Electrochemistry Communications 23 (2012) 63–67

Contents lists available at SciVerse ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Electrooxidation of substoichiometric titanium nitrides, TiN_{1-x}, $0<x<0.5$

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ARTICLE INFO

Article history:
Received 4 May 2012
Received in revised form 13 June 2012
Accepted 26 June 2012
Available online 7 July 2012

Keywords:
Titanium nitride
Titanium oxynitride
Substoichiometry
Nitrogen vacancies
Non-oxide ceramics
Electrochemical oxidation

ABSTRACT

We show that stable titanium oxynitride, $TiN_{1-x}O_x$, may be easily obtained by aqueous electrochemical oxidation of substoichiometric titanium nitride, TiN_{1-x}, for all compositions x comprised between 0 and 0.5. This happens at lower potentials than oxidation into titanium dioxide. Hence, titanium oxynitride free from TiO_2 may be synthesized. A two-step mechanism is proposed for the complete oxidation of the nitride into dioxide: first, the oxynitride is formed on the electrode surface by oxidation of nitrogen vacancies. Then, once formed, the oxynitride can be fully oxidized, to give the dioxide. Measurements of charges associated to voltammetric peaks corroborate this mechanism.

1. Introduction

Titanium nitride, TiN, is a non-oxide ceramic exhibiting outstanding physicochemical properties such as ultrahigh melting point ($\gtrsim$3000 °C), high hardness (H_V~20 GPa), good resistance to aqueous corrosion (j_{corr}~0.1 μA cm^{-2} in 1 M H_2SO_4), a gold-like tint, and a good thermal conductivity (from 19 to 28 W m^{-1} K^{-1} between ambient temperature and 1700 °C) [1–3]. As a consequence, it has numerous industrial applications like wear-resistant coatings for cutting tools, diffusion barrier in semiconductor devices, stand-in for gold in jewelry, etc. [1–3]. Moreover, very recently, TiN has been proposed as Pt or Pd catalyst support in hydrogen, methanol or ethanol fuel cells [4–8], and for electroanalytical applications [9]. Two other properties of importance for the present study are, on one hand, its good electronic conductivity ($\rho \sim 1.5\times10^{-8}$ Ω m), and on the other hand, its wide range of substoichiometry, i.e., TiN_{1-x}, $0<x<0.5$.

It is accepted in the literature devoted to TiN electrochemical oxidation [10,11,5], that a single and irreversible wide anodic peak is observed in cyclic voltammetry, and that this peak can be attributed to the following reaction:

$$TiN + 2\,H_2O \rightarrow TiO_2 + \frac{1}{2}N_2 + 4\,H^+ + 4\,e^-. \qquad (1)$$

At high oxidizing potentials, titanium dioxide and gaseous nitrogen have been well characterized experimentally by angular resolved X-ray photoelectron spectroscopy (XPS) measurements [11]. Nevertheless, the XPS signal of titanium oxynitride, $TiN_{1-x}O_x$, has also been observed along the anodic wave, i.e., at intermediate potentials [10,11], and to the best of our knowledge, no clear mechanism for this oxynitride growth has been proposed so far.

We report herein on the preparation of TiN_{1-x} ceramics, with $x=$ 0.11, 0.22 and 0.45, and provide the first insights into the controlled electrochemical synthesis of titanium oxynitride thin films, $TiN_{1-x}O_x$, for all compositions x comprised between 0 and 0.5. Thanks to the use of substoichiometric nitrides, we show the possibility of forming stable and pure oxynitride layers, i.e., without TiO_2, because the dioxide only develops in a well-separated, electrochemical step at higher potentials. Commonly, titanium oxynitride is produced by physical methods like radio frequency or d.c. magnetron sputtering [12,13], vacuum arc discharge [14], or by chemistry, i.e., by the direct nitridation of TiO_2 in nitrogen or ammonia atmospheres, at high temperatures (ca. 600–1000 °C) [1]. Nevertheless, presence of TiO_2 is always detected in the final material [15]. The fabrication of $TiN_{1-x}O_x$ by electrochemistry that we propose here is rapid and simple, and could open interesting prospects in the field of transition metal oxynitride, dye-sensitized

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1388-2481/$ – see front matter
doi:10.1016/j.elecom.2012.06.032

solar cell photoelectrodes, for example titanium oxynitride supported on titanium nitride charge collector [16–20].

2. Experimental

2.1. Synthesis

TiN_{1-x} samples were prepared by reactive hot pressing, directly from powder mixtures of TiN and titanium metal, following the reaction:

$$(1-x)TiN + x\ Ti \rightarrow TiN_{1-x}. \quad (2)$$

Powders of TiN (purity 99.5%, 325 mesh) and Ti (purity 99.95%, <2 μm) were purchased from Neyco, France. Both were used as received, without further purification. Powders were mixed together in ligroin (VWR International) in a 30-kHz ultrasonic bath (Mecasonic, France) to promote intimate mixing.

