Tribology of Duplex Process of Plasma Nitriding Plus Hard Nanostructured Coating for Wear Resistance Applications in Tool Steels

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Abstract

Nowadays, the subject of recycling plastics (especially PET Polyethylene terephthalate, massively used for bottles) becomes an extremely important task from the environmental point of view. However, D2 steel blades commonly used in plastic cutting mills are not perfect regarding their mechanical and wear-resist properties, which causes significant expenses for frequent service / replacement of the tools. This paper is dedicated to tribology studies of WC–Co based coatings deposited on a plasma nitriding surface of D2 tool steel to increase its wear resistance properties. The performance of the coating was related to its microstructure, composition, mechanical and wear-resistance properties. The latter were studied using ball-on-disk experiments for coated samples of D2 and CPM10V steels in order to determine the behavior of the material in a real cutting process. The results obtained demonstrated that the suggested duplex process improved wear resistance of steels in several times, increasing working life of the tool at least in 500%.

Keywords: Wear, Friction Coefficient, Nitriding, WC-Co Coatings.

Introduction

Steel blades used in cutting mills should be manufactured from high-resistive materials to withstand heavy loads, impact, abrasive action, and thermal oscillations [1,2]. These properties can be achieved by applying protective coatings for the tool steels. Among these chromium-based coatings are widely used for textile machine components, tool inserts, sliding applications due to their high wear resistance, to wearing, corrosion and oxidation, as well pronounced hardness [3,4]. Tungsten carbide (WC) has been widely used for cutting tools, allowing to improve their performance and life-time. The most common problem with surface coatings is an insufficient adhesion to the substrate [5,6].

A duplex process consists in plasma nitriding and deposition of thermal spraying of WC-Co to create a protective layer on tool steels. It offers an attractive solution for improving wear resistance of material, if good film adhesion to the surface is achieved. It has been demonstrated [7] that nitriding can improve wear resistance of tool steels AISI D2 and H13 and enhance the working life of milling components. In the plasma nitriding process, a Nitrogen-Hydrogen gas mixture is converted into a plasma by glow discharge with the target piece (the one which should be nitriding) acting as a cathode. The sputtered iron reacts with the Nitrogen in gas phase by forming unstable FeN, which condenses on the surface and dissolves into stable iron nitrides Fe_3N and Fe_4N [8]. Besides, a layer of nitriding improves adhesion between the coating and the substrate of a tool steel [9].

The post-nitriding coating process can be performed by atmospheric plasma spraying (APS), which has several attractive features for producing wear-resistant components [10]. The powder material intended for APS deposition is introduced into a plasma jet with the temperature of about 10,000 K, where it melts and becomes propelled towards the substrate. The molten droplets flatten at the surface and quickly solidify into a coating layer [11].

We considered particularly important to investigate the advantages of hard protective WC-Co coatings obtained by plasma spraying on the substrates of two steels AISI D2 and CPM10V, the first one commonly-used. The properties of the coated material (coefficient of friction, hardness, lifetime and tool steels efficiency) were studied in detail.

Experimental Procedure

The compositions of substrate steels AISI D2 and CPM10V are given in Table I. The samples were cut in plates 25 x 25 x 4 mm in size. The substrate preparation included vacuum quenching and aging heat treatments in order to homogenize its hardness and microstructure. After the preliminary test to obtain reference data for comparison, the specimens were subjected to plasma nitriding process lasting for 60 hours in 50%N_2-50%H_2 atmosphere under 510°C. After the treatment, the samples were slowly cooled in nitrogen atmosphere. The coatings were deposited by plasma spray process (900 A and 40 V) for mixtures of WC-17Co powder provided by Sulzer Metco and 20 wt% of nano-crystalline WC powder with a particle size of 100 nm and purity of 99.95% provided by Inframat Advanced Materials. The mixing was performed with high energy SPEX mill without milling media for 30 minutes in order to obtain good initial chemical homogeneity of initial coating material. Cross-sections of coated steels were made by conventional metallographic techniques. The morphological details were studied with a GX-51 Olympus optical microscope and FEI Nova NanoSEM 200 scanning electron microscope operated at 20 kV. X-ray diffraction (XRD) analysis of the unmodified steel surface, nitrided steels and WC-Co coated samples was made with Philips PW3040/00 X'Pert MPD diffractometer with Cu K_α radiation(λ= 1.5406Å), operated at 40 kV and 25 A in the 2θ range of 10–100°. Cross section hardness was measured using a Clemex indenter with 300 gf load. For tribology study, CSM ball-on-disc (tungsten carbide, 6 mm in diameter) equipment was used. The surface of samples were polished before measurements. The friction test parameters are shown in Table II. The volume loss after the tests was calculated from scar dimensions measured with optical micrometer connected to the optical microscope. The obtained values of volume loss V were used to evaluate wear resistance of the materials according to the formula [12]:

$$V = (\pi * R * D^3)/(6 * r), \tag{1}$$

where: V is average volume of the material worn out due to friction, R is the friction radius, D is wear trace width and r is ball radius (all quantities measured in millimeters). Finally, the working life and investment costs were calculated based on a real cutting process. For the evaluation, 2 sets of tool steels (15 pieces each) were tested with the duplex process presented in this work.

