Interaction of tungsten nanopowders with air under different conditions

Alexander Gromov a, Young-Soon Kwon b,*, Pyuck-Pa Choi b

a Department of Chemical, Tomsk Polytechnic University, 30, Lenin Ave., Tomsk 634050, Russia
b Research Center for Machine Parts and Materials Processing, School of Materials and Metallurgical Engineering, University of Ulsan, San-29, Mugeo-2Dong, Nam-Ku, Ulsan 680-749, South Korea

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Abstract

Different regimes of interaction between tungsten nanopowders, produced by pulsed electric plasma spraying of wires, and air have been studied: passivation (slow-rate oxidation at room temperature), medium-rate oxidation by linear heating (15K/min) and combustion (fast-rate oxidation). A thermochemical oxidation diagram of tungsten nanopowders in air is proposed.

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1. Introduction

In the last decade W nanopowders have attracted great interest as functional materials with advanced characteristics. One of the most common methods for metal nanopowder synthesis is physical vapor deposition (PVD) [1]. Powders produced by this method have a relatively narrow particle size distribution. However, they completely oxidize within a few hours after being exposed to air, and thus, they should be stored in an inert gas atmosphere or under vacuum. Furthermore, the PVD method has a production rate of only a few milligrams per hour and requires high vacuum, liquid nitrogen and complicated facilities [2], making the production of W nanopowders by this method very expensive.

One method with a substantially higher production rate (~200 g/h) and therefore applicable to industrial production of metal nanopowders, is pulsed electric plasma spraying of wires (PEPSW) [3,4]. Nanopowders produced by PEPSW have numerous useful features such as an energy-saturated structure and a high reactivity under high-temperature processing [5]. The formation of metastable W nanoparticles by the PEPSW process occurs under nonequilibrium conditions, with the duration of the metallic wire spraying being 1–10μs, the plasma temperature ~10^4 K, the average cooling rate of particles up to 10^9 K/s and the specific energy entering the wire (elec) more than 1 MJ/kg [5].

PEPSW metal powders have a high metal content (up to 98 wt.% for Al nanoparticles) after slow passivation in air [6]. In fact, the process of oxide layer formation on the particle surface upon slow oxidation in air should be called “passivation-up-to-self-saturation”. The structure of such self-saturated oxide layers was studied for Al nanoparticles produced by PEPSW in Ref. [6]. The hypothesis of the formation of double electric layers with the additional capacity on the ‘metal-oxide’ interface of particles could explain the high metal content in PEPSW particles [6]. However, the only result
achieved by high-resolution electron microscopic study of PEPSW-produced Al nanoparticles was the observation of an amorphous oxide layer [7,8]. Thus, the experimental data on the oxidation of metal nanopowders needs to be accumulated. The formation of a passivation oxide layer on tungsten nanoparticles and subsequent oxidation and combustion in air have been studied for different temperature regimes in this work. Tungsten has been selected for our studies, as it has a similar formation enthalpy of oxide to Al in the highest oxidation degree: \( \Delta H_f(\text{WO}_3) = -836 \text{kJ/(mole W)} \) and \( \Delta H_f(\text{Al}_2\text{O}_3) = -837.5 \text{kJ/(mole Al)} \). On the other hand, tungsten exhibits much lower chemical reactivity than aluminum.

The majority of reports concerning the oxidation of metal nanoparticles provide information on reactive metals such as Al, Ti, Fe [9–12]. To our knowledge, there are no reports on the oxidation of W nanopowders in air. At the same time the oxidation of bulk W is well studied [13–15].

2. Experimental

Production of the W nanopowder was carried out by using an industrial PEPSW machine named UDP-4G© [5]. The machine comprises three parts: an explosion chamber, a powder collector and an electric circuit. The initial raw material for nanopowder production was a W wire 0.27 mm in diameter and of 99.8% purity. The preliminary evacuated explosion chamber was filled with Ar gas at a pressure of 1.5 atm. The rate of W wire feeding was about 70 mm/s. After producing 120 g of powder, the collector with the powder was removed, and the working cycle repeated.

