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Densification behavior, mechanical properties and thermal shock resistance of tungsten alloys fabricated at low temperature

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ABSTRACT

The low-temperature shrinkage of tungsten was greatly accelerated by the addition of trace Nb and Ni, and the addition of trace Nb and Ni also significantly promoted the final sintering density. The 99.1% of theory density for W–0.1 wt.%Nb–0.1 wt.%Ni material sintered at 1600 °C was obviously greater than 93.7% of theory density for W material sintered at 2000 °C. Ball milling treatment played an important role in promoting the sintering densification of W–0.1 wt.%Nb–0.1 wt.%Ni powder, and the powder milled for 10 h (W10) could be sintered to near full density (99.4% of theory density) at 1600 °C. The ball milling for 15 h has no effect in improving the sintering density, but it induced rapid growth of tungsten grains. The microhardness and tensile strength of the sintered tungsten alloys were highly dependent on its sintering density and grain size. Improving the sintering density while controlling the grain growth could effectively promote the microhardness and tensile strength. Furthermore, the improvement of thermal shock resistance of the W10 alloy was due to good microstructure and the increase in the tensile strength.

1. Introduction

Tungsten (W) alloys are widely used as an important candidate material for various structural applications at high temperature [1] due to its excellent properties such as high melting point, high density, high modulus and thermal shock resistance, low coefficient of thermal expansion and good high temperature strength [2]. Various grades of W alloys are classified [3]: pure W, dispersion-strengthened W, and W alloys produced by different fabrication technologies, e.g. sintered, forged, rolled and hot-worked (deformed). Besides the fabrication, the raw powder materials, the alloying elements and dopants/impurities, treatments, and the final shape/geometry have a strong effect on the achieved properties of W and W alloys [4]. Since W alloy is extensively applied in the highly sophisticated field, it is required that the material should have near full densification (>99% of theory density), so as to make full use of its excellent properties [5]. However, an extreme temperature as high as 2700 °C is required for traditional microsized tungsten powder to be sintered to near full density since it has a very high melting point of 3422 °C [6]. In order to fabricate high density W alloys at a low temperature, in recent years, the researchers have used nanotechnology to synthesize nanometer tungsten powder which can provide a large driving force for sintering due to its abundant surface energy and grain-boundary energy, which is called nanometer activation [7]. Although preparing nanometer tungsten powder can theoretically improve its sinterability, the fact that nanometer tungsten powders can be directly sintered to near full density (>97% of theory density) has never been reported.

Furthermore, transition element niobium (Nb) is a ductile and soft refractory metal with low melting point (2468 °C) compared with W [8], low vapor pressure, good chemical stability, and good strength retention at elevated temperatures [9]. It has been extensively applied in aerospace, electronic devices, steel industry, nuclear industry, and chemical engineering industry. In all applications, approximately 75% of all Nb metal is used as an addition to low-alloyed steels. Another 20–25% is used as an additive in nickel base superalloys and heat resisting steels. Only 1–2% is used in the form of pure niobium and Nb-based high temperature alloys [10]. The Nb alloy is made by melting and mixing two or more metals and the mixture has properties different from those of the individual metals [11]. In addition, transition element nickel (Ni, melting point is 1455 °C) is used primarily for the alloys it forms. It is used for making stainless steel and many other corrosion resistant alloys. Nevertheless, up to date, there are only a few papers devoted to the study on addition of Nb and/or Ni to W alloys. Furthermore, niobium and nickel have been theoretically proved

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to be an excellent accelerator for the sintering densification of tungsten, which is called chemical activation, but there has also rarely been reported that tungsten can be sintered to near full density by adding trace niobium and nickel [12].

In the present work, the W alloys with high relative density were produced at low temperature by the combination of the nanometer activation method and chemical activation method. The nanometer tungsten powder (i.e. W–0.1 wt.%Nb–0.1 wt.%Ni composite powder) was first prepared by the physical and chemical method and then the composite powder was ball milled for different times (0 h, 10 h and 20 h), and the activated composite powders were finally achieved. The effects of ball milling time on the densification behavior of the activated composite powder were investigated in detail. Most of W alloys, because of inherently low fracture toughness, are susceptible to catastrophic fracture caused by the thermal stresses in applications at high temperature. Therefore, the thermal shock resistance of the W alloys was evaluated by water quenching method. The purpose of this work is to report a potential method for fabrication of W alloys at low temperature, which can be applied to aid materials engineering design for the development of W alloys, quality assurance, and characterization assessment of durability.

