Comparison of Reciprocating Wear Behavior of Electrolytic Hard Chrome And Arc-PVD CrN Coatings

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Electrolytic hard chrome coatings have been successfully used for long years for surfaces requiring wear resistance under lubricated conditions. However environmental restrictions on the use of hexavalent chromium baths brought up the need for alternatives. CrN coatings, with their higher hardness and toughness can be an alternative to hard chrome coatings. This study is conducted to systematically investigate the wear behaviour of electrolytic hard chrome and arc-PVD coatings under lubricated reciprocating conditions. Experiments are conducted in unformulated base oil and the effects of normal load (5, 10 and 30N) and temperature (room and 60 ^{o}C) on wear behaviour of both electrolytic hard chrome and arc-PVD CrN coatings are investigated. The results indicated that CrN performed better than hard chrome plating under lubricated reciprocating wear conditions used in this study. This effect became more pronounced by the increase of temperature and normal load. Profilometric wear depths on both coatings could not be determined after the tests conducted at room temperature. However at 60°C, wear depths as deep as 3.5 µm (at 30N load) on EHC coating could be recorded by profilometer. Profilometric depth on CrN coated discs could not be detected. The reciprocating sliding tests on brushed CrN coated discs clearly demonstrated the important role of droplets on tribological behaviour of arc PVD coatings.

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1. Introduction

Electrodeposited hard chromium (EHC) coatings have been widely used for improving wear characteristics of engineering tools and components [1, 2,3]. In the electrodeposition processes, in general solutions containing hexavalent chromium have been used. Hexavalent chromium is classified as a carcinogen compound, which causes health risks if used in production, and environmental problems due to the toxic character of the wastes. The environmental concern on the use of hexavalent chromium stimulated the research activities for alternatives of hard chromium [1, 4-8].

Less harmful electrolytic solutions using trivalent Cr [9, 10] and ion implantation methods [1, 6,11,12] for improving wear and corrosion performance of hard chrome have been investigated.

Wear performance of hard chromium coating is better than most metallic coating alternatives such as Ni and electroless Ni coatings [16-18].

Thick alloy coatings produced by high velocity oxygen fuel spray process [5, 8] and hard coatings produced by physical vapour deposition [2, 13-15], known as clean technologies, are also attractive alternatives.

The crack pattern of the hard chrome surfaces is shown as a problem for wear resistance by some researchers [19]; on the other hand in some studies, the beneficial effect of the cracks is observed and explained by the extension of the fraction of area covered by liquid lubricant [18]. According to Martyak and McCaskie micro-cracks in hard chrome surface were not a major factor in wear performance under lubricated conditions [20]. Arieta and Gawne found that its durability decreased with increasing load under lubricated sliding condition and the topography of the chromium plating surface has a major influence on its durability [21].

Recently, the use of physical vapour deposited hard ceramic coatings for wear resistance applications have been increasing [19,22-24]. PVD-CrN coatings have been investigated by several researchers due to their good mechanical and corrosion properties and also low internal stresses [5, 25-28]. Previous studies showed that physical vapour deposited CrN coatings can be an alternative for hard chromium [2, 15, 25, 29, 30]. If CrN coating is compared to electrolytic hard chrome, it is evident from the available results that CrN is at least two times as hard [2, 29], has better corrosion behaviour [29], and shows better wear resistance [25,30]. Broszeit et al [25] and Friedrich et al. [30] compared the corrosion and wear behaviour of hard chromium and CrN coatings under lubricated conditions. According to them the corrosion and wear behaviour of CrN coatings were better than hard chromium and hence a promising substitute for the replacement of EHC. PVD coatings can potentially replace hard chromium partially or completely in wear applications [15, 25].

Although several studies comparing the wear behaviour of EHC and PVD CrN can be found in the literature there is no systematic research on the comparison of these coating under lubricated room and elevated temperature conditions.

Therefore the aim of this study is to compare the wear behaviour of cathodic arc PVD CrN and EHC coatings under lubricated conditions. For this purpose, reciprocating sliding tests in base mineral oil were performed under different normal loads and oil temperatures.

2. Experimental

2.1. Coatings

Cylindrical high-speed steel specimens (9.5mm diameter, 5mm height) were used as substrate materials. Specimens were wet ground and polished. EHC were deposited from conventional commercial hard chromium solution (Table 1). CrN coatings were produced by cathodic arc PVD (Model NVT-12, Moscow). Coating parameters for CrN are given in Table 2.

