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Synthesis, densification and characterization of ultra-fine W-Al_2O_3 composite powder

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ABSTRACT

W-Al_2O_3 composite powder was prepared via hydrothermal synthesis containing doping, annealing and reduction. The precursors WO_3 and AlOOH were synthesized by the two sets of the hydrothermal reactions, respectively. The formation of $Al_2(WO_4)_3$ from these two precursors in an aqueous solution is a key process, which is beneficial to improve the mixing uniformity of final powder to a molecular level. During subsequent reduction, nano-Al_2O_3 coated W particles were obtained, and inhibited the further deposition of reduced W atoms on the adjacent W particles, obtaining ultra-fine Al_2O_3/W composite powder. After sintering, the dense and fine-grained W-Al_2O_3 alloy was obtained due to the high sintering activity of ultra-fine powder. Compared with the pure tungsten, the W-Al_2O_3 alloy displays obvious higher values of both strength and plasticity especially when the Al_2O_3 content is 2 wt%.

1. Introduction

Tungsten and its alloys have received more attention due to their high melting point, and excellent mechanical properties at high temperatures [1,2]. Tungsten alloys are widely used in the fields of military, aerospace and mechanical processing, such as the armour-piercing head and the spacecraft gyroscope rotor [3,4].

In order to improve the service life and stability of tungsten alloys, refining grains and second-phase strengthening have been widely adopt to improve the low-cycle fatigue resistance, toughness, recrystallization temperature and high-temperature strength [5]. With excellent stability and high melting points, the oxides (La_2O_3, Y_2O_3, Al_2O_3, etc.) are usually added to W alloys as reinforced phases [6]. Tungsten doped with La_2O_3 exhibits a higher recrystallization temperature, a better machining capacity, and excellent mechanical properties at elevated temperatures [7]. However, some La_2O_3 particles melt and even lots of microcracks appear on the surfaces of compacts, when the heat flux density increases to 5 MW/m^2 and above during powder-metallurgy sintering [8]. As a stable oxide, fine Y_2O_3 particles in the W matrix can significantly suppress the growth of W grains, and enhance the high-temperature strength and creep resistance [9,10]. Moreover, Y_2O_3 can enhance the sinterability, as manifested by a decrease in sintering temperature [11–14]. However, the volatile Y_2O_3 is poisonous to humans, and thus restricted for addition.

In this paper, Al_2O_3 was took as the second phase to reinforce tungsten on the base of its excellent advantages including high hardness and strength, well chemical stability, outstanding high temperature properties and low cost. W-Al_2O_3 composite powder was successfully produced by hydrothermal synthesis, providing the original powder for preparing good performance tungsten alloys.

2. Experiment Procedures

The mass fraction of Al_2O_3 was firstly designed as 1% in the final Al_2O_3/W powder, and the other contents of Al_2O_3, such as 2 wt% and 3 wt%, could be prepared using the similar method. Commercial powders of $(NH_4)_6H_2W_{12}O_{40}{\cdot}4H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ and $CO(NH_2)_2$, and HNO_3 solution (66 vol% in purity) were used as the raw materials. 303 g of $(NH_4)_6H_2W_{12}O_{40}{\cdot}4H_2O$ was dissolved into 200 ml of deionized water, followed by the addition of 250 ml HNO_3 solution (keeping 9 mol/L). At the same time, 16.5 g of $Al(NO_3)_3{\cdot}9H_2O$ and 3.96 g of $CO(NH_2)_2$ were dissolved into 450 ml of deionized water. The two mixed solutions were stirred and then transferred into 1000 ml PTFE liners of stainless steel autoclaves, where the hydrothermal synthesis took place at 180 °C for 20 h, namely liquid-liquid doping. The pressure is 3 MPa no more than the rated pressure of autoclave. The synthetic products underwent a series of treatments including washing, filtrating via a vacuum filter and drying in a vacuum oven at 80 °C for 12 h.

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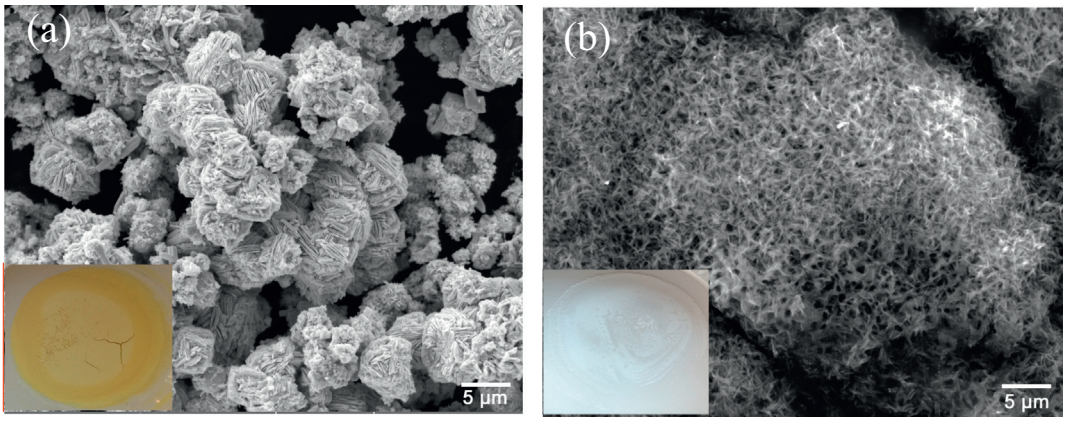

Fig. 1. SEM images of the hydrothermal products (a) I and (b) II.

