Journal of Achievements in Materials and Manufacturing Engineering

VOLUME 23
ISSUE 1
July
2007

Improvement of hardness and corrosion resistance of SS-420 by Cr+TiN coatings

A.J. Novinrooz*, N. Afshari, H. Seyedi
School of material, NRCAM, P.O. Box 31585-4395 Karaj, Iran
* Corresponding author: E-mail address: anovin@aeoi.org.ir

Received 12.04.2007; published in revised form 01.07.2007

Properties

ABSTRACT

Purpose: Double layer Cr+TiN thin films were coated on SS-420 substratum to achieve a corrosion resistive system.
Design/methodology/approach: Ion coating technique was employed for deposition of TiN on stainless steel and subsequently, chromium was coated resulting Cr+TiN composite.
Findings: : In this work we have purposed to improve the natural defect of hard coating material, TiN against corrosion phenomena. This task was fulfilled by formation of a double layer Cr+TiN, which was characterized by glow discharge optical emission spectroscopy (GDOS) for compositional analysis of content elements. X-ray diffraction (XRD) technique was utilized to investigate films crystalline structure. It was revealed that the composite with (111) plane of reflection possess very good corrosion resistive behavior. Scanning electron microscopy (SEM) image showed a double layer configuration.
Research limitations/implications: As the study was carried out on limited surfaces, it is necessary to endeavour further work on larger area.
Practical implications: As the galvanic corrosion is a common problem in thin film technology due to its pinholes and small grains, therefore, any attempt to over come this problem is encouraged.
Originality/value: : Due to limited work and data available on literature about the corrosion resistive thin layers, it may regard this work as a valuable and remarkable approach.
Keywords: Corrosion resistive; Cr+TiN composite; Hardness properties; Galvanic corrosion; Double layer ion coating

1. Introduction

It is well known that Chromium nitride (CrN) and Titanium nitride (TiN) coatings have become important technological materials in the fields of cutting and forming tools, bearing and mechanical devices [1-4]. More over, they have low coefficient of fraction, high surface hardness. So, it is to say that, thin layers of TiN and Cr_xN_y have proven their capability of enhancing mechanical properties in terms of grain size, crystallographic orientation, lattice defect, phase composition and surface morphology. Although, hardness is simple and convenient index employed to evaluate the mechanical properties. But poor corrosion resistance because of pores and pinholes through which the substance would expose to the environment can affect the performance of species. In spite of many reports of investigations on the structure and tribological properties of hard coatings, only limited studies are available on the corrosion phenomena of this compound.

M. Herranen et. al. [5] has employed multilayer coating of Ti/TiN on steel substrates to suppress the corrosion problem. Also, a similar attempt has been made by C.Liu et. al. [6] by applying four layers of TiN or CrN through plasma-assisted PVD deposition. Reported properties of these compounds depend strongly on deposition technique, deposition parameters, controlling film density, stochiometry, microstructure, microchemistry of polycrystalline films, residual stress and texture.

In this article we present our results of double layer of Cr+TiN composite carried out on 420 stainless steel using Hallow Cathode Discharge Gun(HCD-gun). The mechanical properties and corrosion resistance behavior of the samples prepared under experimental condition are investigated.

2. Experimental details

The substrate material for Cr and TiN coating was stainless steel (420 SS) discs of 10 cm in diameter and ~4 mm thickness. They were ultrasonically cleaned in successive rinse of trichloroethylene, acetone, ethanol and dried in hot air blow. The substrates were immediately inserted in to a vacuum chamber for deposition. The chamber was evacuated to the base pressure. The samples were degassed at 500 ºC about one hour. The starting materials (Chromium and Titanium) were grinded and placed in a graphite crucible. Deposition of Cr and TiN carried out in an atmosphere of N2 (99.999% pure) at a pressure of 4.2×10^{-2} Pa. The pressure was monitored with monometer. The coatings were deposited using Hallow Cathode Discharge Gun (model DLKD-1800 with 15 KW power) under experimental condition. Details of experimental setup are given in our previous work [7]. Never the less, some of important parameters are summarized in table 1.

Table 1.
Summery of deposition parameters

Substrate Temp. (ºC)	Pressure before N_2 (Pa)	Pressure after N_2 (Pa)	Bias voltage (V)	Current (A)
400	3.7×10^{-2}	4.2×10^{-2}	50	0.5

To study the crystalline phase structure and phase present in the coating, X-Ray diffraction analysis were carried out by PW 1800 model Philips with monochromatic copper radiation (Cu $K_{\acute{\alpha}}$). To investigate microstructural composition, Scanning electron microscopy (SEM) XL-30 Philips was employed. By performing Vickers microhardness tests, information about hardness of samples were gained.