Table 1. EHC parameters

CrO_3	250g/lt
SO_4^{-2}	%0,3
Temperature	65°C
Current density	30 A/dm^2
Voltage	7 V
Bath Volume	1 m^3

Table 2. Arc PVD parameters for CrN coating

Coating Time (min)	80
Arc Current (A)	90
Bias (V)	150
CoatingTemperature (°C)	250-300
N_2 pressure (torr)	7,5x10^{-3}

2.2. Characterization

Surface roughness of substrate material and coatings were measured by a profilometer (Feinprüf-Perthen F8P) with an optical probe (Focodyn).

The thicknesses of the coatings were determined by ball cratering (Calotest, Wirtz-Buehler).

A dynamic ultra-micro hardness tester (Fisher H100 XYPROG) was used for determining the hardness of the coated samples. In the tests 20mN maximum load was applied in 120 steps, and the step interval was 0.1 s.

2.3. Friction and Wear Test

Wear experiments were conducted under reciprocating sliding conditions. Plint & Partners TE 70 Micro Friction test machine was used. Mineral based oil (without any additive, at 40 °C, 150 cSt) as lubricant and M50 ball (10 mm diameter) as counter body material were selected. Experimental parameters were determined by preliminary experiments. In reciprocating wear experiments, 50 Hz frequency, 1 mm amplitude and 180 min sliding duration were kept constant. 5, 10, 30 N loads, room and 60°C oil temperature were used as variable parameters.

After wear experiments, samples were cleaned with acetone and toluene. Wear scars on the coated samples and balls were investigated by optical microscopy, scanning electron microscopy and profilometer. Diameters of the wear scar on balls were measured by optical microscope, from which wear volumes and rates of the balls were calculated.

3. Results and discussion

3.1. Characterization

CrN coating hardness is approximately two times higher than EHC. Roughness of both coatings is very close to each other. The thickness of EHC is approximately 3.5 times higher (Table 3).

Table 3. Characterization results of the coatings and the substrate

	Thickness (µm)	Ra (µm)	Hardness (kg/mm^2)
Substrate	-	0.06	800±50
EHC	11±1	0.18	1180±150
CrN	3±0.2	0.22	2200±190

3.2. Friction

In room temperature tests the friction coefficients of both coatings were close to each other and decreased with increasing normal loads (Fig. 1). The lowering of friction coefficient with increasing load can be explained by the smoothening of the coating surface or decreasing of the contact pressure by the wear of the ball. Lower loads might also not effective in removal of wear debris from the sliding interface. Friction coefficients varied between 0.1-0.2. This indicated that the lubrication mode was boundary and/or mixed lubrication [31].

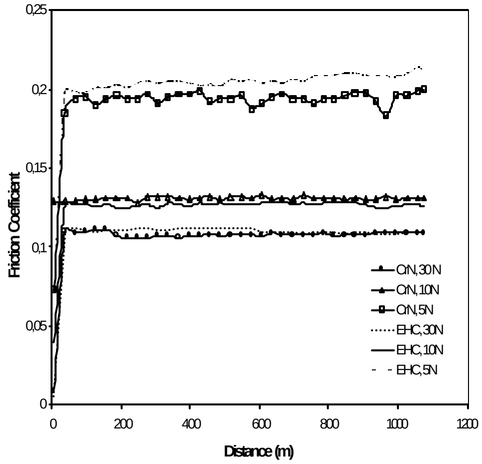


Figure 1. Friction coefficients of CrN and EHC vs. distance (m) at room temperature for all loads

In tests conducted at 60°C the friction coefficients of the coatings also decreased with increasing normal loads. In this case the friction coefficients of EHC are higher than CrN coatings. Moreover the friction coefficient of EHC was not constant; rise and falls were observed (Figure 2). This can be an indication of the adhesion between the contact surfaces during wear.

The coefficient of friction of EHC, increased by the raising of oil temperature, on the contrary the coefficient of friction decreased for CrN coating. The viscosity of oil, the most important lubricant property, decreases with increasing temperature, oil becomes insufficient for disconnecting the sliding surfaces hence coefficient of friction increases [32]. For CrN coating, the lowering of the coefficient of friction with temperature may be attributed to the easier removal of the wear debris from the sliding interface through low viscosity oil.

