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Chemically produced tungsten–praseodymium oxide composite sintered by spark plasma sintering

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HIGHLIGHTS

- Wet chemical method was used to prepare highly uniform Pr_2O_3 doped W–Pr_2O_3 powder.
- The Pr_2O_3 particles significantly refine the grain size of tungsten alloy.
- The tensile strength of Pr_2O_3/W samples were higher than those of pure W samples.

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ABSTRACT

Pr_2O_3 doped W composite were synthesized by a novel wet chemical method and spark plasma sintering. The grain size, relative density and the Vicker hardness $HV_{0.2}$ of Pr_2O_3/W samples were 4 μm, 98.3% and 377.2, respectively. The tensile strength values of Pr_2O_3/W were higher than those of pure W. As the temperature rises from 25 °C to 800 °C, the conductivity of pure W and W–1 wt% Pr_2O_3 composites decreased with the same trend, was above 150 W/m K.

1. Introduction

As a refractory metal with the highest melting point (3440 °C), tungsten is supposed to be the most promising candidate for plasma facing first wall material in future fusion reactors due to its superiority to other materials in many respects, including good thermal conductivity, low thermal expansion coefficient, high moduli of elasticity, good thermal shock resistances, high strength at elevated temperatures, low sputtering yield, high sputtering resistance and low tritium inventory [1–8]. Tungsten materials, however, are facing serious challenge of brittleness in different aspects i.e. low-temperature brittleness, recrystallization brittleness and radiation induced brittleness [9–13]. Second-phase particles (La_2O_3, Y_2O_3, TiC, HfC, Ta_2C, TiN, etc.) [14–16] dispersoids can play a major role in mitigating these problems. Rare-earth oxide particles are particularly effective, because they can gather solutes owing to strong rare-earth–oxygen interactions. They can refine the grains by promoting grain nucleation and hindering grain growth. The refined microstructure will result in not only a significant increase in strength, but also abundant grain boundary areas that can depress the concentration of deleterious solutes in the lattice [17].

A commonly used method to produce nanosized oxide dispersed strengthened (ODS) tungsten powders is mechanical milling (MM) or mechanical alloying (MA). However, the oxide nanoparticles still tend to be agglomerated to some extent because of the high surface energies introduced, typically with submicron or micron size [18,19]. The milling processing also results in contamination by the wear of the milling equipment and media. Nanostructure tungsten based powders can also be made by bottom-up methods starting from the atomic or molecular level. The wet-chemical process has been proved to be effective in fabricating complex nanostructured materials, and has shown high promise for the preparation of nanomaterials with precise composition with very high purity and homogeneity [18–22]. The method is also suited for the fabrication of tungsten based composites. A major challenge in the sintering of nanopowders is to achieve full densification while preserving the nanoscale. One such recent technological innovation is the use of spark plasma sintering (SPS), which is a pressure-assisted sintering that utilizes a large pulsed DC current (1000–5000 A) to heat the compacts and molds. SPS process provides fast heating rate (up to 1000 °C/min) and

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short sintering time, and allows the consolidation of powder materials into dense fine-grained products at lower sintering temperature [23–25].

In this paper, we have developed a novel method for the synthesis of nano ODS-W powders, in which a precursor of tungsten and metal oxides is prepared by the reaction of tungsten and praseodymium salts in aqueous solution at room temperature. The obtained precursor is highly homogenous where the two components are mixed at the molecular level. The doped precursor was reduced in hydrogen atmosphere and the reduced powders were then sintered into W–Pr_2O_3 composites by SPS to demonstrate their homogenous distribution and the sinterability of the as-synthesized Pr_2O_3/W powders. It is concluded that the powder could be consolidated to a uniform ultrafine bulk material with oxide particles dispersed both inside and at the boundaries of the tungsten grains.

2. Experimental procedure

2.1. Precursor synthesis, reduction and sintering

Ammonium paratungstate hydrate (APT, Aladdin) was suspended in an aqueous solution of praseodymium nitrate hexahydrate (Aladdin) to synthesize praseodymium doped tungsten precursors with praseodymium content corresponding to W–1 wt% Pr_2O_3. About 30 g of APT ($H_{42}N_{10}O_{42}W_{12}{\cdot}xH_2O$) and 0.56 g of praseodymium nitrate ($PrN_3O_9{\cdot}6H_2O$) were dissolved in sequence in 150 ml of deionized water under vigorous stirring at room temperature. The solution was filtered after 24 h reaction to ensure complete reaction between APT and Pr ions and the obtained powder was dried at 60 °C for 2 h. The powder was then calcined under nitrogen atmosphere at 450 °C for 1 h whereby the powder was transformed into oxide mixture. Next, the precursor was reduced by high purity hydrogen in a single-tube electrically heated furnace. The boat containing the precursor was placed in the central section of the furnace tube and heated to 800 °C at 5 °C/min in a gas flow, then maintained at that temperature for 6 h. After that, the sample was cooled to room temperature, still under a hydrogen flow. In a separate experiment, the as-received APT was reduced to pure tungsten powder under the same conditions.