Results and Discussion

Figure 1 shows the SEM microstructure and EDXS spectrum of the initial powder material that represents a mixture of large and small grains of irregular shape. The nanocrystalline WC is irregular with grain size under 100 nm. The composition of larger particles, as detected with EDXS analysis, is mainly WC-Co. Thus, the nanoparticles form agglomerates on the surface of the bigger grains.

Figure 2(a) shows the XRD patterns of AISI D2 and CPM10V substrates before and after nitriding. The AISI D2 steel displays its characteristics peaks at 43, 51, 75 and 90° of 2θ angle for the phases of (Fe,C). The CPM10V steel shows the peaks corresponding to the phases Fe and (Fe,C). Nitriding process creates a clearly identifiable layer on the surface of the samples with nitriding phases Fe_4N at angle 48° and Fe_3N at angles 38.4, 41.3, 44, 57.8, 63.3, 69.6, 77.1, 84.2 and 86.1°. Figure 2(b) shows X-ray diffraction patterns for the initial powder, mixed material and WC-Co spray-coating. The main peaks for WC-Co powder correspond to the phases WC, W_2C and Co_3W_3C. The mixture with nanocrystalline WC shows essentially the same peaks, with pronouncedly increased intensity of those responsible for WC. After the spraying over both types of substrates, the phases WC and W_2C forms the coatings, and the complex carbide component Co_3W_3C observable in the initial powder vanishes.

Figure 3 shows the SEM micrographs of as-sprayed WC-Co coating for CPM10V steel and its EDXS spectrum. In general, the coating is homogeneous, the particles melt well so that only low porosity is observed. Our studies revealed that the dark spots correspond to the WC nanocrystalline powder added to the mixture.

Figure 4 presents SEM micrographs for the profile sections of WC–Co coating on D2 and CPM10V steels (a and b, respectively), as well as more detailed view of the coating layer itself (Figure 4c). As one can see from the figure, WC–Co coating is more dense and compact for CPM10V steel, while the layer formed on D2 substrate features miniature pores and microcracks. These are most probably caused by thermal stress induced during plasma spraying process. Coating thickness was approximately 35 μm for both types of substrates. The average chemical compositions of different cross section areas are listed in Table III showing that coating primarily consists of W, C, and Co. The additional nanocrystalline WC can be observed as dark spots with grains less than 100 nm in size (Fig. 4c). The nitriding zone is not clearly seen in Fig 4a, but the chemical composition of zones 3-5 records nitrogen content of approximately 5 wt% (Table III). In this way one can estimate the penetration of nitriding zone into D2 steel being about 70 μm. For the case of CPM10V steel, the nitriding zone, some 40 μm thick is seen clearly due to the formation of steel precipitates at the interface (Fig. 4b).

The mechanical properties in cross sections were determined using hardness measurements for the both types of substrates. The hardness results are presented in Figure 5. In general, as far as hardness improvement is concerned, the duplex process of nitriding with WC-Co coating appears to be more beneficial for CPM10V than for D2 steel. The coating for the former has a hardness between 2700 and 3000 HV in comparison with 2400 to 2800 HV for the latter. The nitriding region in CPM10V steel has an average hardness of 1800 HV, in contrast to 1700 HV for D2 steel. The observed difference naturally is related to the microstructure of steel which is denser for CPM10V.

Friction test conducted for the surface of non-modified tool steels, samples with nitriding layer and tungsten carbide layer are illustrated in Figures 6 and 7. As one can see, the value of friction coefficient increases linearly with higher loads for all samples studied (Fig. 6). For a particular load the mean friction coefficient for D2 steel is higher than that for CPM10V steel. It is evident that the coefficient of friction for both coated steels is very similar due to same composition in coatings. It is important that duplex process of plasma nitriding with subsequent coating deposition results in lower friction coefficient in comparison with uncoated steels. Figure 7 shows the variation of wear rate calculated with Equation (1) using material volume loss estimations. Again, CPM10V nitriding with coating features the lowest wearing rates, whereas uncoated D2 steel is the most susceptible to wearing. This behavior could be related to the hardness properties discussed for Figure 5, taking into account that wear rate and hardness are inversely proportional. In general, our comparative studies revealed a pronounced improvement of CPM10V steel with tungsten carbide coating, which gained an excellent wear and mechanical properties.

