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Thermal Fatigue Resistance Studies of Multilayer CrN and AlTiN Coatings Deposited on Plasma Nitrided H-13 Hot Work Steel

Chetan Gurada ¹, Rajesh Mundotia ², Umesh Mhatre ², Ashwin Kale ² and Dushyant Kothari ^{1,*} ¹ Department of Physics, University of Mumbai, Santacruz (E), Mumbai 400 098, Maharashtra, India² Surface Modification Technologies Pvt. Ltd., Emerald Premises, Sativali Road, Vasai (East), Palghar 401 208, Maharashtra, India

* Correspondence: kothari@physics.mu.ac.in

Abstract: H-13 steel surface was duplex-treated using Plasma Nitriding (PN) and PVD coatings to solve the thermal fatigue problem faced in die-casting applications. Chromium-based multilayer CrN/Cr (m-CrN) coatings and multi-component aluminium–titanium-based AlTiN (m-AlTiN) coatings were deposited using a cathodic arc deposition technique after plasma nitriding the H-13 steel surface with different case-depths of 50 μm and 200 μm . The structural, tribological, corrosion, and mechanical properties of the duplex-treated samples were studied. The thermal fatigue (TF) test was conducted by heating the sample to 600 °C and rapidly cooling it to room temperature, simulating the die-casting process conditions. After multiple cycles, it was observed that the oxide layer thickness formed was lower on duplex-treated samples compared to that on the uncoated plasma nitride sample. In addition, the mechanical properties were improved with the increase in PN diffusion depth. The duplex-treated samples showed better mechanical and thermal fatigue properties compared to untreated and only coated samples. The sample with m-AlTiN deposited on plasma nitrided H-13 with 200 μm case depth displays better thermal fatigue properties compared to the other samples.

Keywords: duplex-treatment; corrosion; die-casting; hot work steel; plasma nitriding; PVD coatings; thermal fatigue; wear rate; hardness



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1. Introduction

High-pressure die casting (HPDC) process is prominently used for the mass production of high-precision castings of plastic, rubber, and light alloy components with acceptable quality at competitive prices [1]. The high pressure or velocity of the molten casting material injected within the cavity affects the die surface because of erosion, corrosion, soldering, and sticking [2,3]. In the die-casting process, dies undergo thermal cyclic loads from 70 °C to 600 °C. The rapid cooling process after injecting the molten material causes thermal stress and dimensional variation, reducing die life [4]. Therefore, the die surface needs to be protected from deterioration to maintain consistent product quality for a longer duration.

Various surface treatments, such as lubricants, surface nitriding, shot pinning, electroplating, PVD coating, etc., have been introduced [4–9] to protect the die surface from high-temperature wear, corrosion, oxidation, and soldering. One such technique is the plasma nitriding process which forms the nitrides with the surface elements, such as Cr, V, Mo, etc., resulting in improved mechanical properties. Metallurgy of the material to be plasma nitrided is crucial for its effectiveness. Therefore, few materials can be plasma nitrided. One such material is H-13 grade hot work tool steel which is the most suitable metallurgy for such applications [10]. The plasma nitriding process on H-13 steel before coating (i.e., duplex treatment) further improves wear resistance with a lower friction coefficient [11]. Duplex treatment shows improved adhesion between coating and substrate [12] increased load-bearing capability, and high-temperature stability [13].

Various studies have been carried out on duplex-treated samples for Al die-casting applications [1,8,14–18]. Batista et al. [16] studied duplex and non-duplex TiAlN and CrN PVD coatings. However, there is still a need to understand vital properties, such as structure, oxidation, wear resistance, and adhesion of the coating after thermal fatigue. Various types of multilayer and nano-layered PVD coatings are well-known to protect the casting dies from erosion, corrosion, soldering, and sticking [8,14,19–21]. In addition, it is known that the oxidation temperature of multilayer coating is higher compared to that of single-layer coatings [22]. Therefore, we have focused our study on multilayer coating solutions.

AlTiN/TiN multilayer coatings support longer tool life with lower residual stress, wear resistance, and mechanical performance depending on the Al/(Al + Ti) ratio, and multi-layered structure. These coatings are useful in an erosive–corrosive environment and have higher plasticity and improved impact fatigue [23]. Multilayer Cr/CrN coatings show a mixture of CrN, Cr₂N, and Cr phases. High-temperature annealing further decomposes the CrN phase into Cr, and moderate formation of Cr₂O₃ was observed by Polcar et al. [24]. Formation of intermetallic compounds and soldering layer of Al cast alloy has been observed in die casting application; however, the Cr/CrN multilayer shows a low friction coefficient and lower amount of intermetallic compound formation [25].

From various studies [22,26–30], it was observed that the CrN coating oxidizes around 700 °C, whereas AlTiN (ternary metal nitrides) coating oxidizes around 900 °C. The incorporation of Al in the TiN coating structure improves the oxidation and wear resistance properties of the coating at high temperatures. The formation of a hard Al₂O₃ layer at the surface inhibits further diffusion of oxygen within the coating and improves wear resistance [31–34]. For hard coating, such as TiAlN, the hardness value of coating was found to increase from 18.9 GPa to 23.9 GPa with Al content increasing from 51% to 66.7% respectively [35], whereas multilayer coatings of Cr/CrN showed hardness of 29 GPa [36], TiN/AlTiN 31.5 GPa [35], and 39 GPa [37].

Jose Mario Paiva et al. [7] and Aneta Wilczek et al. [38] studied high-temperature tribological and wear properties of nano-composite and nano-multilayer coatings, respectively, for die-casting molds, core pins, and blocks. In both studies, the effect of thermal cycles on coating properties was not carried out. Therefore, we have undertaken the present study to understand coating properties after thermal fatigue which is the most prominent cause of die failure.

The objective of the present work was to determine how the duplex-treated H-13 performs against the thermal fatigue conditions compared to the untreated H-13 and only PVD-coated H-13. To understand the effects of plasma nitriding together with multilayer coatings (duplex-treatment), chromium-based multilayer coating (m-CrN) and multi-component aluminium–titanium-based coating (m-AlTiN) were deposited on hardened H-13 substrate. The coating structure, surface morphology, micro-hardness, and corrosion properties of the sample were studied. A thermal fatigue test was carried out on untreated, only coated, and duplex-treated samples. These samples were further analyzed to obtain structural variations, oxidation, wear rate, and adhesion properties. The results obtained are expected to indicate the failure of the samples undergoing thermal fatigue and the performance of the considered duplex treatments for die-casting applications.

2. Materials and Methods

2.1. Plasma Nitrided H-13 Substrate Preparation

H-13 samples (Size: 25 mm dia. × 8 mm thick) were hardened to 53–54 HRC by the vacuum hardening method. These samples were ground and polished to a surface roughness of $R_a = 0.015 \pm 0.002 \mu\text{m}$. Further, samples were plasma nitride with intended 50- and 200-micron case depth. After plasma nitriding, an increase in the surface roughness of the samples was observed (near $R_a = 0.10 \mu\text{m}$). As reported in the literature, after plasma nitriding treatment, the top nitriding compound layer formed is loose which is responsible for spalling during scratch [39]. Post-polishing after nitriding was carried out by various

authors [8], which reduces roughness as well as improves adhesion between the coating and the substrate [40]. Therefore, we also followed the same procedure and polished the samples after plasma nitriding to obtain a roughness value of $0.04 \pm 0.005 \mu\text{m}$. The case depth measurements of plasma nitride samples were calculated by etching the cross section using marble's reagent and then observed under an optical microscope at $100\times$ mag (Figure 1). The case depths measured were $55 \pm 5 \mu\text{m}$ and $195 \pm 5 \mu\text{m}$ for hardened PN50 and PN 200 H-13 samples, respectively. As can be seen in Figure 1, the nitrogen diffusion layer is visible under optical microscope images (at $100\times$ mag). After PN treatment, the hardness of the H-13 hardened sample increased from 589 HV (54 HRC) to 1130 HV0.02 for H-13_PN50 samples and 1140 HV0.02 for H-13_PN200 samples.

