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A new method for non-destructive stripping of coatings on titanium substrates

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ABSTRACT

This work proposed a new method to prepare undamaged cross-sectional samples of coatings on titanium substrates. First, various kinds of coatings were fabricated on titanium substrates by electrochemical, chemical and physical methods. Then the coated samples were anodized in glycerol electrolyte containing NH_4F (1 wt.%) + H_2O (10 vol.%) at 50 V for 2 h, which resulted in coating detachment. Afterwards, coating cross-sectional samples were prepared with detached coating fragments and observed by scanning electron microscopy. The results showed that original internal microstructures of the coatings can be observed from the freshly-broken cross-sections, which might not be observed from samples prepared by existing methods. Finally, we concluded that it was the TiO_2 nanotube layer formed between the coating and titanium substrate that caused the coating's detachment. The new method may be promising in detection, removing or transfer of coatings on titanium substrates.

1. Introduction

Titanium and its alloys have drawn much attention in numerous applications due to their high specific strength, good corrosion resistance and excellent biocompatibility [1,2]. In order to further enhance their performance, they are often coated by various surface modification techniques, including anodic spark oxidation [3–7], sol–gel coating [8,9], chemical vapor deposition [10], hydrothermal treatment [11,12], anodic oxidation [13–16] and others. In order to know the internal structure of the coating on titanium substrates, preparing cross-sectional samples is required, which is a simple-but-not-easy task.

Two methods are available now. Mechanical grinding method is easy to operate and has been widely reported in literatures [3–7,9,10,16]. To put it simply, it is to impregnate the sample with epoxy resin and then grind and polish it along the direction perpendicular to the coating surface until the coating is exposed. Thus, coating diminishment is unavoidable during the procedure and the structure of the coating can hardly be original. Focused ion beam (FIB) is a technique used in many fields for site-specific ablation, analysis, and deposition of materials [17–22]. FIB systems use a finely focused beam of ions (usually gallium) to ablate a coated titanium substrate, conceptually similar to sandblasting, to expose a cross-section for analysis. It is an advanced and sophisticated technique and requires costly equipment. In addition, FIB is inherently destructive to the sample since the high-energy ions will be implanted into the surface, and the surface will be made amorphous. Is there a method to prepare coating cross-sections on titanium substrates that can avoid the as-mentioned disadvantages?

In this work, various kinds of coatings were fabricated on titanium and titanium alloy substrates by different methods, such as electrochemical, chemical and physical treatments. A new method for non-destructive stripping of these coatings from titanium substrates was proposed. Then the cross-section samples of the coatings were prepared with detached coating fragments and observed by a scanning electron microscope (SEM). Finally, the reasonable detachment mechanism was presented.

2. Experimental

2.1. Preparation of coatings on titanium substrates

Pure titanium (TA1) and titanium alloys (TC4 and β-Ti) substrates, with a size of 10 × 10 × 1 mm^3, were carefully polished with No. 400, 600, and 800 SiC abrasive papers. Then they were ultrasonically cleaned with pure acetone, ethanol and distilled water for 5 min, respectively.

First, titanium samples were treated by anodic spark oxidation (ASO) method to obtain titanium oxide coatings. ASO treatment was carried out at room temperature with a direct current power supply system (QUERLI

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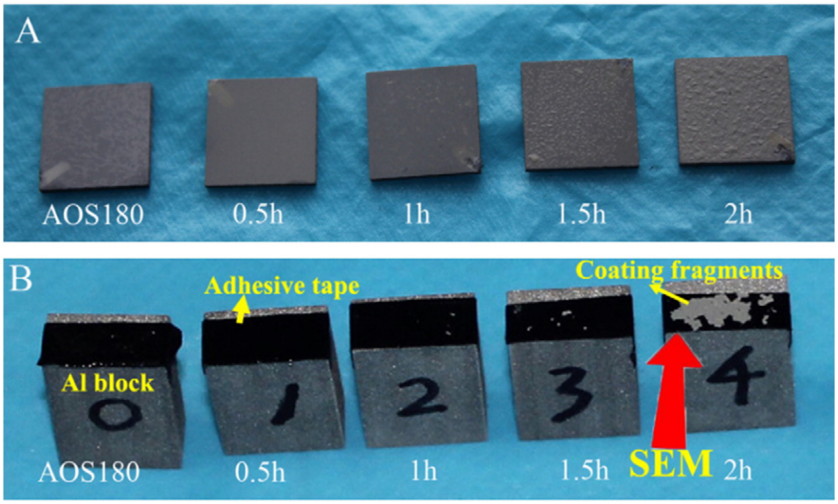

Fig. 1. (A) Appearances of AOS180 samples before and after the anodization treatment for 0.5 to 2 h and (B) attempts to stick the detached coatings to conductive tapes.

