Surface & Coatings Technology 206 (2012) 4417–4424

Contents lists available at SciVerse ScienceDirect

Surface & Coatings Technology

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

Zirconium vacuum arc operation in a mixture of Ar and O_2 gases: Ar effect on the arcing characteristics, deposition rate and coating properties

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ARTICLE INFO

Article history:
Received 9 September 2011
Accepted in revised form 26 April 2012
Available online 4 May 2012

Keywords:
Filtered vacuum arc deposition
Ion current
Arc voltage
Deposition rate
Zirconium dioxide
Argon

ABSTRACT

The effect of oxygen and argon partial pressures (P_{O2}, P_{Ar}) in a Zr vacuum arc on plasma ion current density J_p, arc voltage V_{arc}, deposition rate v_d, and selected coating properties was determined. A d.c. arc current of $I_{arc} = 100$ A was initiated between a Zr cathode and a grounded anode. Cathode spots produced a plasma jet, which entered a 1/8 torus macroparticle (MP) filter. The plasma was guided by a d.c. magnetic field through an aperture to a glass substrate or a flat disk probe, mounted on a rotatable holder. J_p was measured with the probe, negatively biased to $V_b = -60$ V. Coating thickness was measured using a profilometer, and coating properties were investigated using optical microscopy, energy dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), nano-indentation and optical analysis.

The discharge electrical characteristics and the coating deposition rate were found to be significantly influenced by P_{O2} and P_{Ar}. J_p and v_d increased with P_{Ar} until a maximum at $P_{Ar} = 0.27$ Pa and decreased with P_{O2}. V_{arc} decreased with both P_{Ar} and P_{O2}. The changes in J_p, V_{arc}, and v_d, with P_{Ar} were larger at larger P_{O2}. The J_p, V_{arc}, and v_d dependencies suggest that addition of Argon increased the Zr ion emission from the cathode, possibly because Ar ion bombardment reduced Zr surface oxidation and improved plasma conductivity.

Zirconium Oxide (ZrO_2) coatings were transparent and had colored interference rings. Well adhered, MP-free ZrO_2 coatings were deposited with $P_{O2} \geq 1.07$ Pa. Coatings deposited with $P_{O2} = 1.07$ Pa + $P_{Ar} = 0$ were amorphous, whereas those deposited with $P_{O2} = 1.07$ Pa + $P_{Ar} = 0.27$ Pa had some degree of a monoclinic phase. Furthermore, the refractive index (n) and extinction coefficient (k) slightly decreased, from 2.22 to 2.17, and from 0.03 to 0.01, respectively and coating hardness (H) and Young's Modulus (E) decreased from ~12.9 to ~11.6 GPa and from ~153 to ~136 GPa respectively when $P_{Ar} = 0.27$ Pa was added to a $P_{O2} = 1.07$ Pa environment.

1. Introduction

Zirconium dioxide (ZrO_2) is a refractory material (melting point ~ 2700 °C), with a unique combination of properties: low thermal conductivity (4.2 W m^{-1} K^{-1} at room temperature[1]), high hardness (18 GPa for monoclinic phase, 14 to 11 GPa for amorphous [2,3]), excellent chemical and corrosion resistance [2,4], high refractive index (2.2), large band gap (5 eV), high transparency in the 0.3–8 μm range [5], high dielectric constant (~25 [6]), biocompatibility [7] and the ability to work as a photocatalyst [8]. These properties allow ZrO_2 films to protect materials from wear, heat transport and oxidation, and operate as a functional layer, e.g. in optical [5] and electronic devices [6,9].

The crystalline structure of ZrO_2, as well as its optical and mechanical properties, is influenced by the deposition technique and parameters. Amorphous [2,6,10,11], cubic [12,13], monoclinic [2,4,6,7,11,12,14], tetragonal [7,15,16] and orthorombic [9,17] structures were reported for various techniques including Sol–gel [13], Chemical Vapor Deposition (CVD) [18], Sputtering [15,19,20], Electron Beam Physical Vapor Deposition (EB-PVD) [12,16], and Vacuum Arc Deposition (VAD) [2,5,10,17].

