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## Microstructure, Mechanical and Corrosion Properties of Chromium Nitride (CrN) Coating

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### ABSTRACT

Chromium nitride (CrN) films exhibit excellent corrosion and wear properties with thermal stability. CrN films are deposited on silicon (100) and EN 24 steel substrates using DC reactive magnetron sputtering. The pure Cr is used as target and films are deposited at Ar, and N<sub>2</sub> mixtures. The N<sub>2</sub> flow rate is kept at 10 sccm and Ar flow rate is kept at 30 sccm constant. The structural property of the films is studied using the X-ray diffraction (XRD). The average crystallite size of the films is 40 nm as calculated from Scherer's formula. The SEM images show the formation of the grains with smooth surface morphology. The hardness is studied using the microvicker hardness tester and found to increase from 260 HV to 370 HV as the temperature increased. The corrosion studies of the CrN film is studied using the salt spray test and found to have the higher corrosion resistant property.

**Keywords:** Magnetron sputtering, Chromium nitride, thin films, X-ray diffraction, salt spray test.

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### 1. INTRODUCTION

The chemical compound chromium nitride (CrN) is a chromium-nitrogen compound. It has a high hardness and a high corrosion resistance. Nitrogen atoms fill the octahedral holes in the chromium lattice, making it an interstitial compound. Chromium generates a dichromium nitride, Cr<sub>2</sub>N, which is a second interstitial nitride. CrN and Cr<sub>2</sub>N have a high melting point, less electrical resistivity, strong microhardness, and good abrasion, corrosion, and oxidation resistance [1]. Because of its mechanical qualities and refractory nature, chromium nitride (CrN) is a desirable coating material. Because of its melting point, hardness, thermal conductivity, and corrosion resistance, it is employed as a protective coating. Because chromium nitride thin films exist in both cubic (CrN) and hexagonal (Cr<sub>2</sub>N) crystalline phases, their characteristics are determined by the crystalline phase [2]. The deposition conditions [3], which can change the film characteristics, play a critical role in metallization and wear-resistant coatings applications [4-7]. CrN coating was created to address wear

issues in regions where titanium-based coatings had failed. Adhesive wear, corrosion, and oxidation are all resistant to CrN. It is more durable than standard chrome plating, and the PVD coating procedure used to apply CrN has no negative environmental consequences. On medical implants and tools, CrN is frequently used. CrN is also used in innovative multicomponent coating systems for strong, wear-resistant cutting tool applications, such as CrAlN. It has improved thermal stability, oxidation resistance, and corrosion resistance, as well as low internal coating stress, resulting in excellent adhesion under high loads. [8]. Balzers et al. [9] developed a CrN coating that is thermally stable up to 700 degrees Celsius. Cr<sub>2</sub>O<sub>3</sub> appears in CrN films beyond 700°C, according to Almer et al. [10], and only this oxide persists at 900°C. At high temperatures, nitrides films oxidise, which leads to mechanical property deterioration [11-14].  $2\text{CrN} + (3/2) \text{O}_2 \rightarrow \text{Cr}_2\text{O}_3 + \text{N}_2$  is the chemical equation for the reaction of chromium nitride with oxygen. Chang et al. [15] investigated the mechanical characteristics of CrN systems after oxidation at high temperatures and in various atmospheres. Cr<sub>2</sub>N thin films are sputtered using a DC reactive magnetron at various substrate temperatures in this work. The influence of temperature on the structure, surface morphology and mechanical properties is investigated.

## **2. EXPERIMENTAL DETAILS**

### **MATERIALS AND METHODS**

Mild steel EN-24 substrates were cut to a size of 10 x 3 cm, then ground with SiC papers to remove oxides and other pollutants. The polished substrates were degreased with acetone for 2 minutes, then rinsed with triple distilled water. Following that, the substrates were dipped in a 5 percent H<sub>2</sub>SO<sub>4</sub> solution for 1 minute before being completely washed in triple distilled water. Using HIND HIVAC DC magnetron sputtering device, CrN coatings were deposited on the substrates. The cathode was a 5.0 cm diameter high purity (99.999 percent) Cr target. The chamber's base pressure was kept constant at 10<sup>-6</sup> mbar. For all depositions, the substrates were etched for 15 min with 50 W DC power and Ar was fed into the chamber for deposition, with 3x10<sup>-3</sup> mbar pressure. Using CuK1 radiation, the structural properties of the films were investigated using an X-ray diffractometer (X'pert PW 3040 D-8, PANalytical). The salt spray test is employed in this study, which follows the ASTM B117 standard. The wear test is performed using a pin-on-disc machine (Model: Pin on Disc Wear & Friction Test Rig) provided by Micromatic Technologies, Bangalore, in accordance with ASTM G99.

## **3. RESULTS AND DISCUSSION**

### **3.1 X-Ray diffraction (XRD)**

The structural property of the coatings deposited at different temperature was analyzed by  $\theta$ -2 $\theta$  scans in the range 20°-90°. XRD pattern of the CrN films deposited on steel substrates at different temperatures (Fig.1). XRD pattern clearly indicating the polycrystalline nature. XRD pattern indicating the polycrystalline nature of CrN film. The films deposited at 300°C shows the mixed phase of Cr<sub>2</sub>N and CrN. The Cubic CrN (200) and hexagonal Cr<sub>2</sub>N (110), (111), (002), (302) is observed and it changes with temperatures. The crystalline sizes were evaluated from Scherrer formula and found to be 40 nm for film deposited at 300° C [16-19].

### **3.2 Scanning electron microscopy**

Figure 2 shows the SEM images of CrN coating deposited on mild steel. It shows the grains, which are uniformly distributed with smooth morphology of the coatings.

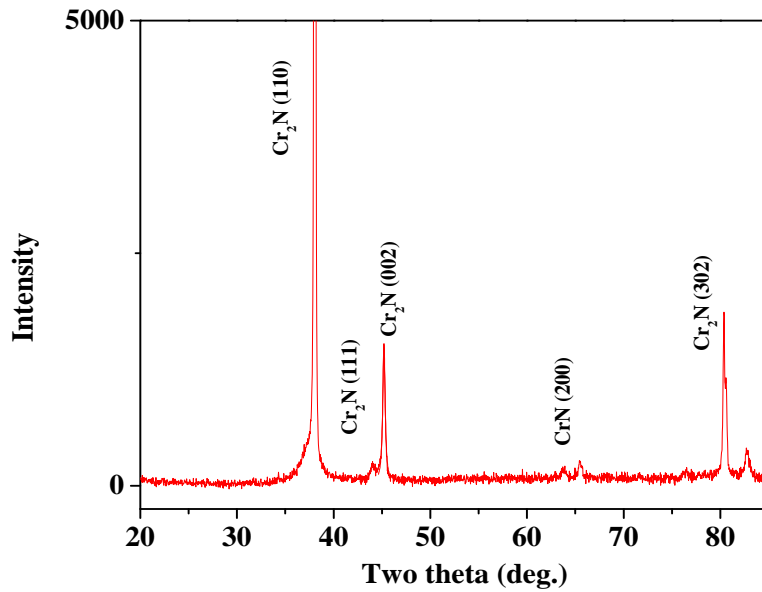


Fig.1 XRD pattern of the CrN coating

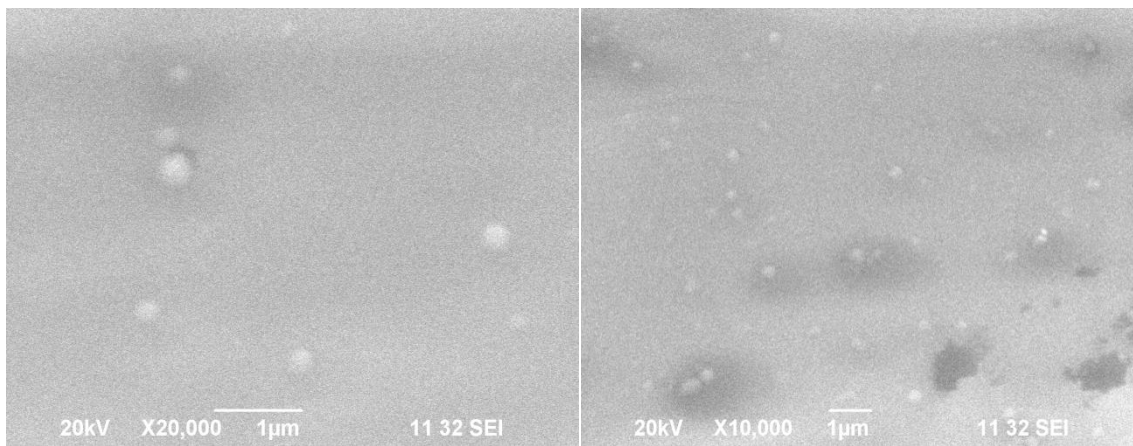


Fig.2 SEM images of the CrN coating deposited at 300°C

### 3.3 Microvicker indentation

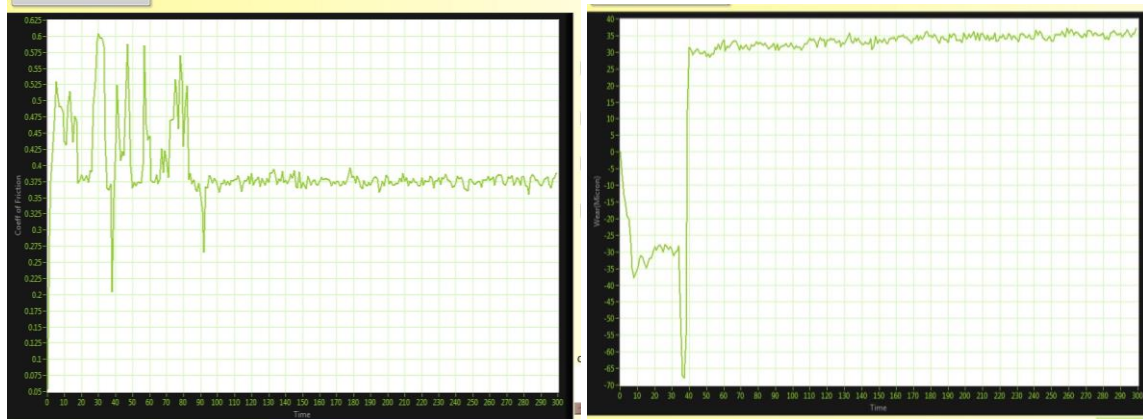
The hardness of the bare substrate is 230 HV. The CrN coating prepared at room temperature exhibits the hardness of 253 HV, while it is 360 HV for the coating deposited at 300°C. As the temperature increased to 500 C, hardness is increased to 371 HV. The hardness increased is observed with the increase of deposition temperature. This increase is due to the effects of fine-grained morphology of the coating annealed at higher temperature [20-22].

### 3.4 Corrosion studies

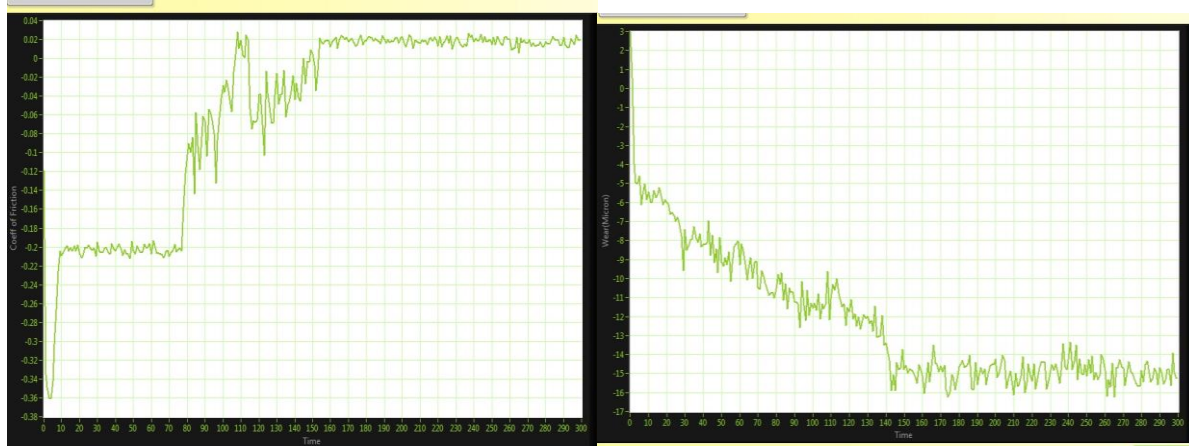
#### Details of testing parameters:

Before coating, the EN-24 steel is corroded after 2 hrs of salt spray test, while the CrN coated sample is not corroded even after 12 hrs but there is a formation of red colour after 24 hrs of the salt spray test. The sample deposited 300°C showed the higher corrosion resistant property compared with other sample.

### 3.5 Pin on disc - Wear properties



**Fig.3 and 4 Co-efficient of friction and Wear of CrN coating deposited at room temperature**



**Fig.5 and 6 Co-efficient of friction and wear of CrN coating deposited at 500°C temperature**

The graph depicts the progression of the COF during wear test. It has a time dependent rising tendency that lasts 90 seconds. The curve then settles into a fairly constant value. The COFs' average value for the early and steady state stage is 0.39 (Fig.3). Averaging the experimental values yielded the values of the initial friction coefficient. The steady state friction coefficients were calculated using the same method. It demonstrates that the coated disc has a lower friction coefficient than the untreated one. The coefficient of friction is lowered when CrN is deposited at a higher temperature. The mild sample's wear behaviour is depicted in Figure 4. It illustrates that the wear increases with time, and that after 40 seconds, the wear remains constant with time. This examination shows that due to particles, dirt, or any contamination, wear increased for a short period of time. After then, the wear is nearly continuous, and it displays 30 micron wear over time. This is because the EN surface on EN-24 steel is dense due to the CrN coating [20-24].

### 4. CONCLUSIONS

Chromium nitride coatings were deposited on EN-24 steel substrates with reactive DC magnetron sputtering. The argon flow rate was 30 sccm, while the nitrogen flow rate was set at 10 sccm, and the samples are annealed at temperatures ranging from 300 to 500 degrees Celsius. The XRD results show the formation of

both CrN and Cr<sub>2</sub>N phases in the coatings and many peaks appear at higher deposition temperature. The crystallite size is calculated for the film deposited at 300°C and found to be 40 nm. SEM images show the smooth morphology of the coatings and formation of the grains. The hardness of the coating deposited at room temperature is 253 HV, while the coatings annealed at 500°C indicated the hardness of 371 HV. The increased hardness at higher temperature is due to the improved density of the coatings and also due to the changes from the cubic to hexagonal phase. The covalent bonding present in the Cr<sub>2</sub>N phase causes increasing in the hardness of the coating. The wear test showed the COF of 0.39 and wear is 30 micron for the coating deposited at room temperature.

#### **REFERENCES**

- [1] Z.B. Zhao, Z.U. Rek, S.M. Yalliso, J.C. Bilello, *Thin Solid Films* 472 (2005) 96.
- [2] J. Lin, Z.L. Wu, X.H. Zhang, B. Mishra, J.J. Moore, and W.D. Sproul, *Thin Solid Films*, 517 (2009) 1887.
- [3] Z.B. Qi, B. Liu, Z.T. Wu, F.P. Zhu, Z.C. Wang, and C.H. Wu, *Thin Solid Films*, 544 (2013) 515.
- [4] B.W. Karr, I. Petrov, D.G. Cahill, and J.E. Appl. Phys. Lett., 70 (1997) 1703.
- [5] S. Logothetidis, P. Patsalas, K. Sarakinos, C. Charitidis, and C. Metaxa, *Surf. Coat. Technol.*, 180-181 (2004) 637.
- [6] M. Sikkens, A.A.M.T. van Heereveld, E. Vogelzang, and C.A. Boose, *Thin Solid Films*, 108 (1983) 229.
- [7] D. Gall, C.S. Shin, R.T. Haasch, I. Petrov, and J.E. Greene, *J. Appl. Phys.* 91(2002) 5882.
- [8] J. Vetter, *Surf. Coat. Technol.* 76 (2005) 719
- [9] B.Balzers, [www.balinit.balzers.com](http://www.balinit.balzers.com), 21 March (2001).
- [10] J. Almer, M. Oden, L. Hultman, G. Håkansson, *J. Vac. Sci. Technol. A* 18, (2000) 121.
- [11] E. Huber, S. Hofmann, *Surf. Coat. Technol.* 68-69 (1994) 64.
- [12] P. Panjan, B. Navinek, A. Cvelbar, A. Zalar, I. Miloev, *Thin Solid Films* 281-282 (1996) 298.
- [13] F.-H. Lu, H.-Y. Chen, *Thin Solid Films* 398-399 (2001) 368.
- [14] W.P. Hsieh, C.C. Wang, C.H. Lin, F.S. Shieu, *J. Electrochem. Soc.* 149 (2002) B234.
- [15] K.-L. Chang, S.-C. Chung, S.-H. Lai, H.-C. Shih, *Appl. Surf. Sci.* 236 (2004) 406.
- [16] R. Glang, "Vacuum Evaporation," in *Handbook of Thin Film Technology*, L. I. Maissel and R. Glang, Eds., McGraw-Hill, New York, 1970.
- [17] V.D.Ovcharenko,A.S.Kuprin,G.N. Tolmachova,I.V.Kolodiy,A.Gilewicz,O.Lupicka,J.Rochowicz, B.Warcholinski, *Vacuum* 117 (2015) 27.
- [18] Danielle de Villiers, Alison Traynor, Simon N.Collins, Sarah Banfield, Jonathan Housden, Julia Shelton, *Wear*, 328–329 (2015) 363.
- [19] P.Angerer, J.M. Lackner, M. Wiessner, G.A.Maier, L.Major, *Thin Solid Films* Volume 562 (2014) 159.
- [20] VolkerFrancoSteier, Remy Kalombo Badibanga, Cosme Roberto Moreirada Silva, Murilo Magalhães Nogueira, José Alexander Araújo, *Electric Power Systems Research*, 116 (2014) 322.
- [21] P.Angerer, J.M.Lackner, M.Wiessner, G.A.Maier, *Int. J. Refract. Met. Hard Mater.* 36 (2013) 101.

- [22] W. Ensinger, S.Flege, M. Kiuchi, K. Honjo, Nucl. Instrum. Meth. B: 272 (2012) 437.
- [23] Hetalkumar N. Shah, Int. J. Automot. Mech. 14 (2017) 3872.
- [24] Jyh-Wei Lee, Jen-Ching Huang and Jenq-Gong Duh, Tamkang J. Sci. Engg. 7 (2004) 237.