Finally, the working life of tool steels was calculated to determine the performance of the materials in a real cutting process (Figure 8). For both types of steels, the nitriding process with subsequent coating increases the working life-time of the material by 500%, which definitely will reduce the financial losses due to production time off required for service / replacement of tools. The investment costs required for D2 Steel ($ per ton) are much higher due to the lower tool life expectance, while for CPM10V steel the investment costs are significantly reduced by 400% due to duplex process reported in this paper.

Conclusions

We performed successful formation of high-quality tungsten carbide coating with a very good adhesion to the surface of tool steel material. Such protective coatings are extremely important to improve tribological behavior of steel surfaces. Both friction coefficient and wear rate of the materials tested increased with increasing load; samples with higher hardness featured lower friction coefficient. The discussed duplex coating process allowed to achieve the most pronounced improvement to CPM10V steel, increasing its wear resistance in several times and extending working life at least in 500%.

Acknowledgments

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12. ASTM International, G99-05 Standard Test Method for Wear Testing with a Pin-on-Disk Apparatus.

Table I. Chemical compositions of steels substrates.

Tool steel	Chemical composition (Wt %)							
	C	Mn	Si	Cr	Ni	Mo	V	S
AISI D2	1.58	0.25	0.32	10.55	0.22	0.51	0.142	-
CPM10V	2.59	-	-	5.64	-	1.43	9.43	0.105

Table II. Tribology test parameters.

Friction test parameters	Selected value
Applied load (N)	1, 3 and 5
Velocity (ms^{-1})	0.125
Acquisition rate (hz)	2.0
Distance (m)	200.0
Environment	Air
Temperature (°C)	25 ± 2
Humidity (%)	35 ± 5
Duration (min)	26.6
Test ball diameter (mm)	6.0

Table III. Chemical compositions of different zones in cross section of coated steels.

Zones	Average chemical composition (Wt%)								
	C	Co	W	Cr	N	Mo	Fe	V	Mn
AISI D2									
1	2.75	9.63	87.62	-	-	-	-	-	-
2	6.86	12.98	80.16	-	-	-	-	-	-
3	8.39	-	0.83	7.53	5.27	0.72	77.26	-	-
4	4.73	-	0.95	9.38	5.69	-	79.25	-	-
5	5.60	-	1.43	7.60	4.07	-	81.30	-	-
CPM10V									
1	3.44	13.07	83.49	-	-	-	-	-	-
2	4.07	11.92	84.01	-	-	-	-	-	-
3	3.58	7.43	82.92	-	-	-	5.6	0.48	-
4	11.68	-	-	5.65	4.73	1.89	65.28	10.77	-
5	7.99	-	-	5.59	-	2.10	73.48	10.0	0.85
Coating									
1	7.40	9.12	83.47	-	-	-	-	-	-
2	5.21	8.05	87.46	-	-	-	-	-	-
3	6.33	8.72	84.95	-	-	-	-	-	-

List of figure captions

Figure 1. SEM microstructure and EDXS spectrum of initial powder material.

Figure 2. XRD diffraction patterns; (a) substrates before and after nitriding; (b) initial WC-Co material and sprayed coatings for D2 and CPM10V steels.

Figure 3. SEM micrographs of as-sprayed WC-Co coating on CPM10V steel with the corresponding EDXS spectrum.

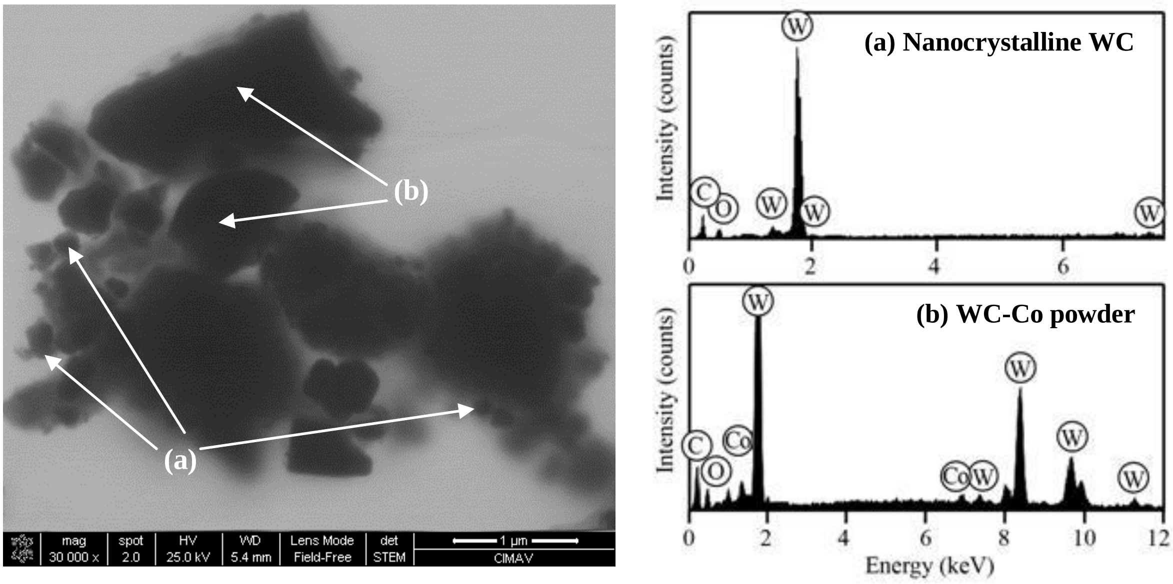
Figure 4. SEM micrographs; (a) cross-section of WC–Co coating on D2 steel; (b) cross-section of WC-Co coating on CPM10V steel; (c) cross section of WC–Co sprayed coating at higher magnification.

