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In situ oxide dispersion strengthened tungsten alloys with high compressive strength and high strain-to-failure

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ABSTRACT

In this work a novel process methodology to concurrently improve the compressive strength (2078 MPa at a strain rate of 5×10^{-4} s^{-1}) and strain-to-failure (over 40%) of bulk tungsten materials has been described. The process involves the in situ formation of intragranular tungsten oxide nanoparticles, facilitated by the application of a pressure of 1 GPa at a low sintering temperature of 1200 °C during spark plasma sintering (SPS). The results show that the application of a high pressure of 1 GPa during SPS significantly accelerates the densification process. Concurrently, the second phase oxide nanoparticles with an average grain size of 108 nm, which are distributed within the interiors of the W grains, simultaneously provide strengthening and plasticity by inhibiting grain growth, and generating, blocking, and storing dislocations.

1. Introduction

Tungsten (W) is a refractory metal with a melting point of 3422 °C, the highest among all the metals [1]. Alloys based on W, also known as tungsten heavy alloys (WHA), can offer high strength at room and elevated temperatures, high thermal conductivity, low vapor pressure, and low sputtering yield, and are thus attractive for industrial- and aerospace-engineering, military applications, and in the nuclear industry [2–6]. In spite of these advantages, however, although W is inherently strong and increasing strength is easy to achieve in WHAs, polycrystalline W and WHAs suffer from a major drawback: their limited plasticity at temperatures near room temperature. This limited plasticity is attributed to the fact that polycrystalline W is notorious for its high susceptibility to soluble interstitial impurities that tend to segregate at grain boundaries, leading to grain boundary brittleness [4]. This inadequate plasticity is in fact a well-known bottleneck that limits the widespread engineering application of WHAs [4,7].

In the past few decades, improving the plasticity at temperatures close to room temperature without sacrificing high strength has evolved into a key goal in research related to high strength metals or alloys. To that effect, research efforts have resulted in a number of strategies that are actively being pursued. For instance, there are studies that describe strategies that involve a redistribution or reduction in the impurity concentration at grain boundaries through the creation of more grain boundaries [2,4]. In related work, Wei et al. applied a one-step top-down approach, namely the severe plastic deformation (SPD) technique of equal channel angular pressing (ECAP), to produce W samples with significantly increased grain boundary volumes by refining the microstructure to the ultrafine-grained regime [2]. Their results included a compressive strain-to-failure of over 30% and a high strength of 1.5 GPa [2].

A second approach involves enhancing plasticity by introducing second-phase particles into a matrix alloy. To that effect, related studies involving Al and Mo alloys suggest that it is possible to improve plastic deformation while maintaining strength, only if

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such second-phase particles are distributed within the matrix grains, rather than at grain boundaries [8,9]. In contrast, when second-phase particles are located intergranularly, published results show that plasticity is generally degraded because these particles act as stress concentrators that promote crack formation [10]. Interestingly, there appears to be no published studies on the application of this approach to W or WHAs.

In view of the above discussion, the present study was motivated by the following research questions. First, can a synthesis strategy be formulated to fabricate W samples with enhanced strength and plasticity? Second, can fundamental insight into the mechanisms controlling the deformation behavior be provided?

In order to accomplish these objectives, the following approach was implemented. First, W samples were consolidated from commercially available W powder by the application of the high pressure spark plasma sintering (HP-SPS) technique. HP-SPS can achieve a sintering pressure as high as up to 1 GPa, which is significantly higher than the pressure used in previous studies involving the application of SPS techniques to consolidate W powder [6,10,11]. The effects of different sintering conditions on the microstructure evolution of the consolidated samples were also studied in the current research. Furthermore, the compressive behavior of the consolidated W samples was investigated and was compared to samples fabricated by other techniques including hot isostatic pressing (HIP), ECAP [2,12], and ECAP + cold rolling (ECAP + CR) [2].

2. Experimental procedures

The feedstock powder used in this study was commercially available M10 tungsten (W) powder supplied by Global Tungsten and Powders Corporation (USA). The chemical composition, morphology and particle size distribution of the feedstock powder was characterized by scanning electron microscopy (SEM, XL30FEG, FEI). The composition was further evaluated using X-Ray diffraction (XRD, Scintag XDS2000) and chemical analysis (Leco Corporation, St. Joseph, Michigan).

