Original Research Article

Wear resistant Anti-Corrosion nanostructured coating for cultivator shovels

Abstract

Agriculture is the economy of Indian population and the principal source of income. Primary and secondary operations such as ploughing are the basic actions and extensive usage of cultivators for secondary tillage operation causes wear of the shovels because they are subjected to high tillage forces. An ample amount of material is lost due to wear and abrasion. Therefore, control and prevention of wear of cultivator shovels are vitally important for agro applications because wear of critical components has an economic significance. In this work CrN coating is deposited over cultivator reversible shovels using the DC magnetron sputtering technique and the structure, morphological, hydrophobic and wear characteristics are determined. It is observed that the working life of the agricultural tool is increased up to a significant level by depositing the desired coating on the substrate.

Keywords: Wear, DC Magnetron Sputtering, Tillage, Secondary Equipments

1. Introduction

Agriculture is the backbone of Indian economy and about half of the Indian population relies on agriculture as its principal source of income. Farm Mechanization has been well received in India as one of the important elements of modernization of agriculture. Country witnessed unprecedented growth in food grain productivity from 0.636 t/ha in year 1965-66 to 2.111 t/ha in 2013-14. This growth is mainly due to the agricultural technology used in farms. Average farm power availability in India has increased from about 0.30 kW/ha in 1960-61 to about 2.02 kW/ha in 2013-14 **[1]**.

Primary and secondary operations such as ploughing are the basic actions required for cultivation of any kind of crop. Universally farmers use different implements such as (mouldboard ploughs, disc ploughs and cultivators) extensively under different field conditions. Among them, cultivator is a kind of soil engaging tool that is used as secondary tillage implement due to its large soil coverage area between two furrows. The extensive usage of cultivators for secondary tillage operation causes wear of the shovels because they are subjected to high tillage forces **[2-6]**. An estimation of material loss in cereal cultivation in Turkey indicates that for cultivating an area of 13422000 ha twice, an amount of 9700 t of steel is lost due to wear and abrasion and the energy equivalent of this material loss has been found to be 897 GJ **[7]**. Therefore, control and prevention of wear of cultivator shovels are vitally important for agro applications because wear of critical components has an economic significance.

The wear and abrasion of agricultural implement can be largely controlled by surface modification such as coating to increase the useful life shell of agricultural tools. It is highly desirable to deposit hard protective coatings to increase the cost effectiveness, life and performance of the shovel. Various conventional techniques like electroplating, thermal plasma spraying, sol-gel technique, cathodic arc depostion (CAD), chemical vapour deposition (CVD) are utilized for depositing the desired material on substrate to achieve surface modification **[8-9]**. These techniques have good process stability as well as economical and they have been adapted for industrial production, but the above mentioned technique are not environmental friendly and coatings exhibit poor properties. Physical vapour deposition (PVD) processes are deposition processes in which ions or molecules of a material are vaporized from a solid or liquid source, transported in the form of a vapour through a vacuum or low pressure gaseous environment and condense on a substrate. PVD processes are used to deposit films with the thickness range of a few angstroms to several dozen nanometres **[10-13]**. Some of the widely used PVD techniques are vacuum evaporation, magnetron sputtering, sputter deposition, arc evaporation, low voltage electron beam evaporation, cathode arc deposition, triode high voltage electron beam evaporation and ion planting. Moreover nanostructured thin films have attracted considerable attention in several applications like octoelectroics, electronics **[14-17]**.

Magnetron sputtering is a physical vapour deposition (PVD) coating technique that can overcome many disadvantages that were prevailing with different techniques such as low density, poor adhesion, and poor properties Sputtering is a very flexible and effective deposition process for depositing various metallic and compound thin films for surface engineering applications. It holds many advantages like contamination free deposition, reproducibility, uniform deposition rate and good quality of film.

Hard protective coatings deposited by sputtering shows excellent physical properties such as high hardness, strength, toughness, chemical stability, wear and corrosion resistance **[18-19]**. It has been widely used as a thin protective film **[20]**.Sputter deposition technique has the ability to deposit coatings at low substrate temperatures or to control the structure and properties of the deposited coatings by controlling the deposition parameters **[21]**.