Generally, coatings deposited by FVAD are characterized by high deposition rate, high density and good adhesion [21]. Zhao et al. reported that the optical properties and homogeneity of ZrO_2 coatings obtained with FVAD were better than obtained with other techniques [5]. They also reported that the deposition rate decreased from 75 to 35 nm/min with increasing O_2 flow rate. Yu et al. reported that the film evolved from amorphous, through monoclinic phase and to amorphous again with increasing O_2 flow rate. They also reported smoother morphology, lower hardness (~13.4 GPa) and lower Young's Modulus (~190 GPa) in the amorphous phase [6]. Similarly, Martin et al. also reported lower hardness (~11 GPa) and lower Young's Modulus (~125 GPa) in the amorphous phase [3]. Zukerman et al. reported that the ion current decreased, and the arc became unstable with increasing O_2 pressure [22].

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doi:10.1016/j.surfcoat.2012.04.082

It was shown previously that Ar addition may significantly improve the stability of Zr vacuum arcs in the presence of O_2 and could even be necessary to achieve stable arcing. Yukimura et al. reported that in a pure O_2 environment the arc was unstable, and had a shorter lifetime than an arc in a mixed O_2+Ar environment [23]. Similarly, Zukerman et al. reported that addition of Ar to the oxygen improved the arc stability, generally increased the ion current and decreased the arc voltage and its fluctuations, characterizing more stable arc operation [22]. Furthermore, Huang et al. showed that coatings produced in both mixed O_2+Ar and in pure O_2, on heated substrates, were crystallized in an orthorhombic phase, and Ar addition reduced the deposition rate [17].

Although it is often observed that during vacuum arc operation in a background gas, the ion current density produced at cathode spots, J_p, generally decreases with increasing background gas pressure, J_p in pure Ar may increase with P_{Ar}. Puchert et al. studied the influence of Argon on filtered Cu vacuum arcs and reported that the ion current increased until a maximum and then decreased with P_{Ar}, whereas the deposition rate decreased as P_{Ar} was increased [24]. Similarly, Zhitomirsky et al. showed that J_p first increased, and then decreased with increasing He and Ar pressure for Ti plasma in their FVAD system [25], however, the influence of P_{Ar} on deposition rate was not presented. The influence of Ar and O_2 partial pressures, P_{Ar} and $P_{O2,}$ on the electrical characteristics of the plasma (ion current density, J_p, and arc voltage, V_{arc}), and on the deposition rate, v_d, was not previously determined. The objective of this paper is to determine J_p, V_{arc} and v_d during Zr FVAD as a function of P_{Ar} and P_{O2}, to present and discuss the inter-relationship between J_p and v_d and to determine the effect of Ar addition on the chemical, structural, mechanical and optical properties of selected coatings.

2. Experimental apparatus and procedure

A schematic diagram of the FVAD system with a 1/8 torus magnetic macroparticle (MP) filter used in the present study is shown in Fig. 1. Details of this system and its multi-cathode plasma gun were presented previously [26,27].

The end flange of the plasma gun was equipped with a 99.5% Zr cathode, offset by 50 mm from the gun axis. The Zr cathode had a frustum cone shape with front and back base diameters of 49 and 54 mm, respectively, and a height of 15 mm. DC arc current was applied between the cathode and a grounded anode by a welding power supply (Miller XMT®-400 CC/CV). The arc current, $I_{arc}=100$ A, was initiated by momentarily contacting the cathode with a mechanical trigger electrode, which was connected to the anode via a current limiting resistor. Cathode spots on the cathode surface produced a plasma jet, which entered the 1/8 torus via a 54 mm diameter hole in the anode, coaxial with the cathode. The jet was guided to the deposition chamber by a d.c. magnetic field of about 12 mT, generally parallel to the duct wall, produced by electro-magnetic coils 1–5. The duct filters MPs by magnetically bending the plasma beam while allowing the MPs to fly straight onto the duct wall (Fig. 1). The 1/8 torus had a major radius of 240 mm and minor radius of 80 mm.

