Composites Science and Technology 82 (2013) 15–22

Contents lists available at SciVerse ScienceDirect

Composites Science and Technology

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

Surface microstructures and epoxy bonded shear strength of Ti6Al4V alloy anodized at various temperatures

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ARTICLE INFO

Article history:
Received 4 December 2012
Received in revised form 24 March 2013
Accepted 5 April 2013
Available online 16 April 2013

Keywords:
A. Hybrid composites
B. Debonding
B. Interface
B. Surface treatments
D. Fractography

ABSTRACT

In this paper, the effects of anodizing temperature on the microstructure, composition and surface profile of Ti6Al4V were systematically investigated. Apparent shear strengths of the anodized alloy bonded with epoxy were measured and the fracture mechanisms were analyzed. With increasing anodizing temperatures from 0 °C to 40 °C, the thicknesses of the oxide layer decreased from ~1200 nm to ~200 nm, indicating accelerated dissolution process of oxide caused by increased ionic mobility at higher temperature. After anodization at 40 °C, a honeycomb-like oxide layer with pore diameter of 100–200 nm was uniformly developed on Ti6Al4V's surface. Surface roughness of the oxide layers ranged from 657.0 nm to 817.2 nm. The apparent shear strengths of the specimens anodized at 0 °C, 25 °C and 40 °C were improved by 217.7%, 225.0%, and 317.2%, respectively, in comparison with that of specimen without anodization. From SEM fractomicrographic analysis, pristine specimen showed adhesive failure between epoxy–alloy interface; for specimen anodized at 40 °C cohesive failure of epoxy was dominant; whereas mixed fracture modes, i.e., oxide layer failure, epoxy–alloy interface adhesive failure, and epoxy cohesive failure, were observed for specimens anodized at 0 °C and 25 °C. The nano-engineered honeycomb-like structure contributed to the improved shear strength due to the interlock between anodized Ti alloy and epoxy adhesive, which provides practical solution to tune Ti-based metal-composite interface property for its application to our on-going deepwater composite pipe project.

1. Introduction

Ti6Al4V possesses many desirable properties such as high fatigue strength, merchantability, weldability, and corrosion resistance. Therefore, it is currently the most widely used among all titanium alloys as marine components, steam turbine blades, structural forgings, and fasteners [1]. Recently large amount of efforts has been made on developing hybrid composite structures such as fiber-metal laminates (FMLs) to take advantages of combined benefits from metals of their ease of manufacturability, impact and fire resistance and fiber reinforced plastic (FRP) composites of their excellent fatigue and corrosion resistance, high specific strength and stiffness, and diverse failure modes [2]. Among those, titanium-based FMLs have been put special attention due to their unique properties including durability, reliable anti-permeability and promising structural applications [3–5]. To achieve the above desired properties, excellent adhesion between Ti layer and composite is necessary. Thus Ti-composite interface property is a critical issue in determining the overall performance (mechanical properties, anti-permeability, and so on) of the hybrid Ti-FRP composite laminate. However, the original Ti6Al4V surface is not suitable for load-bearing conditions because of its poor adhesive properties to polymers.

In order to produce a strong and durable adhesive joint between Ti6Al4V specimen and composites, surface treatment to Ti6Al4V is necessary to tune the surface. Several ways to adjust surface tension, surface roughness, or surface chemistry are used to increase the bond strength between metal and composite [6]. Till now, a wide range of mechanical, chemical, electrochemical and energetic surface treatments have been developed, such as abrasion and grit blasting [7–9], etching [10,11], coupling agent [12,13], plasma-spray and laser treatment [14–16], sol/gel methods [17,18], anodization [19–26], microarc oxidation [27,28], Laser shock peening [29], and so on, to modify the surface physico-chemical characteristics of titanium alloy. Among those, anodization is one of the most promising methods with ease of microstructural design and elemental adjustment of the oxide layer, which yields the best bonding strength and durability [6,20,22]. According to the nature of the electrolytes, anodization can be divided into three groups: (1) acid-based, (2) fluoride-based, and (3) hydroxide-based. In comparison with the other two, hydroxide-based electrolyte involves less hazardous chemicals and was much more environmentally friendly. Matz [20], Garcia et al. [21] and Mertens et al. [22] reported that the oxide layer produced on Ti6Al4V by anodization in NaTESi electrolyte (NaOH + Na-tartrate + EDTA + Na_2SiO_3)

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http://dx.doi.org/10.1016/j.compscitech.2013.04.007