Figure 5. Hardness profiles of tested materials.

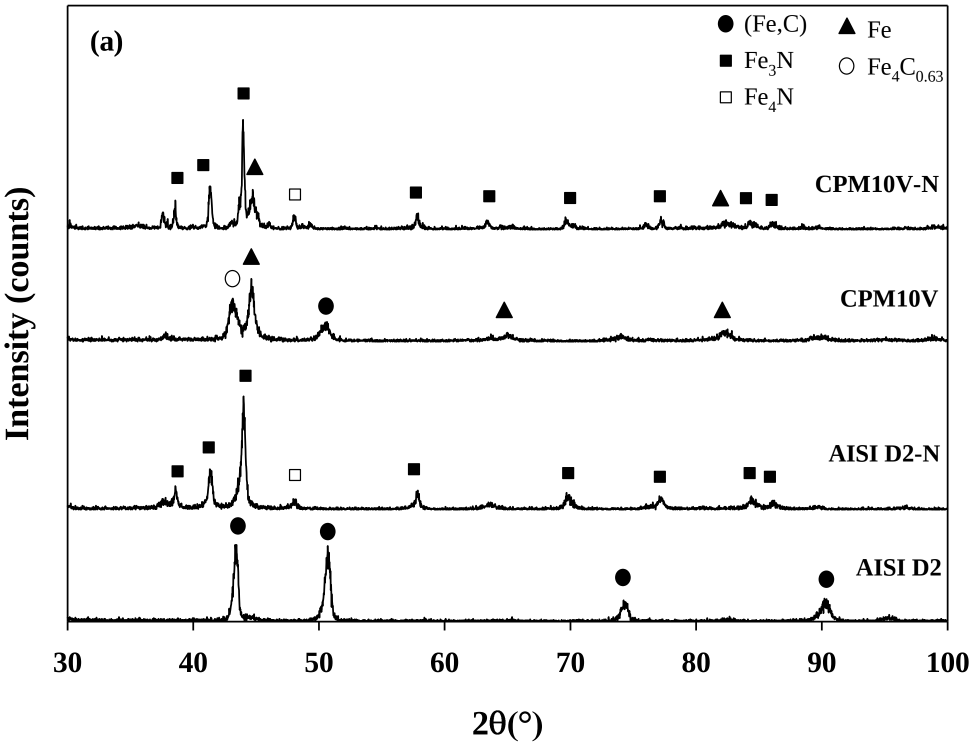
Figure 6. Friction test results for the surface of tool steels, nitriding layer and tungsten carbide layer on steels versus load.