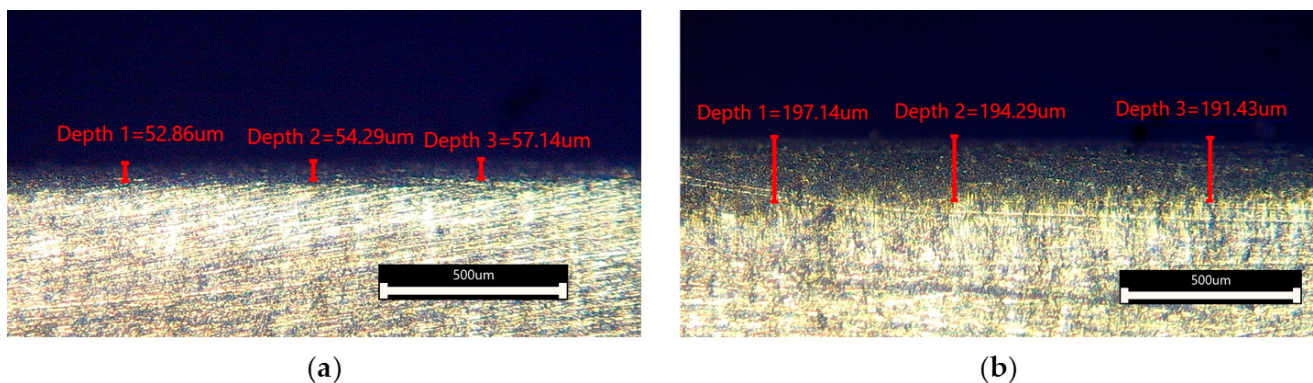


Figure 1. Optical images of an etched cross section of the plasma nitrided H-13 samples were taken for case depth measurement of: (a) H-13_PN50; (b) H-13_PN200.

2.2. PVD Coating Process Details

A duplex system of plasma nitrided H-13 steel with multilayered Cr/CrN (m-CrN) and AlTiN/TiN (m-AlTiN) coatings was developed. The substrates were ultrasonically cleaned in an alkaline solution and degreased in a water-based soap solution followed by DI water rinsing. Oven drying was performed at 80°C temperature for 30 min. These substrates were placed in a vacuum chamber for depositing two types of multilayer coatings, namely Cr/CrN (of 14 bilayers) (m-CrN) and AlTiN/TiN (of 360 bilayers) (m-AlTiN). The details of the coating process are given in reference [41]. After achieving a base vacuum of $8.0 \times 10^{-3} \text{ Pa}$, the samples were etched (i.e., in situ cleaning) with Cr ions (60 A current) for m-CrN coating and with Ti ions (60 A current) for m-AlTiN coating by applying a high bias voltage of (-900 V) between the substrate and the chamber. This process was carried out in ultra-high pure argon (99.95%) atmosphere. A base layer of Cr was deposited to improve the adhesion of CrN with the substrate for duplex m-CrN coatings; similarly, a base layer of TiN was deposited before the deposition of m-AlTiN coatings.

For m-CrN coating deposition, ultra-high pure N_2 gas was used to form the chromium nitride phase deposited for 4 min. By switching Ar and N_2 gas, CrN/Cr multi-layered (14/14) coating was deposited. The final layer of the CrN coating was deposited thicker (20 min) to block the pin holes. During the deposition process, the bias voltage was kept in the range of -100 V to -120 V at a chamber pressure of 1.3 Pa and temperature of 350°C .

For m-AlTiN coating deposition, AlTi (67:33%) composition cathodes (at 70 A current) and Ti targets (at 60 A current) were simultaneously used in ultra-high pure N_2 gas for 2 h. to deposit AlTiN/TiN nano-layered coating at a carousel rotation speed of 3 rpm. Various authors have used a similar method to deposit multilayer structures [41,42]. The final layer of the AlTiN coating was deposited thicker (20 min) to block the pin holes. During the deposition process, the bias voltage was kept in the range of -100 V to -150 V at a chamber pressure of 3.0 Pa and temperature of 450°C .

Table 1 shows the details of samples prepared to study their performance under cyclic thermal fatigue conditions generated during die-casting applications. Hardened H-13 hot work steel is plasma nitrided for 2 different case depths of $50 \mu\text{m}$ and $200 \mu\text{m}$; some of those

nitrided samples are then coated with 2 types of multilayers namely, Cr/CrN (m-CrN) and TiN/AlTiN (m-AlTiN). The names given for various samples will be used hereafter. The coating thickness and roughness values of the respective samples are also presented in Table 1.

Table 1. Details of the plasma nitrided H-13 samples with and without m-CrN and m-AlTiN coatings.

Sr. No	Sample Description	Sample Name	Coating Thickness (μm)	Average Roughness (μm)
1	Hardened + PN (50 μm)	H-13_PN50	NA	0.035 ± 0.005
2	Hardened + PN (200 μm)	H-13_PN200	NA	0.040 ± 0.005
3	Hardened + PN (50 μm) + m-CrN	m-CrN_PN50	2.75	0.10 ± 0.01
4	Hardened + PN (200 μm) + m-CrN	m-CrN_PN200	2.75	0.14 ± 0.01
5	Hardened + PN (50 μm) + (TiN/AlTiN)	m-AlTiN_PN50	3.20	0.17 ± 0.01
6	Hardened + PN(200 μm) + (TiN/AlTiN)	m-AlTiN_PN200	3.20	0.19 ± 0.01

PN: plasma nitriding; m-CrN; multilayer Cr/CrN; m-AlTiN: multilayer TiN/AlTiN; NA: not applicable.

The hardened H-13 samples show a roughness of $0.015 \pm 0.005 \mu\text{m}$ measured using a surface profilometer (Mitutoyo SJ-210 model). After PN treatment, samples were again polished to obtain a roughness value of $0.04 \pm 0.005 \mu\text{m}$. However, duplex treatment further increases the roughness to 0.100 and 0.141 μm for m-CrN_PN50 and m-CrN_PN200 coatings respectively and that of 0.169 μm and 0.193 μm for m-AlTiN_PN50 and m-AlTiN_PN200 coating respectively. The coating thickness of the samples was determined by the ball crater method as per ISO 26,424 standard. The measured thickness for m-CrN was $2.75 \pm 0.1 \mu\text{m}$ and that of m-AlTiN was $3.20 \pm 0.1 \mu\text{m}$ (Table 1).

The duplex treatment further increases the roughness for both types of coatings, and it shows nitriding case dependence. As the case depth increases, the roughness of the sample surface is found to increase.

2.3. Characterisation Details

The surface morphology of the samples was observed using a scanning electron microscope. The composition of the coated samples was measured by energy-dispersive X-ray spectroscopy (EDS). Surface roughness measurements of the prepared samples were carried out using a high-precision surface profilometer (Mitutoyo SJ-210 model) having the least count of 0.005 μm . The samples were cleaned using ethanol and then tested at five different random locations to obtain the average roughness value (Table 1).

The thickness and wear rate of the m-CrN and m-AlTiN coatings were measured using Calo-Wear SMT CT-01 instrument. A total of 5 craters with different sliding distances were created on each sample for 240 s, 180 s, 120 s, 60 s, and 30 s durations. Abrasive diamond particles suspended in distilled water (20 wt.%) were fed at the interface. After the micro-abrasion test, the crater sizes were measured under an optical microscope at $50\times$ mag. Wear rate measurements were calculated using the Rutherford model [43] using the measured crater sizes. The estimated error in the wear measurement was below 10%.

Micro-hardness measurements were carried out using a Fischerscope HM-2000 instrument using the loading and unloading curve method at a rate of 20 mN/20 sec. Measurements were calculated based on the Oliver and Pharr method [44,45]. Multiple indentations were made at different locations for each sample to obtain the average hardness value. The penetration depth of the indenter was kept well below the 10% value of the coating thickness [46].

Corrosion properties of the samples were tested using Digi-Ivy DY2300 series potentiostat with a three-electrode cell consisting of graphite (counter electrode), a saturated calomel reference electrode (SCE), and a test sample as the working electrode. The samples were tested using 1.0 M HCl electrolyte solution prepared in double distilled water at ambient temperature. The potentiostat was used in linear sweep voltammetry (LSV) mode

and varied from -0.7 to 0 V in steps of 5 mV/s. E_{corr} and I_{corr} values were measured using a Tafel plot to calculate the corrosion rate in mm/yr. using the Faraday law [47].

A thermal fatigue test (TF) was carried out on the uncoated and duplex-treated samples. Samples were placed in a preheated furnace at 850°C for 73 s resulting in a surface temperature of 600°C and then dipped in the water at room temperature for 20 s. This procedure of thermal fatigue test was adopted to simulate the die-casting process [10,41]. These cycles were repeated 100 , 300 , and 500 times (named TF100, TF300, and TF500 samples, respectively). After the TF test, samples were inspected for thermal cracks or coating chip-off on the surface under an optical microscope. The samples were further characterized for structural changes using XRD, oxide layer formation using the Calo test [30], and a scratch adhesion test to assess the durability of these duplex-treated samples [41].

