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Nanostructured tungsten through cryogenic attrition

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ABSTRACT

Nanostructured pure tungsten (W) powders have been fabricated through cryogenic attrition (i.e., cryomilling) in a liquid nitrogen medium for the first time. The microstructure and chemistry of W powders before and after 4 and 12 h of cryomilling were thoroughly examined by gas fusion chemical analysis, X-ray diffraction, scanning electron microscopy, and transmission electron microscopy (TEM). Cryomilling in liquid nitrogen protected the tungsten from oxygen and hydrogen contamination while introducing nitrogen. Results showed that the W grain size decreased with cryomilling time, and reached approximately 5 nm after 12 h of cryomilling. High resolution TEM suggested that nitrogen reacted with W to form tungsten nitride (WN). Additionally, amorphous W was identified in the 12 h cryomilled W powder. Tungsten carbide (WC) contamination from the milling media and minor Fe–Cr–Ni-containing impurities from the stainless steel vessel were also documented. The WC had grain size ranging from 20 nm to 150 nm, and was homogeneously dispersed in W matrix.

1. Introduction

Tungsten is a refractory metal that exhibits a high melting point and good high temperature mechanical behavior. It has been widely used in high temperature applications, in the form of tungsten carbide or as alloy additions [1–3]. Tungsten alloys have also attracted increasing interests in recent years due to applications as kinetic energy penetrators, counter-weights, radiation shields, and vibration damping devices [4–6]. Usually in tungsten alloys, a certain amount of Fe, Ni, Co or Cu is added to increase the ductility and decrease the sintering temperature [7–9]. Oxide dispersoids such as partially stabilized zirconia and yttria can be also introduced to form oxide dispersion strengthened tungsten alloys, which further improves the strength and penetration performance [10,11].

The fabrication of fully dense tungsten alloys has been one of the challenges because of their high melting temperature and hardness. Powder metallurgy followed by high temperature liquid phase sintering is the most common process for consolidation [12–14]. Alloying elements are typically added to achieve liquid-phase sintering above the eutectic temperature, but adding them diminishes the properties of pure tungsten such as density and erosion resistance [15]. On the other hand, reducing the grain size of tungsten to the nanoscale can help enhance the sintering kinetics and decrease the processing temperature [16,17]. Compared to coarse grain tungsten, nanostructured tungsten has a lower ductile-to-brittle-transition temperature and improved low (near room) temperature ductility [18]. At the same time, grain refinement is beneficial to the final microstructure and mechanical properties of tungsten alloys. Therefore, efforts have been made to produce nanoscale tungsten powders.

Nanoscale tungsten powders have been fabricated by various techniques including mechanical alloying [9,10,19], wire explosion process [20], mechanochemical synthesis [21] and laser irradiation [22]. Among these techniques, mechanical milling is most commonly employed. It has been shown that nanostructured tungsten, having average crystallite size of as small as 8 nm, calculated from X-ray diffraction line profile analysis, can be obtained as through high energy mechanical milling [17].

Cryogenic attrition often referred to as cryomilling is a method that can produce nanoscale materials. During cryomilling, powders are mechanically milled within a cryogenic liquid, so that the grain size is refined [23]. The physical mechanisms for the reduction of grain size using cryomilling is similar to other milling technique, which has been explained by Fecht [24] to be a three step process: (1) localization of deformation into shear bands with high dislocation density; (2) annihilation and recombination of dislocations to form sub-grains; and (3) transformation of sub-grain boundaries into high angle grain boundaries. Compared to conventional mechanical milling techniques, cryomilling has the advantage of minimizing the oxidation of powders, reducing powder agglomeration, easing scalability, and potentially introducing nanoscale dispersoids which may help improve grain stability during sintering [25]. Cryomilling techniques have been successfully applied to increase the strength of lightweight structural materials such as Al or Mg alloys [26,27]. Other cryomilled powders

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that have been investigated include Fe [28], Ni [29], Zn [30], Ti [31], WC–Co [32,33] and Pd–10Rh [34] powders. However, to the best of the author's knowledge, there has not been any report of processing of nanostructured tungsten powders employing cryomilling.

Ample evidence exists that cryomilling may help further decrease the minimum grain size of powders compared to that obtained if milled at ambient temperature. For example, the grain size of nanocrystalline Cu decreased from 26 nm to 17 nm when the milling temperature changes from 300 K to 188 K [35]. A dislocation model was proposed to predict the minimum grain size obtainable by milling. This model postulated that the minimum grain size is achieved when the hardening rate introduced by dislocation generation equals to the recovery rate from dislocation annihilation and recombination [36]. The minimum grain size following this model can be expressed by [36,37]:

$$\frac{d_{min}}{b} = A_1 \exp\left[-\frac{\beta Q}{4RT}\right]\left[\frac{D_{p0}Gb^2}{v_0 kT}\right]^{0.25}\left[\frac{\gamma}{Gb}\right]^{0.5}\left[\frac{G}{H}\right]^{1.25} \quad (1)$$

where b is the Burgers vector, A_1 and β are the constants, R is the gas constant, k is the Boltzmann constant, Q is the activation energy for self diffusion, D_{p0} is the pre-exponential factor for pipe diffusion, G is the shear modulus, v_0 is the dislocation velocity, γ is the stacking fault energy and H is the hardness. Eq. [1] can be simplified by assuming the temperature effect on the materials constants can be ignored, and is expressed by [36]:

$$d_{min} = A_2 \frac{\exp\left[-\frac{\beta Q}{4RT}\right]}{T^{0.25}} \quad (2)$$

where A_2 is a constant. This equation where the exponential term governs d_{min} demonstrates that a decrease in grain size can be achieved by lowering the milling temperature.