Subsequently, this dried powder was annealed at 550 °C in air for 5 h at a heating rate of 5 °C/min, and then the annealed powder was reduced in sequence at 580 °C for 2 h and 900 °C for 2 h under the atmosphere of H_2. For the sake of comparison, the pure W powder was also obtained by the hydrothermal Method. The densification of W-Al_2O_3 composite powder was conducted via cold isostatic pressing and then sintering in H2 atmosphere at 2200 °C. The compression samples (8 mm in diameter and 12 mm in length) were investigated on a mechanical testing machine (CCS-44100) at room temperature at a strain rate of 0.5 mm/min.

Morphologies of the powder were observed using scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). The phases of the powder were analyzed using X-ray diffraction (XRD) and transmission electron microscopy (TEM).

3. Results and Discussion

3.1. Hydrothermal Synthesis

The morphologies of the products from two sets of hydrothermal reactions are shown in Fig. 1(a) and (b), respectively. The product I is light yellow in color and irregular blocky in shape. From XRD analysis in Fig. 2, the product I is identified to be mainly composed of WO_3 and $WO_3(H_2O)$ with a small amount of NH_4NO_3. Therefore, $(NH_4)_6H_2W_{12}O_{40}{\cdot}4H_2O$ reacted with HNO_3 to form WO_3 during hydrothermal synthesis, and exactly to form a mix of stable monoclinic WO_3, metastable hexagonal WO_3 and $WO_3(H_2O)$ (see Eqs. (2) and (3)). The product II is light white, and exists in the shape of fibrous nanoplates. NH_4NO_3 and AlOOH peaks were detected by XRD, indicating that $Al(NO_3)_3{\cdot}9H_2O$ reacted with $CO(NH_2)_2$ to synthesize AlOOH and NH_4NO_3 (see Eq. (3)).

Chemical reactions of hydrothermal synthesis can be determined as

$$(NH_4)_6H_2W_{12}O_{40} + 6HNO_3 = 12WO_3 + 6NH_4NO_3 + 4H_2O \quad (1)$$

$$WO_3 + H_2O \rightleftharpoons WO_3(H_2O) \rightleftharpoons H_2WO_4 \rightleftharpoons 2H^+ + WO_4^{2-} \quad (2)$$

$$2Al(NO_3)_3 9H_2O + 3CO(NH_2)_2 = 2AlOOH + 3CO_2 + 6NH_4NO_3 + 2H_2O \quad (3)$$

3.2. Liquid-Liquid Doping

Fig. 3(a) is the XRD results of the product after liquid-liquid doping. Other than the disappearance of $WO_3(H_2O)$, there are no obvious changes in phases after liquid-liquid doping, i.e. WO_3 particles still exists as a mix of monoclinic and hexagonal structures. From the SEM images of doped product in Fig. 3(b), the particles transform into regular spheres from the previous irregular clumps, and display well dispersibility and homogeneous.

Based on the Colloid adsorption theory [15], WO_3 and WO_4^{2-} can absorb each other and then form a new colloid group with negative charges because of their similar structure. The Zeta potential value of hydrothermal product I measured experimentally is −22.7 mV, which proves the above speculation. In term of the Zeta potential value of 46.1 mV, AlOOH colloid particles have high positive electricity and are easy to cover on the surfaces of WO_3-WO_4^{2-} colloid groups. The WO_3-WO_4^{2-} colloid groups are thus isolated each other by this coated structure, refining and homogenizing WO_3 particles. Fig. 4 illustrates the mixing process of the two colloid groups.

3.3. Annealing Treatment

The XRD pattern of the annealed powder is shown in Fig. 5. After annealing at 550 °C for 5 h, nearly all of the metastable hexagonal and

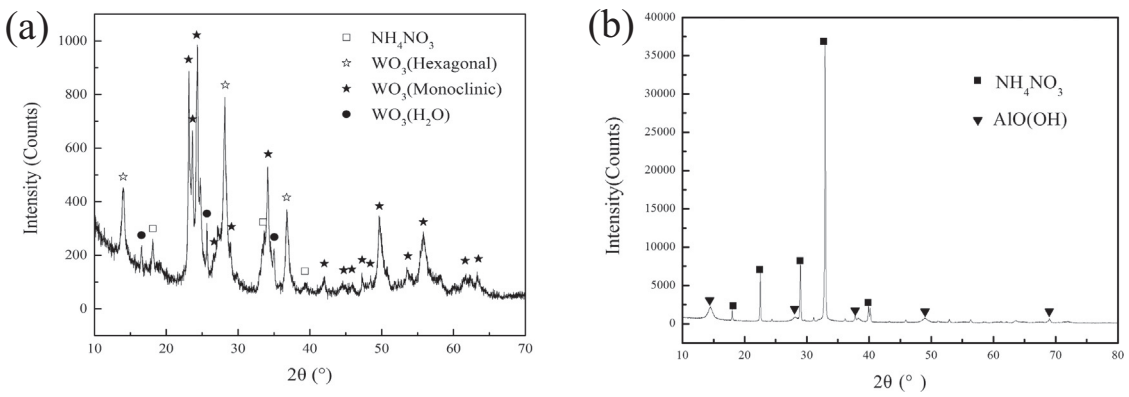

Fig. 2. XRD patterns of the hydrothermal products (a) I and (b) II.