In most of the experiments, a mask (Fig. 2(a–b)) was mounted in the deposition chamber ~150 mm from the toroidal duct exit, i.e. approximately midway between coils 4 and 5 (Fig. 1). The mask had a 26×26 mm^2 square aperture, located at $Y=30$ mm from the straight duct axis. The thickness of the aperture neck (Fig. 2a) was 10 mm. A rotatable substrate holder (Fig. 2c) equipped with 4 glass slide substrates (each 25×25 mm^2) or with an ion current probe (20 mm diameter disk) was mounted behind the mask, i.e. ~160 mm from the 1/8 torus exit (Figs. 1 and 2a). The substrates or the ion probe were mounted on the rotatable holder, 30 mm from its axis (Fig. 2c). The holder could be rotated to align the ion probe or substrate to be coated with the mask aperture. The mask aperture was designed to transfer plasma flux only to the desired substrate, while obstructing the path to the other substrates. This arrangement allowed coating 4 samples, each under different conditions, in one pump-down cycle. When no mask was used, one substrate was mounted on the holder center, i.e., on the straight duct axis. Beam steering coils X and Y (Fig. 1) were used to guide the plasma beam center to the substrate or ion probe by producing a magnetic field normal to the chamber axis [27].

Before arc ignition, the vacuum chamber was pumped down to an initial residual pressure of 27 mPa. The arcs were operated in vacuum, Ar, O_2 or an $Ar+O_2$ mixture. The gases were introduced in the vicinity of the sample chamber (Fig. 1). Ar ($P_{Ar}=0$–0.4 Pa) was introduced via a mass flow controller to produce the desired P_{Ar} before arc ignition. The Ar flow rate was held constant until the end of each experiment. O_2 ($P_{O2}=0$–1.34 Pa) was introduced via a needle valve, with the O_2 flow rate controlled by a computerized control loop based on a LabView program which regulated the total pressure $P=P_{Ar}+P_{O2}$.

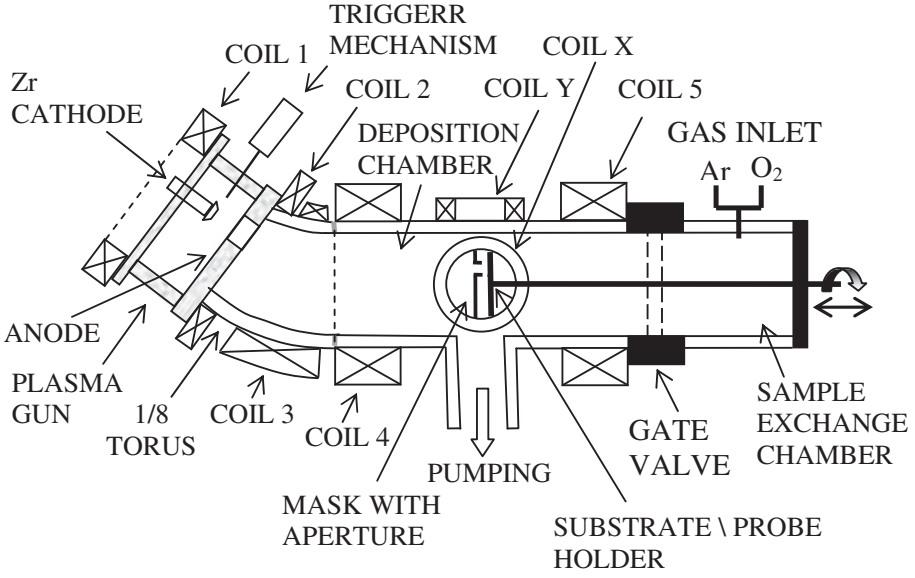

Fig. 1. Schematic diagram of the vacuum arc deposition system.