Physical vapour deposition (PVD) of chromium nitride in comparison to other nitride coatings through magnetron sputtering technique is a good alternative to other conventional surface treatments for protection against wear and corrosion. CrN has good hardness, toughness and good tribological properties. Hard coatings are characterised by a relatively low friction coefficient, good wear resistance and a high corrosion resistance . The aim of this research was to deposit nanostructured coating material to enhance the life shell of the cultivator shovels **[22-24]**.

In this study we have deposited CrN over agriculture tool named reversible shovel on using the DC magnetron sputtering technique and investigated structure, morphological, hydrophobic and wear characteristics at different substrate temperatures as (100 ^{0}C, 150 ^{0}C, 200 ^{0}C). The coatings were characterized by X-Ray diffraction (XRD), Scanning electron microscopy (SEM) nanoroughness and hydrophobicity were determined using atomic force microscopy and contact angle goniometer. Wear test was carried out in a custom designed circular soil bin.

2. Experimental details

2.1 CrN film Processing

The CrN films were deposited by DC-magnetron sputtering technique on shovel (mild steel) as substrate in a custom designed 35 inch diameter chamber (Milman thin film systems). A 4 inch diameter and 6 mm thick chromium target of 99.99% purity was used for the sputtering. The substrate was thoroughly cleaned by rinsing in acetone and methanol and dried under nitrogen gas. The chamber was initially evacuated by a turbo molecular pump backed by a rotary pump. During each deposition, the base pressure was kept less than 5×10^{-6} Torr and the distance between the substrate and the target was kept 110 mm**.** The CrN coating was fabricated at As-deposited and 200 ^{0}C substrate temperature . The sputtering was carried out in an argon (99.99% pure) atmosphere while nitrogen was used as a reactive gas. The flow rate of nitrogen and argon in the chamber was 20 sccm and 20 sccm, respectively. The gas pressure was kept 10 m Torr for all depositions.

2.2. Characterization details

The structure properties of CrN films were characterized by X-ray diffractometer (XRD) with Cu Kα radiation. Scan rate used was 2^{0} min^{-1} and the scan range was from 10 to 70^{0}. The surface topography and elemental analysis of the film was studied using Scanning electron microscope (SEM) (Carl Zeiss) was carried out by using energy dispersive X-ray analysis (EDS). The surface morphology of the CrN films was studied using atomic force microscope (NT-MDT, Ntegra) operated in semi contact (tapping) mode. To determine whether the films are hydrophilic or hydrophobic by nature, contact angle measurement system (Kruss DSA 100 Easy Drop) was used to find contact angle of water with the films. Wear analysis was carried out in custom designed soil bin. A circular soil bin had an outer diameter of 5520 mm, inner diameter of 3490 mm and a depth of 900 mm.

3. Results and discussion

3.1. Structural analysis

X-ray diffraction analysis was carried out to determine the orientations and structural transformation of CrN films deposited at three different temperatures. Fig.1 shows the XRD of the nanostructured films of chromium nitride deposited at 100 ^{0}C, 150 ^{0}C and 200 ^{0}C. The XRD curve clearly reveals that CrN film deposited at different temperatures are polycrystalline in nature and dominant peak occurs at 2Θ = 37.56^o which corresponds to (1,1,1) orientation of cubic phase of CrN (JCPDS 11-0065). At 200 ^{0}C temperature the deposited film exhibited an intense and sharper diffraction pattern. The average crystallite size of the thin film was calculated using the Debye–Scherrer formula **[25]**.

$$t = \frac{0.9\,\lambda}{\beta cos\Theta} \qquad ....(1)$$

where t is the crystallite size, λ the wavelength of X-ray (1.54056A˚), β the line width at half maximum of the most dominant peak and Θ Bragg diffraction angle. The crystallite size for 100 ^{0}C, 150 ^{0}C , 200 ^{0}C substrate temperature coating were 18.97 nm, 20.44 nm and 25.47 nm respectively. Crystal size found to increase with increase in substrate temperature. The enhancement in the crystal size of chromium nitride films can be associated with the change in the kinetic energy of the sputtered particles with the temperature.

