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Porous nanocrystalline Ti(C_xN_{1-x}) thick films by plasma electrolytic carbonitriding

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Abstract

Nanocrystalline Ti(C_xN_{1-x}) films on titanium were prepared by plasma electrolytic carbonitriding (PEC/N) at 600 V in an electrolytic solution containing triethanolamine and formamide using a pulse power supply. XRD, EDAX, FESEM and TEM were employed to characterize the phase components, element composition, and microstructure of the films. Rockwell C indenter and Vicker's indentation test were used to evaluate the adhesion and hardness of the films. The obtained results show that the films are porous and composed of Ti(C_xN_{1-x}), without apparent discontinuity in the interfaces adjacent to the titanium substrate. The thickness, ratios of C/N and pores sizes of the films tend to increase with the discharge time. When discharge-treated for 2.5 h, the film is about 15 μm thick and exhibits nanocrystalline characterization with grain size of 40–60 nm. Its hardness is Hv 2083 at the load of 0.2 N and the adhesion, Pc value, is more than 500 N. The formation process and mechanism of the Ti(C_xN_{1-x}) films are discussed.

Keywords: Plasma electrolytic carbonitriding; Ti(C_xN_{1-x}) thick film; Nanocrystalline

1. Introduction

Titanium carbide/nitride, such as TiC, TiN and Ti(C_xN_{1-x}) films have high hardness, low friction coefficient, and good corrosion resistance and biocompatibility [1–3]. They can improve the load-bearing capacity and wear resistance of titanium components, which are widely used in engineering and orthopedic applications. Up to now, various technologies have been developed to deposit or form titanium carbide/nitride, such as physical vapor deposition [4], chemical vapor deposition [5], ion beam assisted deposition [6], and plasma carbiding/nitriding [2,7]. However, the titanium carbide/nitride films on titanium produced by the aforementioned deposition methods are thin (generally less than 3 μm), otherwise the adhesion of the films is insufficient due to the increased internal stresses in the films, and thereby delamination of the films has been observed under wear condition. Although plasma carbiding/nitriding treatment of titanium at 700–900 °C leads to firmly adhered titanium carbide/nitride layer, the formation of the compound layer with the thickness more than 10 μm requires much higher temperature and longer treatment time [2], which results in worse fatigue behavior and earlier fracture due to the aging of the substrate material [8]. It has been proved that the improvement efficacy of the wear resistance and load-bearing capacity strongly depend on the thickness and adhesion of the hard films [1,9,10], thus alternative methods to produce thick and firmly adhered titanium carbide/nitride films on titanium at low temperature are still worth exploring.

It is found that plasma electrolytic oxidation (PEO) can achieve a relatively fast conversion of titanium surface, at near-to-ambient bulk temperature, into a titanium oxide ceramic layer [11–13]. These layers are up to tens micrometers in thickness and firmly bond to the titanium substrate. Essentially, the PEO process combines electrochemical oxidation with spark discharge treatment [12], and it is thought that the generation of oxygen vapor envelope

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around a piecework and its ionization by virtue of spark discharge at high applied voltage play an important role in the formation of the oxide layer [11]. Recently, plasma electrolytic carbonitriding (PEC/N) has been developed for surface modification of steels [11,14], however, it has not been successfully applied to other metals, especially to titanium and titanium alloys. Based on the principle involved in PEO, we suppose that it is possible to form titanium carbonitride films by generation of carbon- and nitrogen-containing vapor envelope instead of oxygen envelope in PEO. The present work reports our effort to produce thick titanium carbonitride films by PEC/N, focuses on the microstructure, phase composition, adhesion and hardness, especially on the formation process and mechanism of the films.

2. Experimental

Commercially pure titanium (99.305 wt% Ti, 0.25 wt% Fe, 0.08 wt% C, 0.30 wt% O, 0.05 wt% N and 0.015 wt% H) plates with sizes of $30 \times 10 \times 1$ mm^3 were used as substrates material. The plates were polished to a mirror finish with an aqueous silica suspension, and ultrasonically cleaned with acetone and distilled water. For PEC/N treatment, a pulse power supply was employed, and a titanium plate was used as a cathode while a graphite plate was used as an anode in an electrolytic cell. A mixed organic solution of triethanolamine [$N(CH_2CH_2OH)_3$] and formamide [$HCONH_2$], and other proprietary ingredients (added primarily for adjustment of electrical conductivity) was chosen as an electrolyte. The applied voltage, pulse frequency and duty cycle were fixed at 600 V, 100 Hz and 40%, respectively, and the titanium plates were discharge-treated for 0.35–2.5 h. The electrolyte bath was water-cooled and its temperature was maintained lower than 30 °C. After the PEC/N treatment, the obtained samples were washed with distilled water and dried at room temperature, and parts of them were subsequently annealed at 750 °C for 1 h in a vacuum oven.