XRD analysis: The phase analysis was conducted with the SmartLab (Rigaku) X-ray diffractometer with a $\text{Cu K}\alpha$ source (1.54 Å). The scan range was 20 – 80 degrees with a scan rate of $5^{\circ}/\text{min}$.

Scratch adhesion tests were carried out using DUCOM Scratch Tester TR-101 on the coated samples. A progressive load was applied to start from 20 N to 80 N at a speed of 0.28 mm/s. The total scratch length was fixed to 10 mm. Critical failure loads (the failure onset) of the coating adhesion were identified by an abrupt rise in frictional force data and further verified by optical microscope imaging [41].

3. Results

3.1. Surface Morphology and EDS Analysis

Figure 2 shows the SEM images of coated samples and their EDS analyses carried out in the marked area for elemental composition. Surface defects, such as droplets and pinholes, were less visible in the case of m-CrN coating (Figure 2a) compared to m-AlTiN coating (Figure 2c). Therefore, the surface roughness of m-CrN_PN50 is low compared to m-AlTiN_PN50 samples (Table 1). Fewer surface defects in coating structure result in better corrosion and wear resistance properties [48]. In the case of the m-AlTiN_PN50 sample, the Al:Ti composition ratio was found to be $57:43$ (Figure 2d), whereas the target (cathode) composition was $67:33$. Higher Ti content in the m-AlTiN_PN50 sample compared to the target composition is due to the presence of the TiN layer in the multilayer structure which results in overall higher Ti composition in the structure.

A similar study was also conducted by Ebrahimzadeh et.al [49] on the duplex-treated H-13 sample with 3.0 μm thickness of TiN/TiAlN coating deposited at 0.1 Pa nitrogen pressure. They reported very high surface defects, such as droplets and pinholes, which result in a higher roughness value of 0.330 μm . It is known that surface defects become reduced with the increase in nitrogen pressure during AlTiN deposition [50]. Therefore, in the m-AlTiN coating process, nitrogen was deliberately kept higher at 3 Pa to reduce surface defects.

The surface morphology of the sample shows surface defects, such as droplets and pinholes, which cause higher surface roughness. These defects were reduced by increasing the nitrogen pressure during the m-AlTiN coating process. Higher Ti composition compared to the target composition was detected for the m-AlTiN_PN50 sample which is due to the internal TiN/AlTiN multilayer structure of the coating.

3.2. Thickness

The coating thickness measurement of individual layer thicknesses was calculated using the Calo-test instrument. Figure 3 shows the optical images of wear craters created by the Calo test. The results of the measurement are presented schematically in Figure 4 for more clarity. In the case of m-CrN coating (Figure 3a,b), the adhesive Cr layer, CrN/Cr multilayer ($14/14$ layer), and the final layer of CrN were visible under an optical microscope. The measured thickness of a CrN/Cr bilayer coating is presented in the schematic diagram (Figure 4a). The thickness of each CrN/Cr bilayer was 0.140 μm .

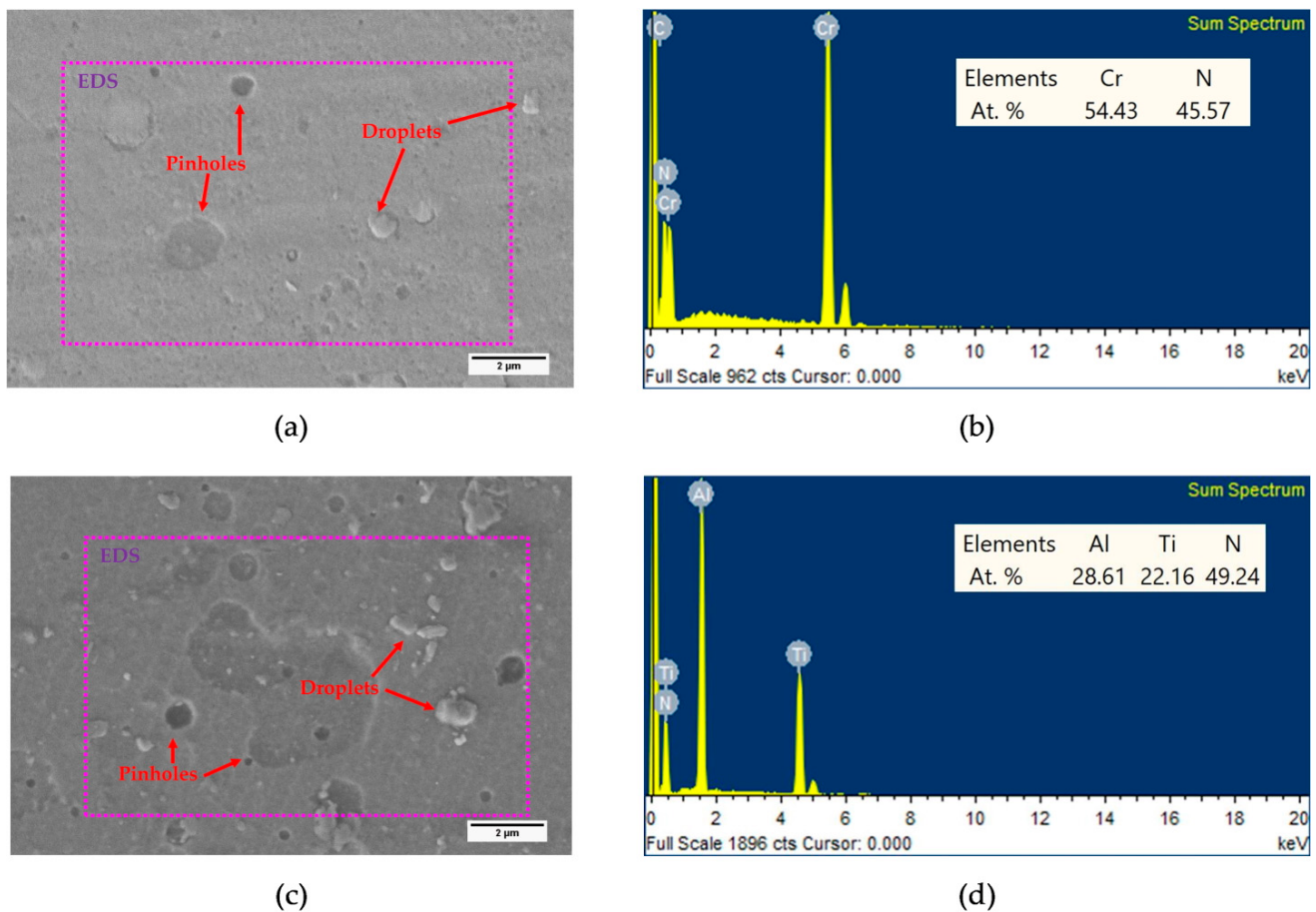


Figure 2. SEM images and EDS analyses of duplex-treated H-13 samples: m-CrN_PN50 (a,b); m-AlTiN_PN50 (c,d).

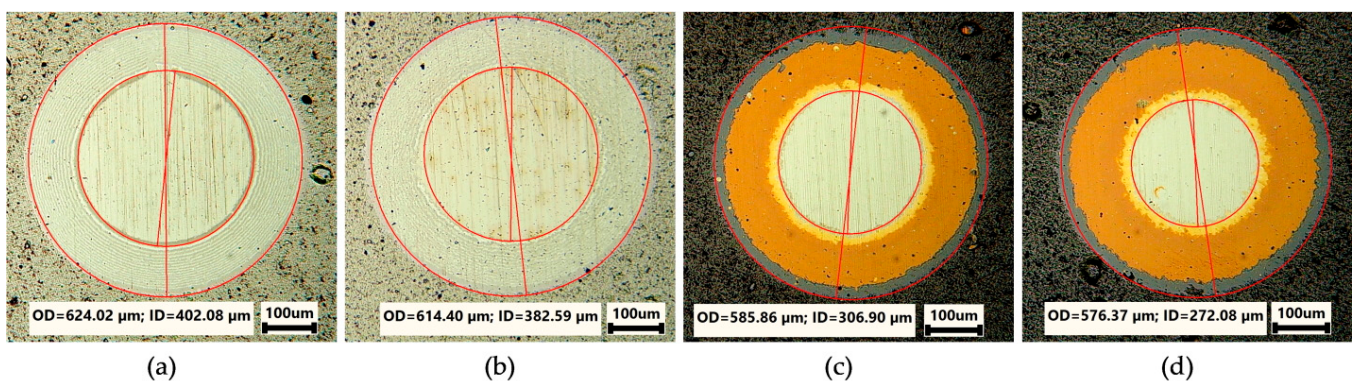


Figure 3. Optical images (taken at $50\times$ mag.) of wear craters for various samples. The crater formation time was kept at 240 s: (a) m-CrN_PN50; (b) m-CrN_PN200; (c) m-AlTiN_PN50; (d) m-AlTiN_PN200.