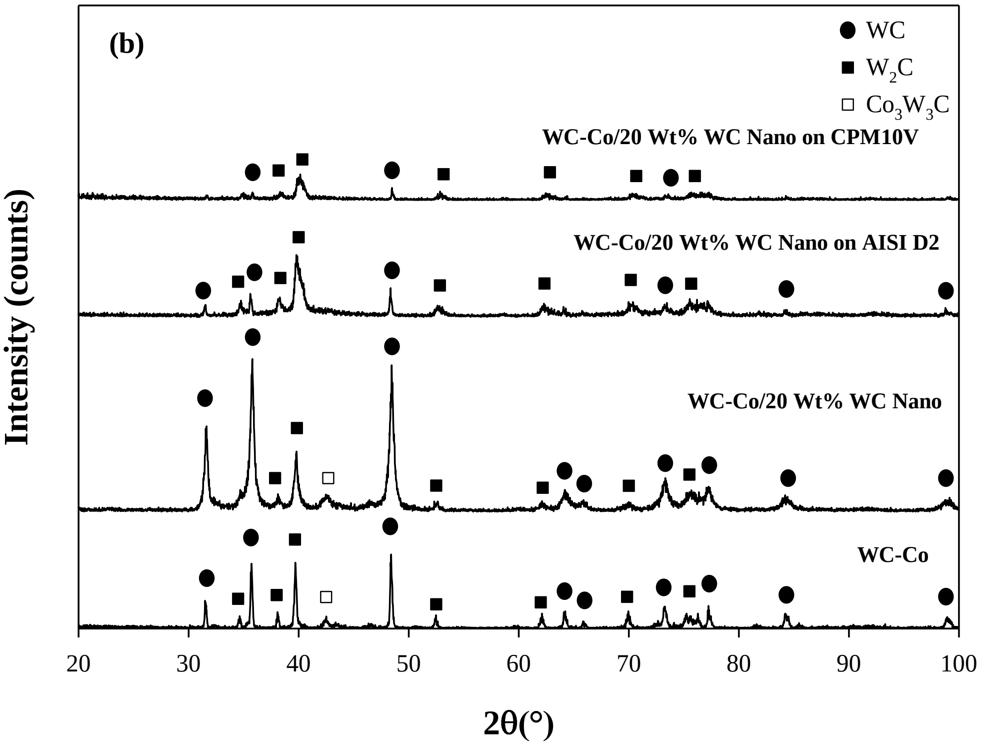
Figure 7. Volume of material removed due to friction for different loads.

Figure 8. Working life and investment costs calculated for the tested materials in real cutting process. HT: Heat Treated, N: Nitriding, and C: Coating.

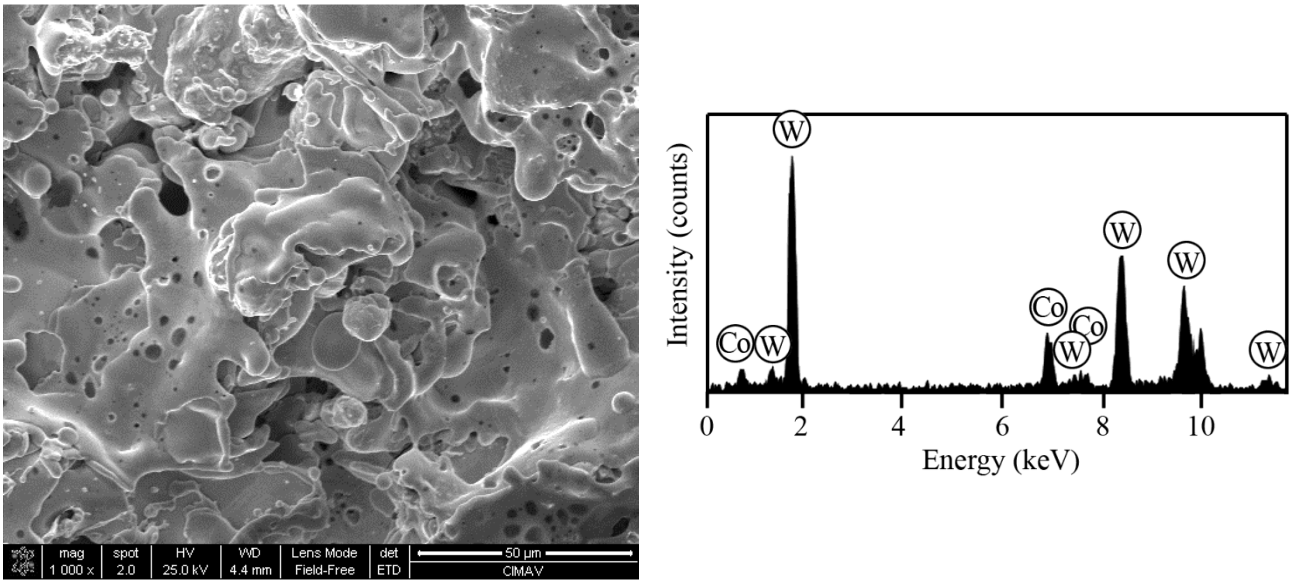

(b)
(a)
mag 30 000 x
spot 2.0
HV 25.0 kV
WD 5.4 mm
Lens Mode Field-Free
det STEM
1 µm
CIMAV
(a) Nanocrystalline WC
(b) WC-Co powder
Intensity (counts)
Energy (keV)
W
C
O
Co
0
2
4
6
8
10
12

