Surface & Coatings Technology 206 (2012) 4230–4234

Contents lists available at SciVerse ScienceDirect

Surface & Coatings Technology

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

Two-phase single layer Al-O-N nanocomposite films with enhanced resistance to cracking

J. Musil *, R. Jílek, M. Meissner, T. Tölg, R. Čerstvý

Department of Physics, Faculty of Applied Sciences, University of West Bohemia, Univerzitní 22, CZ-306 14 Plzeň, Czech Republic

ARTICLE INFO

Article history:
Received 20 December 2011
Accepted in revised form 10 April 2012
Available online 20 April 2012

Keywords:
Two-phase nanocomposites
Oxynitride
Al-based composites
Mechanical properties
Reactive sputtering
Pulsed inlet of oxygen

ABSTRACT

The article reports on dc pulsed reactive sputtering of *two-phase single layer* Al-O-N nanocomposite films using dual magnetron in a mixture of N_2+O_2 with pulsed inlet of oxygen. Two kinds of nanocomposite films were sputtered: (1) nc-AlN/a-(Al-O-N) film and (2) nc-(γ-Al_2O_3)/a-(Al-O-N) nanocomposite film; here nc- and a-denotes the nanocrystalline and amorphous phase, respectively. The transition from the nc-AlN/a-(Al-O-N) nanocomposite to the nc-(γ-Al_2O_3)/a-(Al-O-N) nanocomposite was controlled by the length of the period of oxygen pulses T_{O2}. It was found that both nanocomposites are highly elastic films with relatively high hardness H = 15 to 20 GPa, low effective Young's modulus E^* satisfying the condition that the ratio $H/E^* > 0.1$, high elastic recovery $W_e > 60\%$ and high resistance to cracking in bending. Correlations between the film structure and its mechanical properties are discussed in detail.

1. Introduction

AlON is the aluminium oxynitride spinel ceramic material which exhibits technologically interesting physical properties, particularly optical, mechanical and thermal properties [1–7]. These properties of the Al-O-N material such as thermal, chemical and mechanical stability, refractive index, band-gap, transparency can be controlled and optimized by its elemental composition. Therefore, the Al-O-N material is successfully used in many applications, for instance, as transparent armor, military aircraft and missile domes, IR and laser windows, etc. The Al-O-N is produced not only as a bulk material [1,2] but also as thin films and coatings [3–7]. The Al-O-N thin films are used for optical applications, optoelectronic and microelectronic devices, the Al-O-N coatings as protective coatings against wear, diffusion and corrosion [3].

The Al-O-N material is a very complex system and not all correlations between the mechanical and optical properties and its elemental and phase composition were found. Our study is concentrated on a systematic investigation of the mechanical properties of the Al-O-N coatings only. For enhancement of the mechanical properties of the Al-O-N coating is very important in the relation between its hardness H and the effective Young's modulus E^* because the ratio H/E^* makes it possible to assess a toughness of the coating by measurement of a resistance of the coating to cracking; here $E^* = E/(1-\nu^2)$, E is the Young's modulus and ν is the Poisson's ratio. A formation of hard coatings with enhanced toughness is now a new task in the development of new generation of hard coatings [8–12]. No such investigation was performed so far. Up to now, an attention was devoted mainly to the increase of H of the AlON material by its incorporation in nanomultilayers, e.g. ZrN/AlON [5], VN/AlON [6].

A simple way on how to increase the hardness H of the Al-O-N coating is to control its structure. Therefore, a main attention in our study was concentrated on the structure, hardness H, effective Young's modulus E^*, elastic recovery W_e of the Al-O-N coating and the relation between the ratio H/E^* and the cracking of the coating during bending. The Al-O-N coating is a two-phase nc-grains/a-matrix nanocomposite composed of nanocrystalline grains embedded in the amorphous matrix. H and E^* of the Al-O-N coating is determined by its structure which is controlled by the relative content of the nanocrystalline and amorphous phase.

This article reports on new single-layer nc-AlN/a-(Al-O-N) and nc-(γ-Al_2O_3)/a-(Al-O-N) two-phase composite thin films composed of either AlN or Al_2O_3 nanograins embedded in an X-ray amorphous (Al-O-N) matrix which were reactively sputtered by DC pulsed dual magnetron in a mixture of N_2+O_2 gases. The main aim of this investigation is to determine the mechanical properties (the hardness H and the effective Young's modulus E^*) and mechanical behavior (the elastic recovery W_e and the ratio H/E^*) of these nitride/oxide and oxide/oxide nanocomposite films and to find conditions under which the hard Al-O-N nanocomposite films resistant to cracking in bending can be formed.

2. Experimental

The Al-O-N films were reactively sputtered using a DC pulsed dual magnetron, operated in a bipolar mode and equipped with Al targets

* Corresponding author.
E-mail address: musil@kfy.zcu.cz (J. Musil).

0257-8972/$ – see front matter
doi:10.1016/j.surfcoat.2012.04.028

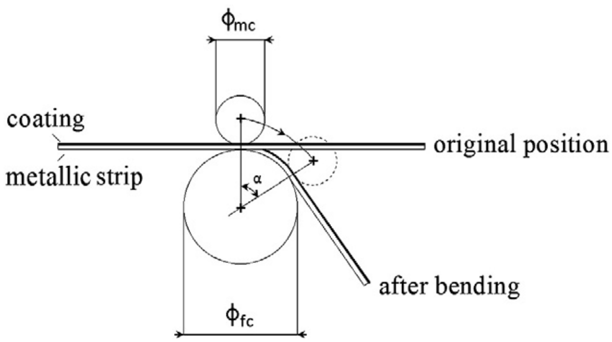

Fig. 1. (a) Schematic illustration of bending test used to create cracks in the film deposited on a metallic strip. $\varnothing_{mc}$ and $\varnothing_{fc}$ is the diameter of moving and fixed cylinder, respectively.

($\varnothing = 50$ mm), in a mixture $N_2 + O_2$ gases. During the film deposition the nitrogen N_2 gas was introduced continuously and the O_2 gas in pulses into the deposition chamber. The pulsing of oxygen enabled to form AlN nanocrystals due to lower affinity of N to Al (the formation enthalpy of the AlN nitride $\Delta H_{AlN} = -318.6$ kJ/mol [13]) compared to that of O to Al ($\Delta H_{Al2O3} = -1678.2$ kJ/mol [13]). The AlN nanocrystals were embedded in the amorphous Al_2O_3 matrix and the nc-AlN/a-Al_2O_3 nitride/oxide nanocomposite film was formed.

The dual magnetron was supplied by an Advanced Energy pulsed power supply at a repetition frequency $f_r = 100$ kHz, the magnetron current $I_{da} = 3$ A averaged over the pulse period $T = 1/f_r$ and the duty cycle $\tau/T = 0.5$ in bipolar mode; here τ is the length of the magnetron pulse. The pumping speed v of the deposition chamber is approximately 33 l/s. The sputtering process was carried out as follows. At first, prior to the magnetron discharge ignition Ar gas was introduced in the deposition chamber at a flow rate $\phi_{Ar} = 20$ sccm. Then, the discharge was started and held at the argon pressure $p_{Ar} = 1$ Pa. Then the argon was fully replaced with nitrogen and held at the pressure $p_{N2} = 1$ Pa with a flow rate $\phi_{N2} = 27$ sccm. The oxygen was introduced in pulses with the oxygen pulse-on time $\tau_{O2} = 2$ s and the repetition frequency $f_{r\ O2} = 1/T_{O2}$ increasing with increasing oxygen flow rate ϕ_{O2} from 0 (pure nitride film) to 5 sccm (pure oxide film); here T_{O2} is the period of oxygen pulses. The oxygen pulse-on time $\tau_{O2} = 2$ s was kept constant. Films were deposited on a floating substrate, i.e. at the substrate bias $U_s = U_{fl}$, two values of the substrate temperature $T_s = $ RT (unheated substrates) and $T_s = 500$ °C, the substrate-to-target distance $d_{s\text{-}t} =$ 100 mm and the partial pressure of nitrogen $p_{N2} = 1$ Pa; here U_{fl} is the floating potential and RT is the room temperature. The Si(100) plates ($20 \times 20 \times 0.3$ mm^3 for XRD measurements and $30 \times 5 \times 0.3$ mm^3 for the measurement of a macrostress σ in the film), microscopic glass ($25 \times 25 \times 1$ mm^3 for the measurement of an optical transparency) and Mo strips ($80 \times 15 \times 0.1$ mm^3 for the measurement of a resistance of the film to cracking) were used as substrates.

The film thickness h was measured using a stylus profilometer DEKTAK 8. The film structure was characterized using an XRD spectrometer PANalytical X Pert PRO in Bragg–Brentano configuration with CuKα radiation. The elemental composition was determined by X-ray Fluorescence (XRF) spectroscopy with PANalytical XRF Spectrometer MagiX PRO. Mechanical properties were determined from load vs. displacement curves measured by a microhardness tester Fischerscope H100 with a Vicker's diamond indenter at a load $L =$ 30 mN. The transparency of Al-O-N films was measured using a spectrometer Specord M400. The resistance of the film to cracking was investigated in a bending test. The principle of the bending test is shown in Fig. 1. The film was deposited on a Mo strip ($80 \times 15 \times 0.1$ mm^3) and the coated strip was bended along a fixed cylinder of diameter $\varnothing_{fc}$ up to angle α at which cracks in the film occurred. The bending of the coated strip was performed in a bending apparatus developed in our labs.

3. Results and discussion

3.1. Structure of sputtered films

3.1.1. Effect of substrate temperature

The structure of the Al-O-N film depends on the period T_{O2} of oxygen pulses and the substrate temperature T_s used in the film sputtering, see Figs. 2 and 3. Fig. 2 compares the structure of Al-O-N films sputtered on unheated substrates ($U_s = $ RT) and the substrates heated at $T_s = 500$ °C. The films deposited on heated substrates exhibit a lower crystallinity (lower intensities of X-ray reflections) compared to those deposited on the unheated substrate. It is due to a release of oxygen from the chamber walls heated by a hot substrate holder, enhanced dissociation of O_2 on the surface of heated substrates, incorporation of more O into the film and by the formation of a higher amount of the a-Al_2O_3 phase in the film at $T_s = 500$ °C. Moreover, it is worthwhile to note that already a small amount of oxygen contained in a residual atmosphere of the deposition chamber after its evacuation to a base pressure p_0 and/or evolved from the chamber walls at $T_s = 500$ °C is sufficient to react with sputtered Al. Therefore, a good reproducibility of properties of the Al-O-N films sputtered under the same conditions is difficult problem; the film properties are strongly influenced by the value of residual pressure p_0, i.e. by the efficiency and time of the evacuation of the deposition chamber, and the state of chamber walls prior to the film deposition. Therefore, a longer series with finer steps in T_{O2} was prepared to see better the evolution of the film structure, see Fig. 3.

3.1.2. Effect of duty cycle of oxygen pulses

The structure of the Al-O-N film strongly depends on a duty cycle of the oxygen pulses τ_{O2}/T_{O2}, i.e. on the amount of oxygen incorporated in the film. The films produced at $\tau_{O2}/T_{O2} = 1$ (the deposition at continuous inlet of oxygen) are nc-(γ-Al_2O_3)/a-(Al-O-N) composites.

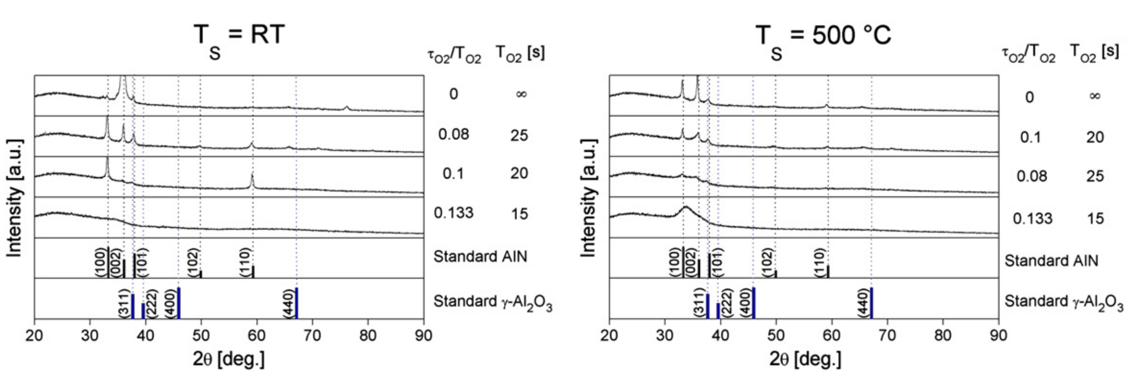

Fig. 2. XRD patterns of Al-O-N films sputtered on glass substrate as a function of repetition frequency of oxygen pulses $f_{r\ O2}$ at $\tau_{O2} = 2$ s and two values of the substrate temperature $T_s = $ RT (unheated substrate) and $T_s = 500$ °C.