The phase components of the samples were analyzed with X-ray diffraction (XRD) using a Cu Kα radiation. Scanning electron microscopy (SEM) and field emission scanning electron microscopy (FESEM), together with transmission electron microscopy (TEM) were employed to observe the morphologies, thicknesses and grain sizes of the films. Thin foils for TEM observation were electropolished using a twin jet electropolisher at 50 V in a solution composed of methanol, ethylene alcohol and perchloric acid. The element compositions on the cross-sections of the films were detected with energy dispersive X-ray spectrometer (EDAX). Rockwell C indenter (conical diamond with 120° included angle and 0.2 mm tip radius) was used to evaluate the adhesion of the films. In the indentation method, the force which separates a film from a substrate, expressed by Pc value, can characterize the adhesion of a film [1]. A series of loads in the range of 300–900 N were applied to the PEC/N formed films, and the resulting damage of the films around the indentations was examined using SEM. Hardness measurements of the films were performed on the surfaces using a Vickers indentation test at a load of 0.2 N.

3. Results and discussion

The XRD patterns of the PEC/N treated samples for different time are shown in Fig. 1. The samples treated for 0.5–1.5 h all exhibit Ti(C_xN_{1-x}) and TiH_2 peaks, and the intensity of Ti(C_xN_{1-x}) peaks tend to increase while that of TiH_2 peaks tend to decrease with increasing the treatment time. When discharge-treated for 2.5 h, the sample only show Ti(C_xN_{1-x}) peaks. The peeling results suggest that the PEC/N formed films consist of two layers, and the TiH_2-riched layer locates beneath the Ti(C_xN_{1-x}) layer, as shown in Fig. 2. In addition, it can be observed from Fig. 1 that as the treatment time prolongs, Ti(C_xN_{1-x}) peaks shift to lower angles, indicating that more car-

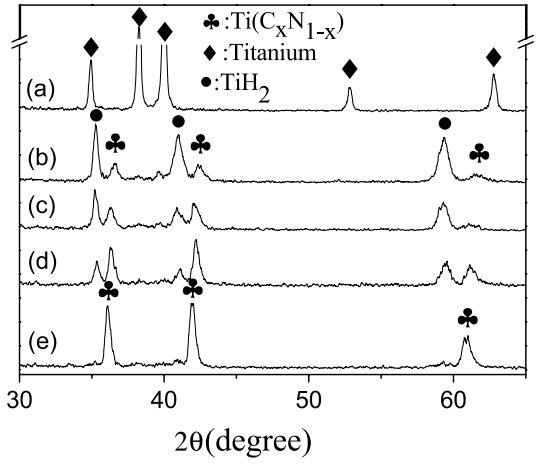

Fig. 1. XRD patterns of the PEC/N-treated samples for the discharge time of: (a) 0; (b) 0.5; (c) 1; (d) 1.5; (e) 2.5 h.

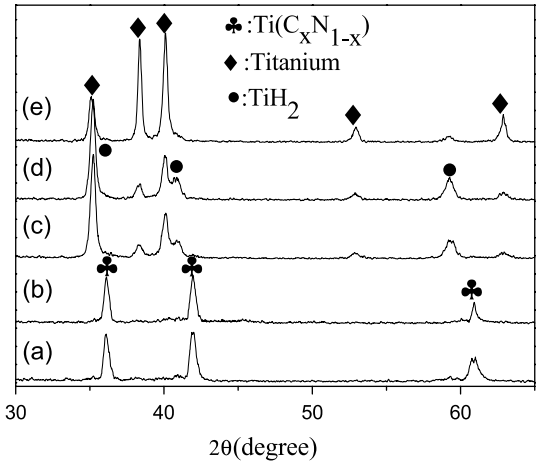

Fig. 2. XRD patterns of 2.5 h discharge-treated sample, subsequently ground to remove: (a) 0; (b) 10; (c) 16; (d) 27; (e) 43 μm in thickness.