3.2. Surface morphology and chemical composition

The surface topography and chemical composition analysis was done through EDS and SEM as shown in Table 1. It shows the atomic (%) of chromium and nitrogen of deposited film at different substrate temperatures. It is clear from that the elements of Cr and N is dependent upon temperature. SEM images of film deposited at substrate temperatures are shown in Fig. 2. The Cr/N ratio is approximately 1 for film deposited at temperature 200^{o}C while that of As-deposited is less than one. The surface nano roughness of the CrN films was studied using atomic force microscopy (AFM). The AFM micrographs correspond to a scan area of 2μm×2μm and two dimensional AFM images obtained for CrN films deposited at 100 ^{0}C, 150 ^{0}C, 200 ^{0}C are shown in Fig. 3. It is clear from the figure 3 that CrN films are constituted with a large number of nanograins. The surface roughness was calculated using the software attached with AFM and is shown in Table 1. It is clear that as substrate temperature was increased from 100 ^{0}C to 150 ^{0}C and 150 ^{0}C to 200 ^{0}C roughness value was also increased from 6.35, 8.48, 11.17 nm respectively. This behaviour of roughness is very well correlated to the particle size which was earlier calculated through XRD. The increment in substrate temperature increases the particle size which in turn enhances the roughness, while decrement in particle size reduces the roughness.

3.3. Hydrophobic properties

The wettability of CrN coatings were evaluated by measuring the water contact angle goniometer at ambient room temperature. The distilled water droplets were dropped on the deposited coating surfaces using a microsyringe. Average value of the water contact angle was determined by experimental drop profiles at different positions for the same sample. The water contact angle as a function of sputtering temperature was measured and is shown in Fig.4. A graph in Fig.4 shows relation between roughness, contact angle and substrate temperature. Water contact angle as measured of 100 ^{0}C, 150 ^{0}C and 200 ^{0}C was 100^{0}, 102^{0} and 105^{0} respectively which confirms that CrN coating is hydrophilic in nature.

4.1. Effect of coating on wear of cultivator shovels by abrasive sand

The effect of coating on gravimetric wear of reversible cultivator shovels was observed in a circular soil bin by using sand as abrasive medium. Test shovels S_1, S_2, S_3 with substrate temperature 100^{0}C, 150^{0}C and 200^{0}C respectively and almost equal hardness of 371 BHN were mounted on the tool frame for continuous testing in the soil bin. The moisture content of sand was kept 9-10 per-cent. Operating speed and depth of operation were 1m/s, 100 mm respectively

4.1.1. Effect of working period

The results obtained during the study are depicted in Fig.5. It is clear from the figure that the weight of shovels decreased with increase in working period for all tested shovels. Shovels with different substrate temperatures coating deposited after 100 h are shown in Fig.6. This result are with the findings of **[26,27]** who also reported that wear increases with increase in period of work. Wear rate was gradually increasing with time. The higher average wear rate of 2.41 mg/min was observed during 100 h of operation in non coated shovel, and the same was reduced for 100 ^{0}C, 150 ^{0}C and 200 ^{0}C that was 2.02 mg/min, 1.77 mg/min and 1.36 mg/min respectively. This may be due to the reason that as substrate temperature increases adhesiveness of the coating increases. The results are in agreement with (Lufitha,2001) who also reported that adhesion strength of the coating increased when substrate temperature was raised.

A statistical analysis was also carried out to find the significant effect of substrate temperature based coating and time on wear of shovels (Table 2). ANOVA shows that the main effects of time and temperature were highly significant on wear loss. The analysis further reveals that the interaction S x t was also significant. Table 3 showing mean values interaction effect of substrate temperature based coating and time on gravimetric wear.