Nine bulk W samples were sintered via SPS/HP-SPS (SPS-825S DR. SINTER, SPS Syntex Inc., Kawasaki City, Japan) using a matrix of temperatures and pressures (1200 °C, 1300 °C and 1400 °C; 200 MPa, 500 MPa and 1 GPa), applying a 5 min hold and a heating rate of 100 °C/min for each. A double acting die set was applied in the current research by combining both SiC and graphite die sets, a schematic of which is shown in Fig. S1 in the supplementary information. A sintering pressure as high as 1 GPa was achieved. The pressures were gradually applied during the heating stage when the temperature was greater than 700 °C. Temperature was measured by an optical pyrometer focused on the outer surface of the sintering die. The vacuum level in the SPS chamber was 1–6 Pa. The default pulse pattern (on:off ratio of 12:2) was applied during sintering. The consolidated samples were characterized by XRD, SEM, electron backscattered diffraction (EBSD, Scios, FEI) and transmission electron microscopy (TEM, JEOL2500). The relative densities (RD) were measured according to Archimedes' principle. TEM samples used to characterize the microstructure of the consolidated W samples were prepared by utilizing focused ion beam (FIB, Scios, FEI).

The consolidated bulk W samples were sectioned into 1 mm × 1 mm x (1.2–1.5) mm samples by using the electrical discharge machining (EDM) technique. The thickness of the samples depended on the sintering conditions. The samples sintered under 200 MPa at each sintering temperature were 1.5 mm thick, and the samples sintered under 500 MPa were approximately 1.45 mm thick. The sample sintered under 1 GPa at 1200 °C was 1.2 mm thick after sintering. The samples sintered under 1 GPa at 1300 °C and 1400 °C were 0.7 mm thick after sintering, which is not sufficient for the following mechanical property tests. Quasi-static compressive tests were conducted by applying a hydraulic Instron instrument (Instron Electropuls 3000) at room temperature. In order to make a comparison, a hot-isostatic-pressed (HIP) coarse grained W sample with an average grain size of 4.5 μm and a relative density of 98.0% was also fabricated from the M10 powder (HIP conditions: 1500 °C, 200 MPa, 1 h). The sample was sectioned by EDM to obtain the dimensions of 1 mm × 1 mm x 1.5 mm and tested under identical conditions after machining. Samples were carefully polished to a mirror finish before conducting the compression tests. A series of strain rates from 5×10^{-4} s^{-1} through 5×10^{-1} s^{-1} were applied. Because of the high strength of W, SiC platens were used to protect the instrument from plastic yielding. The interfaces between the samples and the platens were carefully lubricated to minimize the effect of friction during a test.

3. Results

3.1. Characterization of M10 tungsten powder

The composition of the feedstock powder was determined to be 0.028 wt% oxygen, 0.016 wt% nitrogen, 0.006 wt% carbon, and balance (99.950 wt%) W. The W powder was characterized to exhibit an equiaxed morphology and an average particle size of 288 nm, with approximately 90% of the powder ranging from 100 to 600 nm in size and exhibiting a certain degree of agglomeration. The SEM and XRD results are provided in Fig. S2 in the supplementary information.

3.2. Effects of sintering conditions on the microstructure evolution of the bulk tungsten samples consolidated by SPS/HP-SPS

The effect of sintering temperature and applied pressure can be observed through the comparison of the microstructure of the as-sintered W samples. Fig. 1a to i present the typical fracture morphologies and the corresponding grain size histograms of the samples consolidated under different sintering temperatures and pressures. The average grain size (AGS) values show a single normal distribution with the AGS increasing from 599 to 930 nm for the samples sintered at 1200 °C under 200 MPa and 500 MPa, respectively, indicating a 55% increase in grain size caused by the accelerated diffusion process due to the application of a higher pressure. However, it is interesting to note that the sample sintered at 1200 °C under 1 GPa shows a noticeably different microstructure and grain size distribution. The AGS of W in this sample is 984 nm, only 5.8% larger than the one sintered at less than 500 MPa. Furthermore, a new phase with a significantly finer AGS of 144 nm has appeared in the sample, leading to the formation of an unexpected microstructure in the sample. The formation of the new phase effectively inhibits and controls grain growth in the W, acting as a second-phase particle for grain boundary pinning based on the Zener pinning effect [4,13]. When the sintering temperature is increased to 1300 °C, all three samples under different pressures show the unexpected and distinct microstructures with the appearance of both the newly formed secondary phase and the W phase. The AGS of W exhibits an increase with sintering temperature, and the grain size distribution for the W phase is much broader in the samples sintered at less than 500 MPa and at 1 GPa, which is possibly caused by the broad grain size distribution in the feedstock W powder. Similar results are also observed for the samples sintered at 1400 °C.

The effects of sintering temperature and pressure on the AGS of W and the new phase with finer grains are summarized in Fig. S3 in the supplementary information. Overall, the AGS of W exhibits an