



ELSEVIER

Contents lists available at ScienceDirect

Ceramics International

journal homepage: [www.elsevier.com/locate/ceramint](http://www.elsevier.com/locate/ceramint)

# The synthesis of micro and nano WO<sub>3</sub> powders under the sparks of plasma electrolytic oxidation of Al in a tungstate electrolyte

Tingyan Zhan, Wenbin Tu, Yulin Cheng, Junxiang Han, Bin Su, Yingliang Cheng\*

College of Materials Science and Engineering, Hunan University, Changsha 410082, China

## ARTICLE INFO

### Keywords:

Plasma electrolytic oxidation

WO<sub>3</sub>

Al

Micro and nano sized powders

Sublimation

## ABSTRACT

Plasma electrolytic oxidation (PEO) is commonly known as a coating technique. However, the present study shows that PEO of pure Al in 10 g l<sup>-1</sup> Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O leads to the synthesis of micro and nano sized powders of WO<sub>3</sub>. The as-synthesized WO<sub>3</sub> powders have been characterized by SEM, TEM and photocatalytic tests. The plasma discharges during the PEO process have been investigated by real-time imaging and spectrographic method. The energetic features of the single discharge at different stages of PEO have been evaluated. It was suggested that the electrolyte species were directly decomposed into tungsten oxides within the discharge channels and then the oxides re-entered the electrolyte due to the lower melting and boiling points of WO<sub>3</sub>, and more importantly, its tendency of sublimation.

## 1. Introduction

Great efforts have been made to develop the clean, green and renewable energy related technologies, such as photocatalysis, supercapacitors, lithium ion batteries, solar and fuel cells and photothermal conversion [1]. Tungsten oxides (WO<sub>x</sub>, x ≤ 3) are a group of materials that can be used in these technologies [2]. As an n-type semiconductor, WO<sub>x</sub>, x ≤ 3 shows narrower band gaps (2.4–2.8 eV) in comparison with the commonly investigated TiO<sub>2</sub>, and hence can in theory absorb visible light up to a wavelength of 500 nm [3,4]. As a result, a recent publication shows that the deposition of WO<sub>3</sub> nanoparticles onto a TiO<sub>2</sub> nanotube film improves the photoelectrochemical properties of the film [5]. Up to now, many methods have been used to fabricate WO<sub>3</sub> in the form of powders, thin films or colloids, including sol-gel [6], thermal evaporation [7], sputtering [8], hydrothermal method [9], plasma enhanced chemical vapour deposition [10], gas evaporation [11], electrochemical deposition [12] and anodic oxidation [13]. Among these methods, the last two methods offer a simple and low temperature route to prepare thin films [13].

It is known that the scope of applications of WO<sub>3</sub> can be considerably widened by the micro and nano architectures due to an enhanced surface area [13,14]. However, the earlier studies using anodic electrodeposition usually lead to the formation of thin, compact oxide films on the parent metal (tungsten) surface [13]. Later studies show that nanoporous anodic films can be grown on tungsten foils or tungsten thin films by anodization in oxalic acid, NaF, perchlorate, fluoride ion-containing electrolyte or chloride containing electrolytes [13,15–18].

As a technique evolved from conventional anodization, plasma electrolytic oxidation (PEO), which is also called micro arc oxidation (MAO) or spark anodizing (SA), has attracted the interest of material scientists in recent years due to the environmentally-friendly electrolytes, the simple operating procedure and the capability to form coatings with a series of functional properties, such as wear and corrosion resistance, as well as catalysis [19–23]. PEO works under much higher voltages than conventional anodizing, and as a result, plasma discharges occur on the treated specimen, which will exert great influence on the coating formation mechanism [24,25]. The nature of the plasma discharges, such as its composition, temperature, charge densities, spatial distribution, duration of individual discharges, and bubble growth associated with the discharges, has been investigated by many authors, using the spectrographic method [25–31] or synchronized electrical monitoring, real time imaging or high speed video methods [32–34]. Traditionally, PEO is viewed as a coating technology and there are also several reports that tungsten-containing oxide layers can be fabricated on Al or Ti alloys by this method [35–37].