4.1.2. Effect of substrate temperature based coating on wear of shovels.

The cumulative wear observed was 14.48, 12.13, 10.59 and 8.15 gm for shovel with non coated and substrate temperature coating at 100 ^{0}C, 150 ^{0}C and 200 ^{0}C respectively after 100 hrs of working period. It was found that the wear loss decreased with increase in substrate temperature based coating. Minimum weight loss due to wear was observed in shovel with temperature 200 ^{0}C. Thus, with the increase in temperature from 100 ^{0}C to 200 ^{0}C the cumulative wear was decreased by 43.71 per cent. Further wear rate was calculated for the tested shovels (Table 4.). The wear rate was minimum i.e., 1.36 mg/min for shovel with 200 ^{0}C substrate temperature and for shovel 100^{0}C it was 2.02 mg/min. These results are in agreement with the findings of **[28-30]**. Fig.7 shows graph between wear rate and time.

4. Conclusions

The diffraction patterns confirms that the coating deposited on the shovel was chromium nitrite (CrN) and exhibits cubic structure. Crystal size was found to increase with increase in substrate temperature. Cr/N ratio was approximately one for film deposited at temperature 200^{o}C, while for other deposited temperatures at 100^{o}C and 150^{o}C it was less than one. Roughness value was found to increase with temperature. Water contact angle were observed 100^0, 102^0 and 105^0 at 100 ^{0}C, 150 ^{0}C and 200 ^{0}C substrate temperature respectively, which confirms that CrN coating was hydrophilic in nature. The effect of temperature was found significant and the wear loss decreased with increase in substrate temperature coating. Minimum weight loss due to wear was observed in shovel with maximum substrate coating temperature at (200 ^{0}C). The shovels with different substrate coating temperatures wore along the thickness. There was negligible change in length and width. The reduction in thickness in all shovels followed the same pattern. Wear loss was maximum at the tip of the shovel and it gradually decreased while moving away from the tip of the shovel. Minimum dimensional wear loss was observed in shovel with substrate coating temperature at (200 ^{0}C). On the basis of the above findings, it was concluded that the DC magnetron sputtering coating technique can be used to deposit antiwear, corrosion free and hydrophobic coating at 200 ^{0}C substrate temperature on agricultural tools. The working life of the agricultural tool can be increased upto a significant level by depositing the desired coating on the substrate.

COMPETING INTERESTS DISCLAIMER:

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

References

1. S. Singh, R.S. Singh, S.P. Singh, Farm Power Availability on Indian Farms, Agricultural Engineering Today, 38 (2014): 44-52.
2. Z. Owsiak, Wear of symmetrical wedge shaped tillage tools. Soil Tillage and Research, 43(1997): 295-308.
3. A. K. Gupta, D. M. Jesudas, P. K. Das, and K. Basu, Performance evaluation of different types of steel for duck foor sweep apllication, Biosystems Engineering, 88(2004), 63-74.
4. S. A. Ferguson, J. M. Fielke, and T. W. Riley, Wear of Cultivator Shares in Abrasive South Australian Soils. Journal of Agricultural Engineering Research, 69(1998): 99-105.
5. S. Karoonboonyanan, V. M. Salokhe, and P. Niranatlumpong, Wear resistance of thermally sprayed rotary tiller blades. Wear, 263(2007): 604-608.

