, the high-quality W powders doped with rare earth were prepared by the liquid-solid doping method in which Ce doped APT was employed as the raw materials in the present work. The effects of Ce doping contents on microstructure, grain size and formation of new phase were systematically discussed from the stage of calcined to hydrogen reduction.

1 Experimental

The commercially APT was used as raw materials to fabricate tungsten oxide (WO_3). Analytically pure $Ce(NO_3)_3 \cdot 6H_2O$ with the property of easy soluble in water acted as the dopant. According to the stoichiometric ratio calculation, the weights 50, 100, 1000 and 10000 ppm of Ce were dissolved in the right amount of deionized water, respectively. Before drying at 80 °C in an oven, the four solutions were all fully mixed with the right amount of APT. Then the pure and doped APT powders were calcined at 600 °C for 2 h in a muffle furnace to remove organic salt components. Finally, the obtained W-Ce composite oxide powders were reduced into

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tungsten powders by hydrogen atmosphere at 800 °C for 3 h in a tube reduction furnace and cooled with the furnace in the H₂ protection atmosphere. The dew point of hydrogen was -40 °C and its flow rate was 0.4 m³/h. The boat load was about 3–4 g in the reduction boat with the size of 60 mm×30 mm×14 mm and oxide layer height was approximately 1.5–2mm.

The phase composition of calcined and reduced W-Ce composite oxide powders were determined by X-ray diffraction (XRD D8-Focus Bruker-AXS). Morphology and particle size of doped powder were characterized by field emission scanning electron microscopy (FESEM Nova NanoSEM450 FEI) with energy dispersed spectroscopy (EDS INCA Energy 250 X-max 50 Oxford Instruments). Further morphology observation and structure analysis of reduced tungsten powders were carried out by high resolution transmission electron microscopy (HRTEM JEM-2100F JEOL) equipped with energy dispersed spectroscopy (EDS INCA Energy 300 mics/x-stream Oxford Instruments).

2 Results and discussion

2.1 Microstructure of Ce doped tungsten oxide

Fig. 1 shows the XRD patterns of tungsten oxide powders and Ce doped powders both calcined at 600 °C for 2 h. The diffraction spectrum (1) shows that tungsten oxide powders contain WO₃ phase. As shown in pattern (2), Ce doped tungsten oxide powders consisted of WO₃ phase and Ce₄W₉O₃₃ phase. It indicates that a new phase of Ce₄W₉O₃₃ is formed at this temperature during the process of calcination due to the rare earth element Ce reacted with WO₃.

SEM images of tungsten oxide powders calcined at 600 °C for 2 h are shown in Fig. 2. It is observed that the size of Ce doped tungsten oxide powder is smaller than that of undoped tungsten oxide powder (Fig. 2(a) and (b)). The reason is likely ascribed to the effect of Ce₄W₉O₃₃ particles, which can increase the number of the nucleation and inhibit grain growth of tungsten oxide. In addition, it is also noted that the size of the area contained Ce (Fig. 2(c)) is smaller than that of the area with-

out Ce (Fig. 2(b)), which further illustrates the effect of Ce₄W₉O₃₃ particles.

2.2 Reduction of Ce doped tungsten oxide

The XRD patterns of tungsten oxide powders and Ce doped powders both reduced at 800 °C for 3 h are shown in Fig. 3. The tungsten powders (Fig. 3(1)) show a single W phase. Curves (2) and (3) show that Ce doped tungsten powders mainly exist as W phase and the rest of the samples exist as Ce₂W₂O₉ phase and Ce₂(WO₄)₃ phase. The phase of Ce₄W₉O₃₃ is reduced to Ce₂W₂O₉ phase and Ce₂(WO₄)₃ phase during the process of hydrogen reduction. From these spectroscopic results, the hydrogen reduction of Ce doped tungsten powders is basically accomplished at 800 °C for 3 h.

After ultrasonic dispersion, SEM images of Ce doped tungsten powders reduced at 800 °C for 3 h are presented in Fig. 4. The morphology of W particles (Fig. 4(a)) is basically polyhedron and the size is non-uniform at the range from dozens of nanometers to 3 μm. It can be found that most surfaces of bigger polyhedron have a layered growth structure as shown in the white arrow, which results from the growth model of chemical vapor transport and condensation during the reduction process^[19]. With the addition of Ce, the size of W particles is remarkably decreased and the morphology is spherized (Fig. 4(b), (c) and (d)) compared with that of undoped W particles.

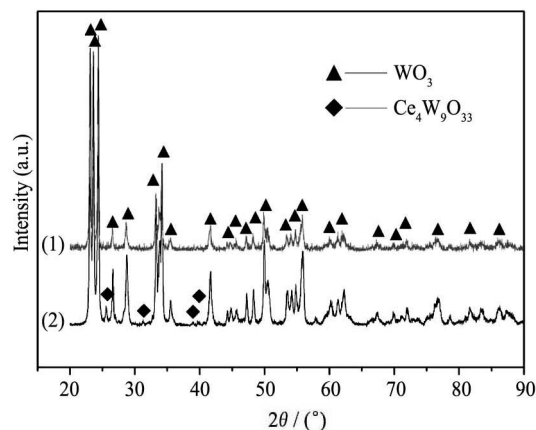


Fig. 1 XRD patterns of undoped (1) and 10000 ppm Ce doped (2) tungsten oxide powders calcined at 600 °C for 2 h

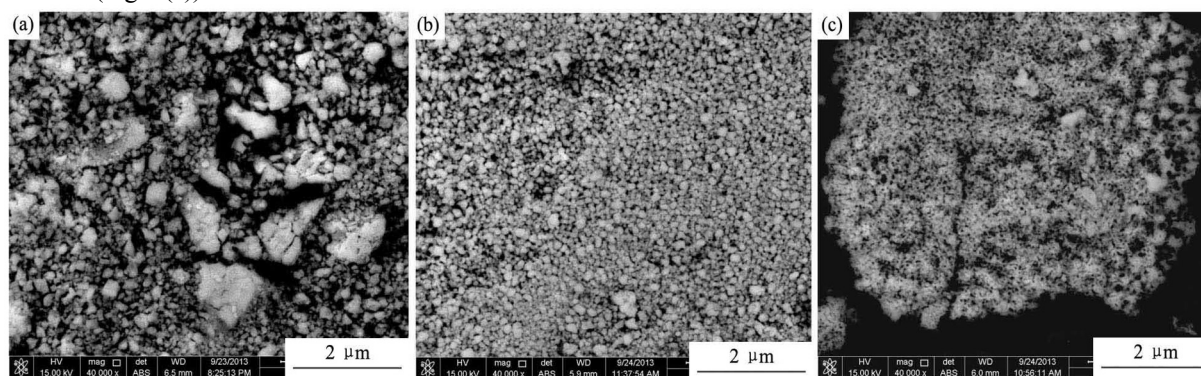


Fig. 2 SEM images of tungsten oxide powders calcined at 600 °C for 2 h (a) Undoped; (b, c) 10000 ppm Ce doped

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