Applied Surface Science 264 (2013) 507–515

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

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

Adsorption behavior of glycidoxypropyl-trimethoxy-silane on titanium alloy Ti–6.5Al–1Mo–1V–2Zr

Jian-hua Liu, Zhong-wei Zhan, Mei Yu*, Song-mei Li

School of Materials Science and Engineering, Beihang University, Beijing 100191, China

ARTICLE INFO

Article history:
Received 27 May 2011
Received in revised form 9 October 2012
Accepted 10 October 2012
Available online 17 October 2012

Keywords:
Glycidoxypropyl-trimethoxy-silane (GTMS)
Titanium alloy
Adsorption isotherm
XPS
Tafel
EIS

ABSTRACT

The adsorption behavior of glycidoxypropyl-trimethoxy-silane (GTMS) on titanium alloy Ti–6.5Al–1Mo–1V–2Zr was investigated by using X-ray photoelectron spectroscopy (XPS), Tafel polarization test, and electrochemical impedance spectroscopy (EIS). From the XPS results, it was found that the silane coverage on the titanium surface generally increased with GTMS concentration, with a slight decrease at concentration of 0.1%. Based on the relationship between isoelectronic point (IEP) of titanium surface and the pH values of silane solutions, adsorption mechanisms at different concentrations were proposed. The surface coverage data of GTMS on titanium surface was also derived from electrochemical measurements. By linear fitting the coverage data, it revealed that the adsorption of GTMS on the titanium alloy surface at 30 °C was of a physisorption-based mechanism, and obeyed Langmuir adsorption isotherm. The adsorption equilibrium constant (K_{ads}) and free energy of adsorption process (ΔG_{ads}) were calculated to elaborate the mechanism of GTMS adsorption.

1. Introduction

The organosilanes are the mostly used precursors in sol–gel chemistry. A variety of organosilanes with specific functional groups have been employed as adhesion promoters between metallic substrates and organic resins [1]. More recently, organosilane-based coatings are extensively developed for anti-corrosion, wear-resistant, and optical applications [2–4]. The popularity of organosilane-based coatings is attributed to its "bridge" effect between organic and inorganic phases. Many researchers pointed out that silanol, product of organosilane hydrolysis reaction (Fig. 1a), in principle chemically bonds with metallic and organic substrates [1,5]. A widely accepted theory [6–11] of the bonding mechanism postulated that during immersion, the silane molecules adsorbed on the metal surface via hydrogen bonding between the silanols (—SiOH) and the hydroxyl groups (—MeOH) on the metal surface (Fig. 1b). And then condensation took place to form strong covalent metallo-siloxane (Me—O—Si) bonds in the consequent drying process (Fig. 1b). It had been proved [12,13] that the chemical heterogeneity at the metal surface, the pre-treatments of metallic substrate and the pH value of silane solution strongly affected the adsorption behavior of silane, which directly governed the integrity and uniformity of resulting silane coatings.

The structure of glycidoxypropyl-trimethoxy-silane (GTMS) was shown in Fig. 2. The ending epoxy group enables GTMS molecules to chemically bond with or incorporate into most epoxy- and amine-based resins. Therefore, GTMS is widely used to prepare silane coatings on aluminum [14,15], magnesium [16,17], and titanium [18] alloys. An important application of GTMS [19–22] significantly improved the adhesion strength and durability of the epoxy/metallic interfaces. The titanium alloy served as substrate in this study is Ti–6.5Al–1Mo–1V–2Zr alloy, which is extensively applied in the aerospace and automobile industries. To help design proper formulation of silane solution applied on titanium alloy Ti–6.5Al–1Mo–1V–2Zr, it is of significant importance to investigate the adsorption mechanism of GTMS on this alloy.

In this work, the adsorption mechanism of GTMS on the surface of titanium alloy Ti–6.5Al–1Mo–1V–2Zr was investigated. The quantitative surface compositions of GTMS-treated titanium alloy were acquired from XPS analysis, to draw the adsorption isotherm and further establish the adsorption type of GTMS. The XPS measurement can also provide information of oxidation state of silicon through high resolution spectra, which is helpful in understanding the condensation of silane molecules and film formation with GTMS concentrations. Besides, electrochemical methods are applied to illustrate the in situ adsorption process of GTMS. Based on the parameters derived from Tafel polarization and EIS measurement, surface coverage of GTMS on titanium alloy surface is estimated and thermodynamic aspect of the adsorption process is highlighted.

* Corresponding author. Tel.: +86 10 82317103; fax: +86 10 82317103.
E-mail address: yumei@buaa.edu.cn (M. Yu).

