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Short communication

High-pressure preparation of bulk tungsten material with near-full densification and high fracture toughness

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ABSTRACT

In this work, we present a novel method to sinter tungsten bulk material under high pressure without any additives. The sintering temperatures were greatly reduced in our experiments. The sintered samples can achieve near-full densification (relative density of 99.5%), and have fracture toughness of about 50% higher than that from the traditional methods, without sacrificing hardness. Moreover, the grain sizes of the sintered samples maintained in the initio range. The sintering kinetics, microstructure evolutions, and relationships of mechanical properties versus pressure–temperature conditions were also discussed.

1. Introduction

Tungsten (W) has been regarded as an important candidate material for various structural applications at elevated temperatures, owing to its excellent properties such as high melting point (3410 °C), high density, high elastic modulus, great resistance to thermal shock, excellent thermal conductivity, low thermal expansion coefficient, and good high temperature strength. In addition, because of its high density and high atomic number ("high-Z"), considerable applications are also involved in medical X-ray as well as in nuclear components, including shielding [1–3].

Since tungsten possesses a very high melting point, fabrication of its fully dense bulk material with desirable properties through conventional powder metallurgy method, in general, involves relatively high temperature and long time. In the meantime, this in turn leads to considerable grain growth, and thus difficult to maintain the scale of starting grain size in the sintered products [4]. As reported, in a conventional process, a fully dense tungsten body is difficult to achieve even at the sintering temperature as high as 2500 °C [5]. Yih et al. also reported that, to get the relative density close to 96% by conventional sintering method, the 1.05 μm tungsten powder had to be sintered at 2200 °C for 10 h [6]. Various approaches were tried to improve the sinterability of tungsten. For example, Jain et al. sintered submicron tungsten powder in a microwave field method [7]. In their experiments, relative density of the sintered bodies could be reached up to 98.5%, with sintering temperature of 1450 °C for 20 min, followed by isostatic pressing at 1500 °C, 100 MPa for 60 min. But the grain size grew up to around 24 μm. Wang et al. reported that mechanical milling could improve the sinterability of nano-tungsten powder in pressureless sintering [8]. In their work, relative density of 97% was obtained, with the sintering temperature as low as 1100 °C and the holding time of 60 min. But unfortunately, the final grain size was not reported yet.

To minimal the grain growth, and produce a fully dense tungsten body, a number of efforts have been done in recent years. It is reported that additives could enhance densification of tungsten [5,9]. For the W—5 wt.% Y_2O_3 composites, which were sintered at 1700 °C and 30 MPa for 3 min [9], the grain size of the achieved fully dense body was reduced from 18.8 μm (for the sintered tungsten without additive, and with relative density of 96%) to 3.7 μm. Field assisted sintering technology (FAST) was also employed by Chanthapan et al. [4]. For the W—10 vol.% WC system, with the initio grain sizes of 0.6–0.9 μm, the corresponding grain size and the relative density of the sintered body were 3.1 μm and 99.6%, respectively, after a sintered process at 1800 °C and 85 MPa for 5 min. Han et al. [10] reported that the ball milled W—0.1 wt.% Ni powder can achieve relative density of 99.4% when sintered at 1600 °C for 5 h, but the grain size was increased from the nano-scale to micro-scale.

As mentioned above, it is clear that, when using the conventional sintering methods without any additives, controlling both density and grain size of the sintered tungsten at the same time is a challenging job. Although adding transition metals or oxides as activators may reduce the sintering temperature and achieve fully dense body with minima grain growth, however, the additives may affect properties of sintered tungsten, and thus limited its applications. In this work, we present a novel method to prepare tungsten bulk material at high

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pressure without any additives. The as sintered tungsten materials could achieve near-full densification (relative density of 99.5%) and have high fracture toughness. Moreover, the grain growth of the tungsten particles was effectively inhibited, with the grain sizes of the sintered samples maintaining in the initio range. The feasibility of this method to consolidate tungsten compacts at different temperatures and pressures was demonstrated systematically, and the sintering kinetics and microstructure evolution were also studied in detail.

2. Experiment

The tungsten powder (99.98% purity, Aladdin Co., Ltd., China), with particle sizes in the range of 1–5 μm was used as the starting material. The scanning electron microscope (SEM) images and X-ray diffraction (XRD) patterns of the powder are shown Fig. 1. High pressure sintering experiments were carried out on a DS6 × 14MN cubic press. The cell assembly and experimental methods were described elsewhere [11]. Before each high pressure sintering experiment, the tungsten powder was first precompressed into cylinders, and then treated by reduction with hydrogen at 900 °C for 30 min. In the sintering processes, the samples were firstly compressed under some pressure, and then start heating. After the samples were treated at 3.0 to 5.5 GPa and 1000 °C to 1500 °C for 30 min, the temperature was then reduced to ambient temperature, with a decrease rate of 100 °C·min^{-1}, and then the pressure was released. Archimedes method was used to measure the density of the sintered samples, and the average grain sizes were attained by scanning the fracture section of the samples with the Field Emission Scanning Electron Microscope (S-4800 II, Hitachi, Japan). Knoop hardness of the samples was studied using the Vickers indenter hardness tester (HV-10, Shanghai Taiming Optical Instrument Co., Ltd., China), and three point method was used to test the fracture toughness using Electronic Universal Test Machine (AG-10TA, Shimadzu, Japan).

