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Tantalum oxynitride thin films: Mechanical properties and wear behavior dependence on growth conditions

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ABSTRACT

Tantalum oxynitride (TaN_xO_y) thin films were produced by magnetron sputtering. This work analyzes and compares the mechanical properties and the wear behavior of the films, taking into account the differences promoted by changes in composition and structure, caused by the variation of the partial pressure of the reactive gases ($P(N_2 + O_2)$) and by the polarization of the substrate holder.

Besides the change in composition, the variation of $P(N_2 + O_2)$ causes significant changes in the morphology and structure of the films. Those produced with low $P(N_2 + O_2)$ evidence a higher crystallinity and, in these conditions, the films exhibit hardness around 20 GPa. Films produced with higher $P(N_2 + O_2)$ exhibit higher O content, are amorphous and the hardness is significantly lower.

The substrate bias does not influence the adhesion of the films to the high speed steel substrate, but influences the mechanical properties, particularly the hardness, at low $P(N_2 + O_2)$ regime. Films with higher crystallinity exhibit higher hardness, but in the low $P(N_2 + O_2)$ regime, those who were produced with polarization are harder. Although some dependence may be established for set B films, the hardness is not as influent on the wear resistance of the TaN_xO_y films as the friction coefficient.

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1. Introduction

Ceramic thin solid films, out of which one can pinpoint the transition metal nitride family of compounds, have been used for several decades as hard, adhesive, wear resistant coatings. Several studies about mechanical and wear behavior of transition metal nitrides are very well known. The reference material, for long time and the most studied one, is TiN [1], but other nitrides and oxides were object of deep analysis, such as ZrN, CrN, or others [2–4]. In some of these families of nitrides, the increase of mechanical and tribological properties was obtained by adding a third element, such as Al or Si, (TiSiN, TiAlN, CrAlN) [5–7]. In the case of tantalum nitride, the literature is not so large as in the case of TiN, ZrN, CrN, but some studies may be found [8], including super-hardness [9]. However, along with the previously mentioned characteristics, one might require certain optical or electrical properties. Transition metal oxynitride thin films possess the main advantage of tuning the oxygen/nitrogen content, thus leading to films suited for a large number of applications. The effect of oxygen addition to transition metal nitrides on the mechanical properties has been previously reported for molybdenum compounds [10], titanium compounds [11–14] and zirconium compounds [15–17], among others.

Molybdenum oxynitride thin films, studied by J. Barbosa et al. [10], using DC reactive magnetron sputtering, revealed a strong decrease of the hardness, from ~25 GPa to values lower than 5 GPa, and of Young's modulus, from ~275 GPa to ~50 GPa, with the increase of oxygen content in the films. Titanium oxynitride thin films seem to exhibit a similar trend concerning the mechanical properties as a function of oxygen content. For titanium oxynitride films, deposited by pulsed laser deposition (PLD) [11], the hardness decreases from ~15 GPa to ~7 GPa with increasing oxygen flow rate, while the critical loads concerning the adhesion to the substrate (in particular the emergence of the first cracks) varied from 3.4 N to 1.5 N. Similar behavior is reported by F. Maury et al. [12], where titanium oxynitride thin films, produced by atmospheric pressure MOCVD using tetra-iso-propoxide (TTIP) and N_2H_4 as reactive gases, exhibit hardness values up to ~19 GPa with the increase of the nitrogen content, while, concerning the adhesion aspect, for loads of up to 3.2 N the authors did not observe any damage on the thin films. The increase of the duty cycle during pulsed DC reactive sputtering is translated in higher oxygen content, as reported by J.-M. Chappé et al. [13]. This leads to a decrease in hardness and Young's modulus values, from ~16 GPa to ~5 GPa, and from ~270 GPa to ~140 GPa, respectively. The connection of the substrate to a negative voltage during RF sputtering seems to have a noticeable effect on the mechanical properties, as reported by F. Vaz et al. [14], with measured hardness values ranging from ~20 GPa to ~36 GPa,

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and Young's modulus ranging from ~240 GPa and ~360 GPa. These results are significantly higher than those reported by the other techniques; however, it is noticed a consistent pattern in all cases: the decrease of mechanical properties when the oxygen content of the films increases. Zirconium oxynitride thin films exhibit this same pattern; however, there is an observation that deserves to be mentioned. Both J.-H. Huang et al. [15,16] and F. Vaz et al. [17] report a slight increase in hardness for low oxygen fraction samples, compared to the nitride compounds, explained by the solid solution hardening mechanism. With oxygen insertion, an increased strength of the material is expected [18], due to lattice distortion. The distortion inhibits the mobility of the dislocations, inducing a hardness enhancement.

For pure tantalum films, hardness values between 10 GPa and 20 GPa and Young's modulus values close to 250 GPa, dependent on the thickness of the film and the structure occurrence (α-Ta or β-Ta), have been reported [19]. Tantalum nitride thin films, deposited by DC magnetron sputtering [20], display hardness values between ~25 GPa and ~40 GPa, dependent on the bias voltage. The highest value was obtained for a substrate polarization voltage of -50 V, as is the case for the samples presented in this paper, albeit with a significant measuring error, of ± 9 GPa.

For tantalum nitride thin films, deposited by DC magnetron sputtering, where both the sputtering power and the nitrogen flow were varied [21], hardness values between ~21.5 GPa and ~32.3 GPa were reported. The abrasive wear rate was between 1.4×10^{-14} m^2/N and 6.2×10^{-14} m^2/N, as a function of nitrogen flow increase. The critical normal forces applied on the stainless steel substrate samples were reported to be between 20 and 57 N, depending on the N_2 flow. Higher flows resulted in lower cohesive critical loads. Up to 100 N, no adhesive failure was observed, only cohesive failures, mentioned above. Similar values, concerning the adhesion critical loads, are reported by A. Aryasomayajula et al. [22], with a maximum load of 20 N for a tantalum nitride coating, deposited with an intermediate layer of pure Ta.

