Corrosion and Wear Behavior of ZrN Thin Films

J. Menghani, K. B. Pai, M.K. Totlani, N. Jalgoankar

Abstract— **ZrN coating is an alternative candidate to replace the conventional TiN coating especially for high temperature oxidation-resistance applications. ZrN coatings of varying thickness (1.5, 2.0, 2.5, 3.0, 4.0)μ were deposited on 316 stainless substrates by cathode arc Evaporation, in a reactive nitrogen atmosphere. The influences of lamellae thickness on the microstructure, tribological and corrosive properties of the films were investigated. The coefficient of steady-state friction of the films ranged from 0.213 to 0.659.The corrosion resistance of coatings tested in 1 N H_2SO_4 solution. The results indicate that microstructure, wear and corrosion properties of the films were dependent on lamellae thicknesses in film structure.**

Index Terms— **Cathode arc evaporation technique; XRD; Potentiodynamic test; Pin on disc, SEM**

I. INTRODUCTION

In many tribological applications, hard coatings of metal nitrides are now commonly used.[1,2] The first generation PVD coated tools featured TiN as the hard coating and were applied in interrupted cutting such as milling of steels. The superior performance of PVD TiN coated tools prompted their use in other machining applications, such as turning, threading, and boring, as well as in industries as a wear resistant or protective layer on the dies. The continued success of PVD coated tools led to the commercial development of second and third generation PVD coatings (TiCN and TiAlN) which offer even higher machining productivity. Recently, zirconium nitride (ZrN) films have attracted increasing interests for various applications. [3].

TiN and ZrN are thermodynamically stable but are susceptible to oxidation, which can be inferred from the heats of formation of TiN (-80 kcal/ mol) and ZrN(-87.3 kcal /mol).TiN is most widely used but at temperature$>600^0$C TiO_2 (Titanium dioxide)layer is formed. Due to large difference in molar volume between TiO_2 and TiN, compressive stresses are developed in oxide layer this results in spallation and exposure of unoxidised nitride to further oxidation. Zirconium base thin films have high Melting point, high Hardness (30% harder than TiN),high hot hardness and high Corrosion and Abrasion resistance. ZrN coated tools have shown significant performance advantages over TiN coated tools during drilling tests. [4-11]

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In recent years, cathodic arc plasma evaporation techniques are most widely applied in industrial processes, because of excellent adhesive properties with various substrates also due to high current density, ionization ratio and flexibility of target arrangements [12-16]

The purpose of this study is to deposit ZrN thin films of varying thickness on 316 Stainless steel by a cathodic arc plasma evaporation technique from Zr target source. SEM is used to characterize wear scar and corrosion behavior. The phase analysis and average grain size measurement was done with the help of XRD. The influences of lamellae thickness on the wear (by using pin on disc wear test) and corrosion (potentiodynamic test in $1NH_2SO_4$) performances of ZrN coatings were investigated.

II EXPERIMENTAL PART:

The ZrN coatings were deposited on polished 316 stainless steels by using cathodic arc evaporation (CAE) system at Multi arc (I) Ltd, Umargaon. In this study, 99.95% Zr target was used as cathode material. The distance between the cathode and the substrate was 180 mm. The experimental parameters of the deposition process are shown in Table 1. A series of ZrN coatings with different thickness were deposited. The cathode current and bias voltage were kept at 60 A and −150 V, respectively.

Table I: Process Parameters of ZrN coatings by cathodic arc deposition

Base pressure (Pa)	5.0×10^{-5}
Source to substrate distance (cm)	17
Substrate bias voltage(-V)	150
Evaporator current (A)	60
Reactive gas	N_2
Reactive gas pressure (Pa)	0.007-0.008Mbar
Deposition time (min)	45min Depending on thickness