In order to estimate the corrosion behavior of TiN and Cr+TiN deposited on steel substrates electrochemical test were performed in an aqueous solution of 3.5% NaCl. Comparison study was made with and without Chromium samples. Finally, glow discharge optical emission spectroscopy (GDOES) was utilized to quantities study of coating elements.

3. Results and discussion

Compositional quantitive analysis of Cr/TiN double layer deposited on ss-420 substrates is carried out by glow discharge optical emission spectroscopy (GDS). On the basis of this operation, the coated film was sputtered from the sample and spread in to the glowing torque and then constituent particles were analyzed from top to bottom of the surface as a function of sputtering time by optical emission spectroscopy process, which was measured with respect to standard values. As shown in Fig (1), the presence of Cr, Ti, and N confirm the Cr/TiN constituents.

The XRD diffraction pattern of individual TiN and Cr/TiN is given in Fig (2). The host matrix (TiN) was strongly effected by Cr guest elements forming Cr+TiN complex. As shown in Fig (2), preferential growth of TiN is (200) plan of reflection with crystalline NaCl structure [8]. It is well known that the crystal structure depends on many factors like strain energy, surface energy and etc. J. Pelleg and L. Zevin [9] have shown that, Thin films of TiN with lowest surface energy corresponds to (200) plane. By increasing thickness of films, the elastic strain energy and other defects are naturally increased. Reduction of these defects is a matter of challenge towards the researchers and requires lot of efforts. Our attempt on investigation of many specimens has revealed that presence of chromium in TiN matrix and formation of Cr+TiN composite enhances growth of TiN (100) orientation (fig 2). Our studies on this composite confirmed that very hard and corrosion resistive layers are yielded. The similar arguments about the hardness and surface energy relating to (111) plane of TiN have been given by references (10, 11 and 12).

