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Niobium addition enhancing the corrosion resistance of nanocrystalline Ti_5Si_3 coating in H_2SO_4 solution

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Abstract

In this paper, novel Nb-containing Ti_5Si_3 (i.e., $Ti_{56.2}Nb_{6.3}Si_{37.5}$ and $Ti_{50.0}Nb_{12.5}Si_{37.5}$) nanocrystalline coatings were deposited onto Ti–6Al–4V substrates by a double glow discharge plasma technique. The effects of Nb alloying on the electrochemical behavior of the Ti_5Si_3 nanocrystalline coatings were systematically investigated in a naturally aerated 5 wt.% H_2SO_4 solution, for which various electrochemical techniques, including potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), potentiostatic polarization and Mott–Schottky analysis, were employed. Moreover, to evaluate the corrosion performance of the as-deposited coatings over an extended period, their corrosion resistance was analyzed after 7 days' immersion in a 5 wt.% H_2SO_4 solution by EIS measurements and observations of corroded surface morphologies. The results showed that the $Ti_{62.5-x}Nb_xSi_{37.5}$ ($x = 0$, 6.3, 12.5) nanocrystalline coatings exhibit superior corrosion resistance compared with Ti–6Al–4V, and their corrosion resistance is enhanced with increasing Nb content, suggesting that Nb alloying is an effective strategy for improving the corrosion protection ability of the Ti_5Si_3 nanocrystalline coating. The roles of Nb additions in enhancing the corrosion resistance of the Ti_5Si_3 nanocrystalline coatings can be summarized as: (a) reducing the residual tensile stresses of the as-deposited coatings and (b) tailoring the composition, compactness and electronic structure of the passive films formed. These findings are expected to broaden the application of Ti_5Si_3 as a highly corrosion-resistant coating for engineering components operating under aggressive conditions.

Keywords: Nanocrystalline film; Sputter deposition; Electrochemical impedance; Corrosion; Transition-metal silicides

1. Introduction

Titanium alloys are relatively new engineering materials, possessing an extraordinary combination of properties, such as high specific strength, good corrosion resistance and biocompatibility. They are commonly used in aerospace structures, space vehicles and medical devices, and in the petroleum and chemical industries [1,2]. The excellent corrosion resistance of titanium alloys in many industrial environments arises from the existence of a protective oxide film that forms naturally upon exposure to air [3]. However, titanium alloys exhibit low corrosion resistance in strong reducing acids such as sulfuric acids, which has restricted their use for safety–critical applications [4]. Furthermore, under the application of static or dynamic contact loads, the thin passive film would be easily destroyed. Because bare titanium alloys have a strongly negative standard electrode potential (−1.63 V), they often suffer galvanic and crevice corrosion as well as corrosion

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embrittlement caused by intensive interactions with the interface material and/or the surrounding environment [5]. In the past decade, various surface modification techniques, including micro-plasma oxidation [6], laser treatment [7], chemical vapor deposition [8], physical vapor deposition [9] and ion implantation [10], have been developed to improve the resistance of titanium alloys against abrasion and corrosion damage. Among these methods, the application of a double glow discharge plasma technique, through the synthesis of nanocrystalline transition metal silicide coatings, has proved to be an economical and effective way to enhance the surface properties of titanium alloys [11,12].