2.1 Wear testing: Pin on disk tester

The specimens were tested under dry (unlubricated) conditions and at room temperature on pin-on-disc sliding machine (Model TR-20, DUCOM-Bangalore). The flat side of the coated substrate was attached to standard 6 mm cylindrical pins using an adhesive. These pins were then held at fixed position while the counter face disk (SAE 52100 steel (Rc 55) disc of diameter 60 cm) rotated at a constant velocity. The geometry is shown in Fig. 1. The configuration ensures that a point (Hertzian) contact is established initially for the wear test, regardless of any small misalignment of the pin. From Hertzian contact theory, the contact pressure was calculated to be in the range of 700– 800 MPa, which is similar to the contact pressures that industrial coatings are normally subjected to in service. The films were worn without any lubrication and in ambient air atmosphere.[17] A fresh surface of specimen was used each time and before each test. Both the disc and the specimens were cleaned with

acetone to remove any possible traces of grease and other surface contaminants. The testing conditions consist of applied Load of 4Kg, rotating speed of 200rpm and time for 20 minutes.
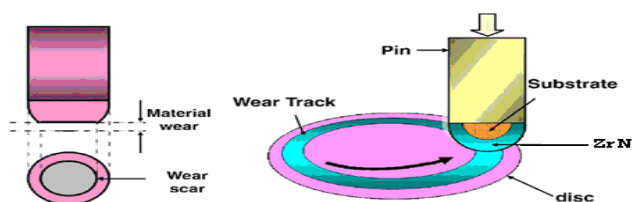

Fig. 1 Wear Testing Geometry

2.2 Corrosion Testing:

The electrochemical evaluation was carried out at room temperature using a standard three-electrode (reference, counter and working) configuration, saturated calomel electrode as the reference electrode, graphite electrodes as the counter electrode and the specimen as the working electrode. The experiments were performed using a potentiostat controlled with a computer. The potentiodynamic polarization tests were conducted in 1000 ml solutions of 1N H_2SO_4 at a constant scan rate of 0.5mV/s. prior to polarization, the samples were allowed to stabilize to obtain a stable open circuit potential (OCP). The surface area contacting electrolyte was 1 cm^2.

2.3 SEM and XRD characterization

Coating morphology and wear and corroded surface topography were studied using a Hitachi 3400S Scanning Electron Microscope (SEM). The phase and average grain size of the coating layers were identified by X-ray diffraction (XRD: PHILIPS PANalytica X'Per PRO MRD). The Cu Kα line at 0.15405 nm was used as the source for diffraction pattern analysis

III.RESULTS AND DISCUSSION

A basic disadvantage of the Cathode arc evaporation(CAE) method (from the point of view of the corrosion protective and wear behavior of the deposited coatings), compared to the reactive magnetron sputtering and chemical vapour deposition is the obtention of the so-called "drop phase" sprays of the locally melted surface of the titanium Zirconium cathode that causes increased coating porosity. Further presence of droplets leads to defect in film uniformity and increased surface roughness of coating. By using electrochemical techniques, it is possible to estimate , the protective efficiency, P_i (%),which is opposite of porosity of the films can be calculated by eq. 1. [18]

$$P_i(\%) = \left[1 - \left(\frac{i_{corr}}{i^0_{corr}} \right) \right] \times 100 \quad \text{---(1)}$$

Where i_{corr} and i^0_{corr} represent the corrosion current density in the presence and absence of coating, respectively.
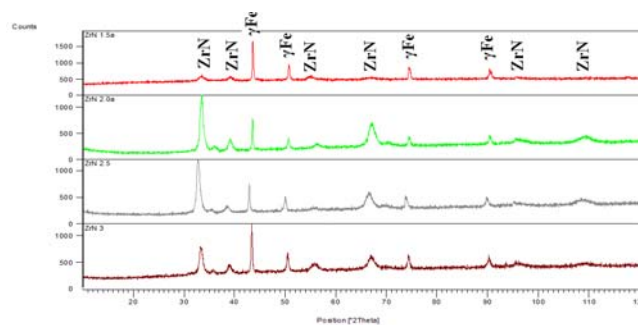
3.1 XRD Analysis