The consolidation of the samples was carried out through SPS (FCT Group, SE-607, Germany) technique. The temperature profile of the sintering program in this study was illustrated in Fig. 1. Under the action of a uniaxial pressure increased slowly to 43.3 MPa, the powders were heated by pulse current to 450 °C. Then under the constant pressure of 43.3 MPa, the powders were heated to 700 °C with a heating rate of 50 °C/min. The powders were held at 700 °C for 2 min and the pressure was increased from 43.3 MPa to 57 MPa at the same time. All these above sintering processes were conducted in vacuum. Then a flowing gas mixture of argon and hydrogen atmosphere was used for the following sintering processes. The samples were heated to 1300 °C with a heating rate of 100 °C/min and held at 1300 °C for 20 min. Subsequently, the samples were heated to 1800 °C at a heating rate of about 100 °C/min, and after 2 min soaking they were cooled down to room temperature with a cooling rate of 100 °C/min. The size of the sintered samples was about 20 mm in diameter and 2.0–3.0 mm in thickness. Densities measurements of sintered samples were conducted by the Archimedes method. The relative densities (RD) were calculated using theoretical densities of tungsten and Pr_2O_3 as 19.3 g/cm^3 and 6.85 g/cm^3 respectively. Polished sintered samples were subjected to Vickers microhardness testing under 200 g loads and a dwell time of 20 s at room temperature. The Vickers microhardness was calculated as a mean of ten measurements.

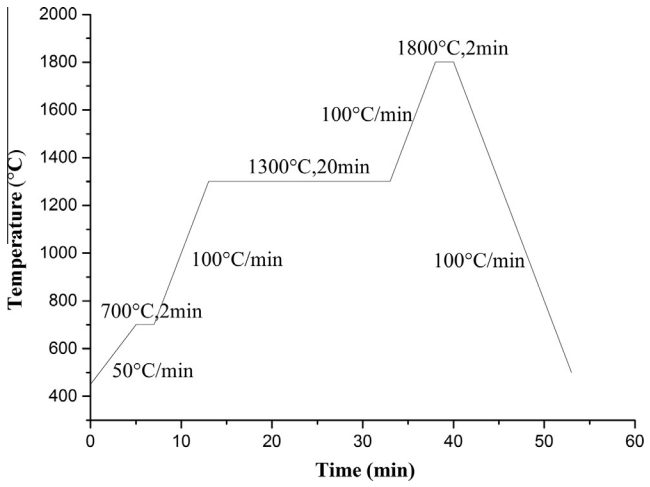

Fig. 1. Temperature profile of SPS process for the pure tungsten and W–Pr_2O_3 composites.

2.2. Microstructure characterization

The microstructure and particle morphology of the precursor and reduced powders were studied by field emission scanning electron microscope (FE-SEM, SU8020) and energy dispersive X-ray spectrometer (EDS) analysis detectors. X-Ray diffraction (D/MAX 2500V) was employed for the characterization of the prepared materials. The morphologies of the SPS-sintered bulk tungsten materials were characterized by FE-SEM and transmission electron microscopy (TEM, JEF-2100F). Energy-dispersive X-ray spectroscopy (EDX) analytical system installed on TEM was used for elemental analysis. Grain sizes were measured from Secondary Electrons (SE) images of fractured samples. TEM samples were sectioned with a diamond saw and mechanically ground to about 50 μm thick circular discs with 3 mm in diameter. The samples were dimpled to about 20 μm and then ion thinned with Ar^+ ions until perforation occurred.

2.3. Tensile property test

Tensile testing was performed using Instron testing machine (Instron 5967). The tensile test specimens are dog-bone shaped with an overall length of 16 mm, a gauge length of 5 mm and an effective cross section of 4 × 0.75 mm as shown in Fig. 2. The behaviors of BCC metals show a strong dependence of the yield stress on the strain rate and temperature. Moreover, the yield stress of W is strongly temperature dependent, and one expects a strong rate dependence of the flow stress. Therefore, the tests were performed with strain control and deformation speed of 0.05 mm/min was applied. For the alignment of the specimen, a preloading of 5 N was applied.

2.4. Thermophysical properties test

Thermal conductivity test was performed using laserflash thermal analyzer (LFA 457, Germany). Measurements of thermal diffusivity (α) of the materials from room temperature to 800 °C

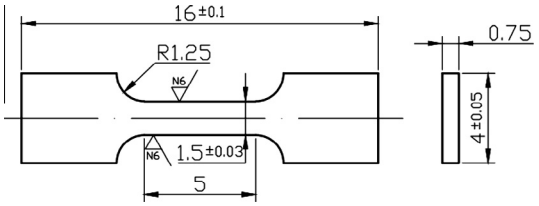

Fig. 2. Drawing of the tensile specimen with dimensions.