6. M.B. Karamis,. Energy losses resulting from tillage tool wear in Turkish agricultural fields. In: Third International Symposium Ismir, Turkey, October 26-29, Mechanization and energy in agriculture, Proceedings. (1987):211-219.
7. J. Lin, W. D. Sproul, J. J. Moore, S. Lee, and S. Myers, High rate deposition of thick CrN and Cr_2N coatings using modulated pulse power (MPP) magnetron sputtering. Surface and Coatings Technology, 205(2011), 3226-3234.
8. J. Jagielski, A. S. Khanna , J. Kucinski, D. S. Mishra, P. Racolta, P. Sioshansi, E. Tobin, J. Thereska, V. Uglov, T. Vilaithong, J. Viviente, Si.Ze. Yang, and A. Zalar, Effect of chromium nitride coating on the corrosion and wear resistance of stainless steel. Applied surface science, 156(2000), 47-64.
9. K. Lukaszkowicz, L.A. Dobrzański, A. Zarychta, L. Cunha, Mechanical properties o multilayer coatings deposited by PVD techniques onto the brass substrate. Journal of Achievements in Materials and Manufacturing Engineering, 15(2006), 47-52.
10. L.A. Dobrzański, K. Gołombek, J. Mikuła, D. Pauma, Multilayer and gradient PVD coatings on the sintered tool materials. Journal of Achievements in Materials and Manufacturing Engineering, 31(2008), 170-190.
11. D. Pakuła, L.A. Dobrzańsk, Investigation of the structure and properties of PVD and CVD coatings deposited on the Si_3N_4 nitride ceramics. Journal of Achievements in Materials and Manufacturing Engineering, 24(2007), 79-82.
12. L.A. Dobrzański, L. Wosińska, K. Gołombek, J. Mikuła, Structure of multicomponent and gradient PVD coatings deposited on sintered tool materials, Journal of Achievements in Materials and Manufacturing Engineering, 20(2007), 99-102.
13. S. Gulizia, M.Z. Jahedi, E.D. Doyle, Performance evaluation of PVD coatings for high pressure die casting, Surface and Coatings Technology, 140(2001), 200-205.
14. S. Jellad, C. Labdi, G. Malibert, G. Renou, Nanomechanical and nanowear properties of Cr_3C_2 thin film deposited by RF sputtering, Wear, 264(2008), 893-898.
15. J. Esteve, J. Romero, M. Gomez, A. Lousa, Cathodic chromium carbide coatings for molding die applications, Surface and Coatings Technology, 188(2004), 506-510.
16. M. Roy, A. Pauschitz, R. Polak, F. Franek, Comparative evaluation of ambient temperature friction behavior of thermal sprayed Cr_3C_2 - 25(Ni20Cr) coatings with conventional and nano-crystalline grains, Tribology International, 39(2006), 29-38.

17. V. Dave, H.O. Gupta, R. Chandra, Nanostructured hydrophobic DC sputtered inorganic oxide coating for outdoor glass insulators, Applied Surface Science, 295(2014), 231-239.
18. B. Warcholinski and A. Gilewicz, Tribological properties of CrNx coatings. Journal of Achievements in Materials and Manufacturing Engineering, 37(2009), 498-504.
19. S. Gulizia, M.Z. Jahedi, E.D. Doyle, Performance evaluation of PVD coatings for high pressure die casting, Surface and Coatings Technology, 140 (2001), 200-205.
20. S.A. Ferguson, J.M. Fielke, T.W. Riley, Wear of Cultivator Shares in Abrasive South Australian Soils, Journal of Agricultural Engineering Research 69 (1998), 99-105.
21. M.B. Karamis, Energy losses resulting from tillage wear in Turkish agricultural fields. In: Third International Symposium Ismir, Turkey, October 26-29, Mechanization and energy in agriculture : Proceedings. 1987, 211-219.
22. Z. Owsiak, Wear of spring tine cultivator points in sandy loam and light clay soils in southern Poland. Soil and Tillage Research, 50(1999): 333-340.
23. G. G. Fuentes, R. Rodriguez, J. Avelar Batista, C. Housden, J. Montala, F. Carreras, L. J. Carreras, A.B. Cristobal, J.J. Damborenea, and T. J. Tate, Recent advances in the chromium nitride PVD process for forming and machining surface protection, Journal of materials processing technology, *167*(2005), 415-421.
24. S. M. Musameh, and S. W. Jodeh, Tribological behavior of chromium nitride coating by unbalanced magnetron sputtering, Journal of Active and Passive Electronic Devices, 2(2007): 93-103.
25. Lufitha, M. (2001). Effect of Substrate Temperature on Coating Adhesion. Pub.Phd.Thesis. University of Toronto, Canada.
26. M.P. Rubiniec, L.A. Dobrzanski, M. Adamiak, Comparison of the PVD coatings deposited onto plasma nitrited steel, Journal of Achievements in Materials and Manufacturing Engineering, 42(2010), 172-179.
27. M. Richert, A. Mazurkiewicz, J. Smolik, Chromium carbide coatings obtained by the hybrid PVD methods. Journal of Achievements in Materials and Manufacturing Engineering,43(2010), 145-152.
28. M.P. Rubiniec, L.A. Dobrzański, M. Adamiak, (2007). Comparison of the adhesion and wear resistance of the PVD coatings. Journal of Achievements in Materials and Manufacturing Engineering, 20(2007), 279-282.