Fig 2 Combined XRD spectra of ZrN films of varying thickness

In the present case it can be seen that a single phase of ZrN films was formed after deposition on the substrate. ZrN has a higher negative free energy of formation than TiN, hence ZrN seemed to form itself more easily than TiN. The average grain size can be estimated from the full-width at half-maximum (FWHM) of peak by Sherrer's relation [19]

$$D = \frac{k\lambda}{\beta \cos \theta} \quad \text{____(2)}$$

where λ, θ, and B are the X-ray wavelength, Bragg diffraction angle and FWHM in radians, respectively. The average grain size, Coefficient of friction and electrochemical results are, as listed in Table 2
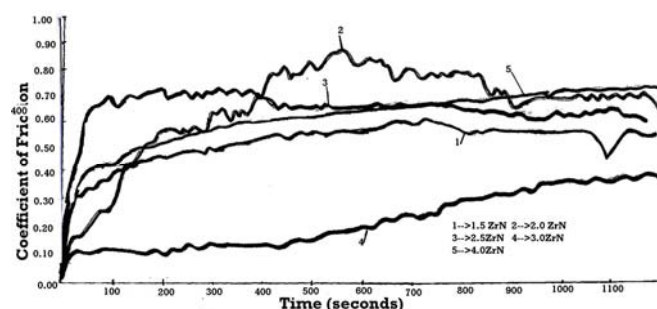
3.2 Tribological performance

Fig 3 Variation in Coefficient of Friction(COF) with time for ZrN of varying thickness during wear testing.

Typical curves of coefficient of friction vs. Sliding distance and time for all thickness is illustrated in Fig4(abcde).The changes in wear resistance due to increase in thickness is due to difference in hardness of resultant coating and the adhesive strength between film and substrate. During sliding, changes in the conditions of mating surfaces occur which affect friction and wear properties. After some period, the so- called "run-in," "break-in" or "wearing-in" period, the friction force generally stabilizes into what is called steady-state sliding. [20] This wearing period is usually taken as the criterion for evaluating the wear. The internal stresses within the coating contribute to the wear resistance of coating. Hard debris delaminated from the coating layers or the oxides which were formed in the atmosphere are partly entrapped between rubbing surfaces. Friction coefficients are related to the change of the wear debris contour. The three-body rolling wear process enables the friction coefficients in the wear process fluctuating with large amplitudes. Highest COF and

hence highest wear was observed for 2 μ ZrN. Fig 4,SEM of 2.0 ZrN after wear test indicates the presence of cracks signifying large internal stresses. This large internal stresses are responsible for high COF as indicated in table 2. Although lowest COF is observed in case of 3μ ZrN (0.213), the COF continuously increase with time and no steady state region was observed. However 1.5μ ZrN had low COF(0.489) and long and steady wearing period.
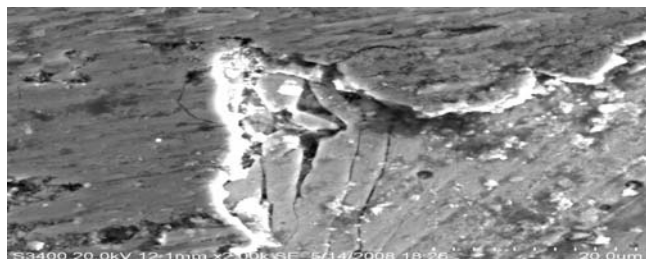

Fig 4 SEM of 2.0μ ZrN after wear testing

3.3. Electrochemical properties

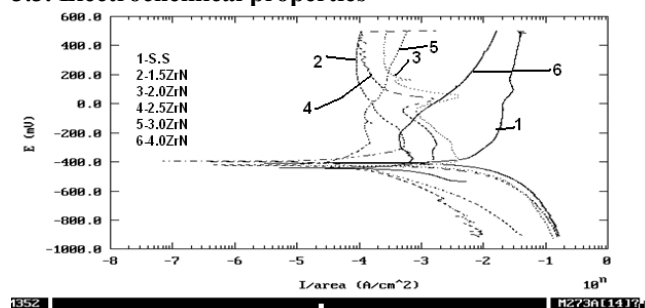*Fig 5 Potentiodynamic plot of ZrN of varying thickness in 1NH₂SO₄*

The corrosion potential of the steel substrate is about −0.408 V. Each sample's open circuit potential is approximately in the same position. The corrosion potentials (Ecorr) of the coated specimens are only slightly away from that of stainless steel, within 25 mV, which indicates that, the corrosion of the ZrN coated-specimens are mainly from the dissolution of the metal substrate and not from the ZrN film. Since corrosion potential is a thermodynamic property of the substrate material the variation of Ecorr is not supposed to be far away from that of bare steel. [21, 22]

The corrosion current density (icorr) is an important parameter to evaluate the kinetics of corrosion reactions, normally proportional to the corrosion current density measured via polarization. The lower the icorr, the lower corrosion rate the sample is [23]. In the present test the icorr value obtained is always less than bare Stainless steel substrate except for 2μ ZrN may be due to high internal stresses within the coating.

The compositional analysis of coatings after potentiodynamic test was done using EDX attached to SEM.
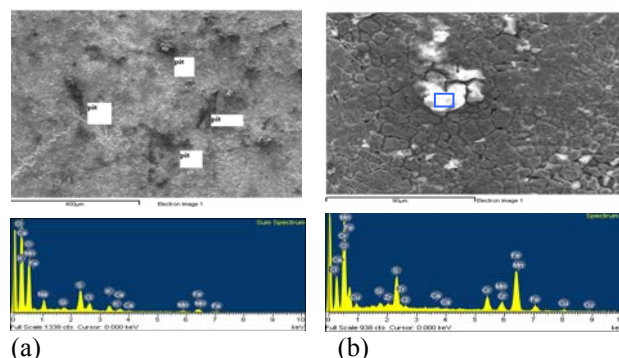

(a)   (b)

Fig. 6 The EDX analysis of 2μ ZrN (a) corroded sample and (b) small region in corroded sample in 1N H2SO4

The SEM and EDX analysis in fig 6 (I) shows large number of corrosion pits in the 2μ ZrN coating This indicates that the 2μ ZrN coating is too thin to inhibit the aggressive action of corrosion media with the presence of physical defects running through the coating. The intense and small peaks of Fe and Mn are observed.As seen in SEM micrograph in Fig 6 (II) after potentiodynamic test some micro-cracks were formed and complete removal of coating in certain region have occurred. PVD coatings are always under the compressive residual stress. The thermal expansion coefficient of ZrN is 7.24×10^{-6} while that for S.S is 10.4×10^{-6}. This difference in thermal expansion might give rise to compressive stresses in the films when samples are cooled down after deposition. Under the synergetic effect of compressive residual stresses and thermal stresses cracks are formed on 2μ ZrN coating when subjected to potentiodynamic test. Hovsepian et al notified that the deposition of PVD coatings nearly always results in generating compressive stress state in the coatings and stress-corrosion cracking will be promoted in an aggressive environment, resulting in severe corrosion failure. [24,25]

IV. CONCLUSION

(1)The characteristics and performance of ZrN coatings developed as a function of lamellae thickness by cathodic arc plasma evaporation were achieved.
(2)Corrosion and wear resistance are not only dependent on thickness but also on the deposition parameters. internal stresses and high porosity within coating

Table II: Average grain size, Coefficient of friction and electrochemical results

No.	Sample	Grain Size (nm)	COF	E_corr (mV)	I_corr (μA/cm²)	Protective efficiency, P_i (%)
1	S.S Substrate			-408	31.05 mA/cm²	
2	1.5 ZrN	7.83	0.489	-427.4	3.768 mA/cm²	88%
3.	2.0 ZrN	7.13	0.659	-429.0	68.23 mA/cm²	
4.	2.5 ZrN	6.872	0.616	-396.0	52.84	99.82
5.	3.0 ZrN	6.49	0.213	-422.1	145.1	99.54
6.	4.0 ZrN	5.466	0.519	-442.1	1.767 mA/cm²	94.4

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