Non-passivated W nanopowder as well as other metal nanopowders immediately self-ignites if exposed to air, making passivation essential. Hence, the powder-collector was placed into a separate hermetic passivation chamber immediately after powder production. Passivation was carried out at room temperature in the medium of argon gas (pressure of 1.1 atm) having an air content of about 0.1 vol.%. These conditions of air-passivation for metal nanopowder were discussed in a previous paper [6]. The W nanopowder sample (noted as “WNP-air”) was completely passivated by the Ar + 0.1 vol.% air mixture after 25 h. The end of the passivation period was determined as the moment when the nanopowder stopped reacting with air, i.e., when the pressure of the gas mixture in the passivation chamber stopped decreasing. Another sample, noted as “WNP-StAc”, was passivated by a 0.1 mass% stearic acid (StAc, C\(_{18}\)H\(_{36}\)O\(_2\)) solution in toluene (C\(_6\)H\(_6\)O). The solution for passivation was added to the fresh powder immediately after production, and the powder solution was mechanically stirred for \(~2\) h. The temperature was maintained at temperatures lower than 30°C in order to avoid partial self-sintering of the powder.

DTA–TGA analyses of samples were performed using a STA-409 apparatus (Netzsch Gersebau GmbH Thermal Analysis, Germany) at temperatures up to 1300°C in air. XRD analyses were carried out using a “MAX-B” diffractometer (Rigaku, Japan) with CuK\(_{\alpha}\) radiation (Ni-monochromated). The “Mastersizer 2000” by Malvern Instruments, UK was used for the determination of the particle size distribution. The powders were suspended in ethanol and ultrasonically treated for 15 min before analysis. Scanning electron microscope (SEM) investigations were performed with the “JSM-6500 F” (Jeol, Japan) apparatus, which includes a field emission gun. XPS analyses were carried out with a “ESCALAB 250” spectrometer, using monochromated AlK\(_{\alpha}\) radiation under a acceleration voltage of 15 kV. In addition, the W nanopowder samples, burned in air, were observed with a video camera.

For combustion one gram from each of the powder samples was put onto a BN plate (see Figs 1 and 2) in a cone-like shape. For three statistically studied samples of equal mass the ignition temperature determined by a pyrometer was 350–420 K. Local ignition was initiated.

Fig. 1. Video images of the combustion process of tungsten nanopowder in open air (“WNP-air”): (a) 50 s after ignition; (b) 200 s after ignition.
by an electrically heated Ni–Cr alloy wire, which was placed at the top of the sample. After the ignition, combustion occurs as a non-stationary layer-by-layer process (Fig. 1). From the ignition point, combustion waves of red color propagated through the surface and inside the sample “WNP-air” (Fig. 1(a) and (b)) whereas for the sample “WNP-StAc” the process is similar to a “volcanic eruption”-like burning (Fig. 2(a) and (b)). The maximal combustion temperatures for the studied samples are 1235K for the sample “WNP-air” and 1360K for the “WNP-StAc” sample. The duration of the burning process was 455s for “WNP-air” and only 7s for “WNP-StAc”.

XRD, TGA and chemical analysis showed that the final combustion product of both samples consisted of two phases: unreacted tungsten and WO₃ (residual tungsten content C_W = 35.4 ± 0.3 mass% for the sample “WNP-air” and C_W = 73.6 ± 0.3 mass% for the sample “WNP-StAc”). It is noticeable that the XRD patterns of the final combustion product of both samples are alike: the most intensive peaks belong to the residual W phase. Microstructures of the final combustion product of the sample “WNP-air” are shown in Fig. 3. The spherical particles of the initial WNP (Fig. 3(a)) completely changed their morphology during the combustion: the final products consist of porous aggregates of micron size (Fig. 3(b)).

3. Results and discussion

W nanopowders studied in this work were produced under identical electric conditions in Ar (1.5atm) in the explosive chamber of the PEPSW machine. The pressure of Ar in the explosive chamber was slightly higher than atmospheric, which leads to gas adsorption on the surface of particles immediately after they form from the plasma gas. The probable mechanism of particle formation during PEPSW process is described elsewhere [16,17]. Adsorbed Ar prevents cooled particles from coming into contact with each other and sintering in the powder collector, as well as from reacting with air and water when the chamber is opened. Before passivation W nanopowders contained about 4mass% of adsorbed Ar as determined with DTA–TGA.