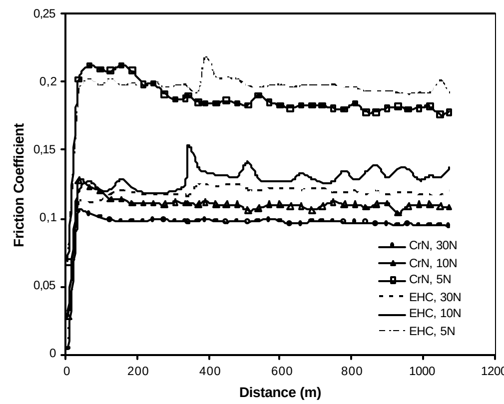


Figure 2. Friction coefficients of CrN and EHC vs. distance (m), at room temperature for all loads

From friction point of view, at room temperature both EHC and CrN coatings showed similar characteristics. However at 60 °C CrN showed better and more stable friction behaviour than EHC coatings.

3.3. Wear

3.3.1. At room temperature

Wear rates of balls decreased with the reducing load. In addition, wear rates of balls sliding against CrN coating were lower than the values of balls' sliding against hard chromium (Figure 3).

In the profilometric measurements conducted on all coated discs, wear depths cannot be determined due to low wear amounts.

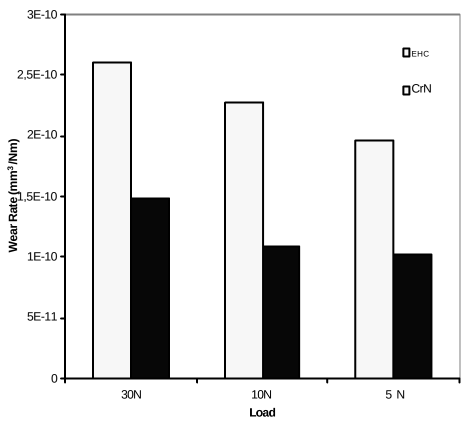
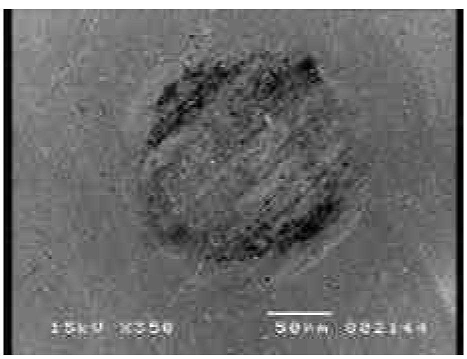
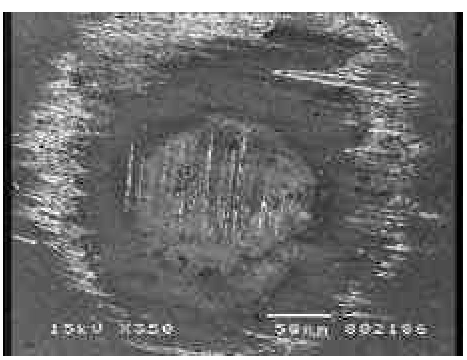


Fig. 3. Wear rates of steel balls sliding against EHC and CrN coatings, for all loads at room temperature



(a)



(b)

Figure 4. SEM images of wear scars on steel balls sliding against; (a) hard chromium, (b) CrN coating, at 30 N load and room temperature.

The wear scar on ball against EHC is given in Fig. 4 (a). On the dark regions of this scar high Cr concentration was detected by EDS analysis which can be explained by the transfer of chrome from hard chrome coating to the steel ball. These regions became smaller with decreasing load.

At 30N load, around the sliding contact area of the steel balls sliding against CrN coating, a region formed by wear debris was observed (Fig. 4b). This area extended with decreasing load which can be attributed to the free movement of abrasive particles i.e. droplets in the sliding interface.

In the wear tracks of EHC coated discs scratches and grooves in the direction of movement were observed but the natural cracked structure of hard chromium could still be observed in the wear scar.

In wear tracks of CrN coatings it was observed that the droplets on CrN coatings were not present. Grooves or scratches were hardly observable in these coatings.

3.3.2. At 60 °C

In comparison to room temperature experiment results, at 60°C wear rates of balls were higher.

In 60^{o}C experiments, wear rates of balls used against EHC coating decreased with decreasing load as in room temperature conditions, but amount of wear was 1-2 order of magnitude higher. Under 30N load the wear rates for room temperature and 60 °C were 2.5x 10^{-10} and 8.8 x 10^{-9} mm^3/Nm respectively.