29. V.K. Chahar, and G.S. Tiwari, Effect of soil moisture content on wear characteristics of reversible shovels of tractor drawn cultivator, Journal of Institution of Engineers India, 46(2008): 3-4.
30. V.K. Chahar, G. S. Tiwari and R. N. Verma, Wear characteristics of reversible shovels of tractor drawn cultivator, *Journal of Agricultural Engineering*, 46(2009) :17-24.

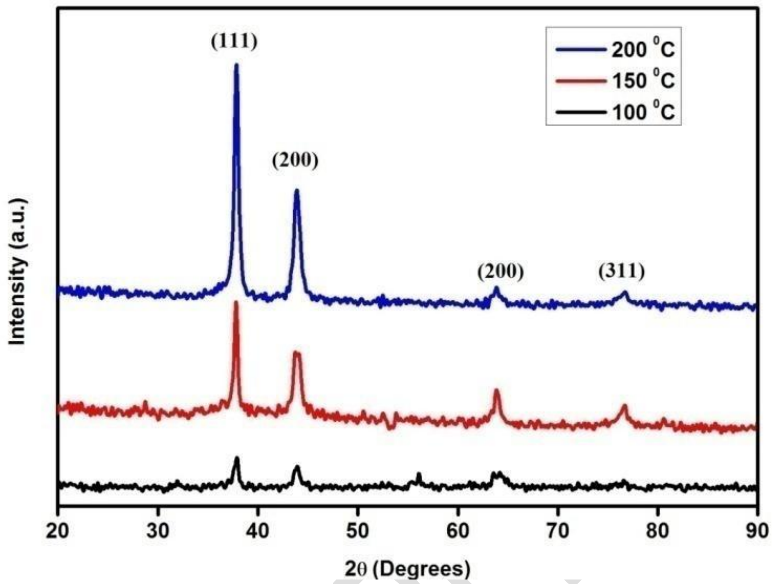


Fig. 1. XRD patterns of CrN films deposited at different temperatures.

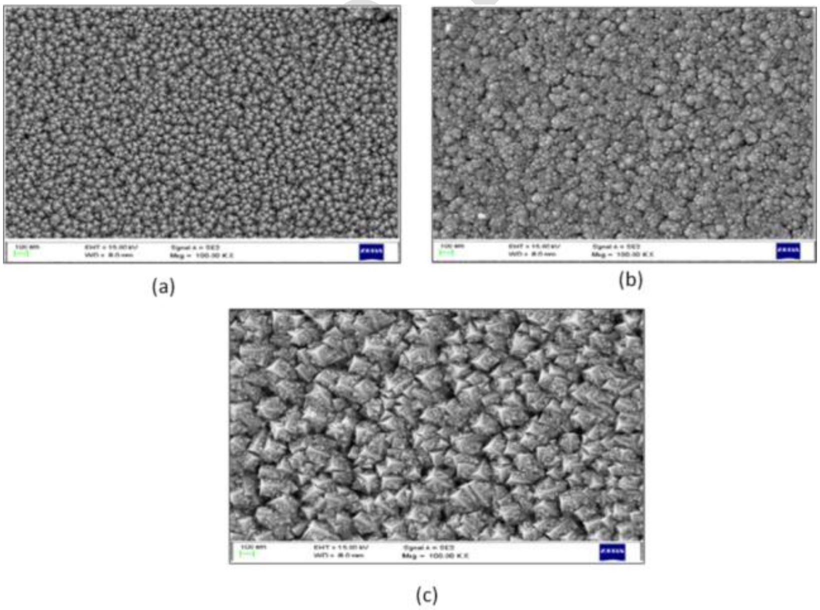
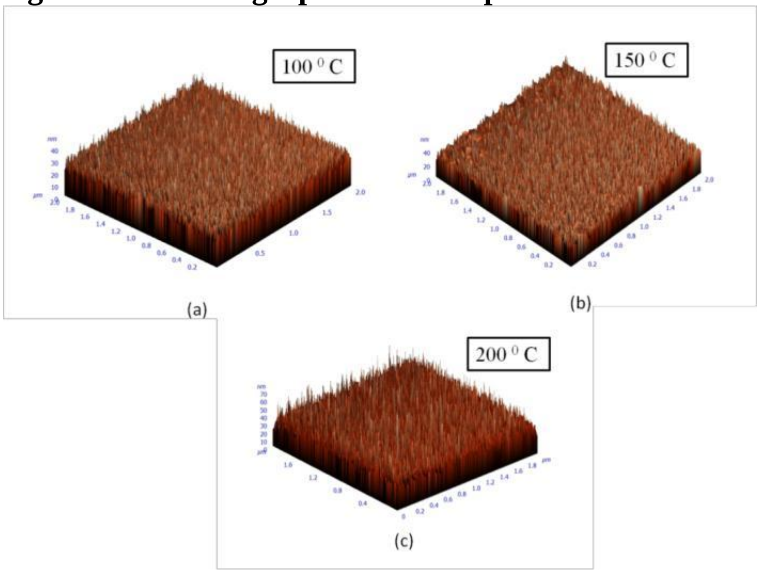


