Influence Bias Voltage and Working Pressure on the Microstructure, Scratch and Wear Properties of TiAlZrN Films Prepared by CFUBMS Technique

Yaşar Sert*, Levent Kara+, Tevfik Küçükömeroğlu*

*Karadeniz Technical University, Department of Mechanical Engineering
Karadeniz Technical University, 61080, Trabzon, Turkey
yasarsert@ktu.edu.tr, tkomer@ktu.edu.tr

+Department of Mechanical Engineering, Erzincan Binali Yıldırım University
Fatih Street, 24100 / Erzincan, Turkey
leventkara61@gmail.com

***Abstract*— In this paper, TiAlZrN coatings were deposited on AISI H13 steels with various bias voltage and working pressure ranging between -50 V to -90 V and 2 x10-3 to 3x10-3 Torr respectively. Closed field unbalanced magnetron sputtering technique which is a kind of PVD was used for the deposition process. Among the different PVD methods, closed field unbalanced magnetron sputtering method is one of the most successful and sophisticated technology for the metal, alloy and ceramic coatings to control microstructure, surface morphology and phase composition. After the deposition process, the effects of bias voltage and working pressure on the microstructure, hardness, scracth and wear properties were investigated by SEM, EDS, nanoindentation, scratch and wear volume measurements. All produced films exhibited classic surface of granular structure and the cross-sectional morphology showed that all films have columnar structure which was altered from massive columnar to denser columnar structure due to increase the bias voltage and working pressure. TiAlZrN films deposited at -90 V and 3x10-3 Torr exhibited dentest structure, besides possessed the best nano hardness, scratch and wear properties. The highest nano hardness of 42 GPa is obtained under highest bias and working pressure. Also compared untreated AISI H13 steel which is the substrate, the produced TiAlZrN with aforementioned coating parameters considerably enhance the wear resistance.**

***Keywords*— PVD, CFUMBS, TiAlZrN, scratch, wear volume**

I. Introduction

Closed field unbalanced magnetron sputtering method is commenly used for producing thin hard coating films because of its lots of advantages amongst the other PVD technique such as high rate deposition, control microstructure and phase composition, low levels of impurities etc [1-3]. Thanks to this deposition method lots of thin hard coating films can be produced to increase the wear resistance of substrate material. Amongst these thin hard coating films, especially TiN is one of the most well-known and used in various industrial areas [4]. In following times, due to developing technology and industrial needs, the improvement of the properties of TiN coatings have become a necessity. For this purpose, ternary coatings such as; TiAlN, TiCrN, TiVN and TiNbN were developed. It was observed that addition of Al increases the thermal stability and mechanical properties of TiN [5,6]. On the other hand, it was determined that the aforementioned properties of the quaternary coatings produced by adding some elements were higher than the ternary coatings [7]. Conducted studies showed that adding Si, Cr V, Y to TiAlN enhanced the wear resistance [8-10]. However wear and scratch properties and the effect of the deposition parameters on these properties of TiAlZrN were not investigated efficaciously. This deficiency in the literature has inspired our paper. So in this paper, the effect of the bias voltage and working pressure on the morphological, hardness, scrath and wear resistance of TiAlZrN coatings was investigated.

II. Experimental Details

Closed field unbalanced magnetron sputtering method was applied with the aim of depositing TiAlZrN films on the nitreded AISI H13 steel. Ti, Al, Zr pure disks (%99,9) were used as a targets, also nitrogen and argon were used as a reactive gas and discharge (sputtering) gas, respectively. In addition to the adventages such as high coating quality, high plasma density, the most important reason for using this method is that graded coatings are enabled to be produced. This provides high adhesion performance between film and the substrate. Bias voltage and working pressure were selected as a variable deposition parameters and frequency, deposition duration, turget currents and target current of interlayer were keep constant as shown in Table I.

TABLE I
DEPOSITION PARAMETERS

Parameters	Sample No		
	Zr1	Zr2	Zr3
Ti/Al/Zr Target Current (A)	6/2/2	6/2/2	6/2/2
Frequency (kHz)	100	100	100
Bias Voltage (V)	50	75	90
Working Pressure (Torr)	$2x10^{-3}$	$2,5x10^{-3}$	$3x10^{-3}$

The surface and cross-section morphology were observed and characterized by using scanning electron microscopy (SEM). The elemental analysis of coatings was performed with energy dispersive spectroscopy (EDS) using ZAF correction method (Z: Atomic number effect, A: Absorption effect and F: Flerosan excitation effect). Nano indentation values were measured by nano hardness tester at 15mN indentation load and 10s dwell time. The scratch properties of TiAlZrN films were evaluated by scratch tester-CSM Revester equipped with a Rockwell C diamond stylus. And lastly the wear properties of this films were conducted by using ball-on disc tribometer. The wear experiment parameters are given in Table II. Wear volumes were measured by using optical microscopy which is produced by Nanofocus, Germany. After that, the wear rate of the coatings were calculated using related equation;

$W= V/Pxd$ (mm^3/N.m)

In this equation: V: Wear volume
P: Load
m: Sliding distance

TABLE II
WEAR EXPERIMENT PARAMETERS

Normal Load (N)	2
Track Diameter (mm)	10
Sliding Speed (mm/sn)	60
Cycle	1600
Counter Body	Al_2O_3

III. RESULTS AND DISCUSSIONS

SEM was used for the observation of the surface morphology of the coatings. SEM photos are shown in Fig 1. The grain size of this coatings were measured by using Image analysis on these SEM images and are given in Table III.

