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The microstructure and mechanical properties of tantalum nitride coatings deposited by a plasma assisted bias sputtering deposition process

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ABSTRACT

In this study, two tantalum nitride-based coatings were synthesized onto Ti-6Al-4V substrates with two different Ar/N_2 flux ratios using a form of plasma assisted bias sputtering deposition termed the double cathode glow discharge deposition technique. Their microstructures and mechanical properties were characterized by X-ray diffraction, scanning electron microscopy (SEM), transmission electron microscopy and nanoindentation tests. At a low nitrogen partial pressure, the tantalum nitride coating consists of a hexagonal Ta_2N phase, with a preferred (101) orientation, while at a high nitrogen partial pressure, the as-deposited coating is composed of a face-centered cubic (fcc) TaN phase with a strongly (200) oriented texture. The two as-deposited coatings exhibited striated nanostructured composed of equiaxed grains about ~10 nm in diameter, embedded with an array of homogenously distributed nanopores. The mechanical properties and damage resistance of the coatings were evaluated by nanoindentation techniques. The hardness and elastic modulus of the Ta_2N coating was higher than those of the TaN coating, indicating that the Ta_2N coating may offer better protection ability for the underlying metal substrate under load-bearing conditions. In addition, the presence of nanopores is beneficial to the contact damage resistance for both coatings.

1. Introduction

Transition metal nitrides, such as TiN, CrN and ZrN, have been widely used as coating materials owing to their combination of excellent mechanical properties with other attractive characteristics such as thermal stability, chemical inertness and electrical resistance [1]. In recent decades, with the ever-increasing demand for high performance protective coatings applied under various harsh operating conditions, considerable efforts have been made to develop hard yet tough coatings [2]. Unlike titanium, chromium and zirconium-based nitrides, tantalum nitride has attracted less attention as a coating material. This is presumably because of the high cost and more stringent deposition conditions required for this material [3]. Even so, tantalum nitride has recently attracted interest as protective coatings in a wide variety of technological applications, such as mechanical, microelectronic and biomedical applications [4]. Further, some studies have demonstrated that tantalum nitride-based coatings have better histocompatibility and blood compatibility than some widely used biomedical alloys, making them promising candidates for medical applications [5]. Such coatings have been prepared by a range of deposition methods including DC/RF magnetron sputtering, ion-beam-assisted deposition, reactive-electron-beam evaporation etc. [6]. Their mechanical properties have been investigated in a number of studies [7–11]. The results showed that mechanical properties of these coatings were dependent strongly upon the deposition method and the process parameters employed, the hardness values for tantalum nitride coatings normally range from ~20 GPa to ~45 GPa.

Commonly, tantalum nitride coatings are deposited using magnetron sputtering deposition methods [7,10,12]. In this case, with variations in nitrogen partial pressure, the resultant coatings can frequently exhibit complex microstructures containing a number of equilibrium and metastable phases. Phases such as β-Ta (tetragonal-structured), hexagonal Ta_2N, hexagonal ε-TaN, and fcc TaN are often observed, in addition to a variety of other phases, including α-Ta (bcc-structured), hexagonal δ-TaN, having a WC-type structure, hexagonal-Ta_5N_6, tetragonal-Ta_4N_5 and orthorhombic-Ta_3N_5 [3,9,13]. Since the mechanical properties of a tantalum nitride-based coating are related to its

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phase composition, it is important to understand the development of coating microstructure under different deposition methods and conditions.

Our recent studies have demonstrated that double cathode glow discharge technique, a form of plasma assisted bias sputtering deposition, is a simple, yet effective, deposition method to enhance the surface properties of Ti-6Al-4V alloy [14]. The metal silicide or metal nitride coatings prepared using this technique exhibited a nanocrystalline structure, with strong adhesion to the substrate [15,16]. In the present study tantalum nitride coatings were deposited by a double cathode glow discharge technique. A relatively high deposition temperature was used in this study to reduce the degree of residual stress in the coating and allow much higher coating thicknesses to be deposited [14]. In addition, it would be expected that the higher deposition temperature would reduce the incidence of artefacts in the as-deposited coatings [17]. Following the deposition process, the microstructures of the as-deposited coatings were characterized in detail and the mechanical properties of these coatings were assessed by indentation testing. The relationship between mechanical properties, deposition conditions and microstructure is discussed and compared with other studies focused on TaN-based coatings. The structure and mechanical properties of these coatings were then compared with similar coatings prepared by magnetron sputtering and other methods, which involve lower substrate deposition temperatures.

2. Experimental methods

The substrate material was Ti-6Al-4V in the form of disks with a diameter of 40 mm and a thickness of 3 mm. The nominal composition of this alloy in wt.% is given as: Al, 6.42; V, 4.19; Fe, 0.198; O, 0.101; C, 0.011; N, 0.006; and the balance, Ti. Before sputter deposition, the substrates were ground and then polished consecutively with silicon carbide papers down to 1200 grit, followed by cleaning with pure acetone and distilled water in an ultrasonic bath. A 99.99% purity Ta disk, which was 100 mm in diameter and 5 mm thick, was used as the target in the deposition process. Tantalum nitride coatings were deposited onto the polished Ti-6Al-4V substrates using double cathode glow discharge apparatus. During the process of sputter-deposition, one cathode was the target composed of the desired sputtering material, and the other was the substrate. When voltages are applied to the two cathodes, glow discharge occurred, as described elsewhere [18,19]. The base pressure in the chamber was 5×10^{-4} Pa, and the working pressure was 35 Pa at a constant Ar gas flow rate of 100 sccm during depositions. Synthesis of the two coatings was conducted in a flowing Ar + N_2 gas mixture, with the Ar:N_2 flux ratios of 20:1 and 20:3, respectively. Other deposition parameters were as follows: target electrode bias voltage with direct current, −750 V; substrate bias voltage with impulse current, −300 V; substrate temperature, 700 °C; parallel distance between the target and the substrate, 10 mm; and treatment time, 2 h.