In the case of m-AlTiN coating (Figure 3c,d), the TiN adhesive layer, AlTiN/TiN multi-layer, and the final layer of AlTiN were visible under an optical microscope. However, the thickness of the individual AlTiN/TiN bilayer was not visible under an optical microscope. It can be estimated by the deposition time, total thickness, and the number of rotations/min of the sample during the coating process [42]. With each rotation of the sample in the chamber, a layer of AlTiN and TiN is deposited (one bilayer). The total number of rotations at 3 rpm for 120 min is 360 bilayers of AlTiN/TiN. Therefore, the estimated bilayer layer thickness is approx. ~ 5.5 nm (Figure 4b). Optical images of the craters with m-CrN coating

(Figure 4c) and m-ALTiN coating (Figure 4d) were taken at high (500 $\times$) magnification to see the multilayer structures.

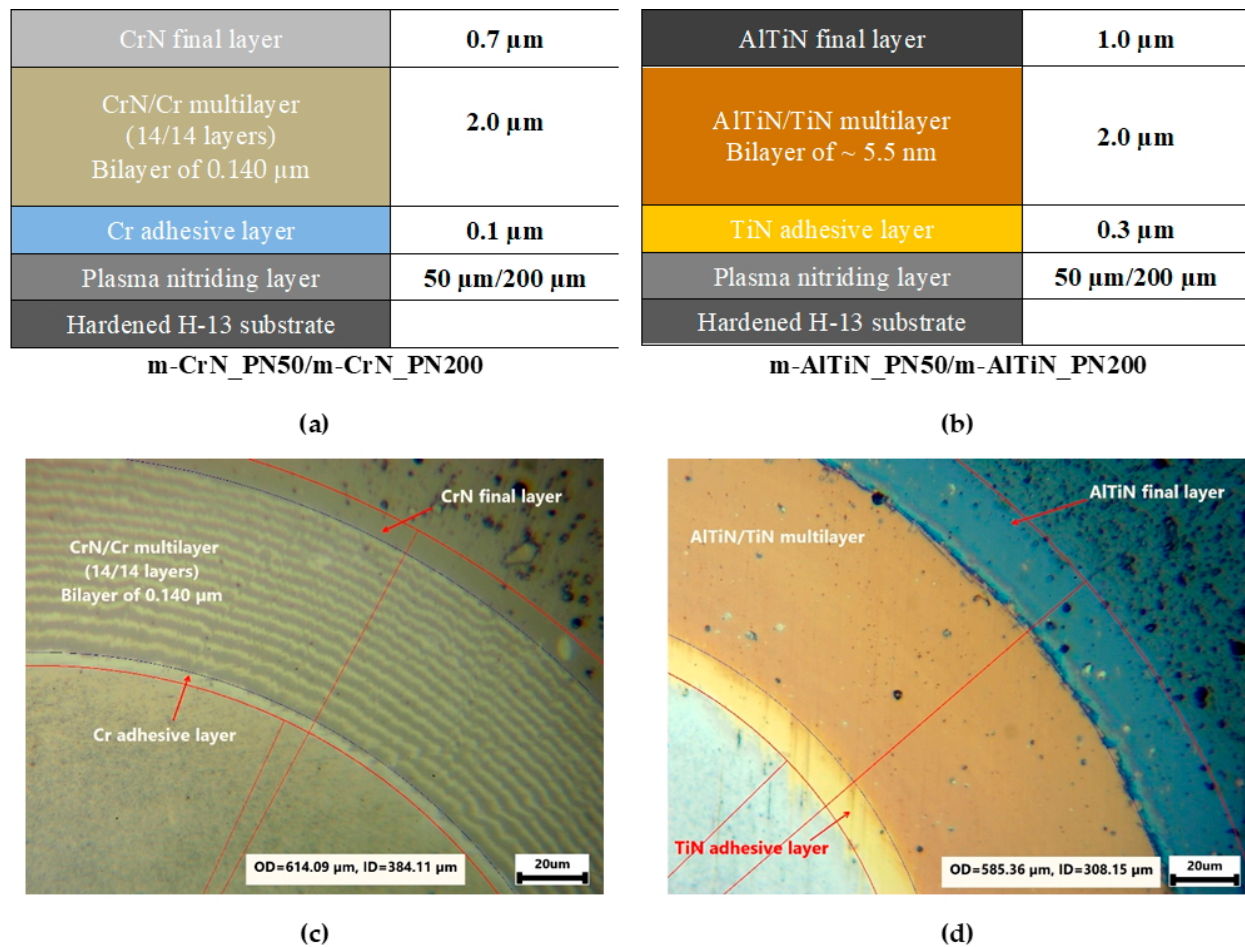


Figure 4. Schematic representation and optical crater images (taken at 500 $\times$ mag.) of various duplex-treated samples with m-CrN coating (a,c) and m-ALTiN coating (b,d) structures, respectively.

3.3. Wear

Wear rate measurements of the samples were calculated on the prepared samples using a micro-abrasion test [43]. Figure 3 contains the optical images of the crater taken for 240 sec. It was observed that the crater size (diameters) was in order: m-CrN_PN50 > m-CrN_PN200 > m-ALTiN_PN50 > m-ALTiN_PN200. Similarly, five craters were made for each sample. Higher crater size implies a higher wear rate [43] (Figure 5).

It was observed that the wear rate of the m-CrN_PN50 sample (Figure 3a) was higher compared to the m-CrN_PN200 sample (Figure 3b). It implies that the wear rate of the sample decreases with the increase in the plasma nitriding depth. Similar results were observed for the m-ALTiN coating for different PN samples (Figure 3c,d). In addition, the wear rate of the m-CrN coating was higher compared to m-ALTiN coated samples. It is due to the lower bilayer structure of the m-ALTiN coating which reduces the wear rate (Figure 4b). The wear properties of the coating improve with the decrease in the bilayer layer thickness of the multilayer system [51–54]. From the results, it is visible that the wear rate can be reduced by treating the H-13 substrate with the combination of thicker plasma nitriding and better coating structure (duplex treatment).

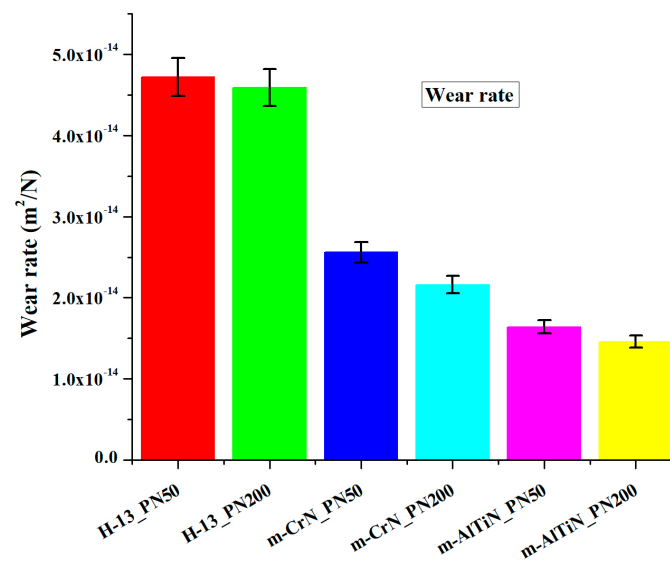


Figure 5. Wear rate values of with and without duplex-treated H-13 samples.

Wear rates of coating systems with plasma nitrided substrates were lower than that of non-nitrided (Figure 5). Similar results were observed by W. Tillmann et al. [15] in a wear study of their Ti/TiAlN multilayer structure with plasma nitrided H-13 samples. It can be correlated with the high hardness of plasma nitrided substrates resulting in lower plastic deformation as compared to without plasma nitride samples. Our samples with different coatings had similar hardness values (Figure 6). However, m-AlTiN coating displays better wear resistance compared to m-CrN coating. Therefore, the wear rate is dependent upon the coating structure [51–54].