0169-4332/$ – see front matter.
http://dx.doi.org/10.1016/j.apsusc.2012.10.054

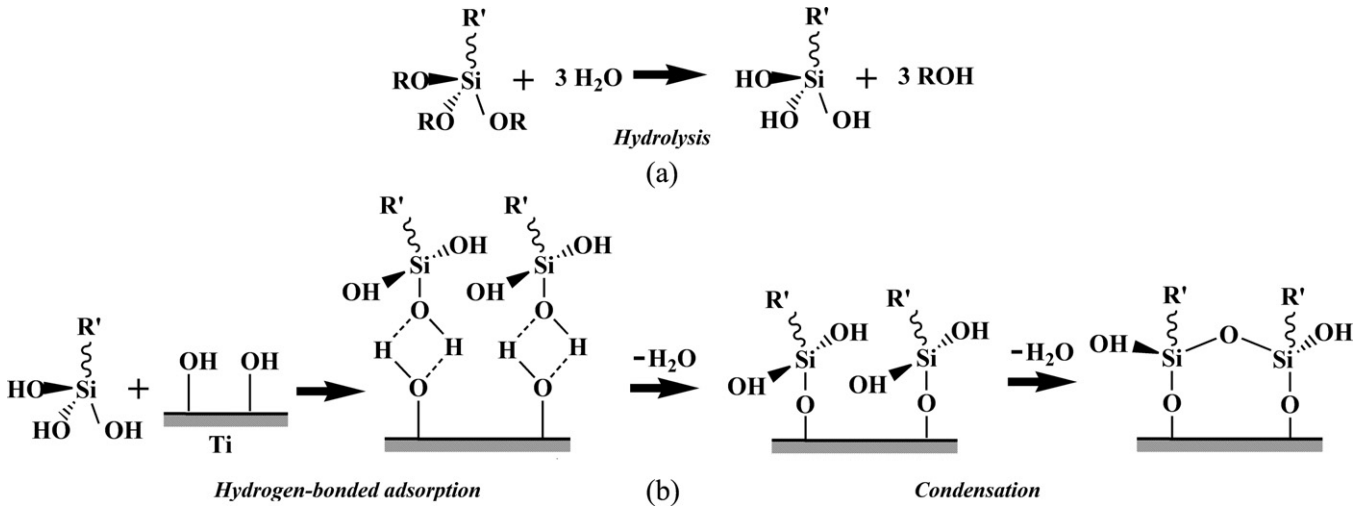

Fig. 1. Schematic illustrations of hydrolysis, hydrogen-bonded adsorption and condensation of silane on metal surface.

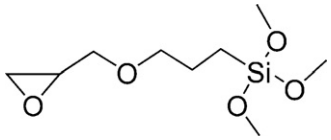

Fig. 2. Structure of GTMS.

2. Experimental

2.1. Sample preparation

The nominal composition of titanium alloy Ti–6.5Al–1Mo–1V–2Zr was given in Table 1. They were cut into 1 cm^2 round samples, sealed with epoxy resin and sanded to 5000# grade by waterproof abrasive papers. After that, the samples were mechanically polished using diamond paste to a mirror polish, and cleaned with deionized water (10 min), ethanol (10 min, analytical) and acetone (15 min, analytical) prior to being used in the following surface analysis and electrochemical tests.

The silane solutions were prepared by mixing glycidoxypropyltrimethoxy-silane (GTMS, analytical, Nanjing Capatue Chemical Co., Ltd., China), glacial acetic acid (0.1 M, analytical, Beijing Chemical Works, China) and deionized water. The GTMS concentrations *c* were 0%, 0.01%, 0.05%, 0.1%, 0.5% and 1% by volume. The mixtures were then stirred for 2 h at room temperature to ensure complete hydrolysis of GTMS.

The cleaned samples for XPS analysis were immersed into the hydrolyzed silane solutions for 5 min and then dried in air for 15 min, followed by oven dry at 60 °C for 30 min.

2.2. XPS analysis

X-ray photoelectron spectroscopy (XPS) was analyzed on a PHI-1600 spectrometer (U.S.A.) equipped with Mg Kα radiation for exciting photoelectrons. X-ray source was operated at an accelerating voltage of 15 kV and 250 W. The pressure in the ion-pumped analysis chamber was maintained at 1.1×10^{-7} Pa during data acquisition. All binding energies (BE) were referenced to the adventitious C 1s line at 284.6 eV. The samples were analyzed at the take-off angle of 45° relative to the surface normal. The peak fitting of Si 2p was conducted by using an XPSPeaks 4.1 program. The surface composition (in atomic%) of various samples was determined by considering the integrated peak areas of C ls, Si 2s, Si 2p, O ls and Ti 2p peaks, and their respective experimental sensitivity factors. These sensitivity factors were derived from a large set of organic and inorganic compounds of well-defined stoichiometries. The fractional concentration of a particular element *E* (%*E*) is calculated by using Eq. (1) [23]:

$$\%E = \frac{(I_E/s_E)}{\sum(I_n/s_n)} \times 100\% \quad (1)$$

in which *I* and *s* are the integrated peak area and the sensitivity factor, respectively; *n* stands for the *n*th element considered in the quantitative analysis.

The XPS measurements were taken on several panels of samples independently. Each panel contained a series of coated samples treated with different GTMS concentrations. The XPS data of each panel was analyzed and fitted to confirm reproducibility of the tests. The XPS data of the panel with best fitted result were presented here.

Table 1
Nominal composition of Ti–6.5Al–1Mo–1V–2Zr alloy.

Element	Al	Mo	V	Zr	Other	Ti
Concentration (wt.%)	6.5	1	1	2	0.30	Balance

2.3. Electrochemical measurements

The electrochemical measurements were carried out by using an Advanced Electrochemical System (PARSTAT 2273, Princeton, USA). A three-electrode cell was employed, consisting of a saturated calomel reference electrode (SCE), a platinum foil as counter electrode and the cleaned sample as working electrode with a surface area of 1 cm^2. The test solutions were the GTMS solutions with different concentrations mentioned above. All electrochemical tests were carried out at constant temperature (30 ± 1 °C) by putting the cell into water bath.

Tafel polarization curves were recorded at constant sweep rate of 1 mV/s and the scanning range was from −250 to +250 mV with respect to the open circuit potential. The cathodic and anodic branches were separately performed on two fresh electrodes scanning from the open circuit potential, in order to avoid the influence by each other. Before each experiment, the working electrode was immersed in the test cell for 30 min until to reach steady state condition. The measurements were repeated three times for each condition and the average values were presented.

The electrochemical impedance spectroscopy (EIS) measurements were conducted with an AC excitation amplitude of 10 mV