2

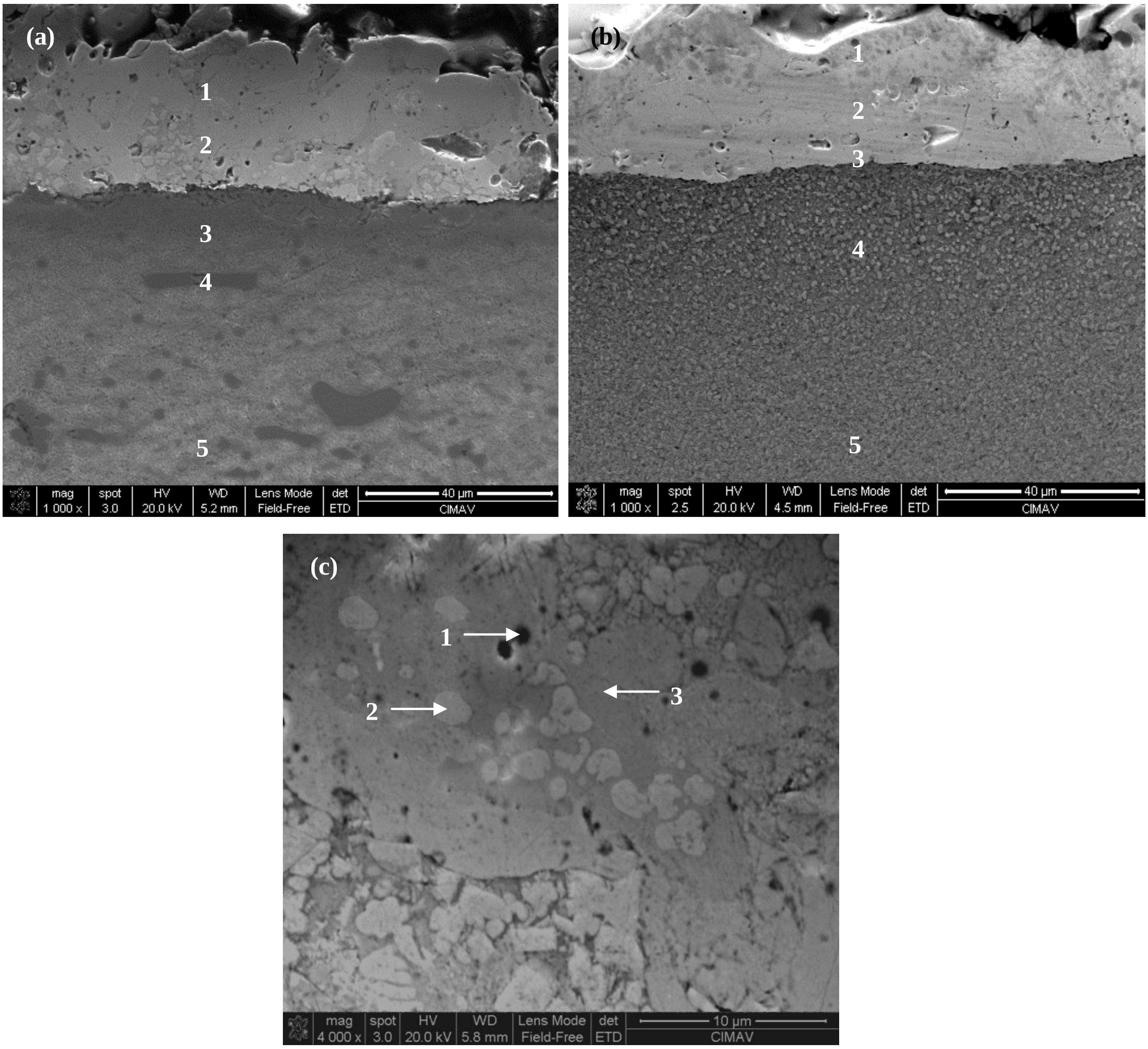

(a)
● (Fe,C)
■ Fe_3N
□ Fe_4N
▲ Fe
○ $Fe_4C_{0.63}$
CPM10V-N
CPM10V
AISI D2-N
AISI D2
Intensity (counts)
30
40
50
60
70
80
90
100
2θ(°)


(b)
● WC
■ W_2C
□ Co_3W_3C
WC-Co/20 Wt% WC Nano on CPM10V
WC-Co/20 Wt% WC Nano on AISI D2
WC-Co/20 Wt% WC Nano
WC-Co
Intensity (counts)
20
30
40
50
60
70
80
90
100
2θ(°)