In this study, the feasibility of applying cryogenic attrition to the nanostructuring of tungsten powders was explored. The morphology and grain size of the powder was examined via transmission electron microscopy (TEM), scanning electron microscopy (SEM), and powder X-ray diffraction (XRD). Inert gas fusion infrared and thermal conductivity detection was also used to determine the oxygen, hydrogen, and nitrogen concentration of the powder before and after cryomilling.

2. Experimental details

Pure W powders (15–40 μm, 99.95%) obtained from Global Tungsten and Powders Corporation (Towanda, PA, USA) were cryomilled in a Szegvari Union Process 1-S attritor modified for continuous flow of liquid nitrogen. Powders were cryomilled in the presence of liquid nitrogen with WC satellites (0.25″ diameter, Union Process) and a starting ball-to-powder weight ratio of 32:1. The cryomilled W powder was sampled at 4 h, and the run was concluded after 12 h of cryomilling. The powders before cryomilling, after 4 h of cryomilling and 12 h of cryomilling are hereafter designated as CM0, CM4 and CM12, respectively. After cryomilling, the W powders were immediately transferred to an atmosphere-controlled glove box where the liquid nitrogen was allowed to boil off.

A Leco OHN836 inert gas fusion infrared and thermal conductivity detection unit was used to measure the nitrogen, oxygen and hydrogen content of the W powders before and after cryomilling. The powders were subjected to conventional powder X-ray diffraction (Panalytical MRD Pro system) with Cu K_α radiation to determine the crystallite size and strain. The morphology of the powders was examined via a Zeiss Ultra-55 field emission scanning electron microscopy (FE-SEM) by sprinkling powders on the carbon tape. Powders were also carefully mounted in epoxy and metallographically ground using SiC paper and polished down to 0.25 μm using an oil-based diamond paste. The cross sections of the powders were examined by SEM and X-ray energy dispersive spectroscopy (XEDS).

TEM (FEI™ Tecnai F30 TEM) and scanning TEM equipped with a Fischione™ high angle annular dark field (HAADF) detector, operating with accelerating voltage of 300 keV were employed to examine the details of grain size and morphology of the powders. All of the TEM foils were prepared from the cross-sectional powders mounted in epoxy via focused ion beam (FIB-FEI™ 200 TEM) utilizing an in-situ lift-out (INLO) technique.

Table 1
Oxygen, nitrogen and hydrogen contents measured by gas fusion chemical analysis in the tungsten powders before (CM0) and after 4 (CM4) and 12 (CM12) h of cryomilling.

Powder	Measurement	O (wt.%)	N (wt.%)	H (ppm)
CM0	1	0.016	0.001	0.092
	2	0.015	0.000	0.481
	3	0.017	0.001	0.030
	Average	0.016 ± 0.001	0.001 ± 0.000	0.202 ± 0.244
CM4	1	0.306	0.378	89.283
	2	0.308	0.378	85.500
	3	0.306	0.378	83.674
	Average	0.307 ± 0.001	0.378 ± 0.000	86.152 ± 2.861
CM12	1	0.385	4.255	103.940
	2	0.386	4.265	103.200
	3	0.386	4.281	110.600
	Average	0.386 ± 0.001	4.267 ± 0.014	105.913 ± 4.076

3. Results

The O, N and H concentrations were measured three times by inert gas fusion technique for each powder and the results are summarized in Table 1. The starting W powder contained a negligible amount of O, N and H. For the CM4 powder, O and N content increased to 0.307 and 0.378 wt.%, respectively, while H increases to 86.2 ppm. Extending the cryomilling time to 12 h only slightly increases O content to 0.386 wt.% and H to 105.9 ppm. However, the N content increased significantly to about 4.267 wt.% for the CM12 powder.

Fig. 1 presents the XRD patterns for the CM0, CM4 and CM12 powders at room temperature. Peak broadening occurred for the CM4 powder, indicating that the cryomilling successfully reduced the crystallite size. A further decrease of the crystallite size was observed after 12 h of cryomilling, which is evident from the broadening of the diffraction peaks for the CM12 powder. Meanwhile, the intensity of the diffraction peaks for the CM12 powder also drops significantly compared to those for CM0 and CM4 powders. This may imply that some regions of the CM12 powder become amorphous during the cryomilling process.

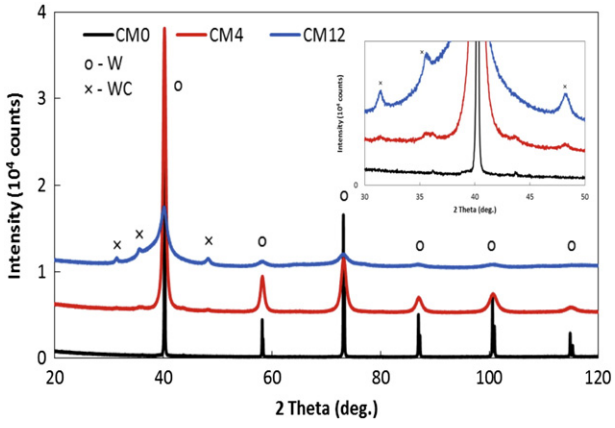

Fig. 1. Powder X-ray diffraction patterns of W powders before (CM0), and after 4 h (CM4) and 12 h (CM12) of cryomilling.