Journal of Physics and Chemistry of Solids 71 (2010) 1754–1759

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

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

# Bilayer period effect on corrosion–erosion resistance for $[TiN/AlTiN]_n$ multilayered growth on AISI 1045 steel

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ARTICLE INFO

*Article history:*
Received 14 April 2010
Received in revised form
21 August 2010
Accepted 29 August 2010

*Keywords:*
A. Metals
A. Multilayers
A. Surfaces
B. Plasma deposition
D. Electrochemical properties

ABSTRACT

The aim of this work is to study the electrochemical behavior, under a corrosion–erosion condition, of $[TiN/AlTiN]_n$ multilayer coatings with bilayers periods of 1, 6, 12 and 24, deposited by a magnetron sputtering technique on Si (1 0 0) and AISI 1045 steel substrates.

The TiN and AlTiN structure for multilayer coatings were evaluated via X-ray diffraction (XRD) analysis. Silica particles were used as an abrasive in the corrosion–erosion test within a 0.5 M $H_2SO_4$ solution at an impact angle of 30° over the surface. The electrochemical characterization was carried out using a polarization resistance technique (Tafel), in order to observe changes in the corrosion rate as a function of the bilayers number ($n$) or bilayer period ($\Lambda$). Corrosion rate values of 359 mpy in uncoated steel substrate and $1.016 \times 10^{-6}$ mpy for substrate coated with $[TiN/AlTiN]_{24}$ under impact angle of 30° were found. This behavior was related with the mass loss curve for all coatings and the surface damage was analyzed using SEM images. These results indicate that TiN/AlTiN multilayer coatings deposited on AISI 1045 steel provide a practical solution for applications in erosive–corrosive environments.


## 1. Introduction

Erosion–corrosion is an accelerated corrosion of metals due to a combination of a chemical and mechanical abrasive attack by the physical movement of fluids with suspended solids on the surface of the metal. Therefore, alloys that form a film surface under a corrosive environment commonly have a corrosion speed limit but this film is susceptible to delamination; hence, corrosion is accelerated rapidly. Erosion–corrosion is associated with a current induced by the mechanical removal of the surface of the protective film that results in a further increase of the corrosion rate for chemical or electrochemical processes. Surface engineering of metallic substrates with a protective film calls unanimous attention from industry and researchers, as it produces a host of properties such as wear protection, erosion resistance, oxidation protection, and corrosion resistance. On other hand, the hard coating and multilayer coatings are highly functional if the interface between the film and the substrate present good adherence [1]. Moreover, the multilayer coatings are extensively used in metallurgy industries and are becoming of increasing importance in wear and corrosion protection. The interest on multilayered via Physical Vapor Deposition (PVD) is based on their considerably enhanced mechanical properties [2–5]. Although, previous studies have reported that the concept of multilayer coatings offers a potent solution for tribological properties in hard coatings. The coatings deposited via PVD based on nitrides

AlCN [6], CrAlN [7], TiNbCN [8] and AlTiN with high aluminum content provide high wear resistance, stability under high service temperature, oxidation resistance and low thermal conductivity. Furthermore, TiN/TiAlN and TiN/AlTiN multilayer coatings deposited on cutting tools produce good mechanical and corrosion resistance [9]. Currently, the literature shows aluminum titanium nitride (AlTiN) as a material with better mechanical properties compared to TiN, due to the inclusion of aluminum atoms in TiN crystalline structure generating increase in oxidation resistance by formation of the stable ternary material AlTiN [10]. In recent years, there have been considerable efforts to develop coating multilayered to improve mechanical properties (e.g. TiCN/TiNbCN) [11], wear and oxidation resistance for many components. The improvements were presented in alternating deposition of two (or more) different layers to avoid the fracture movement; therefore, the multilayer structure may act as nano-cracks inhibitors [12,13]. The aim of this work is to study the behavior of TiN/AlTiN multilayer coatings with a thickness of 3 μm, under corrosive–erosive fluid, as a function of increasing of the bilayer number ($n$) or decreasing of the bilayer period ($\Lambda$). Also, this work compared the corrosion–erosion behavior presented by the AISI 1045 steel uncoated substrate with all TiN/AlTiN multilayered.

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0022-3697/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jpcs.2010.08.019