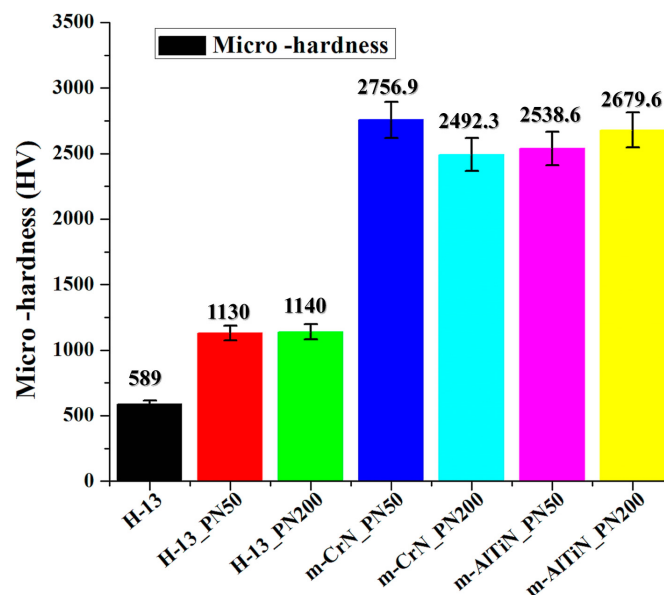


Figure 6. Microhardness values and indenter penetration depth for with and without duplex-treated H-13 samples.

For both the coatings, the wear rate of the samples with less PN depth is higher compared to higher PN depth (Figure 5). In addition, the m-AlTiN exhibits better wear resistance compared to the m-CrN coating. It can be attributed to lower bilayer thickness in the m-AlTiN coating structure (Figure 4).

3.4. Microhardness

Microhardness measurements were carried out at multiple locations for each sample based on the loading and unloading curve (Figure S1) [44,45]. The average micro-hardness values of with and without duplex-treated samples are presented in Figure 6. In addition, the penetration depth of the indenter is well under the 10% value of the coating thickness (See Figure S1) [45].

From the microhardness values (Figure 6), it is visible that after PN treatment, substrate hardness increases. After the duplex treatment, the micro-hardness value of the samples increases further. It is noted that not much variation in hardness values of the samples with different PN case depths was observed. It could be due to lower penetration of the indenter (<5% of coating thickness) during measurement excluding the substrate effect from the results [45]. For both the m-CrN and m-AlTiN coatings, hardness values were in a similar range (Figure 6). However, m-AlTiN coated samples exhibit a lower wear rate than m-CrN coated samples. This can be correlated to m-AlTiN coating's nano-layered coating structure which improves its wear-resistant properties [51–54].

It is visible that PN treatment on H-13 improves the microhardness, and it is double that of hardened H-13. Further improvement in the micro-hardness is achieved by the duplex treatment showing an overall 5 to 6 times rise in the hardness values. For both the duplex-treated samples with different coatings, hardness values are in a similar range but the wear resistance of m-AlTiN is better than m-CrN coated samples. This is attributed to the lower bilayer thickness of the m-AlTiN coating (Figure 4).

3.5. Corrosion Study

The corrosion properties of the samples were studied using a potentiostat in 1.0 HCL solution at ambient conditions. Using the data, the Tafel plots of the samples were plotted to obtain the E_{corr} and I_{corr} values (Figure 7). These values were used to calculate the corrosion rate (Table 2).

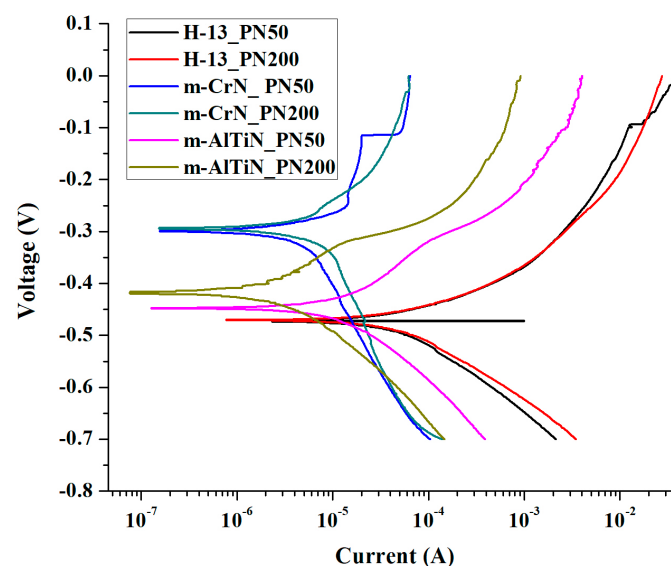


Figure 7. Tafel plots of potentiodynamic study of plasma nitrided and duplex-treated H-13 hot work steel samples tested in 1.0 M HCl corrosive electrolyte solution at ambient temperature.

The results show that duplex-treated samples exhibit better corrosion resistance compared to only plasma-nitrided samples. For the m-AlTiN coated samples, the corrosion rate is much lower than the m-CrN coated samples. It can be attributed to higher total coating thickness and low bilayers of AlTiN/TiN in the m-AlTiN coating structure [55] (Figure 4). This blocks the pinholes and other surface defects and protects the substrate from corrosion [30]. It can be noted that the E_{corr} value of m-CrN duplex-treated samples

is lower than m-AlTiN duplex-treated samples (Table 2). However, the corrosion rate of the m-AlTiN-coated samples is lower compared to the m-CrN-coated samples due to their dense coating structure.

Table 2. Potentiodynamic polarization test data of duplex-treated and nitrided H-13 hot work steel.

Sample	Corrosion Rate (mm/yr)	E_{corr} (V)	I_{corr} (A)
H-13 PN 50	7.63×10^{-1}	−0.472	6.58×10^{-5}
H-13 PN200	7.73×10^{-1}	−0.470	6.67×10^{-5}
m-CrN PN50	6.63×10^{-2}	−0.299	5.72×10^{-6}
m-CrN PN200	7.66×10^{-2}	−0.293	6.61×10^{-6}
m-AlTiN PN50	3.35×10^{-2}	−0.437	2.89×10^{-6}
m-AlTiN PN200	3.08×10^{-2}	−0.416	2.66×10^{-6}

It is observed that duplex treatment reduces the corrosion rate (by one order) protecting the surface of nitrided H-13 in a corrosive environment. The duplex treatment performed with m-AlTiN coating displays superior corrosion resistance owing to its dense coating structure.

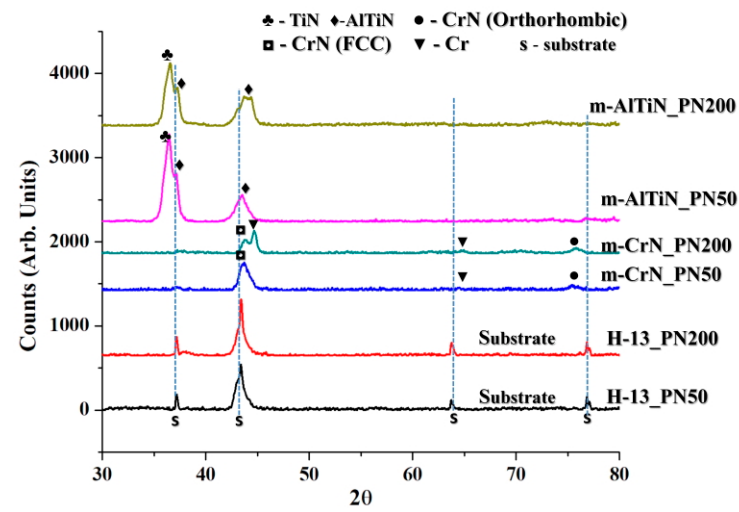
3.6. XRD Phase Analysis

Figure 8a shows the XRD of the duplex-treated and plasma-nitrided H-13 samples. Table 3 compares the observed $2\theta^\circ$ with the $2\theta^\circ$ given in the ICSD data for the phases shown in Figure 8a. Substrate phases observed in the present work are similar to the phases observed by Cruz et al. [56]. The case depth of plasma nitrided substrates mainly contains precipitates of CrN and ϵ -Fe₂₋₃N which are helpful in increasing the hardness by precipitating the hardening mechanism.