DC Power Supply WYJ-300V3A, China). The ASO apparatus was described in detail in our previous work [23]. The TA1 titanium samples were anodized in 1 M H_2SO_4 electrolyte at 80 V (AOS80), 120 V (AOS120), 150 V (AO150), 180 V (AOS180) and 250 V (AOS250) for 1 min, respectively. TC4 and β-Ti titanium samples were anodized in 1 M H_2SO_4 electrolyte at 120 V and 150 V for 1 min, respectively.

Then, some TA1 titanium samples were treated in 30% H_2O_2 solution at 80 °C for 8 h and then aged in 0.25 M HCl solution for 72 h (TiO_2–H_2O_2), according to methods reported in the literature [24].

In addition, TA1 titanium samples with thin diamond coating prepared by glow discharge plasma method were also involved, which were kindly provided by College of Materials Science and Engineering of Sichuan University. Deposition process was carried out in a microwave plasma chemical vapor deposition reactor for 5 h (flow rate of CH_4: 20 sccm, flow rate of H_2: 400 sccm; 1300 W). All the samples were ultrasonically cleaned and dried in oven.

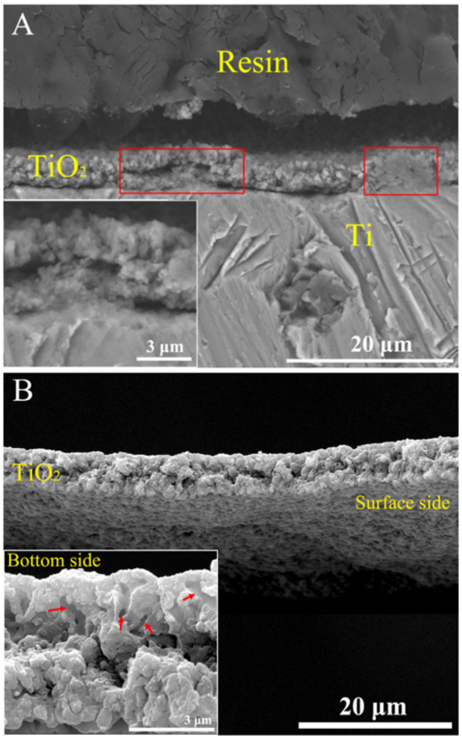

Fig. 2. Cross-sectional SEM micrographs of TiO_2 coating on AOS180 sample prepared by the mechanical grinding (A) and the anodization method (B).

2.2. Coating detachment treatment and cross-sectional sample preparation

The novel coating detachment treatment proposed here was the same as that of the treatment that prepare anodic TiO_2 nanotube (TNT) layer. The anodic oxidation system was mentioned above. All the coated titanium samples were anodized in a glycerol electrolyte solution containing NH_4F(1 wt.%) + H_2O(10 vol.%) at 50 V for 2 h. Afterwards, the samples were gently rinsed in distilled water and then dried in an oven at 50 °C. Coatings were observed to detach by the anodization treatment. To know the essential treatment time, the anodization was carried out at a constant voltage of 50 V for periods ranging from 0.5 to 2 h.

Some detached coating fragments were transferred from titanium substrates to metal blocks to prepare cross-sectional samples. For comparison, cross-sectional samples of some coatings were also prepared by mechanical grinding method.

The surface morphology and chemical composition of the samples were detected by SEM (Inspect F, FEI) and the attached energy dispersive X-ray spectroscopy (EDS), respectively. X-ray diffraction (XRD, Philips, X'Pert MPD 3 kW) was used to analyze the crystal structure of the samples.

3. Results and discussion

Fig. 1A showed appearances of AOS180 samples before and after anodization treatment. After 0.5 h and 1 h of anodization, the surface changed minor in color. When anodized for 1.5 h, the surface exhibited bubbles, and it became more serious when coming to 2 h. Fig. 1B showed that some coating fragments were easily stuck to the conductive tape from the 2 h-anodized sample while seldom from others. The results showed that the required anodization time for coating detachment was 2 h.

From Fig. 2A, we can see that some areas of the coating prepared by mechanical grinding method were damaged to some extent. However, the novel treatment made a coating cross-section sample with high quality, with “real”, “fresh” cross-section morphology. From the inset image in Fig. 2B, pore and channel structures, marked with a red arrow, near the bottom side can be observed clearly. The thicknesses were both measured to be about 3.8 μm, which indicated that the coating thickness was not changed by the anodization treatment.

Fig. 3A, B displayed the surface micrographs and XRD patterns of TiO_2 coatings prepared in H_2SO_4 electrolyte at different voltages.