## 2. Experimental details

$[TiN/AlTiN]_n$ multilayered coatings have been grown onto Si (1 0 0) and AISI 1045 steel substrates using a multi-target magnetron sputtering system, with r.f. source (13.56 MHz) and two stoichiometric targets of Al and Ti with a purity of 99.9%. The optimal deposition parameters were the following: sputtering power of 400 W for Al and 350 W for the Ti target; a substrate temperature of 300 °C; under circular rotation substrate with 60 rpm; to facilitate the formation of the stoichiometric coating, the sputtering gas was a mixture of Ar 93% and $N_2$ 7% with total working pressure of $6\times10^{-3}$ mbar, under a nitrogen gas flow of 3.7 sccm. An unbalanced r.f. bias voltage, which generates a constant voltage offset of -70 V was applied. Moreover, the magnetron sputtering device had a positioning substrate system in relationship to the target spot, this parameter permitted a varying in the bilayer number ($n$) among 1, 6, 12 and 24 or bilayer period ($\Lambda$) among 1.5 μm, 500 nm, 250 nm and 125 nm, respectively. The crystal structure of the coatings was determined by using a D8 Advance Bruker X-ray diffractometer with CuKα ($\lambda$=1.5405 Å) radiation. Chemical composition of the coatings was determined by energy dispersive X-ray spectroscopy (EDX) using a Philips XL 30 FEG. The structural assembly of the multilayered was analyzed by scanning electron microscopy (SEM) (Philips XL 30 FEG) equipped with a light optical magnification range: 525–24.00×. For the analysis of the erosive–corrosive effect a device built for the evaluation of chemical attack in metallic materials was used. Fig. 1 shows the erosive–corrosive test device that consists of a tribometer with a glass container for erosive–corrosive storage, an acrylic cover that is available in the sample holder and electrodes – an impelling of High Ultra Molecular Weight Polyethylene (HUMWPE) – which rests on a teflon shaft that is attached to the main shaft motor which provides fluid motion. The lid of the container allows for located sample exposure under corrosive fluid, and the reference electrode and counter-electrode. The fluid movement is caused by a shaft driver motor. The tangential speed applied to the fluid with erosive particles was fixed to 11.12 m/s, this take into a count that the impeller radius is 0.055 m and the motor speed was fixed to1930 rpm. The electrochemical study was carried out with a Gamry unit, model PCI 4 with DC and AC signals, which generate Tafel polarization curves. These curves were realized at room temperature using a cell that supported one working electrode within an exposed area of 1 $cm^2$, a reference electrode ($Cu/CuSO_4$) and a graphite counter electrode under a 3.5% NaCl+0.5 M $H_2SO_4$ solution, into distilled water. The resting potential was measured during 30 min intervals. The Tafel curves were taken during times, between 15 and 250 min, in which the impact angle on surface samples was 30°. This time was necessary for anodic and cathodic sweep potential. Tafel polarization curves were obtained at a sweep speed of 0.5 mV/s in voltage range from −0.2 to 0.8 V with an exposed area of 1 $cm^2$ [10]. In this project, a silica solution ($SiO_2$) with particle sizes between 210 and 300 μm was used as an abrasive agent. This solution was chosen because it is used to study steel as it facilitates the observation at a defined anodic region and chloride addition guaranteeing an effective attack. Finally, for analyzed corrosion surface process, the superficial morphology was characterized by using a High-Resolution Scanning Electron Microscope (SEM) (Philips XL 30 FEG).

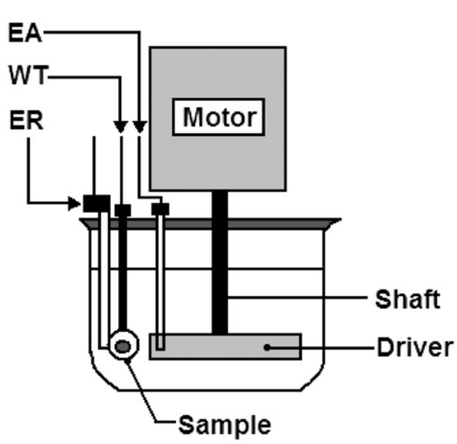


**Fig. 1.** Schematic diagram of the device used at corrosion–erosion wear testing. Auxiliary electrode (EA), working electrode (WT), reference electrode (ER) were used in the test [13].

## 3. Results and discussion

### 3.1. X-ray diffraction analysis

The measured total thickness of the deposited $[TiN/AlTiN]_n$ multilayered was found to be approximately 3 μm. The individual thicknesses varied in function of bilayer number from $n$=1 to 24, producing layered with individual thickness from 1500 to 125 nm, referent to the bilayer period ($\Lambda$). Fig. 2 shows the XRD pattern of TiN/AlTiN coatings deposited with $\Lambda$=250 nm onto a Si (1 0 0) substrate, at a r.f. negative bias voltage of -70 V; the XRD pattern presents a cubic structure where the strongest peak (2 2 0) corresponds to the AlTiN (2 2 0) plane, indicating a light textured growth along this orientation. The other weak peaks correspond to diffractions from TiN (1 1 1), AlTiN (2 0 0) and AlN (2 2 0) planes of the FCC structure. These preferential orientations are in agreement with JCPDF 00-038-1420 and JCPDF 00-037-1140 from TiN and AlTiN ICCD cards, respectively. Regarding the lattice parameter, obtained from the preferential orientation in the TiN and AlTiN single layered coatings was as well as was the multilayered system with bilayers period $\Lambda$=250 nm ($n$=12), in this study the Nelson–Riley extrapolation technique was employed in the refinement procedure to determine the value of $a_0$ (±0.0001 nm), because this technique permits direct precision determination of the lattice constant (see Table 1). The results show an expansion of the cell unit relate to the value reported in the ICCD cards mentioned before for Ti–N (FCC) ($a_0$=0.4241 nm) and Al–Ti–N (FCC) ($a_0$=0.4112 nm), both in powder, when those

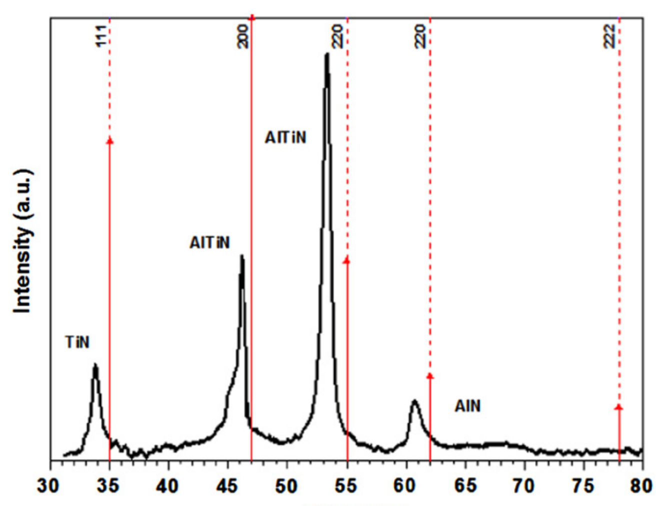


**Fig. 2.** XRD patterns for TiN/AlTiN multilayered grown with $\Lambda$=250 nm. Dash lines indicate the position of the peaks obtained from JCPDF 462553 files from ICDD cards.