On the other hand, wear rates of balls sliding against CrN coatings increased slightly by the decreasing load (Fig 5). An increase of about an order of magnitude was observed by the increase of the temperature on the wear rate of steel balls sliding against CrN coatings (Figs 3 and 5).

The comparison of wear rates for balls sliding against hard chrome and CrN coatings showed that:
The wear rates of balls sliding against hard

chrome coatings under 30 N and 10 N loads were much higher than balls sliding against CrN under same conditions. Ball wear rates, sliding against CrN and hard chromium became closer to each other at 5 N load.

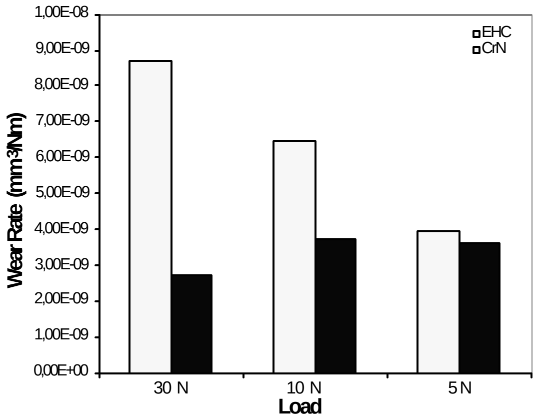


Figure 5. Wear rates of steel balls sliding against EHC and CrN coatings, for all loads at 60°C.

On profilometric examination of CrN coated discs, wear depths were not detected. However, on EHC coated discs wear depths were easily detected and recorded. In Figure 6, 3D and 2D profile images of the wear scar on EHC, which occurred under 30N load is given. The wear scar was not homogenous; hence the wear rate of EHC discs could not be calculated. The maximum wear depth was 3.5µm. The wear depth and width on EHC reduced with decreasing load and the maximum wear depth was 1.5µm at 10N load, 1 µm at 5N. The EDS analysis on the wear scar of balls against EHC showed more chrome transfer from coatings to steel balls than at room temperature experiments. This finding may confirm the adhesion of hard chromium to steel ball during sliding. With decreasing load, wear scars on the balls became smaller and the amount of chromium transfer reduced.

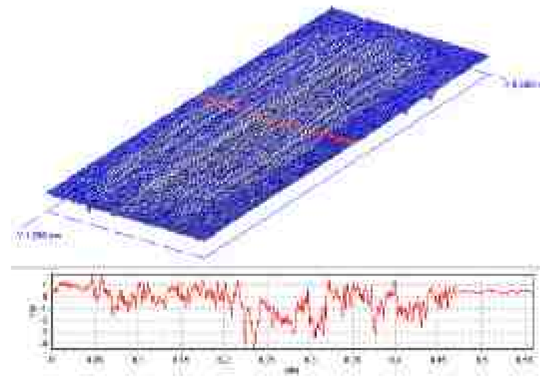
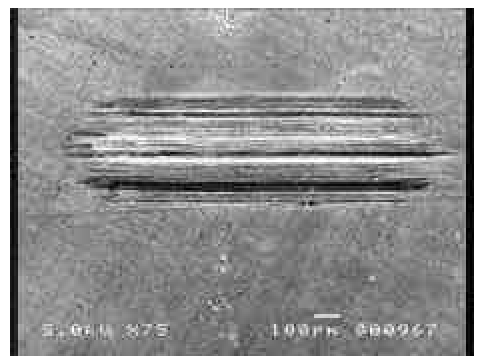
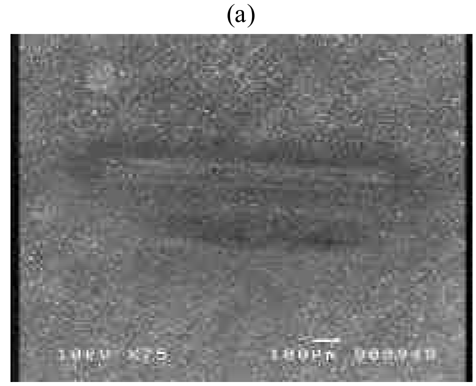


Figure 6. The 3D and 2D wear scar profiles on EHC coated disc, at 30N load and 60°C



(a)