In the present paper, we show for the first time that instead of forming a thick oxide coating, micro and nano sized powders with the main composition of WO<sub>3</sub> have been synthesized by PEO of pure Al in a sodium tungstate electrolyte. The as-prepared WO<sub>3</sub> particles show photocatalytic ability according to a designed experiment for the degradation of methyl orange (MO) aqueous solution.

\* Corresponding author.

E-mail addresses: [chengyingliang@hnu.edu.cn](mailto:chengyingliang@hnu.edu.cn), [deepblacksea@163.com](mailto:deepblacksea@163.com) (Y. Cheng).

<https://doi.org/10.1016/j.ceramint.2018.03.054>

Received 1 October 2017; Received in revised form 15 February 2018; Accepted 7 March 2018  
0272-8842/ © 2018 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

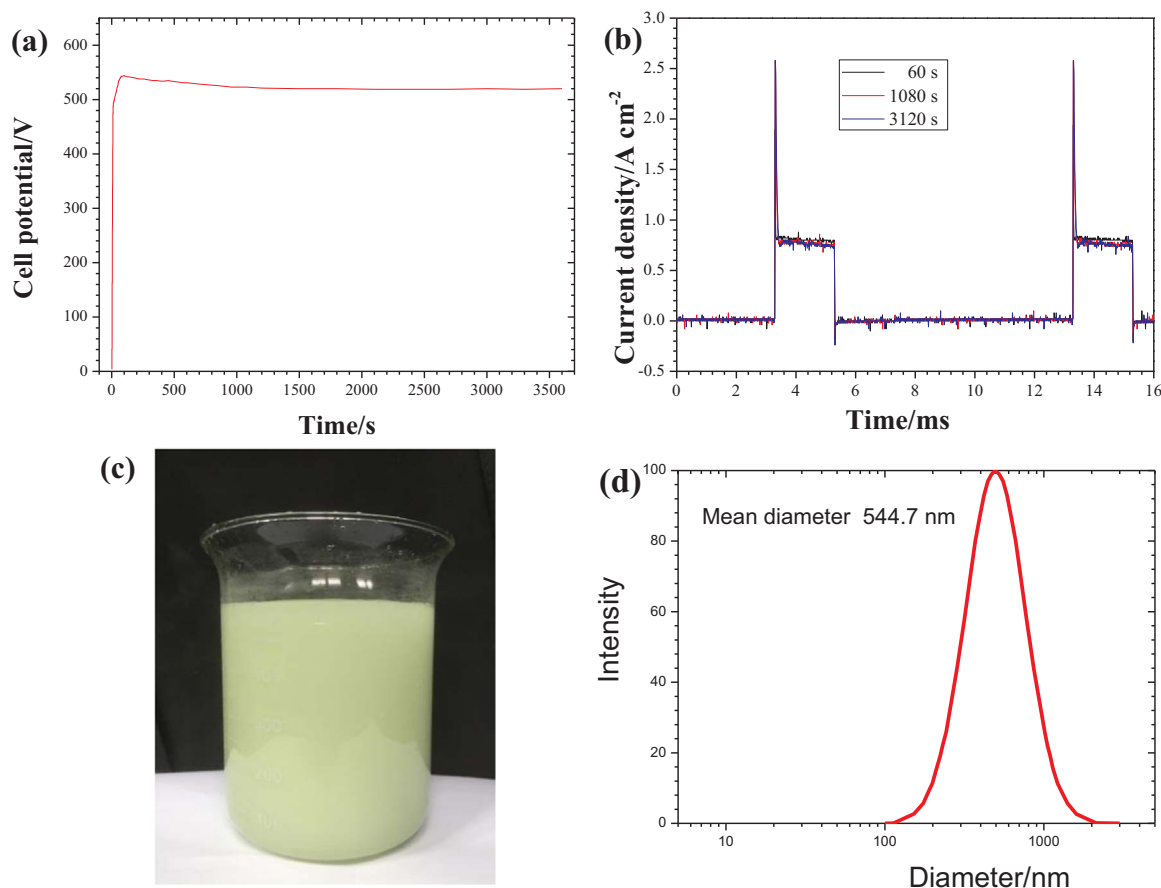


Fig. 1. (a) and (b) are the cell potential-time response and waveforms during the PEO of the Al specimen in  $10 \text{ g l}^{-1} \text{ Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  electrolyte for 3600 s, respectively. (c) and (d) are the appearance of the solution after the 60 min treatment and the corresponding size distribution of the particles in the solution.