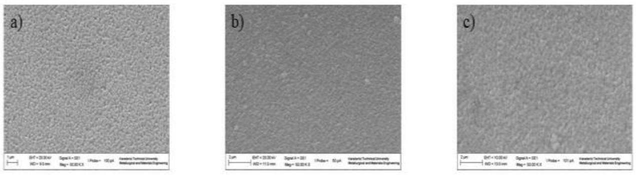

Fig. 1 The surface morphology of the coatings a) Zr1 b) Zr2 c) Zr3

TABLE III
THE GRAIN SIZE OF COATINGS

Sample Number	Grain Size (nm)
Zr1	340±50
Zr2	328±50
Zr3	307±50

It has been known that, each coating parameters have different effects on the coatings [11]. As seen in Fig 1 and Table III, the grain size of the coatings decreases as the bias voltage and working pressure increase. Considering the bias voltage, it has interpreted that as the bias voltage increases, more nucleation regions can be formed by more intense ion bombardment on the substrate surface and a more fine - grained structure can be occured. Several authors reported the same results in their paper. Warcholiski et al. indicated that increasing bias voltage increase the ion fluxes and mobility and results smoother and denser microstructure [12].

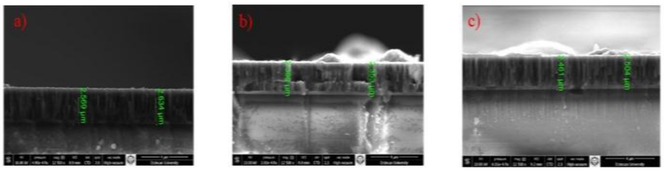

Fig. 2 The cross-section photos and thickness measurements of coatings coatings a) Zr1 b) Zr2 c) Zr3

The cross-sectional SEM micrographs of TiAlZrN coatings deposited on the glass substrate are shown in Fig 2. As seen in Fig 2, all coatings showed columnar morphology. The thicknesses of Zr1, Zr2 and Zr3 coatings are 2,6µm, 2,3 µm and 2,4 µm respectively. The highest coating thickness was obtained at Zr1 which has the lowest bias voltage and working pressure. With the increasing bias voltage, the decreasing in thickness of coating can be explained by ion-peening and re-sputtering effect on the coatings. Similar results observed in several study performed by Devia and Gangopadhyay etc [13,14]. In term of working pressure, the encounter of the sputtering atoms on the way to the substrate surface increases with the increase working pressure, and for this reason, the thickness of coatings due to less atoms can reach the substrate surface. As can be seen the Zr2 and Zr3's coating thickness, increasing bias voltage 75 V to 90 V didn't make a distinct difference.

TABLE IV
EDS ANALYSIS OF COATINGS

Chemaical Composition (%)	Zr1	Zr2	Zr3
Ti	43,52	42,71	46,24
Al	5,18	7,29	9,03
Zr	3,29	7,32	4,08
N	48,01	42,69	40,65

The EDS analysis of the coatings is given in Table IV. As we can see the Table IV, C and O were not detected in the coating structure. And also the nitrogen atomic percentage in the coatings decreased as the bias voltage and working pressure increased. Because the atomic mass of N atoms is lighter than the other elements in the coatings. So enhanced ion flux bombardment due to the increase of bias voltage re-sputters the N atoms and this cause N reduction in the coating.

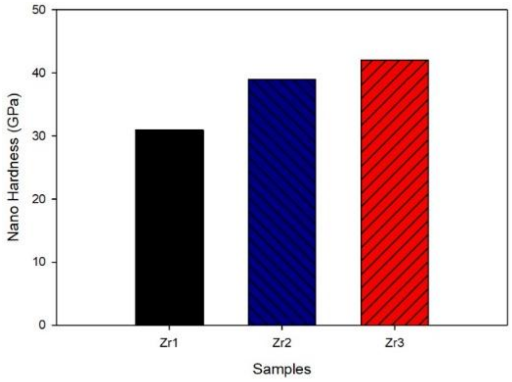

Fig. 3 Nano harndess graphics of the coatings

The nano hardness values of the coatings are given in Fig 3. As can be seen in Fig 3, Zr3 with the highest bias voltage and working pressure showed the highest nano hardness. There are two possible reasons for this result. One of these is the deposition parameter's effect on the coatings. With increase bias voltage and working pressure, tight and dense coating structure was attained by enhanced ion density in plasma. The other reason is related to the decrease of the grain size. As mentioned before, the grain size decreases with the increasing deposition parametres which is used in this study. This is in accordance with the Hall-Petch equation.