An X-ray diffraction (XRD) system (PANalytical Empyrean) equipped with a Cu anode was employed to study the phase composition of the as-deposited Ta-N coatings. Cu Kα ($\lambda = 1.5406$ nm) radiation was used during the analysis, and the instrument was operated at a current of 40 mA and an energy of 45 kV. The X-ray signal was collected over of 2 theta values from 30° to 90°. The cross-sectional morphology of as-deposited coatings was examined by scanning electron microscopy (SEM, Hitachi S3400). The microstructure of two coatings was also investigated by a transmission electron microscope (TEM, Philips CM200) operating at 200 kV. TEM samples were prepared using a dual-beam focused ion beam system (FIB, XT Nova Nanolab 200), using methods described elsewhere [20].

A UMIS (Ultra-Micro Indentation System 2000, CSIRO, Sydney, Australia) workstation equipped with a Berkovich diamond indenter was used to measure the mechanical properties of as-deposited coatings. For hard coatings on ductile substrates, it is generally accepted that to avoid the effect of the substrate the maximum indentation depth should be less than 10% of the coating thickness [21]. Therefore the contact depth was carefully controlled to be less than 10% of the coating thickness to avoid any influence from the substrate during nanoindentation. A maximum load of 400 mN was applied to the surface of each coating with a holding time at maximum load for 10 s. To ensure reproducible data, twelve indentations were performed on three different areas of each coating. The hardness (H) and reduced modulus (E_r) of the coatings were calculated according to the Oliver-Pharr method [22]. Then, the elastic modulus (E) was calculated from E_r from Eq. (1) [22]:

$$\frac{1}{E_r} = \frac{(1-\upsilon^2)}{E} + \frac{(1-\upsilon_i^2)}{E_i} \qquad (1)$$

where E and υ are the elastic modulus and Poisson's ratio for the specimen (normally the Poisson's ratio for tantalum nitride coating is taken as 0.35 [10,23]), and E_i and υ_i are the same parameters for the indenter (1140 GPa, 0.07, respectively).

To investigate contact damage resistance, 200 g and 1000 g loads was applied to each as-deposited coating using a microindentation system (Durascan, Struers, Denmark) equipped with a Vickers diamond indenter. The cross-sectional structures of the coatings under and adjacent to these indents were characterized by a single beam focused ion beam microscope (FEI xP200, FEI instrument, Hillsboro, USA) [20]. All samples were sputter coated with a thin layer of gold prior to the FIB analysis to protect the near surface features and also minimize charging effects.

3. Results

3.1. Microstructure and phase analysis

The X-ray diffraction spectra collected from as-deposited coatings deposited on Ti-6Al-4V substrates are presented in Fig. 1. The results shows that hexagonal Ta_2N (JCPDS No. 26-0985) is the dominant phase in the coating deposited with the Ar:N_2 flux ratio of 20:1, while fcc TaN (JCPDS No. 49-1283) becomes the primary phase for the coating deposited with the Ar:N_2 flux ratio of 20:3. In comparison with the standard powder diffraction file data for Ta_2N and TaN, the diffraction peak intensity for the reflections of (101) Ta_2N and (200) TaN is significantly strong, indicating that the Ta_2N and TaN coatings exhibit strong (101) and (200) preferred orientation, respectively. In addition, the obvious

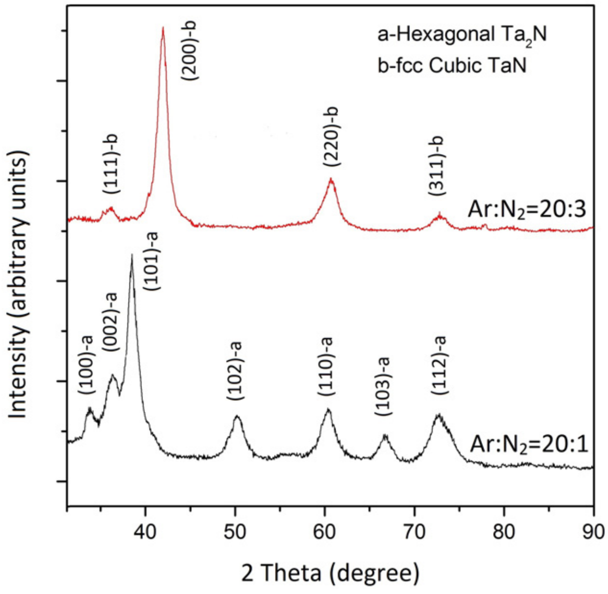

Fig. 1. X-ray diffraction patterns of the Ta-N coatings prepared using two different Ar:N_2 flux ratios.