Fig. 2. SEM images of film deposited at different substrate temperatures, (a) 100°C (b) 150°C (c) 200°C

Fig. 3. AFM micrographs of film deposited at different temperatures.



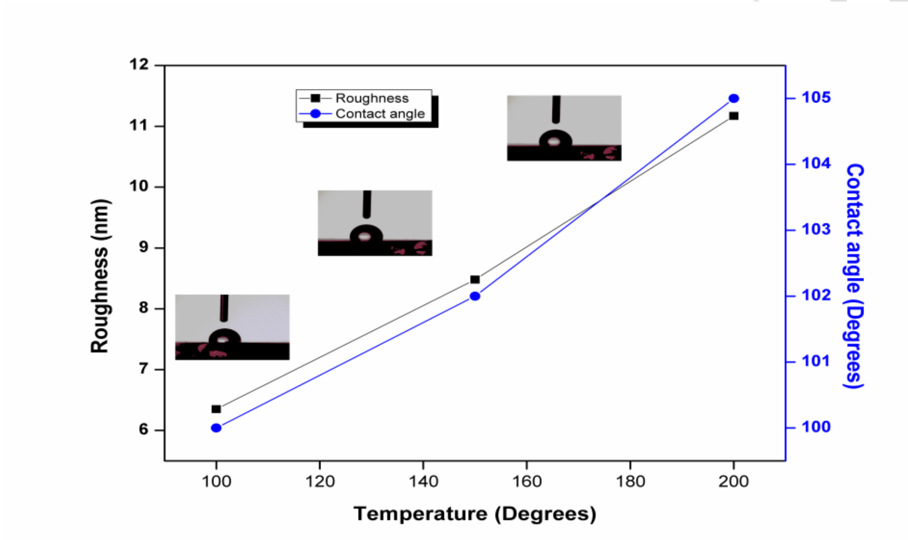


Fig. 4. Contact angle and roughness of film deposited at different temperatures.

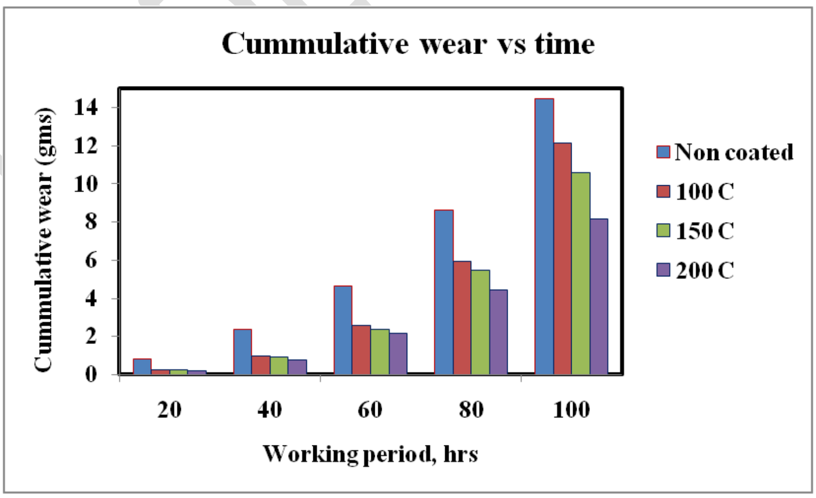


Fig. 5. Cumulative wear in shovels with different substrate temperature coating at different working period.