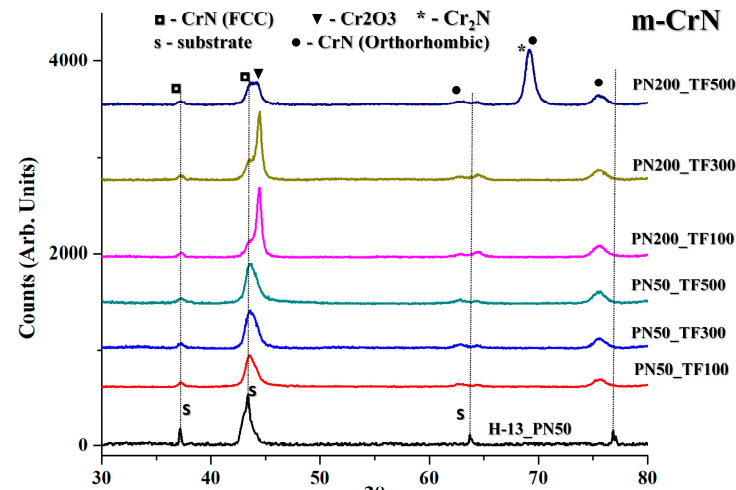
Table 3. Comparison of observed $2\theta^\circ$ and the $2\theta^\circ$ given in the ICSD data for the phases shown in Figure 8a.

No.	Observed $2\theta^\circ$	ICSD Data			Remark
		$2\theta^\circ$	Phase (Plane)	ICSD No.	
1	36.45	36.66	FCC TiN (111)	381420	Substrate Phases
2	37.15	37.31	FCC AlTiN (111)	804072	
3	37.19	37.57	FCC CrN (111)	110065	
4	43.43	43.43	Hexagonal ϵ -Fe ₂₋₃ N (111)	491662	Substrate Phases
5	43.51	43.35	FCC AlTiN (200)	804072	Substrate Phases
6	43.90	43.77	FCC CrN (200)	110065	
7	44.72	44.39	BCC Cr (110)	060694	
8	63.77	63.59	FCC CrN (200)	110065	
9	64.89	64.57	BCC Cr (200)	060694	
10	75.77	75.59	Orthorhombic CrN (211)	702942	Substrate Phases
11	76.86	76.82	Hexagonal ϵ -Fe ₂₋₃ N (113)	491663	

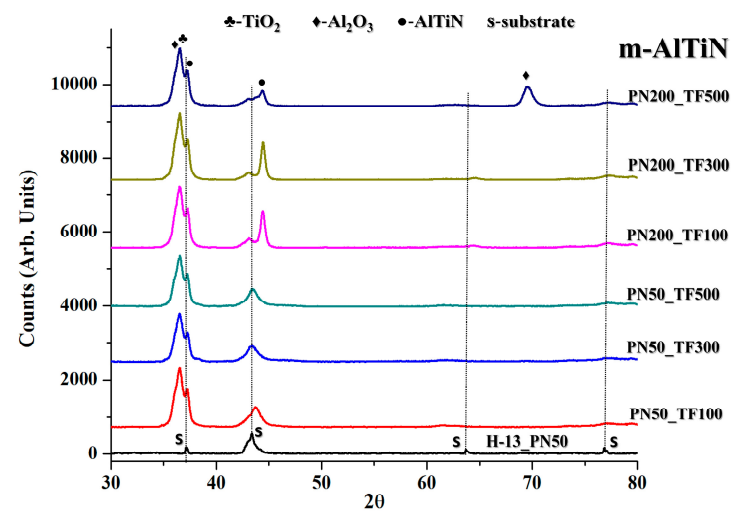
XRD plots of duplex-treated samples after various thermal fatigue cycles are shown in Figure 8b,c. Tables 4 and 5 compare the observed $2\theta^\circ$ with the $2\theta^\circ$ given in the ICSD data for the phases shown in Figure 8b,c. Figure 8b compares the phase change in the m-CrN duplex-treated samples. Similarly, Figure 8c shows the phase information of m-AlTiN duplex-treated samples.



(a)



(b)



(c)

Figure 8. (a) XRD plots of plasma nitrided and duplex-treated samples; (b) XRD plots of duplex-treated m-CrN samples after various thermal fatigue cycles; (c) XRD plots of duplex-treated m-AlTiN samples after various thermal fatigue cycles.

Table 4. Comparison of observed $2\theta^\circ$ and the $2\theta^\circ$ given in the ICSD data for the phases shown in Figure 8b.

No.	Observed $2\theta^\circ$	ICSD Data			Remark
		$2\theta^\circ$	Phase (Plane)	ICSD No.	
1	37.19	37.57	FCC CrN (111)	110065	Substrate Phases
2	43.74	43.77	FCC CrN (200)	110065	
3	44.41	43.43	Hexagonal ϵ -Fe ₂₋₃ N (111)	491662	Substrate Phases
4	44.18	44.207	Rhombohedral Cr ₂ O ₃ (202)	850869	
5	62.79	62.50	Orthorhombic CrN (200)	702942	Substrate Phases
6	64.38	63.59	FCC CrN (200)	110065	
7	68.50	68.32	Hexagonal Cr ₂ N (300)	792159	
8	69.15	69.04	Orthorhombic CrN (012)	702942	
9	75.44	75.59	Orthorhombic CrN (211)	702942	Substrate Phases
10	76.86	76.82	Hexagonal ϵ -Fe ₂₋₃ N (113)	491663	

Table 5. Comparison of observed $2\theta^\circ$ and the $2\theta^\circ$ given in the ICSD data for the phases shown in Figure 8c.

No.	Observed $2\theta^\circ$	ICSD Data			Remark
		$2\theta^\circ$	Phase (Plane)	ICSD No.	
1	35.15	35.15	Rhombohedral Al ₂ O ₃ (104)	821468	Substrate Phases
2	36.59	36.60	Orthorhombic TiO ₂ (200)	841750	
3	37.19	37.57	FCC CrN (111)	110065	
4	37.31	37.31	FCC AlTiN (111)	804072	
5	43.33	43.35	FCC AlTiN (200)	804072	Substrate Phases
6	44.42	43.43	Hexagonal ϵ -Fe ₂₋₃ N (111)	491662	
7	64.43	63.59	FCC CrN (200)	110065	Substrate Phases
8	69.46	68.88	Rhombohedral Al ₂ O ₃ (300)	851337	
9	76.86	76.82	Hexagonal ϵ -Fe ₂₋₃ N (113)	491663	Substrate Phases

Duplex-treated H-13 samples with m-CrN coating show FCC CrN phases, along with the existence of the BCC Cr. Duplex-treated H-13 samples with m-AlTiN coating show various FCC AlTiN and FCC TiN phases. As can be seen in Figure 8b, the amount of Cr₂O₃ phase increases as compared to the other phases as the thermal fatigue cycles increase. The existence of the Cr₂N phase after thermal fatigue indicates that the Cr/CrN multilayer combines to form a hexagonal Cr₂N structure. The orthorhombic CrN phase seen after thermal fatigue indicates the possibility of stress-induced phase transformation. Duplex-treated H-13 samples with m-AlTiN coatings subjected to various thermal fatigue cycles mainly show AlTiN, Al₂O₃, and TiO₂ phases. (Figure 8c). These oxides of aluminium and titanium protect the H-13 steel surface.

3.7. Thermal Fatigue

A thermal fatigue test was carried out on the samples for 100 cycles (TF100), 300 cycles (TF300), and 500 cycles (TF500). The wear behavior of these samples was studied using a micro-abrasion test [43]. Oxide layers were observed for the uncoated plasma nitrided H-13 samples (Figure 9). The measured oxide layer thickness was 0.29 μm , 0.69 μm , 0.27 μm , and 0.57 μm for H-13_PN50 (TF300), H-13_PN50 (TF500), H-13_PN200 (TF300), and H-13_PN200 (TF500), respectively. It was noted that with the increase in the TF cycle, the wear rate also increases (Figure 10).