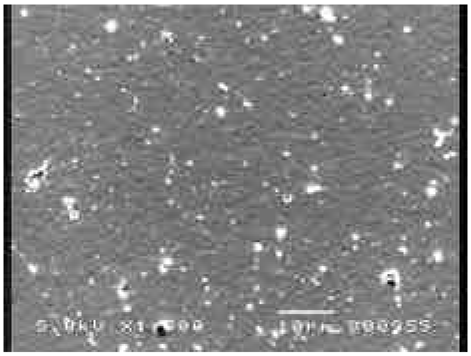
(b)

Figure 7. SEM images of wear scars occurred at 60°C and 30N. on (a) EHC and (b) CrN coating

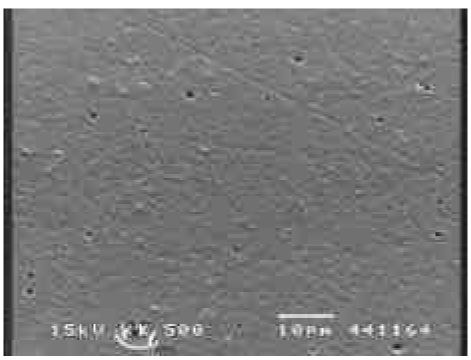
The SEM images of wear tracks on coatings formed at 60 °C under 30 N load are given in Figure 7. In this image the presence of deep grooves were observed on EHC coated discs. However, on CrN coatings only a slight darkening and removal of droplets were observed

3.3.3. Brushed CrN coating

The anomalous scratches observed on the outside of the contact area of the balls sliding against CrN coatings indicated the need for further investigation (Fig.4b). It was thought that droplets on CrN coating (Fig. 8a) could be the reason of these abrasive wear scratches behaving as free moving particles in the sliding interface.



(a)



(b)

Figure 8. SEM images of the coating surfaces (a) CrN, (b) brushed CrN.

To clarify this point of view, a CrN coated specimen was brushed to eliminate the droplets and to find out the effect of droplets on wear. The brushing process was similar to the industrial process applied to arc-PVD coatings; namely the surface of the coating was brushed with a rotating hard polymer bristled brush. As can be observed from Figures 8a and b, brushing removed most of the droplets.

In order to clarify the role of droplets on the wear process, brushed CrN coated discs are subjected to reciprocating sliding tests under 10N load and at room temperature.

The comparison of the friction behaviour of the brushed and original coatings revealed that brushing process by creating a smoother surface gave lower friction coefficient (Figure 9).

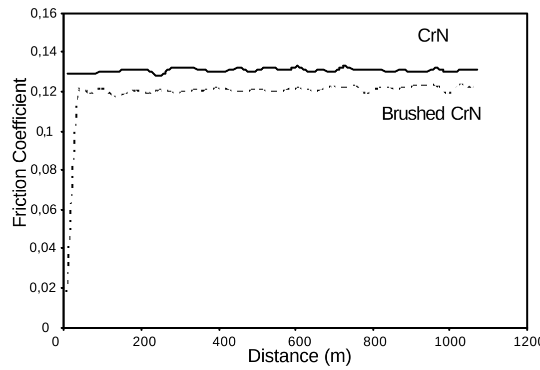


Figure 9. Friction coefficients of CrN and brushed CrN coatings vs. distance

(a)

(b)

Figure 10. Wear scars on steel balls sliding against, (a) original CrN, (b) brushed CrN at 10N load and room temperature.

The scratches observed outside the contact area of the balls sliding against CrN were not present on brushed CrN coatings (Figures 10 a and b). This indicated that droplets on CrN after detaching from the surface acted, outside the contact area, as abrasive particles during sliding.

4. Conclusions

The results of this investigation conducted under boundary or/and mixed lubrication reciprocating sliding conditions showed that:

CrN performed better than hard chrome plating under lubricated reciprocating wear conditions used in this study.

This effect became more pronounced by the increase of temperature and normal load.

Due to low wear rates profilometric wear depths on both EHC and PVD CrN coatings could not be determined after the tests conducted at room temperature.

However at 60°C, wear depths on EHC coating could be recorded by profilometer. Profilometric depth on CrN coated discs could not be detected.

The reciprocating sliding tests on brushed CrN coated discs clearly demonstrates the important role of droplets on CrN coating wear.

References

[1] Chen, A., Qui, X., Sridharan, K., Horne, W.g. Dodd, R.A., 1996, *Surf. and Coat. Technol*., 82, 305-310.