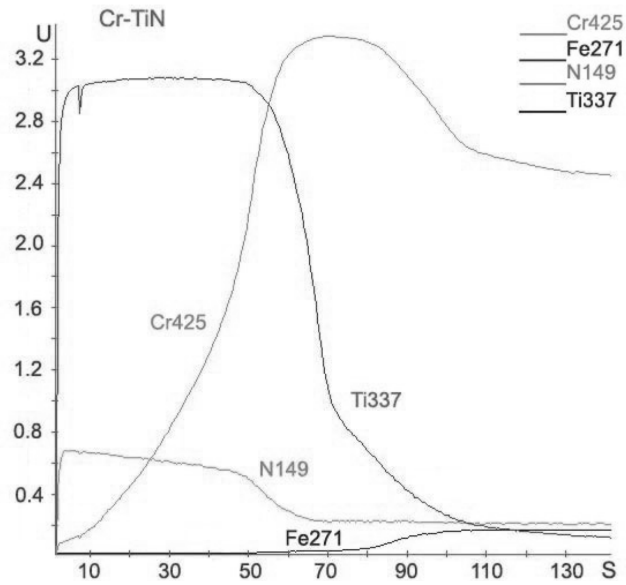


Fig. 1. GD-OES analysis of double layer Cr+TiN

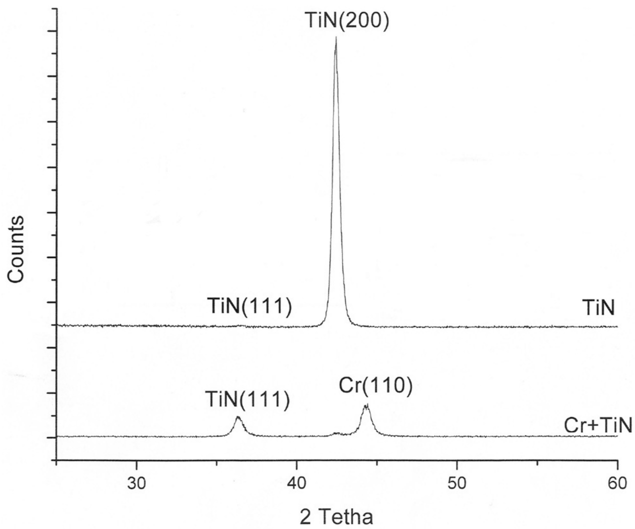


Fig. 2. X-Ray diffraction patterns of TiN (111) plane with and without Chromium

The more detail investigation of the samples indicates that Schmid factor of TiN prepared on (111) crystalline direction is zero. This means that, there is no strain upon the surface, as a result no plastic surface deformation would be imposed, and hence, very hard surface could be obtained. Substantially, hard coating of–naked substrate (in our case SS-420) is proposed to prevent them from corrosive attack, which is mainly depending on nobility ratio of coating and substrate material. Moreover the morphology of coated layers contains many pores and pinholes, through which reaction with the environment takes place resulting deterioration of the materials. According to Structural Zone Model (SZM) [13], the ratio of T_s/T_m determine microstructural feature of deposited coatings. Where T_s is the deposition temperature and T_m is the melting temperature of the material. In present work the ratio for the coated film on SS-420 substrates is 0.2, which is related to the surface with many pinholes and small grains. Through these pinholes, and pores the corrosive materials penetrate and damage the samples, i.e galvanic corrosion. One of ways to overcome this problem is to deposit metallic layer with lower melting point [13]. To incorporate the idea, we have taken chromium metal and coated it, on the TiN films using Ion-Plated Hollow-Cathode Discharge Gun under experimental condition. The details of deposition are given in our previous work [2]. The comparative values of Vickers micro hardness of Cr+TiN and TiN are given in table 3.

Table 2.
Corrosion parameters for different samples

Samples	steel	TiN	Cr+TiN
Corrosion current µA	7.4	4.3	1.8
Corrosion potential mV	-505	-489	-452

It is clear from the table that hardness of specimens has been drastically improved after Cr treatment. TiN coated sample has individually lower wear resistance value; where as, double layer Cr+TiN composite has proven to demonstrate higher value. This simply indicates that the contribution of chromium in TiN matrix has improved the wear resistance. The wear test is carried out on TiN with and without chromium is given in Fig 3 (a, b), respectively.

Corrosion protection is a main attempt has been taken in this work. The corrosion attack on hard coated parts can be reduced by a denser coating texture [14]. In our case, this has been achieved by depositing Cr as a second layer on TiN specimen. Corrosion investigation is accomplished by allowing the Cr+TiN samples to place in an H_2O+NaCl (3.5%) electrolyte. It is well known that the corrosion rate is proportional to the corrosion current density measured through polarization. The optimum potential and current density were determined and summarized in table 2.

Table 3.
Vickers micro hardness of TiN and Cr+TiN at different temperature

Cr+TiN	TiN	Temperature ºC
1400	1057	25
1850	1177	400
1233	724	600

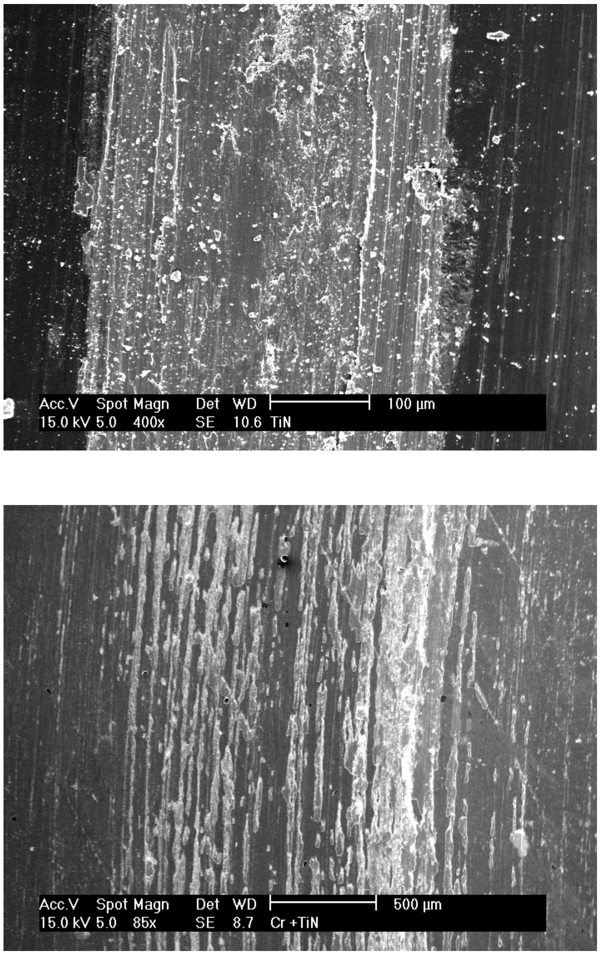
a)
b)