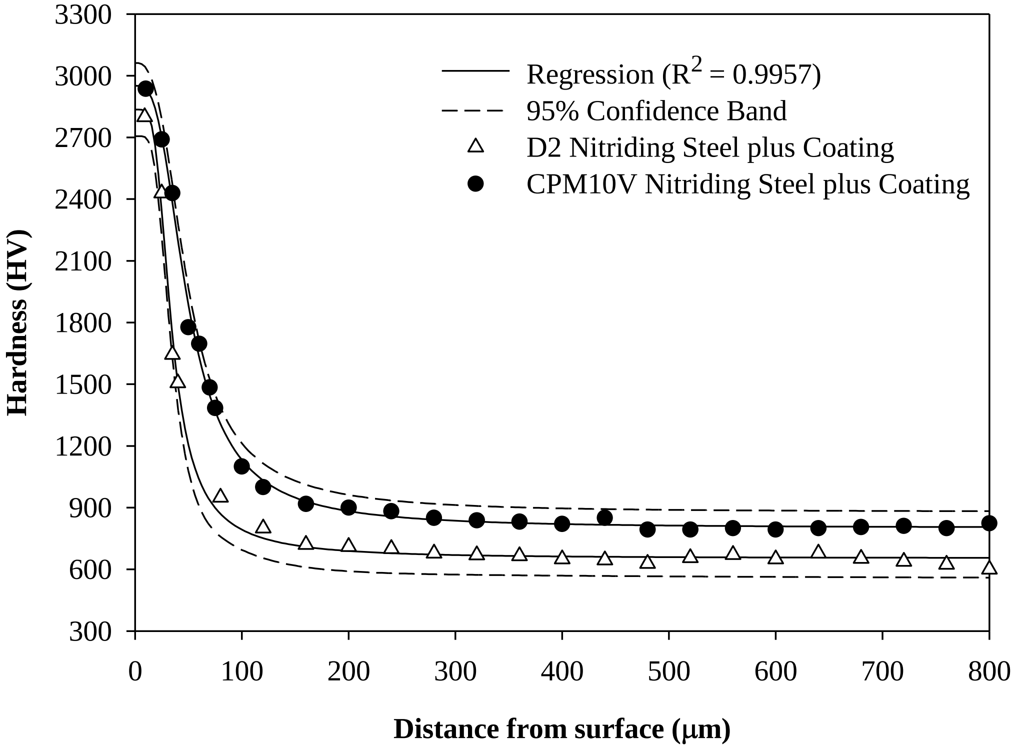
3


mag
1 000 x
spot
2.0
HV
25.0 kV
WD
4.4 mm
Lens Mode
Field-Free
det
ETD
50 µm
CIMAV
Intensity (counts)
Energy (keV)
0
2
4
6
8
10
Co
W
W
Co
Co
W
W
W
W