3. Results and discussion

3.1. Densification

Fig. 2 shows the relative densities of the as sintered tungsten samples at 1000 °C, 1300 °C, and 1500 °C as a function of pressure. It is clear that the tendencies of the three curves are consistent. That is, at a fixed sintering temperature, the relative density of the sintered samples increased with pressure. By sintering at 1000 °C and 3.0 GPa for 30 min, the density obtained was 88.7% of theoretical density. By further increasing the pressure to 4.5 and 5.5 GPa, the relative density increased to 92% and 94.5% respectively. When the samples were sintered at a fixed pressure, we found that the relative density of the

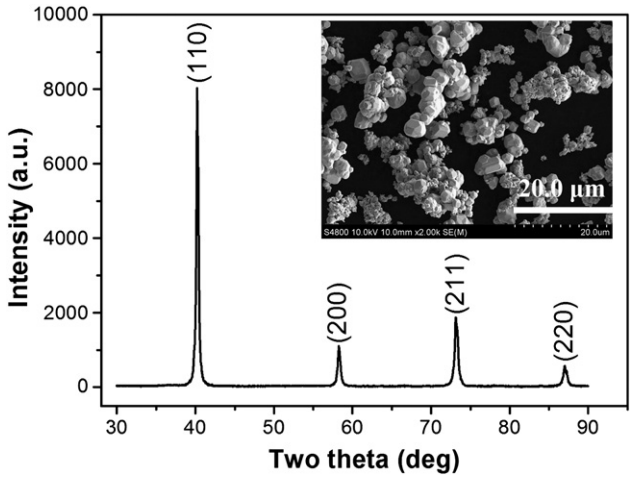

Fig. 1. SEM image and XRD pattern of the initial W powder.

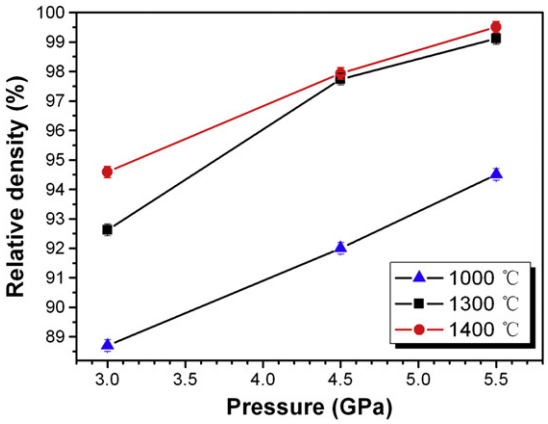

Fig. 2. Relative densities of bulk Tungsten samples sintered at 1000 °C, 1300 °C, and 1500 °C as a function of pressure.

sintered samples also increased with temperatures. By sintering at 5.5 GPa and 1000 °C for 30 min, the relative density obtained was 94.5%. By further increasing the sintering temperature to 1400 °C, the relative density was obviously increased, and finally to a nearly full densification, with a relative density of 99.5%. In our experiments, it is clear that, when ultra high pressure was applied in the sintering procedure, the needed temperature was greatly reduced for sintering a nearly full densification sample.

It is known that yield strength defines the onset of plastic deformation and viscous flow of a material. As He et al. [12] reported, the yield strength of tungsten increases with compression at room temperature, reaching a value of 5.3 GPa at the highest pressure of 69 GPa. Though the yield strength of tungsten under high pressure and high temperature has not yet been reported, it is well known that material's yield strength increases with pressures and decreases with temperatures. Therefore we speculate that in the sintering procedure, when ultra high pressure was firstly loaded on to the tungsten green compacts, the particle rearrangement, sliding, or even distortion and crushing occur quickly. With increasing pressures to 3.0 or 4.5 GPa, the tungsten compacts were subjected to severe deformation, resulting in a local high-stress concentration due to grain-to-grain contacts. At this moment, atomic diffusion and vacancy transport were difficult. Some minor phase, such as pores were still distributed dispersedly between grain boundaries. By heating the sample to a certain temperature under high pressure, tungsten started weakening. Thus the local high-stresses began to relax, and creep deformations of the tungsten grains happened. Higher temperatures promoted the viscous flow of the tungsten grains, vacancy transport as well as the atomic diffusion between grain boundaries, and thus resulting in the bonding and the closing of gaps between the grains. When loading pressure was equal to 5.5 GPa, which may be equal to or exceeding the yield strength of tungsten, part of the local high-stress concentration is expected to diminish, and the total contact areas between individual particles might increase. When the temperature was increased high enough, the entire sample would yield, and the local pores existed in grain/crystalline boundaries were nearly eliminated or closed. Therefore, high pressure and temperature enhanced the densification of tungsten.

3.2. SEM observations

Fig. 3 shows the SEM images of the sintered tungsten samples at various pressures and temperatures. In Fig. 3(a), we find that some finer particles located on the surfaces of the bigger grains. In addition, some grains might be broken as shown in Fig. 3(b). When the pressure was increased up to 5.5 GPa, as shown in Fig. 3(c), obvious cracks of the grains were found. Thus we conclude that some of the tungsten grains