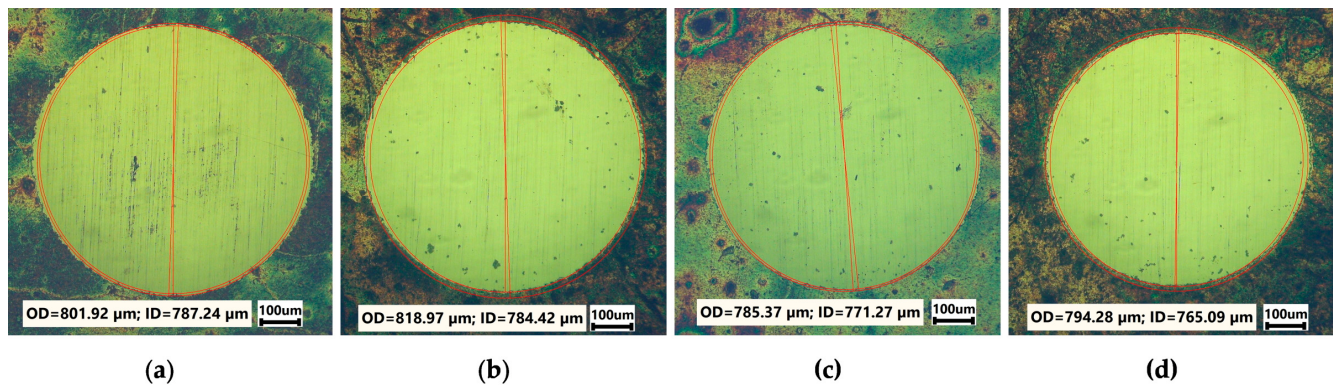


Figure 9. Optical crater images (taken at 50× mag.) of oxide layer after thermal fatigue: (a) H-13_PN50 after TF300; (b) H-13_PN50 after TF500; (c) H-13_PN200 after TF300; (d) m-H-13_PN200 after TF500.

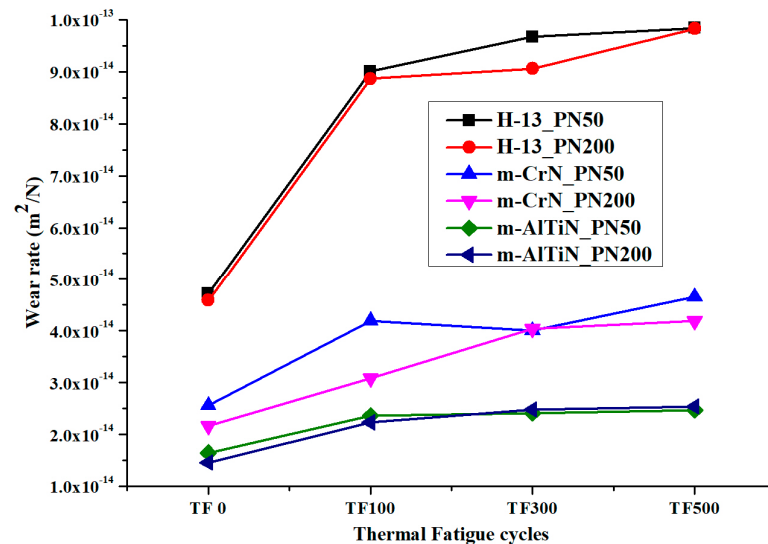


Figure 10. Wear rate of plasma nitrided and duplex-treated H-13 samples with no thermal fatigue (TF0) and subjected to 100, 300, and 500 thermal fatigue cycles (TF100, TF300, and TF500).

The oxide layers formed after the thermal fatigue test (for TF300 and TF500) were clearly visible and measurable for the H-13_PN50 and H-13_PN200 samples. For the duplex-treated sample, only surface discoloration was visible, but no distinct oxide layer was seen. (See Figures S2 and S3). Therefore, m-CrN and m-AlTiN coatings restrict oxidation on the surface.

Formation of Cr_2O_3 oxide and Al_2O_3 oxide on the m-CrN and m-AlTiN coating surface, respectively, reduces further diffusion of oxygen within the substrate [30]. Therefore, m-CrN and m-AlTiN restrict oxide formation at the surface and improve its wear-resistant properties. As the thermal fatigue test simulates the die-casting condition, it is clear that the m-CrN and m-AlTiN coatings could protect the surface from oxidation during the die-casting process.

In Figure 10, it can be seen that the duplex-treated samples exhibit a lower wear rate than only nitride samples. It is seen for all the samples that the wear rate increases with the number of thermal fatigue cycles. For H-13_PN50 and H-13_PN200 samples, the wear rate increases sharply with the TF cycle. The oxide layer was visible for these samples (Figure 9). The soft oxide layer formed on the surface results in a rise in wear rate after thermal fatigue. As m-CrN and m-AlTiN coatings restrict the oxidation on the surface (see Figures S2 and S3), the wear rate does not rise for these samples. It can also be seen that the m-AlTiN-coated samples have better wear resistance after thermal fatigue compared to

other m-CrN-coated samples. It can be concluded that the duplex treatment sample can withstand thermal fatigue conditions for a longer duration. The M-AlTiN_PN200 sample was the most wear-resistant coating in thermal fatigue conditions.

3.8. Scratch Adhesion Test

Scratch adhesion failure modes of duplex-treated H-13 samples tested after the thermal fatigue test are presented in Figure 11. Scratch failure loads for duplex-treated H-13 samples subjected to 100, 300, and 500 thermal fatigue cycles (TF100, TF300, and TF500) are presented in Figure 12. It is observed that with the increase in the thermal fatigue cycles, the adhesion strength of the coating increases. It is noted from Figure 11 that the coating adhesion failure is due to buckling spallation observable in both the duplex-treated samples. Buckling spallation is regularly spaced and shaped annular circles which can extend outside the edges. In the case of the m-AlTiN_PN200 sample, after TF500 it shows some failure modes of recovery spallation which are generated by elastic recovery behind the stylus and depend on plastic deformation in the substrate and cohesive cracking in the coating [57]. With the increase in the TF cycles, the adhesion strength is observed to increase. This increase in the adhesion strength after thermal fatigue can be due to the diffusion of intermediate layers [47,58]. This needs further investigation.