We aimed at preparing three compositions $1-x=0.6$, 0.8, and 0.9. Sintering was performed in a La Physique Appliquée furnace (France) at 1815 °C, using a 40-MPa load, in a 15-mm graphite die, coated inside with boron nitride. Pure argon atmosphere was used, to prevent oxidation. The temperature program was composed of a first segment from ambient to 1600 °C at a rate of 15 °C/min then holding for 1 h at 1600 °C in order to avoid the melting of unreacted titanium metal (Ti melting point: 1670 °C). Subsequently, the sintering temperature was reached at the rate of 15 °C/min, and held for 1.5 h, 3 h, and 3.5 h for the compositions 0.6, 0.8, and 0.9, respectively. Indeed, the higher the amount of nitrogen vacancies, the higher the densification rate. To finish, the cooling from 1815 °C to ambient was done at the rate of 8 °C/min. The 40-MPa load was applied at 1100 °C, and released at the end of the dwell at 1815 °C. A similar protocol was used in Ref. [21] for the preparation of substoichiometric titanium carbides.

2.2. Characterization

X-ray diffraction, XRD, was done on a Siemens D5000 diffractometer (Germany) equipped with a Cu anticathode. Scanning electron microscopy, SEM, was performed using a Philips XL30 apparatus (The Netherlands), with in situ X-ray energy dispersive spectroscopy, EDS. The sintered samples were dense at 91, 95, and 97% for the compositions 0.6, 0.8, and 0.9, respectively, as measured by the Archimedes method.

2.3. Electrochemical apparatus

Cyclic voltammetry was carried out at room temperature (25 °C) in a standard three-electrode cell configuration. A PGSTAT30 potentiostat was used, controlled by GPES 4.9 software (Metrohm Autolab Ecochemie, The Netherlands). The solution was a 1 M H_2SO_4 aqueous solution (Aldrich and Millipore MilliQ + water), deaerated by bubbling pure argon. The reference electrode was a saturated calomel electrode, SCE, equipped with an extension filled with 1 M H_2SO_4. Potentials were recalculated vs. NHE (normal hydrogen electrode, $E_{SCE} = +0.242$ vs. NHE). The counter electrode was a platinum disk (10 mm in diameter)

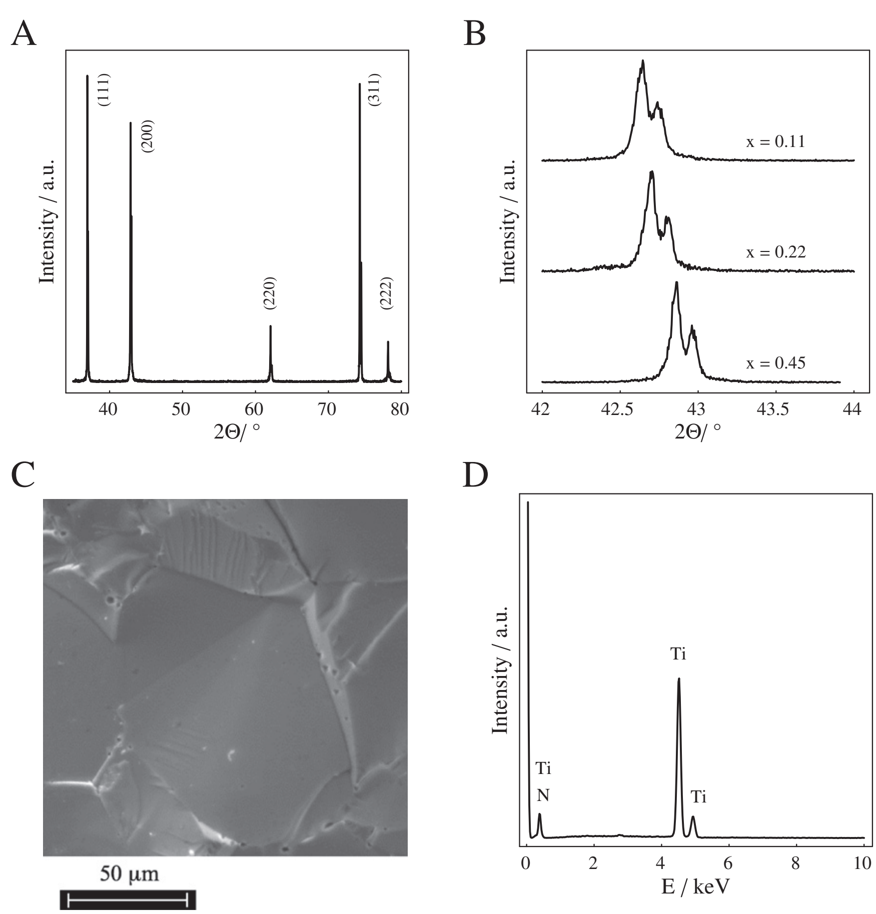

Fig. 1. (A) and (B) XRD patterns of the TiN_{1-x} samples, synthesized as described in Section 2.1. (A) $x=0.45$ ($TiN_{0.55}$). (B) Zoom-ins around diffraction peak (200) for $x=0.11$, 0.22, and 0.45, i.e., for $TiN_{0.89}$, $TiN_{0.78}$, and $TiN_{0.55}$, respectively. (C) SEM micrograph of a fractured pellet. (D) EDS analysis.