Tantalum oxynitride thin films could display beneficial properties from both tantalum nitride and tantalum oxide-type compounds. Reports concerning the mechanical and wear behavior of tantalum oxynitride thin films are, to date, limited. Tantalum oxynitrides deposited by DC reactive magnetron sputtering, where the O_2/N_2 was varied between 0.08 and 1.33 [23], exhibit a decrease of hardness, from 27 GPa to 6 GPa, along with an increase in non-metal content. Similar behavior is reported by O. Banakh et al. [24]. The adhesion to a steel substrate is reported to be poor. Generally, critical loads of 2 N and 4 N for Lc_1 (the load necessary for the appearance of the first cracks) and Lc_2 (the load necessary for the emergence of delaminated sections), respectively, are leading, in this particular case, to mostly cohesive failure, while adhesive failure appears at higher loads (up to 27 N) [23]. The combination of poor adhesion and brittleness leads also to a poor wear behavior for loads of 1 N [23]. The introduction of the reactive gases inside the chamber by keeping the nitrogen flow constant while the oxygen flow is pulsed does not seem to influence greatly the mechanical properties [25]. Hardness and Young's modulus values for this particular case are situated between 14 and 7.3 GPa and 233 and 146 GPa, respectively, both parameters decreasing with the non-metal content.

In this work, we will present findings concerning two sets of samples of tantalum oxynitride (TaN_xO_y) thin films, deposited onto high-speed steel substrates. One set was deposited with a negative bias voltage of -50 V applied to the substrate holder, while the other set was deposited with grounded substrates. In each set the variable factor was the reactive gas mixture flow rate and, as a consequence, the partial pressure of these two reactive gases. The option of using a grounded substrate holder during deposition for one of the sets is related with the interest of obtaining films produced with lower mobility of the adatoms and with lower stress levels. The films produced with substrate bias have the potential to exhibit better mechanical properties, due to a higher level of stresses induced by the ion bombardment.

The results, about mechanical properties and wear behavior, presented in this paper were analyzed in order to see if certain configurations of the tantalum oxynitride thin film system, produced by sputtering, under the described conditions, may be adequate for applications related with optical and decorative coatings, photocatalytic surfaces, or dielectric devices. Therefore, it was not the main intention to explore the conditions to obtain the hardest coating or the best wear resistance.

2. Experimental details

TaN_xO_y thin films were deposited onto silicon (100) wafers and AISI M2 high-speed steel (HSS) substrates, by DC reactive magnetron sputtering, using a laboratory-size deposition chamber. The chamber includes two unbalanced type II magnetrons with a rectangular shape, facing each other. For the production of the TaN_xO_y thin films only one of the magnetrons was used, in a closed field configuration. During all runs, the substrate holder was positioned at a distance of 70 mm, in front of the parallelepiped tantalum target, with dimensions of $200 \times 100 \times 6$ mm and a purity of 99.6%. The films were produced with rotation of the substrate holder, to improve their homogeneity. The base pressure of the chamber before plasma etching was 10^{-3} Pa, or lower. Before each deposition, the substrates were plasma etched during 500 s, using a pulsed current of approximately 0.6 A in a pure argon atmosphere with a partial pressure around 0.3 Pa. Two series of TaN_xO_y films were prepared: set A and set B. The deposition parameters that were kept constant for both sets were: the deposition time (1 h); the argon flow rate (70 sccm); the ratio of the reactive gases ($N_2/O_2 = 17/3$), injected from the same source; the substrate holder temperature (100 °C) and the DC current density (50 A/m^2). The variable deposition parameters, the thickness, the average roughness and the composition of the produced thin films are registered in Table 1. Set A films were produced with an applied substrate polarization of -50 V, while set B was produced with grounded substrate bias (GND), the deposition period for both sets being set at 1 h. In the case of the films from set B, an extra set of films was produced with double the deposition time.

The atomic composition was measured in the samples deposited on Si wafers by Rutherford backscattering spectrometry (RBS). The measurements conditions were: Set A: $^4He^{2+}$ with an energy of 2.0 MeV and protons with an energy of 1.4 MeV at an angle of incidence 0°. Further experiments were made with protons with 1.57 and 2.4 MeV; Set B: Protons with an energy of 2.25 MeV, at an angle of incidence 0°. The resulting profiles were generated using the IBA DataFurnace NDF software program [26].

X-ray diffraction (XRD) patterns were obtained for the samples deposited onto Si substrates, using a Philips diffractometer (CuKα radiation) in a Bragg–Brentano geometry configuration.

Cross-sectional morphologies of thin films were examined with a scanning electron microscope (SEM) ZEISS Supra 55VP, using the signal from the secondary electrons detector, at a working distance of 5 mm and with an applied voltage of 3.0 KV.

The determination of adhesion critical loads, hardness, Young's modulus and wear resistance was done on the samples deposited onto HSS substrates.

The film's adhesion was evaluated on a scratch-test type instrument from CSM Instruments, using a semi-spherical Rockwell indenter with a tip radius of 100 μm. The loading rate was set to 30 N/min, while the scan speed of the indenter on the sample surface was set to 10 mm/min. The wear tracks were analyzed and, as a result, four different critical load values were registered: L_{C1A}—applied load for the first visible minor cracks resultant of first cohesive failure; L_{C1B}—applied load for first major cracks (cohesive failure); L_{C2}—applied load for first detected delamination resultant of adhesive failure; and L_{C3}—applied load for total film destruction. On some of the samples, major cracks

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