## 2. Experimental

A rolled plate of commercial high-purity aluminium (99.97%) was cut and mounted in epoxy resin to provide specimens with working area of  $20 \text{ mm} \times 10 \text{ mm}$ . The specimens were successively polished to a 2000 grit SiC finish, degreased in ethanol, rinsed in distilled water, and finally, dried in a stream of warm air. PEO was carried out in an aqueous electrolyte containing  $10 \text{ g l}^{-1} \text{ Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ , prepared with high purity chemical and distilled water. A 1 l glass vessel, equipped with magnetic stirring and water cooling, was employed for the treatment. The power supply was a 5 kW pulsed power source (MAO-5D, Pulsetech Electrical Co., Ltd., Chengdu, China). Pulsed unipolar constant current regime was used for the anodizing, with an average positive current density of  $\sim 0.16 \text{ A cm}^{-2}$ . The duty cycle of the waveform is 20% and the frequency was 100 Hz. The waveform during anodizing was recorded by a Tektronix TDS1002C-SC oscilloscope. In this research, we found that instead of forming thick coatings on the Al specimen, large amount of fine particles was synthesized and suspended in the electrolyte by the PEO treatment. Scanning electron microscope (SEM, Quanta 650 FEG) was used to examine the surface of the Al sample after the PEO treatment and also the fine particles collected from the solution. An X-ray diffractometer (Rigaku D/max 2500) were used to determine the phase composition of the synthesized powder. A transmission electron microscopy (JEM-3010) was also used to characterize the synthesized particles. The size distribution of the particles was examined by a Zetasizer Nano analyzer (ZetaPlus, Serial No 21487).

In order to have a better understanding the PEO phenomena in this study, the plasma discharges during the PEO process have also been investigated by real-time imaging and spectrographic method. A commercial digital camera, NIKON D7100, was used to record the plasma

discharges, using a fast exposure time of  $125 \mu\text{s}$ . The optical emission spectra (OES) of the PEO discharges were acquired using an Ocean Optics Spectrometer (HR4000), in the wavelength range from 250 to 700 nm. An integration time of 2 s was used for spectra acquisition. Atomic and ionic lines in the collected spectra were identified using the UIST online spectral database [38], and the plasma electron temperature has also been calculated.

Besides the direct observation of the surface of the PEO-treated sample, the oxide film has been stripped electrochemically from the Al substrate and then the backside of the stripped film was also examined by SEM. The cross section of the oxide film has also been observed by mounting the stripped film in epoxy resin, which can avoid the interference from the Al substrate. The oxide film was stripped by immersing the sample in NaCl solution, then a 60 V cell potential was employed to dissolve the Al substrate. The method is similar to that reported by Liu et al. [39]. This method can avoid the attack of the thin oxide film by the strong alkaline solution, which is the chemical used for coating stripping elsewhere [40].

The investigation of the oxide film growth regime can further assist the understanding of the present PEO behaviors. The growth regime of the thin oxide film on the Al sample can be affected by a series of anodic processes. The anodic processes in Al anodizing may include oxide formation, chemical dissolution of aluminium oxide, direct ejection of Al into electrolyte and the oxygen evolution [41]. The coating growth regime, such as the growth direction and consumption of metal substrate during PEO, can be inferred from the observation of the coating cross section with reference to the original metal plane [42]. In this study, a small area of the polished sample surface was protected by a kind of glue and then the Al sample was subjected to PEO treatment for 3600 s. The cross section at the junction of the oxide film/protected

Download English Version:

<https://daneshyari.com/en/article/7887146>

Download Persian Version:

<https://daneshyari.com/article/7887146>

[Daneshyari.com](https://daneshyari.com)