Fig. 3. The wear test performed on (a) TiN and (b) Cr+TiN

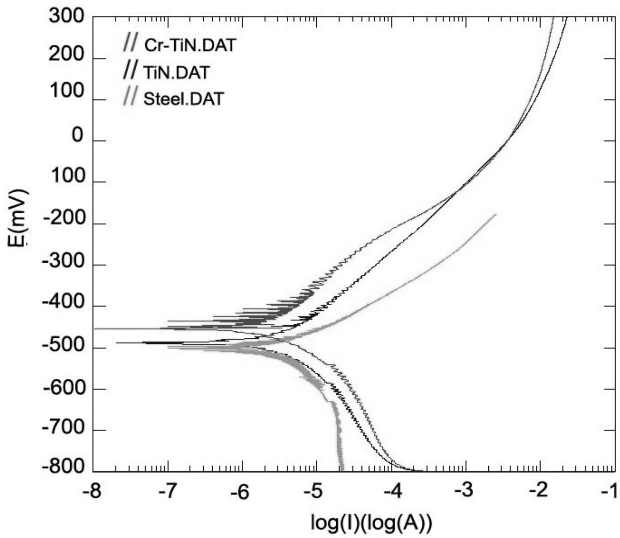


Fig. 4. Polarization curve of TiN and Cr+TiN

The polarization curves and current potential behavior of TiN coated on SS-420 substrate with and without Chromium is illustrated in Fig (4). As shown in the figure, the bare sample (SS-420), also TiN sample are comparatively more corroded than double layer Cr+TiN sample.

It can be deduced from this figure that a remarkable improvement has taken place by introducing Cr to TiN matrix

4. Conclusions

Generally, in the most of hard coating substrate system, due to many pinholes and pores, galvanic corrosion takes place. The ability of a coating to prevent corrosion attacks from the environment closely related to its microstructure properties. In this work we have achieved to good protection stage by formation of a double layer Cr+TiN. The results in a coating that provides corrosion resistance of the substrate as compared to single TiN coating.

Acknowledgements

This work is apart of research project proposed at school of material NRCAM, Karaj. The financial support and collaboration of staff members of NRCAM is greatly acknowledged and appreciate.

References

[1] M. Polok-Rubinec, L.A. Dobrzański, M. Adamiak, Characterization of the CrN, TiN PVD coating, deposited on to plasma nitrided hot work tool steel, Proceedings of the 11th International Scientific Conference on "Contemporary Achievements in Mechanics, Manufacturing and Materials Science" CAM^{3}S 2005, Gliwice-Zakopane, 2005, 265-272.

[2] A.J. Novinrooz, H. Seyedi, Effect of nitrogen flow rate on properties of CrN films prepared by HCD-gun. Journal of Achievements in Materials and Manufacturing Engineering 17 (2006) 189-192.

[3] J. Kusiński, M. Rozmus, J. Bujak, The life-time of drills covered with multi layer Cr/CrN PVD coatings. Proceedings of the 11th International Scientific Conference on "Contemporary Achievements in Mechanics, Manufacturing and Materials Science" CAM^{3}S 2005, Gliwice-Zakopane, 2005, 552-557.

[4] M. Herranen, U. Wiklund, Corrosion behaviour of Ti/TiN multilayer coated tool steel, Surface and Coating Technology 99 (1998) 191-196.

[5] C. Liu, A. Leyland, Q. Bi, A. Matthews, Corrosion resistance of multi-layered plasma-assisted physical vapor deposition TiN and CrN coatings, Surface and Coatings Technology 141 (2001) 164-173.

[6] A.J. Novinrooz, H. Seyedi, M.M. Larigani Microhardness study of Ti(C,N) films by Hallow Cathode Discharge Gun, Journal of Achievements in Materials and Manufacturing Engineering 14 (2006) 59-63.

[7] M.I. Jones, I.R. McColl, Effect of substrate preparation condition of TiN coating by RF sputtering, Surface and Coatings Technology 132 (2000) 143-151.

[8] J. Pelleg, L. Zevin, Reactive-sputter-deposition of TiN films on glass substrates, Thin Solid Films 197 (1991) 117-128.

[9] W.J. Chou, G.P. Yu,J.H. Huang, Mechanical properties of TiN thin films coating on SS-304, Surface and Coatings Technology. 149 (2002) 7-13.

[10] C.T. Chen, Y.C. Song, Microstructure and hardness of hollow cathode discharge ion-plated TiN films, Journal of Material Engineering and Performance 7 (1998) 324-328.

[11] H. Ljungcrantz, M. Hultman, Nanoindentation studies of single-crystal (001) TiN layer on MgO, Journal of Applied Physics 80 (1996) 6725-6733.

[12] I. Petrov, P.B. Barna, Microstructural evalution during film growth, Vacuum Science Technology A21 (2003) 117-123.

[13] H.A. Jehn, Improvement of corrosion resistance of PVD hard coating substrates, Surface and Coatings Technology 125 (2000) 212-217.