According to XRD data (see Fig. 4), particles of the sample “WNP-air” contain three phases: α-W, β-W and W₃O. The formation of β-W is the characteristic feature of W nanopowders produced by PEPSW. Low-temperature phase, β-W, has a lower density of 19.1 g/cm³ compared to α-W (19.3 g/cm³) and transforms to α-W at temperatures above 630°C [18]. According to XPS results obtained by Tikhonov [19] (content of [O] was not determined in that work), the finest fraction of the PEPSW W nanopowders contains a higher
concentration of $\beta$-W. In that work the sample of W nanopowders produced under $e_{\text{c}}/e_{\text{s}} = 0.49$ was divided into three parts with $S_{\text{sp}} = 15.4 \text{ m}^2/\text{g}$, $2.8 \text{ m}^2/\text{g}$ and $0.7 \text{ m}^2/\text{g}$. The quantity of $\beta$-W in the finest sample was $43 \text{ mass}\%$. The sample with $S_{\text{sp}} = 2.8 \text{ m}^2/\text{g}$ contained traces of $\beta$-W while the sample with the largest particles consisted completely of $\alpha$-W. This distribution of $\beta$-W in samples with different $S_{\text{sp}}$ can be attributed to a higher cooling rate for the finest particles during PEPSW as well as a stabilization of lattices of lower density.

$W_3O$ peaks, registered by XRD (Fig. 4), probably correspond to the surface passivation layer. But according to XPS (Fig. 5, viewed surface ~4000 $\mu\text{m}^2$), the oxygen content in the surface layers of these particles is higher than for $W_3O$ (mass ratio $[\text{W}]/[\text{O}]=34.5$). Calculation based on XPS data (Fig. 5) showed that the composition of the surface layer is close to that of $WO_{1.6}$ (mass ratio $[\text{W}]/[\text{O}]=7.1$), which is slightly higher than that for $WO_2$ (mass ratio $[\text{W}]/[\text{O}]=5.8$). This discrepancy between the XRD and XPS data may possibly be due to well-crystallized $W_3O$ layers covering the finest powder particles, while the largest particles are covered by an amorphous oxide layer with a similar composition to $WO_2$. It should be noted that the thickness of the oxide layer on particles is less than $2 \text{ nm}$: oxide peaks are invisible at the etching time of $50 \text{ s}$.

Particle size analyses revealed that the “WNP-air” sample has a relatively narrow size distribution in the range of $20–200 \text{ nm}$ with the maximum at $60 \text{ nm}$ (Fig. 6), in good correspondence with the SEM micrographs in Fig. 3. The calculated thickness of the oxide layer is $0.8 \text{ nm}$ (Table 1).

Fig. 7(a) shows the DTA–TGA curves of the sample “WNP-air” upon linear heating ($15^\circ\text{C}/\text{min}$) in air up to $1300^\circ\text{C}$. Gas desorption occurred (0.4 mass% decrease on TG curve) while the sample was being heated from room temperature to $280^\circ\text{C}$. A DTA curve showed an exothermal peak from the very beginning of heating (Fig. 7(a)). Gas desorption is probably accompanied by oxidation as observed for Al nanopowder [20]. The first stage of W nanopowder oxidation covers the temperature range $280–420^\circ\text{C}$ (weight increase on TG curve, Fig. 7), where the average mass rate of oxidation is $0.6 \text{ mg O}_2/\text{min}$. A quantitative XRD analysis showed that the composition of the oxidized powder after the first stage was $\alpha$-W (81 mass%) and $W_3O$ (19 mass%). This stage of oxidation probably corresponds to an interaction of the finest W particles with oxygen. This is in agreement with the XRD data: $\beta$-W was completely oxidized ($\beta$-W peaks disappeared). The second stage of W oxidation continues up to $520^\circ\text{C}$ (Fig. 7(a)). The average mass rate of oxidation during the second stage was $1.1 \text{ mg O}_2/\text{min}$. After the second stage, the process ends with the $WO_3$ formation. No metallic W was found in the end products of oxidation up to $860^\circ\text{C}$. The con-

![Fig. 4. X-ray diffraction patterns of W nanopowder (“WNP-air”) (CuK$_\alpha$ radiation, $\lambda = 1.54056 \text{ nm}$).](image)

![Fig. 5. XPS images of W nanopowder passivated by air (“WNP-air”); etching time: (a) 0s (surface); (b) 50s (penetration depth 2 nm); (c) 100s (penetration depth 4 nm) and (d) 200s (penetration depth 8 nm).](image)

![Fig. 6. Particle size distribution of W nanopowder passivated by air (“WNP-air”).](image)
tent of metallic W in the initial NP calculated from the TG curve (Fig. 7(a)) is 95.5 mass%. The product of complete oxidation is yellow-colored WO₃, the sublimation of which begins at 890°C (weight decrease on TG curve, Fig. 7). For the bulk WO₃ the sublimation temperature is a little higher ($T_{\text{subl}} = 900°C$) [13]. The melting of WO₃ was observed at 1210°C, almost the same temperature as for bulk WO₃ ($T_{m} = 1200°C$).