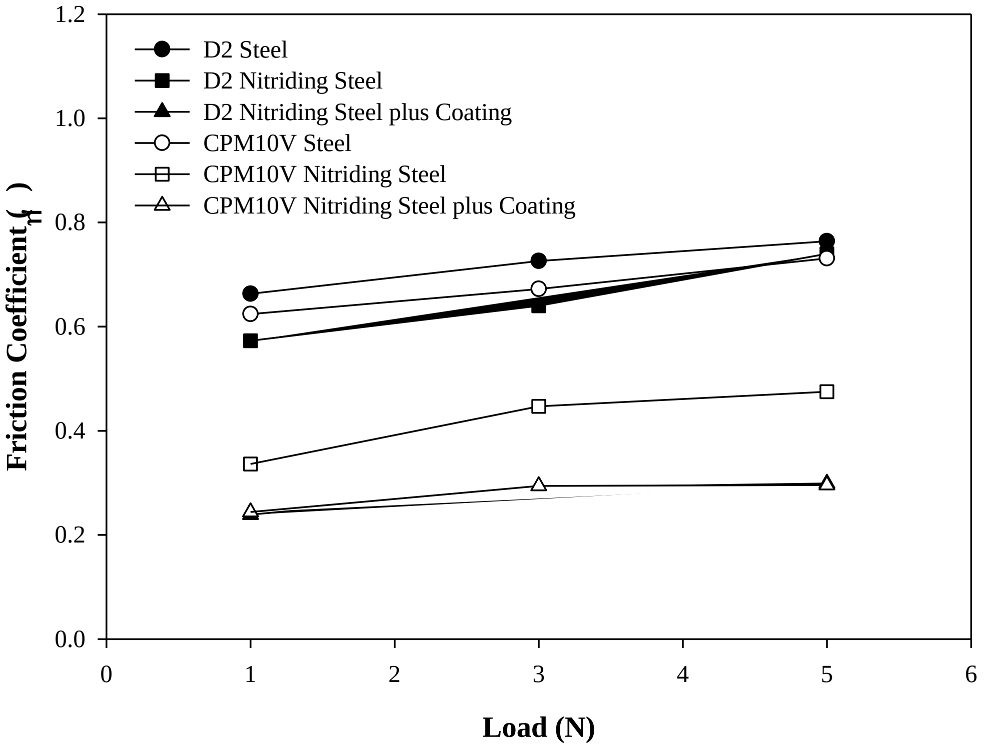
4


(a)
1
2
3
4
5
mag 1 000 x
spot 3.0
HV 20.0 kV
WD 5.2 mm
Lens Mode Field-Free
det ETD
40 µm
CIMAV
(b)
1
2
3
4
5
mag 1 000 x
spot 2.5
HV 20.0 kV
WD 4.5 mm
Lens Mode Field-Free
det ETD
40 µm
CIMAV
(c)
1
2
3
mag 4 000 x
spot 3.0
HV 20.0 kV
WD 5.8 mm
Lens Mode Field-Free
det ETD
10 µm
CIMAV

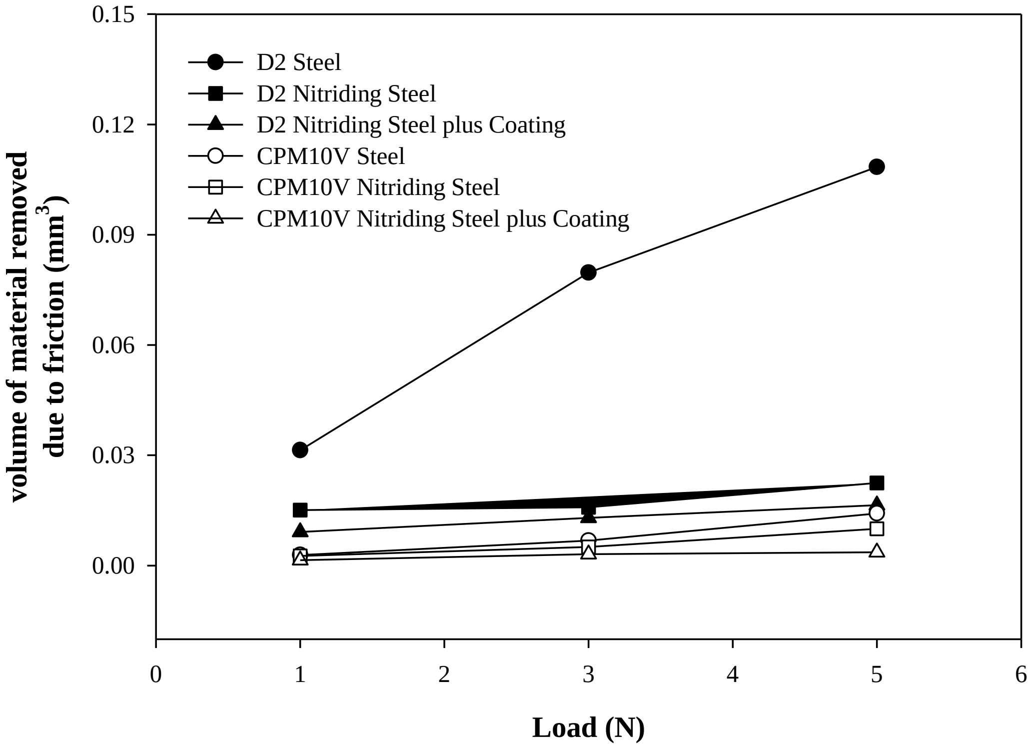
5


3300
3000
2700
2400
2100
1800
1500
1200
900
600
300
Hardness (HV)
0
100
200
300
400
500
600
700
800
Distance from surface (μm)
Regression (R^2 = 0.9957)
95% Confidence Band
D2 Nitriding Steel plus Coating
CPM10V Nitriding Steel plus Coating

6


D2 Steel
D2 Nitriding Steel
D2 Nitriding Steel plus Coating
CPM10V Steel
CPM10V Nitriding Steel
CPM10V Nitriding Steel plus Coating
Friction Coefficient (η)
Load (N)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
0
1
2
3
4
5
6

7


D2 Steel
D2 Nitriding Steel
D2 Nitriding Steel plus Coating
CPM10V Steel
CPM10V Nitriding Steel
CPM10V Nitriding Steel plus Coating
volume of material removed due to friction (mm^3)
0.15
0.12
0.09
0.06
0.03
0.00
0
1
2
3
4
5
6
Load (N)

8


Working Life
Investment Costs
Working Life (Days)
Investment Costs (USD/Ton)
0
20
40
60
80
100
120
0
5
10
15
20
25
30
35
40
D2 HT
D2 HT + N
D2 HT + N + C
CPM10V HT
CPM10V HT + N
CPM10V HT + N + C
Steel Condition