[2] Rebholz, C., Ziegele, H., Leyland, A., Matthews, A., 1999, *Surf. and Coat. Technol.,* 115, 222-229.

[3] ASM Handbook, Vol: 5, 1992, Hard Chromium Plating, ASM Int. USA

[4] Navinsek, B., Panjan, P., Milosev, I., 1999, *Surf. and Coat. Technol*., 116-119, 476-487.

[5] Pastegar, F., Richardson, D.E., 1997, *Surf. and Coat. Technol*., 90, 156-163.

[6] Walter, K.C., Scheuer, J.T., McIntyre, P.C., Kodali, P., Yu, N., Nastasi, M., 1996, *Surf. and Coat. Technol*., 85,1-6.

[7] Walter, K.C., Kern, K.T., Tesmer, J.R., Scarborough, W.K., Woodring, J.S., Nastasi, M., 1997, *Surf. and Coat. Technol*., 97, 250-253.

[8] Legg, K.O., Graham, M., Chang, P., Rastagar, F., Gonzales, A., Sartwell, B., 1996, *Surf. and Coat. Technol*., 81, 99-105.

[9] Brooman, E.W., July 2000, *Metal Finish*., 38-43.

[10] Weis, M., Manty, B., 1995, *Soc .of Vacuum Coaters*, 38.Annual Tech. Conf. Proce., 325-330.

[11] Alexander, R.B., July 1996, *Plating and Surf. Finish*., 9-11.

[12] Onate, J.I., Alonso, F., Garcia, A., 1998, *Thin Solid Films*, 317, 471-476.

[13] Legg, K.O., July 1996, *Plating and Surf. Finish*., 12-14.

[14] Engel, P. Schwarz, G., Wolf, G.K., 1999, *Surf. and Coat. Technol*., 112, 286-290.

[15] Engel, P., Schwarz, G, Wolf, G.K., 1998, *Surf. and Coat. Technol*., 98, 1002-1007.

[16] Komvopoulos, K., Suh, Nam P., Saka, N., 1986, *Wear*, 107, 107-132

[17] Gawne, D.T., Ma, U., 1989, *Wear*, 129, 123-142

[18] Grigorescu, I.C., Gonzalez,Y., Rodrigues ,O., De Vita, Y., 1995, *Surf. and Coat. Technol*., 76-77, 604-608

[19] Menthe, E., Rie, K.T., 1999, *Surf. and Coat. Technol* 112, 217-220.

[20] Martyak, N.M., McCaskie, J.E., 1995, *Jour.of Mater. Sci. Letters*, 14, 1329-1331.

[21] Arieta, F.G., Gawne, D.T., 1995, *Surf. and Coat. Technol.,* 73, 105-110

[22] Su, Y.L., Yao, S.H., Leu, Z.L., Wei, C.S., Wu, C.T., 1997, *Wear*, 213, 165-174

[23] Kubinski, J.A., CEF, Hurkmans, T., Trinkt, T.,Fleischer, W., Van der Kolk, G.J., October 1999, *Plating and Surface Finishing*, 20-25.

[24] Lee, S.C., Ho, W.Y., Lai, F:D., 1996, *Mater. Chem. and Phys*., 43, 266-273
[25] Broszeit, E., Friedrich, C., Berg, G., 1999, *Surf. and Coat. Technol*., 115, 9-16.
[26] Su, Y.L., Yao, S.H., 1997, *Wear*, 205, 112-119.
[27] Fu, Y., Zhu, X., Tang, B., Hu, X., He, J., Xu, K., Batchelor, A.W., 1998, *Wear*, 217, 159-166.
[28] Fu, Y., Loh, N.L., Batchelor, A.W., Zhu, X., Xu, K., He, J., 1999, *Mater. Sci. and Eng*., A265, 224-232.
[29] Navinsek, B., Panjan, P., Milosev, I., 1997, *Surf. and Coat. Technol*., 97, 182-191
[30] Friedrich, C., Berg, G., Broszeit, E., Rick, F., Holland, J., 1997, *Surf. and Coat. Technol*., 97, 661-668.
[31] Bhushan, B., and Gupta B. K., 1991, *Handbook of Tribology*, Mc Graw-Hill
[32] Hutchings, I. M., 1992, *Tribology*: Friction and Wear of Engineering Materials, Edward Arnold, London.