After the desorption of the passivation coating (2.7 mass% decrease on TG curve), the oxidation of the sample “WNP-StAc” has a similar character as to that of the sample “WNP-air” as shown in Fig. 7(b). The oxidation stages of this sample are not separated (DTA curve) and the process has the same scenario (similarity of the TG and DTA curves). The metal W content of the initial sample “WNP-StAc” calculated from TG curve (Fig. 7(b)) was 97.4 mass%. Thus, the passivation of W by stearic acid does not change the onset temperature of oxidation and slightly decreases the metal content in the initial powder, which is probably due to a thicker layer of coating on particles.

It can be assumed that neither of the studied W nanopowders even partially react with nitrogen from the air, since no nitrides were found in the final combustion products. This is the main difference between the burning scenarios of Al and W nanopowders in air [21]. The nitridation process for W nanopowders is limited by a low burning temperature (less than 1400 K) of W and layer-by-layer burning as in the well-studied SHS processes [22]. Furthermore, it is limited by diffusion of oxygen through the surface of oxidation products and consequent WO₃ melting. At low temperatures ($T < 1400 K$) the oxidation process proceeds due to the diffusion of the oxidizers through the layer of products. The difference between combustion regimes of studied samples can be accounted for by different passivation layers on

<table>
<thead>
<tr>
<th>NP</th>
<th>Temperature of the oxidation onset (TGA), °C</th>
<th>Temperature of the oxidation end (TGA), °C</th>
<th>$[\text{W}^+]$, mass%</th>
<th>$S_{\text{BET}}$, (BET), m²/g</th>
<th>Calculated $\alpha_v$, nm</th>
<th>$[\text{WO}<em>{3}+\text{WO}</em>{1.6}]^\ast$, mass%</th>
<th>Calculated thickness of oxide layer, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>280</td>
<td>860</td>
<td>95.5</td>
<td>3.9 ± 0.3</td>
<td>79.1</td>
<td>2.3</td>
<td>0.8</td>
</tr>
</tbody>
</table>

$^\ast [\text{WO}_{3}+\text{WO}_{1.6}] = 100\% – [\text{W}^+] – [\text{adsorbed gases}]$. 

![Fig. 7. DTA-TGA curves of W nanopowder: (a) “WNP-air” and (b) “WNP-StAc” ($m = 119.0mg$, the heating rate in air is 15°C/min, and $\alpha$-Al₂O₃ is the reference).](image)

![Fig. 8. Thermochemical diagram of the W nanopowder passivation, oxidation and combustion in air.](image)
particles. Stearic acid burning results in gasification and combustion not as complete as in the case of burning of oxygen-passivated particles. Particles of the W nanopowder coated by oxides burn together (Fig. 1(a) and (b)) and maintain higher temperatures for a longer period and, as a result, provide a higher oxidation degree of W. Chemical processes that took place during the oxidation and combustion of “WNP-air” are similar to the processes (under DTA–TGA and XRD) shown in Fig. 8.

4. Conclusion

Metal particles of tungsten nanopowder, produced by PEPSW, are spherical with a smooth surface and a diameter less than 1 μm. The explosion of W wires results in β-W phase formation with mainly fine powder particles. Using air and stearic acid as passivators, the passivation period of W nanopowder is about 25h and 2h, respectively. During this period an oxide coating less than 5 nm in thickness forms on W nanoparticles, passivated by air. The composition of oxide layers on fine W particles is W₂O₅, while it is close to WO₂ for the largest particles. The oxidation and combustion scenarios for W nanoparticles covered by stearic acid and tungsten oxide are similar. W nanopowders do not form nitrides during oxidation and combustion in air as aluminum nanopowders do.

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References