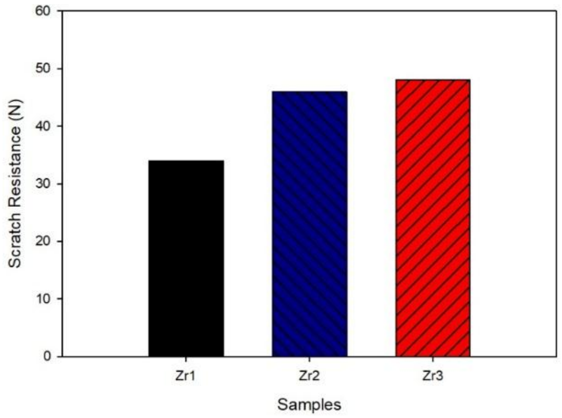

Fig. 4 Scratch resistance graphics of the coatings

The scratch resistance of the coatings is given in Fig 4. As seen in Fig 4, the scratch resistance values are 34N, 46N and 48 N for the coatings deposited on the AISI H13 steel surface with Zr1, Zr2, Zr3 deposition parameters, respectively. As mentioned before, the density of coatings increased with increases bias voltage and working pressure. It was determined that this increase in the density contribute to the increase of scratch resistance [15]. Also, the coating with the highest nano hardness (Zr3) showed the highest scratch resistance. According to this, the value of the scratch resistances improved with the enhance of the resistance to plastic deformation.

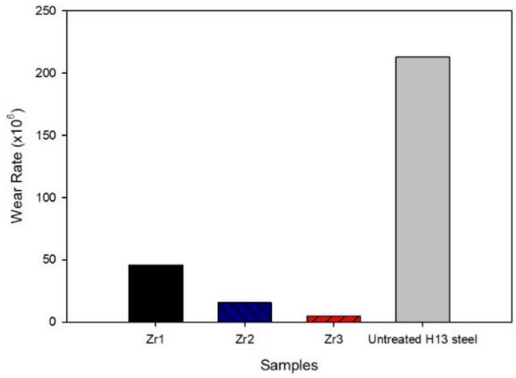

Fig. 5 Wear rate graphics of the coatings

Fig. 6 Optical profilometer photos of the coatings a)Zr1 b)Zr2 c)Zr3

Wear rate comparison and optical profilometer photos of the coatings are shown in Fig 5 and Fig 6, respectively. As seen in Fig 5, all coatings showed higher wear resistance than untreated AISI H13 steel. And also Zr3 which has the highest bias voltage and working pressure showed the highest wear resistance. Increasing bias voltage enhanced the density of film and reduce possible defects inside the coatings [15]. In addition to this, TiAlZrN coatings which was produced using Zr3 deposition parameters enhanced wear resistance of AISI H13 steel approximately 40 times.

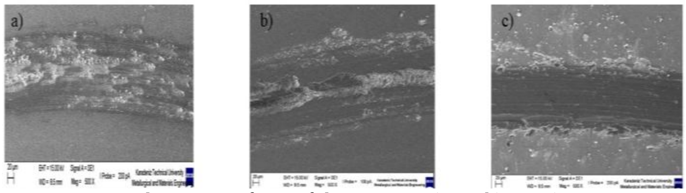

Fig. 7 The worn surfaces of the coatings a) Zr1 b) Zr2 c) Zr3

The SEM photos of the worn surfaces of samples are given in Fig 7. Fig 7 (c) shows the SEM photo of the Zr3 which consists of smooth surface and thin scratches. This is because of high value of hardness and small grain structure of this coating. Fig 7 (b) shows severe adhesive and abrasive wear surface for Zr2. Coating was partly removed from substrate. This can be related with lover hardness value. Fig 7 (a) shows deep abrasive and delamination of coating from substrate.

IV. CONCLUSIONS

AISI H13 steels were coated with TiAlZrN by changing bias voltage and working pressure deposition parameters. Following this, microstructre, hardness, scratch and wear properties of TiAlZrN were investigated. Following conclusions were attained,

- All coatings showed columnar structure.
- The lowest grain size was attained with 90 V bias voltage and $3x10^{-3}$ working pressure deposition parameters.
- The highest hardness was obtained at Zr3 with highest bias and working pressure and the lowest hardness was obtained at Zr1 with lowest bias voltage and working pressure.
- Application of TiAlZrN coatings increased wear resistance of AISI H13 steel when compare with untreated one.
- The highest wear resistance was attained with highest bias voltage and working pressure.

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