2. Experimental details

The ammonium metatungstate, niobium nitrite ($Nb(NO_2)_5$) and nickel nitrite ($Ni(NO_2)_2$) were used as raw materials for the synthesis of nanometer tungsten powder. A sol was prepared by dissolving ammonium metatungstate, niobium nitrite and nickel nitrite with a small amount of polyethylene glycol (PEG-2000) into the distilled water. The nanometer W–0.1 wt.%Nb–0.1 wt.%Ni composite powder was then gained by a multi-step process, consisting of sol–spraying–drying of the solution at 250–350 °C, calcining at 300 °C for 2 h and a subsequent two-step reduction process (600 °C and 750 °C) in hydrogen atmosphere for 1.5 h and 2.5 h, respectively. The calcined composite powder was ball milled in a W alloys bottle for different times, and the milling conditions are listed in Table 1. The ball mill activated nanometer tungsten powders were obtained and a pure tungsten powder without addition of niobium and nickel was also synthesized using the same production process for comparison, the pure tungsten powder, W–0.1 wt.%Nb–0.1 wt.%Ni composite powder, W–0.1 wt.%Nb–0.1 wt.%Ni composite powder ball-milled for 10 h and 15 h were denoted as W, W0, and W10 and W15, respectively.

X-ray diffraction meter (D/ruax2550PC, Japan) was employed to identify the phases of these powders, and ultra high resolution field emission scanning electron microscopy (SEM, NOVA TM NanoSEM 230, Czech) was used to characterize the morphology of these powders. The oxygen content in these powders were determined by a nitrogen/oxygen/hydrogen determination (TCH-600, USA), the specific surface area of each powder was measured by a BET surface area analysis instrument (Monosorb Autosorb-1, USA). The crystalline phase was determined using the X-ray diffraction (XRD) (Rigaku, Japan). The broad–scan analysis was typically conducted within the 2-θ range of 10–80° using the Cu Kα (λ = 1.542 Å) radiation. The narrow scan analysis was conducted within the 2-θ range of 20–30° and was subsequently used to determine "Bragg" grain size. The BET grain size was determined using the surface area measurement technique. It was found that these tungsten powders were difficult to be shaped because of their nanometer particle size, so they were mixed with 0.5 wt.% paraffin prior to forming, then they were pressed into standard tensile samples by two-direction cold pressing with pressure of 250 MPa. The green compacts were pre-sintered at 1000 °C in atmospheric pressure of 5 Pa for 2 h in order to eliminate the paraffin, later pre-sintered compacts were sintered in tungsten rod furnace at different temperatures (1500 °C, 1600 °C, 1700 °C, 1800 °C, 1900 °C, 1950 °C, 2000 °C and 2030 °C) for 2 h, heating rate was 2 °C/min and flowing H_2 was employed as the protective atmosphere. The densities of the sintered specimens were measured by Archimedes principle with deionized water as the immersing medium. The quasi–static mechanical properties of these specimens were measured by a standard Instron 3369 material test machine (USA) and the tensile speed was about 1 mm/min according to ASTM:A356 (6 mm × 3 mm × 60 mm). The hardness of specimen was tested by a nanoindentation method and load of 50 mN.

Table 1
Ball milling parameters used in the present work.

Milling medium	Ethanol
Grinding medium	Tungsten balls (3–10 mm in diameter)
Ball to powder ratio	3:1 (mass ratio)
Liquid to solid ratio	3:1 (volume ratio)
Plate and bowl speed	240 rpm
Milling time	10 h, 15 h

The thermal shock resistance can be appraised by water quenching method based on the definition of the critical thermal shock temperature difference (ΔT_{crit}). The ΔT_{crit} can be measured experimentally by quenching specimens from various elevated temperatures and determining the quenching temperature that results in a reduction of strength for a given specimen geometry [13]. The ΔT_{crit} value is defined as 70% of the room temperature strength, which was determined using linear interpolation of the retained strength values as described in ASTM:C1525-04. Before the water quenching, all samples were ground and polished with diamond slurries down to a 1 μm finish and the edges of all samples were chamfered to minimize the effect of stress concentration due to machining flaws. At least ten samples were tested for each experimental condition and all samples were from same billet. The polished rectangular bars for thermal shock testing were heated in the vacuum up to the desired temperature difference and held for 10 min to eliminate any temperature gradient effect before quenching by dropping parallel to their tensile surface into the water bath. The temperature of the water bath was controlled to about 25 °C by adjusting the cooling water flow. The water quenching temperature differences were 200, 300, 400, 500, 600 and 700 °C. The 5 Pa was kept for the samples heated in vacuum and the time taken for the transfer from the furnace to the water bath was less than 1 s. A digital microhardness tester (HXD-1000T) was employed to determine the microhardness of the sintered tungsten bulk, and the tensile strength was tested by means of mechanical testing machine (Instron3369, USA).

3. Results and discussions

3.1. Phase and performances of these powders

The XRD patterns of four kinds of powders (W, W0, and W10 and W15) are shown in Fig. 1, which indicated an increase in peak broadening with progress of milling. The peaks of Nb and Ni were not detected due to low amounts of Nb and Ni. Using a combination of W(1 1 0) and W(2 1 1) peaks, the grain size and lattice distortion were calculated according to the XRD patterns as shown in the following equation [14]:

$$\beta \cos\theta = 0.94(\lambda/d) + 4\varepsilon \sin\theta \quad (1)$$

where β is the full-width at half-maximum (FWHM), θ is Bragg angle, λ is the X-ray wavelength, d is grain size and ε is lattice distortion. The broadening factors that are not induced by ball milling were taken out by the following equation [14,15]: