OPPORTUNITIES IN DEVELOPMENT OF COMPOUND COATING THIN FILMS AS TRIBOLOGICAL COATINGS

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ABSTRACT

The unusual mechanical and structural properties of transition metal-based nitride thin film coating materials developed in nano-composite structure, exhibiting high hardness, chemical stability also at elevated temperature and special elasto-mechanical properties, envisage for their applicability as wear and corrosion resistant tribological hard coatings used in performance growing of metal cutting tools and working components.

Present paper focus on the outcome results in producing of nanoscaled TiAlN multilayer thin films developed in a fuzzy-controlled dc-reactive magnetron sputtering process.

KEYWORDS: reactive sputtering, nano-structure, multilayer, graded composition, fuzzy-control.

1. INTRODUCTION

Thin film coatings grown in a low pressure plasma environment by vapor phase deposition techniques (PVD and PACVD) are important both from scientific and technical point of view. In the last few years a number of surface engineering techniques have been introduced for preparation of nano-composite thin film materials. Transition metal nitride and carbide based nano-composite coatings, composed of two material phases, represent a composite consisting of nano-crystals embedded in an amorphous matrix, limited in a grain size of 10nm, and smaller. The super-hardness of compositionally graded nc-TiAlN/a-TiAl(N) coatings prepared in a nanoscaled multilayer structure, revealed the preparation possibility for obtaining a new type of coatings with special tribological behaviour [7, 9, 11]. These coatings are thermodynamically unstable displaying a range of non-equilibrium structures [5, 16]. Nano-composite coatings can be prepared by a method that ensures a high rate of nucleation and a low rate of grain growth, e.g. performed in a selective reactive magnetron sputtering process. Co-deposition of components, which can form a tissue phase on the surface of the growing crystals and the process induced segregation of the minority components at the grain boundaries, are controlling the structure evolution during the film preparation [1, 2]. The plasma parameters are strongly interdependent and nonlinear process characteristics generate difficulty in reproducible preparation of ternary and quaternary compound structures.

A fuzzy-logic control technique was adapted for controlling the reactive magnetron sputtering process, and various nitride compound structures were prepared in a multilayer structure [6, 7].

In this paper a short review on adaptation of the fuzzy-logic process control system for controlling the reactive sputtering process and multilayer structure evolution of Ti1-xAlxN coatings prepared at high (Wm) and low (Wm) discharge power will be discussed in connection with the preparation parameters and coating characteristics. Stress relaxation and increased corrosion resistance have been revealed on multilayer structured Ti1-xAlxN (with 44≤x≤61) coatings deposited on steel substrates tested in an aqueous acid solution.

2. BASIC CONSIDERATIONS AND OBJECTIVES

Very recently a group of nanocomposite materials called „MAX-Phases” with a generic formula of Mn+1AXn, where n=1…3 and M indicates the transition metal component, A – is the component of IIIa respectivelly of IVa group, and X means the C or N element of the compound, are considered the fourth generation in the performance evolution of hard coatings material. Dedicated papers talks about prepa-
ration and characterisation of bulk phases Ti₅SiC₂, Ti₅GeC₃, Ti₅AlC₂ for n=2, and Ti₅AlN₃ for n=3 [3, 4]. These new materials indicate very interesting behavior of relative low hardness, high plasti-city, high thermal and electrical conductivity and a nanolayered structure. MAX-Phases are very promising materials in multilayer structure with a bi-layer lattice constant of ~100Å, giving rise to unique behavior for microstructure and tribological point of view [13].

Though many technological success have been reported for large scale preparation of the transition metal nitride-, carbide-, and carbonitride thin film coatings, still there are a considerable spreading in performance of the registered laboratory and field test results. There is a need in understanding of structure forming mechanism and crystal growth of superhard nanostructured crystalline materials with amorphous tissue phase, which can reach high hardness value and high elastic recovery.

To date experimental works have been extended for preparation of multicomponent coatings to investigate process parameters–structure–properties correlation in order to improve the wear resistance of (Ti, Al, Si, C)N coatings. The aim of these study was to show the relevance of control parameters upon grain growth and structure evolution of metastable Ti-Al-N composite coatings. The incorporation of nitrogen into TiAl alloy film indicated a fundamental change in microstructure of nitride compound coating. Therefore, a deeper knowledge is needed in understanding of transition from the crystalline structure to the amorphous one. Deposition and microstructure characterisation of (Ti, Al)N ternary compound coatings produced by a fuzzy-controlled reactive unbalanced magnetron (UM) sputtering was performed in frame of this research work.

3. EXPERIMENTAL WORK CONDITIONS

3.1. Experimental considerations on process control system adapted to reactive unbalanced magnetron (UM) sputtering process

In reactive magnetron sputtering process of a highly active elemental metal target, there are two stable operation modes, namely metallic and reactive sputtering modes. Experimentally it has been proved that in reactive sputtering the run-away transitions are frequently associated with sputtering of cluster molecules from the target surface, which sometime seriously affects nucleation and microstructure evolution of the deposited layer. For a critical value of the reactive gas flow rate \( q^* \), where a stoichiometric compound layers are formed, an abruptly reduction was found in reactive gas consumption by sputtered metal atoms. Target coverage degree, and therefore the coating composition, are controlled by bombarding ion flux on target surface and by the arrival rate of incident atom flux of the reactive gas. These two process-control variables are basically adjustable for a constant composition evolution of reactively sputtered binary component coatings [5, 12, 15, 16].

These two process-control variables together with the energy of species bombarding the growing film surface (mainly controlled by the bias voltage of the substrate) have to be adjusted for supporting the development of phases necessary for the production of the designed structure.

Usually, in reactive sputtering deposition process of homogeneous compound coatings the process conditions have to be controlled inside of the hysteresis loop of the deposition diagram. Therefore, a fast signal processing and a closed loop automatic feedback control of process parameters are a basic requirements. Owing to the strong interdependence of process parameters, classical controller can't be used in these unstable conditions of reactive sputtering process. A fuzzy-logic process control system has been adapted to the unbalanced magnetron reactive sputter deposition of Ti-Al-N coatings, which made possible the dynamic control of the deposition rate, chemical composition and structure of the coatings and provided stable working conditions inside the hysteresis loop of the reactive sputtering also. By applying this control system, single and multilayers of micro- and nanocrystalline composite structures were prepared with compositions of TiN–AlN cubic solid solution phases.

In fuzzy control, using a cognitive approach by linguistic description of human expertise, the process controls are represented as fuzzy rules of relations, and this resource of knowledge is used by an inference mechanism to determine the control action. Fuzzy logic control (FLC) is essentially a way of mapping an input space to an output space of investigated system. The whole task is accomplished by a FLC represented as a three-step process system, shown in figure 1.

Our FLC is a velocity-type controller, where error of deposition rate \( e_{ad} \) and its first difference \( \Delta e_{ad} \) are the inputs and the discharge current correction \( \Delta Id \) is the output. The initial step is the fuzzification where "crisp" measurements of the input variables \( e_{ad} \) and \( \Delta e_{ad} \) are converted into fuzzy input data sets.

The fuzzy inference is the heart of the FLC and holds a database of information defining the linguistic rules. Also in this block, the membership function determines individually the activation level of the output variables for each rule, according to the information in the database.
The final step is the defuzzification. This is the process where "crisp" \( \Delta I_d \) output values, are determined using information about the control variables from the inference stage. The defuzzification task used in our control system is based on the centre of gravity method. The membership functions, which were used to represent the human expert's interpretation of the linguistic variables, have an important effect on the controller performance. A change in the membership functions alters the performance of the controller because the membership function determine when a given rule is eligible to be put into effect. Once the fuzzy control rules are given, the controller performance depends mainly on the membership functions.

In our experiences as diagnostic tool for detecting the narrow processing region, where stoichiometric compound layer is formed, an optical emission spectroscopy technique has been adopted. A monochromator unit for monitoring of glow discharge and a quartz crystal microbalance as deposition rate meter were used. We developed an efficient software program implemented on a microcomputer and succeeded to obtain stable processing conditions in the transition region of reactive sputtering process [10]. In this respect we have used the estimated reactive gas partial pressure as state parameter, which was accomplished by a closed loop control program while reactive gas mass flow was kept constant and discharge power has been controlled in a fuzzy-mode in order to consume all nitrogen excess. Therefore, the monitored signal everytime indicates the onset of reactive sputtering mode, without to be able for transition from metallic to compound sputtering mode. In accordance of fuzzification, for which the pertinent output signal \( \Delta I_d \) determines evolution of system’s state, the arrow in figure 2 indicates that. The spectral line intensity \( I_{sp} \) and deposition rate \( a_D \) have been appointed as output variables. Controlled deposition rate \( a_{Dpr} \) of the system tend to the prescribed value \( a_{Dpr} \), while the reactive gas flow rate \( q_0 \) was kept constant.

Reactive gas input flow rate \( q \) and the target discharge current intensity \( I_d \) were selected as process controlled variables.

Fig. 2 Principle of fuzzy-control applied in reactive sputtering process. Theoretical process curves of the \( a_D \) deposition rate vs. \( q_{N2} \) reactive gas flow rate are simulated for various \( J_0 \) ion current density parameters in sputtering process of TiAlN.

### 3.2. Sample preparation in UM sputtering system

These experiments are related to sample preparation of homogeneous single and/or compositionally graded Ti-Al-N nanostructures of multilayered compound phase, which have been performed for determining the role of parameters in the structure forming mechanism by applying a fuzzy-controlled reactive magnetron sputtering process. The nanoscaled multilayers were deposited on HSS and Si(100) substrates and consisted from a controlled number of individual layers with variable composition ranging between N-doped metallic and stoichiometric compound individual layers.

A sector aligned plane-rectangular composite Ti-Al target structure (with Ti:Al =60:40 area ratio) was adapted in the dc reactive unbalanced magnetron (UM) sputtering source for TiAlN thin films preparation. The experimental set-up used for samples preparation has been presented in detail elsewhere [10]. That is a metal vacuum system evacuated by a turbo-molecular pump for base pressure better than...
10^4 Pa and dynamic pressure of 0.26 Pa. The PVD plasma was excited in dc driving mode for Ar–N gas mixture discharge.

The N2 reactive gas throughput — (measured by GFM 17 Aalborg mass flow meter) was adjusted by a mass flow rate controller (S 216 Granville Phillips APC Controller). The sputtering of the structured Ti–Al target was performed in an unbalanced magnetron (UM) operating mode.

In a sets of experiences the prescribed process variables have been selected for the software-controlled deposition rate of compositionally graded Ti-Al-N multilayers. The same parameters were used at the deposition of single layers. Thermally oxidised Si (100) wafers were used as substrates. Parameters used at the preparation of multilayered TiAlN (Sample A4) as well as at the preparation of single layers (samples A37 and A38) together with the film properties are presented in Table 1.

First the sputtering process was started in pure Ar atmosphere by developing a Ti–Al starting layer deposited on the SiO2 substrate. During the increase of nitrogen flow rate a transition layer formed. In this period the discharge current was held at a constant value. Getting the N2 flow rate at the prescribed value the automatic controller entered into action for fuzzy-mode control of discharge current (power) adjusting it to the prescribed values, also inside the hysteresis loop. The multilayer structure of this sample is composed of a nanocrystalline phase deposited at low discharge power (W_m=440W) and a micro-crystalline structure deposited at high (W_m=975 W) power.

The deposition rate (aD) was monitored by an oscillating quartz-crystal rate-meter while the concentration of sputtered Ti atoms was measured by a plasma emission monitoring (PEM) technique (Isp). The abrupt transition between the nanocrystalline and microcrystalline structures illustrate the sudden response of the discharge conditions on the changes in the ion current intensity.

4. EXPERIMENTAL RESULTS

In investigations of as deposited coatings have been used several methods for composition, structure/microstructure analysis. The crystal structure was analysed by TEM and selected area electron diffraction (SAED) on cross-sectional samples (X-TEM) as well as by X-ray diffraction. The chemical composition was determined by energy dispersive X-ray microanalysis (EDS) of the X-TEM samples. The ‘Process Diffraction’ program [8] was used for the evaluation of patterns. Coating’s thickness was measured by X-TEM and on fractured cross sections by SEM imaging. Coating adhesion was evaluated by scratch test (CSEM Revetest) method. Microstructure X-TEM investigations on ion beam thinned cross section of specimens have performed by using of a 200 keV CM-20 Philips electron microscope. A representative Ti1-xAlxN coating (sample A4) shown in figure 3, revealed a multilayer structure evolution with a wavelength of Λ=20nm. This layer system contains all structures developed from the very first stage of sputtering process. SAD diffraction patterns of specific area evidenced a transition between an amorphous phase and a mixture of very fine grained microstructure imbedded in amorphous phase. EDX compositionally investigation clearly indicate that this two phase composition exist for 44<x<61 at.% Al content in coating, when the discharge parameters were soft-controlled between Ud=440V, Id=1.0A, and Ud=650V, Id=1.5A discharge voltage and discharge current values, respectively. The compressive stress level in the film plane was estimated from the induced strain by XRD investigation of coatings. The strain was found to increase with substrate bias U_s, possibly due to microstructure alterations, related to the energetic ion bombardment during growth.

Figure 4 shows XTEM micrograph of homogeneous TiAlN single layers.

![Figure 3 XTEM micrograph and SAD pattern of Ti-Al-N multilayers (Sample A4), with:](image-url)
Fig. 4 XTEM images of Ti Al N single layers formed in samples A37 and A38. (a) and (b) are dark field (DF) and bright field (BF) images of sample A37 with SAED patterns of V-shaped columnar and small grained structure. (c) and (d) are DF and BF images of sample A38 with SAED pattern.