T_1 = 100 ^{0}C T_2 = 150 ^{0}C T_1 = 200 ^{0}C

Fig. 6. Shovel with different substrate temperature coating after 100 hrs of working period.

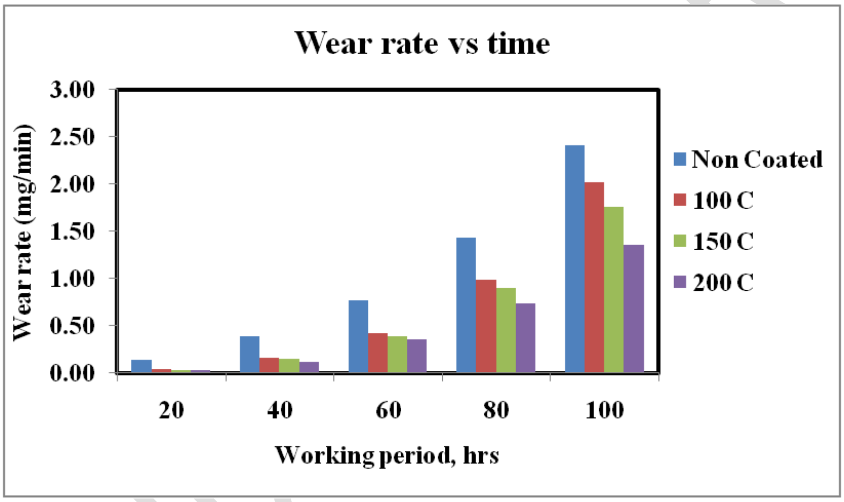


Fig. 7. Wear rate in shovels with different substrate temperature coating at different working period.

Table 1. EDS data of deposited CrN samples at different substrate temperatures.

Substrate temperature (^{0}C)	Atomic % Cr	Atomic % N_2
100	39.56	46.54
150	40.77	44.31
200	42.06	42.48

Table 2. Analysis of Variance for the effect of substrate temperature based coating and time on wear of cultivator shovels.

Source of Variance	DF	SS	MSS	Computed F
Shovel (S)	3	63.42	21.14136	1170.688*
Time (t)	5	1145.58	229.1169	12687.18*
Sxt	15	47.31	3.154078	174.6548*
Error	48	0.87	0.018059	1.000
Total	71			
Grand Mean		11.33		
C V		5.51		

*** Significant at 5 % level**

Table 3. Mean values showing interaction effect (two variables) of substrate temperature based coating and time on gravimetric wear.

Time/Shovel	S_1(Non coated)	S_2(100 ^{0}C)	S_3(150 ^{0}C)	S_4(200 ^{0}C)	Mean
0	0.00	0.00	0.00	0.00	**0.000**
20	0.82	0.25	0.22	0.17	**0.367**
40	2.38	0.95	0.89	0.75	**1.243**
60	4.65	2.55	2.36	2.14	**2.928**
80	8.60	5.92	5.44	4.41	**6.090**
100	14.48	12.13	10.59	8.15	**11.338**
Total	30.94	21.80	19.50	15.62	
Mean	**5.16**	**3.63**	**3.25**	**2.60**	

Table 4. Wear rate of shovels with different substrate temperature based coating.

Sr.No.	Shovel (Temperature)	Wear rate (mg/min)
1	S_1(Non Coated)	2.41 mg/min
2	S_2(100 ^{0}C)	2.02 mg/min
3	S_3(150 ^{0}C)	1.77 mg/min
4	S_4(200 ^{0}C)	1.36 mg/min