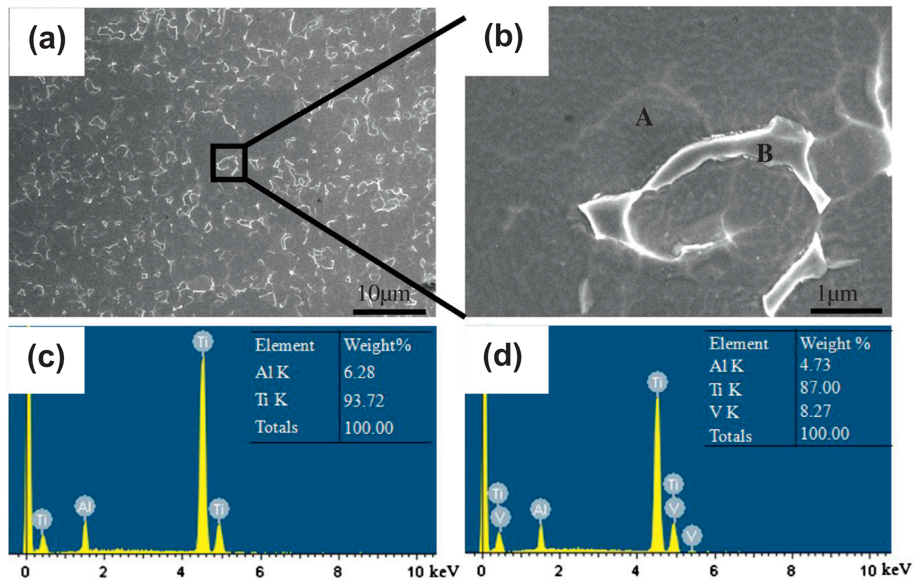

Fig. 1. Microstructure of the studied Ti6Al4V: (a and b) are the SEM images, and (c and d) are the EDX-S results of areas A and B in (b).

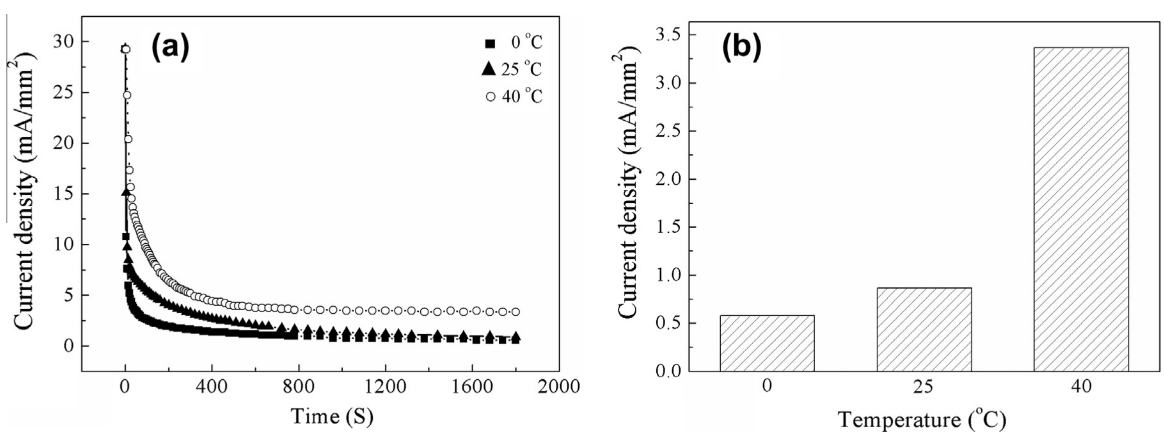

Fig. 2. (a) Dependence of current density on time and (b) stable current density at different temperatures in the anodization process of Ti6Al4V.

exhibited a good bonding strength to polymer and long-term durability. However, till now there are still unknown issues in the hydroxide anodization process of this alloy. For example, effects of different Ti-complexing agents, anodizing temperature, time and voltage on the formation mechanisms, microstructure and mechanical properties of the anodized oxide layer have not been systematically investigated but are critical for practical application.

In the present study, sodium hydroxide-based solution was selected as the electrolyte and the anodizing temperature was taken as the primary parameter in the anodization process. The effects of anodizing temperature on the microstructure, element distribution and chemical composition of the oxide layer were studied. Meanwhile, the temperature effects of the anodized samples on the bonding strength between Ti6Al4V and epoxy together with fracture mechanism were also investigated.

2. Materials and experiments

2.1. Materials

The metal specimens used in the experiment are Ti6Al4V alloy (Grade 5) which was composed of α-Ti (continuous phase) and β-Ti (discontinuous lath-shaped phase), as shown in Fig. 1a and b. Al element presented in both phases, while V element mainly distributed in β-Ti which was confirmed by the EDX-S analysis shown in Fig. 1c and d. The Ti specimens were ground with 800#, 1200#, 2400#, 4000# abrasive papers and SiO_2 polishing paste consecutively, ultrasonically washed with distilled water and acetone, finally dried for anodization and test. Specimens with size of 10 mm × 20 mm × 2 mm were used for surface analyses.

Bisphenol-F epoxy resin (D.E.R. 354, Dow Chemical) was used as polymer adhesive hardened by amine based curing agent (EPOLAM 5015, Huntsman).

2.2. Anodization procedure

Sodium hydroxide-based solution was selected as the electrolyte, and Na-tartrate was used as the Ti-complexing agent, together with a small amount of ethylenediaminetetraacetic acid (EDTA) as impurity-ion complexing agent to prevent precipitation by heterogeneous nucleation on the Ti alloy surface during anodization. The electrolyte was prepared from the solution of NaOH (7.5 M), $Na_2C_4H_4O_6{\cdot}2H_2O$ (0.2 M) and EDTA (0.1 M). A DC power unit was employed to generate voltage of 15 V. A water bath was used to adjust the anodizing temperature from 0 °C to 40 °C.