According to the preliminary RBS analysis the oxygen concentration on the small grained area was higher than that in the area of columnar morphology. The clarification of the role of impurities as well as their in situ forming compound (possibly amorphous phases in the development of V-shaped morphology or in that of the nanocrystalline TN structure needs further analysis.

5. CONCLUSIONS AND DISCUSSIONS

The fuzzy-logic process control system was applied effectively for the dynamic control with short time constant of the working parameters of unbalanced magnetron sputter deposition in TiAIN multilayer systems. This control system can provide stable-working conditions also inside the hysteresis loop of the reactive sputtering. Selecting the discharge current as control parameter one can prepare designed composition and composition modulation related to different micro- or nanocomposite structures. Compositionally-graded multilayer nitride coatings of (Ti+Al)(N)/(TiAl)N have been prepared with nm-scaled individual layers ranging between nitrogen doped metallic and stoichiometric individual layers.

The Ti-Al-N phase prepared at high deposition rate (Sample A 37) by the fuzzy-controlled unbalanced magnetron sputtering, at the present experimental conditions, have cubic solid solution structure with lattice spacing fitting the values which can be derived from the empirical law of Wahlstrom et al. [17] for this composition. In the micro- and nanocrystalline structures with a composition of Ti Al N prepared at low deposition rates (sample A 38) the distorted TN crystalline phases developed (Table 1).

The role of impurities in the formation of these structures is under investigation.

A composite phase of nc-TiAIN nanocrystals embedded in a-TiAl(N) amorphous matrix phase has been evolved for 44 < x < 61 at.% Al content, when the discharge parameters were software-controlled between $U_d=440\ \text{V}$, $I_d=1.0\ \text{A}$, and $U_d=650\ \text{V}$, $I_d=1.5\ \text{A}$.

Adaptive fuzzy-logic control technique applied in reactive magnetron co-sputtering process open new opportunity for preparing of multilayered hard coatings.

By selecting a desired deposition rate and presetting a-prioric correctly established mass flow rate of the reactive gas for stoichiometry of sputtered film, it is possible to achieve a precise control of the process for optimum properties of the nitride coatings.

A comparative study for corrosion resistance of single- and multilayer TiAIN coated steel substrate systems has been performed by applying a modified Sella-method [14]. The corrosion tests were performed for biased steel substrates ($U_{bias}=600\ \text{mV}$ SCE) immersed in 1N H2SO4 aqueous solution in case of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ multilayer deposited on steel substrates (with 44 < x < 61). The test results revealed a many order increased for corrosion resistance of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ multilayer coated steel substrates in contrast with the corrosion resistance behaviour of the single layer coated one, by the same composition, and also better resistance as for TiN multilayer coating structures (Fig. 5).

Fig. 5 Corrosion current intensity measured vs. curvature radius of the mechanically stressed steel substrate specimens with $\text{Ti}_{1-x}\text{Al}_x\text{N}$ and TiN multilayer coatings, performed during of galvanic test for $U_{bias}=600\ \text{mV}$ (SCE) biased samples in 1 N H$_2$SO$_4$ aqueous solution.
Table 1. Preparation parameters and phase composition of Ti$_{1-x}$Al$_x$N$_y$ samples: $T_{\text{substrate}} = 300^\circ\text{C}$, bias voltage $U_B = -90\text{ V}$, $q_{N_2} = 0.35\text{ Nl/h}$

<table>
<thead>
<tr>
<th>Samples</th>
<th>$I_d$ (A)</th>
<th>Discharge power (W)</th>
<th>Deposition rate (nm.s$^{-1}$)</th>
<th>Layer structure</th>
<th>Composition Al at. % / Ti at. %</th>
<th>Crystallographic phases</th>
<th>Lattice parameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A4</td>
<td>1.5</td>
<td>975</td>
<td>1.6</td>
<td>Multi-layer</td>
<td>61/39</td>
<td>Cubic s.s.</td>
<td>0.417 (ED and X-ray)</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>440</td>
<td>0.25</td>
<td></td>
<td>44/56</td>
<td></td>
<td>0.418 (X-ray)</td>
</tr>
<tr>
<td>A37</td>
<td>1.5</td>
<td>975</td>
<td>1.6</td>
<td>Single layer</td>
<td>61/39</td>
<td></td>
<td>0.419 (ED)</td>
</tr>
<tr>
<td>A38</td>
<td>1.0</td>
<td>440</td>
<td>0.25</td>
<td>Single layer</td>
<td>44/56</td>
<td></td>
<td>0.419 (ED)</td>
</tr>
</tbody>
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More detailed information are going to be presented in a future contribution.

REFERENCES


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