As a promising high-temperature engineering material, Ti_5Si_3 has recently attracted much interest because of its high melting temperature (2130 °C), low density (4.32 g cm^{-3}), excellent creep strength and high oxidation resistance [13,14]. Moreover, highly covalent-dominated atomic bonds endow Ti_5Si_3 with good chemical inertness and high hardness, which has generated vigorous pursuit of Ti_5Si_3 as a wear- and corrosion-resistant coating material. Unfortunately, since Ti_5Si_3 has a hexagonal crystal structure, the thermal expansion anisotropy, originating from a large difference between the coefficients of thermal expansion (CTE) in the crystallographic *c* and *a* directions (CTE(*c*)/CTE(*a*) ratios of ~3), results in appreciable residual stresses in the material during heating and cooling that can give rise to microcracking [15,16]. To alleviate or eliminate this problem, alloying by substitutional elements, which acts to change the chemical bond nature and/or refine the crystal size, has been performed to control the degree of strain or microcracking. For example, Thom et al. [17] suggested that a critical grain size of pure Ti_5Si_3 and carbon-containing Ti_5Si_3 is 2–3 μm and 5–6 μm, respectively, needed to completely avoid microcracking. Experimental observations also indicated that the thermal-expansion anisotropy of Ti_5Si_3 exhibits a substantial reduction by replacing some of the titanium by zirconium, niobium or chromium [18,19]. It is worth noting that previous studies focused mainly on physical and mechanical properties, with little attention devoted to understanding the electrochemical behavior of Ti_5Si_3 in aqueous corrosive environments. In an earlier study, the present authors investigated the influence of carbon addition on the electrochemical characteristics of Ti_5Si_3, and found that the small additions of carbon have a significantly positive impact on the corrosion resistance of Ti_5Si_3 in 3.5 wt.% NaCl solution [20]. Considering the fact that Nb not only has a high solubility in Ti_5Si_3 (~21 at.%), but also possesses high passivating ability in diverse aqueous environments [21,22], it is hypothesized that Nb could be a desirable additive to Ti_5Si_3, which acts to reduce both the residual tensile stress and tailor the surface properties of Ti_5Si_3 and, consequently, enhance its corrosion resistance.

To test this hypothesis, two Nb-containing Ti_5Si_3 coatings (i.e., $Ti_{56.2}Nb_{6.3}Si_{37.5}$ and $Ti_{50.0}Nb_{12.5}Si_{37.5}$) were prepared by a double glow discharge plasma technique. The microstructure of the as-deposited coatings was first characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy and transmission electron microscopy (TEM). Subsequently, the electrochemical behavior of the coatings was investigated by potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), potentiostatic polarization and capacitance measurement (Mott–Schottky approach) in a naturally aerated 5 wt.% H_2SO_4 solution. In addition, X-ray photoemission spectroscopy (XPS) was employed to identify the composition and chemical bonding states of the passive films grown on the coatings following potentiostatic polarization tests. For comparative purposes, these measurements were also performed on a Ti_5Si_3 nanocrystalline coating and the uncoated Ti–6Al–4V substrate. Finally, the roles of Nb additions in governing the corrosion mechanisms of the Ti_5Si_3 coatings were elucidated.

2. Experimental

2.1. Specimen preparation

Disk-shaped substrates, 40 mm in diameter and 3 mm thick, were machined from a commercial Ti–6Al–4V alloy rod. The nominal composition of this alloy in weight per cent is: Al, 6.04; V, 4.03; Fe, 0.3; O, 0.1; C, 0.1; N, 0.05; H, 0.015 and the balance Ti. Prior to coating deposition, the substrates were successively ground with a series of silicon carbide papers and finally polished with 1.5 μm diamond paste to obtain a mirror-like surface finish. The polished substrates were then ultrasonically cleaned in ethyl alcohol and dried in cold air. Three types of coatings—$Ti_{62.5}Si_{37.5}$ (i.e., Ti_5Si_3 as a reference), $Ti_{56.2}Nb_{6.3}Si_{37.5}$ and $Ti_{50.0}Nb_{12.5}Si_{37.5}$—were deposited onto the polished substrates by a double cathode glow discharge technique, using three targets with different stoichiometric ratios ($Ti_{50}Si_{50}$, $Ti_{45}Nb_5Si_{50}$ and $Ti_{40}Nb_{10}Si_{50}$, respectively). The targets were fabricated from ball-mill Ti (−300 mesh, 99.9% purity), Nb (−300 mesh, 99.9% purity), and Si (−200 mesh, 99.5% purity) by employing cold compaction under a pressure of 600 MPa. During the deposition process, one cathode was the target composed of the desired sputtering materials, and the other was the substrate. When voltages were applied to the two cathodes, glow discharge occurred, as described elsewhere [20]. The glow discharge sputtering parameters can be described as follows: base pressure, 5×10^{-3} Pa; working pressure, 35 Pa; target–substrate distance, 10 mm; target electrode bias voltage, −800 V; substrate electrode bias voltage, −300 V; substrate temperature, 800 °C; and treatment time, 3 h.

2.2. Microstructure characterization and composition analysis

The phase compositions of the as-deposited coatings were characterized by X-ray diffractometry (XRD; D8 ADVANCE with Cu Kα radiation) operating at 35 kV