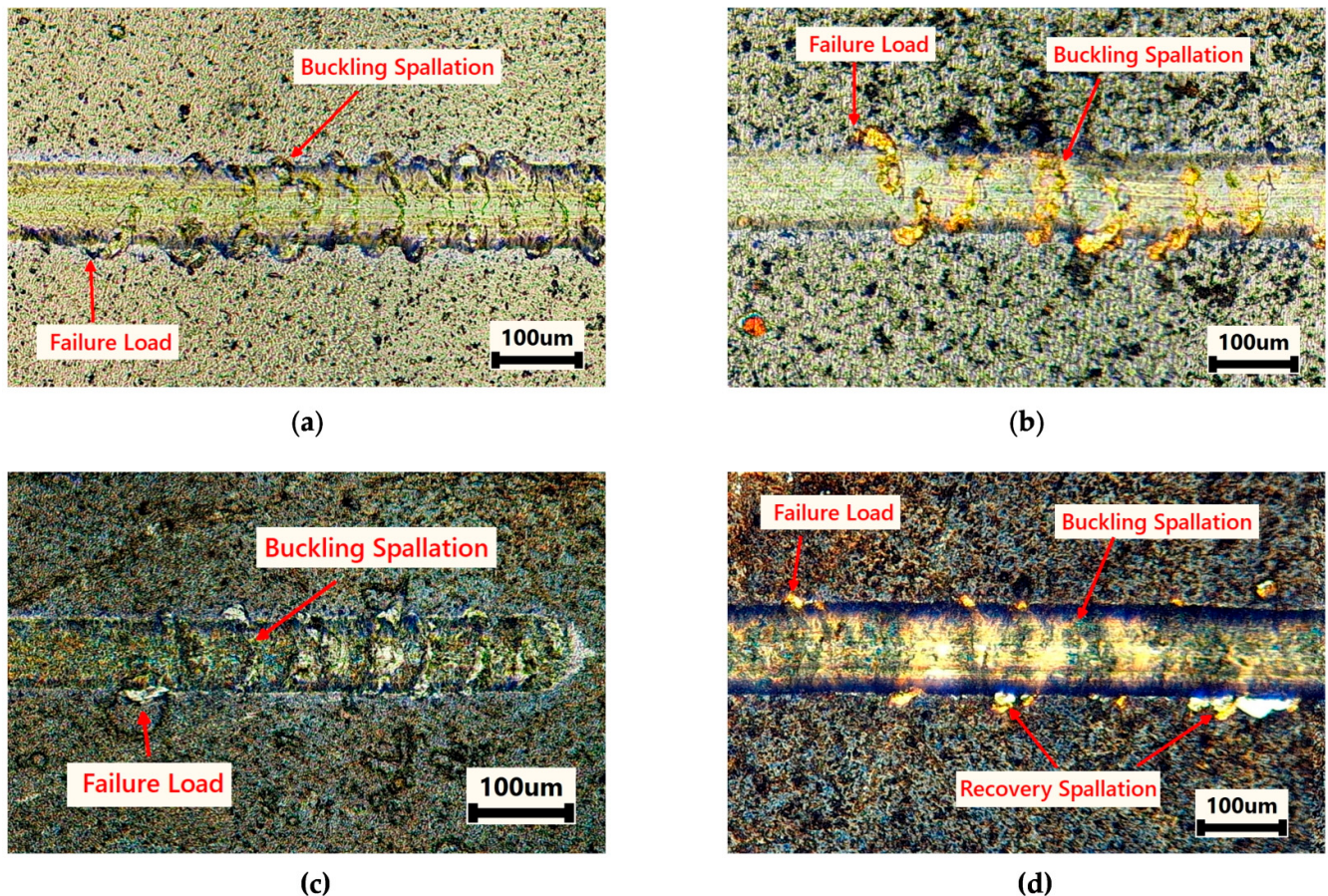


Figure 11. Failure modes of coating scratch adhesion after thermal fatigue for samples: (a) m-CrN_PN50 for TF100; (b) m-CrN_PN50 for TF500; (c) m-AlTiN_PN50 for TF100; (d) m-AlTiN_PN200 for TF500.

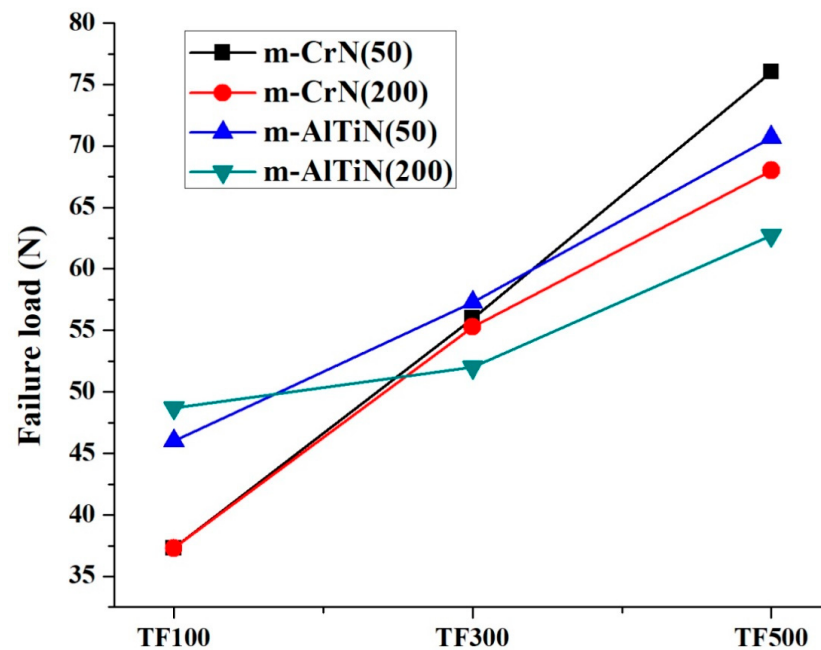


Figure 12. Scratch failure loads for duplex-treated H-13 samples subjected to 100, 300, and 500 thermal fatigue cycles (TF100, TF300, and TF500).

4. Discussion

From the results reported above, it is clear that the duplex treatment improves the mechanical, properties oxidation resistance, wear resistance, and thermal fatigue properties of H-13 steel. Plasma nitriding doubles the microhardness, and duplex treatment quintuples the microhardness of H-13 (Figure 6). Wear resistance of duplex-treated H-13 is two to three times better than that of plasma nitride H-13 (see the wear rate at TF0 in Figure 10).

Hot work tool steel H-13 treated with plasma nitriding shows improved hardness which is attributed to the formation of CrN precipitates in the substrate. With the increase in nitrogen case depth from 50 μm to 200 μm , the amount of CrN precipitates increase, and the hardness increases. The presence of the CrN phase in the nitrided H-13 steel substrate is evident in the XRD (see Figure 8); which is due to the nitrogen diffusion into the H-13 steel and subsequent compound formation [56,59]. The multilayer coatings on the plasma nitrided H-13 steel further improve micro-hardness, wear, and corrosion resistance. The wear rate is lower for the 200 μm case depth duplex-treated H-13 steel than that of 50 μm among the coated samples. The presence of the CrN phase in the nitrided H-13 steel provides better lattice matching with the base layer of the multilayer coatings, namely Cr in m-CrN and TiN in m-AlTiN coating samples further improves the adhesion properties of duplex-treated H-13 steel [15]. In addition, plasma nitriding introduces a buffer layer with intermediate hardness between the soft H-13 substrate and hard PVD coating. Thus, a gradual increase in hardness from the substrate to the coating improves the adhesion between the coating and the substrate.

The oxide layer formed after thermal fatigue (e.g., after 500 cycles) for plasma nitride H-13 has a thickness value ranging from 0.6 to 0.7 microns (Figure 9). However, for duplex-treated steel after 500 thermal fatigue cycles, no oxide layer was visible in the optical microscope. The samples became slightly discolored (see Figures S2 and S3). Duplex-treated samples result in improved corrosion resistance compared to the nitrided H-13 sample (Table 2 and Figure 7); m-AlTiN coating on nitrided H-13 samples shows a higher corrosion resistance among all samples. The m-CrN_PN200 shows less negative corrosion potential compared to the other samples. The enhanced oxidation and corrosion resistance are due to the dense multilayer structure in the coated layers and better adhesion with the plasma nitride layer.

The scratch test results of duplex-treated samples subjected to different thermal fatigue cycles show that failure load increases with an increase in TF cycles. With the increase in the thermal fatigue cycles, the adhesion strength is observed to increase. This increase in the adhesion strength after thermal fatigue can be due to the diffusion of intermediate layers [47,58].

The combined effect of the above improvements can be seen in the wear rate values of duplex-treated H-13, obtained before and after 500 thermal fatigue cycles. Here, we compare our results with the results of Mundotia et al. [41] who reported a similar study of only multilayer-coated H-13. For m-CrN and m-AlTiN samples, the duplex-treated sample has 57% and 43% lower wear rates, respectively, than those of only coated samples in the case of without thermal fatigue. After 500 thermal fatigue cycles, the wear rate increases (wear resistance decreases) for both only coated and duplex-treated samples, but the duplex-treated samples maintain the lead.

The m-CrN coating shows phase change in the XRD after being subjected to various thermal fatigue cycles. Initially, the oxide layer is formed at lower thermal cycles. Therefore, the wear rate tends to increase with the increase in the thermal fatigue cycles. For the sample having 200 μm case depth after 500 thermal fatigue cycles, the Cr_2N phase is formed due to the disappearance of the interface between Cr and CrN multilayers induced by thermal fatigue stress on the coating. In particular, for the m-AlTiN sample, the duplex-treated sample has a 41% lower wear rate than that of the only coated sample, just a decrease of 2% from 43%. XRD measurements give clues for the better performance of the m-AlTiN duplex-treated sample. In this sample, with thermal fatigue cycles, lubricating layers of Al_2O_3 and TiO_2 are formed which improve the wear resistance. The sample with m-AlTiN deposited on plasma nitrided H-13 with 200 μm case depth displays better thermal fatigue properties compared to the other samples. This is seen from the wear rate study at various thermal fatigue cycles. There is a slight increase in wear rate from TF0 to TF100 which then remains constant up to TF500. However additional rhombohedral Al_2O_3 (300) orientation appears for the m-AlTiN deposited on plasma nitrided H-13 with 200 μm case depth which enhances the lubricating effect. As thermal fatigue cycles simulate the die-casting process, it is proposed that the duplex-treated m-AlTiN H-13 would perform better than the other treatments studied so far. Plasma nitriding together with PVD coating improves load bearing capacity of the substrate [60]. The plasma nitride layer reduces stress and hardness gradients between the coating and the substrate which contribute considerably to the increase in performance of the duplex coating [61,62].

5. Conclusions

The present work focused on finding the answer to how the duplex-treated H-13 would perform compared to the untreated H-13 and only PVD-coated H-13 for die-casting applications. Thermal fatigue testing was carried out to simulate the die-casting process. The duplex-treated samples showed better wear resistance and thermal fatigue properties compared to untreated and only coated samples. The sample with m-AlTiN deposited on plasma nitrided H-13 with 200 μm case depth, displayed better thermal fatigue properties compared to the other samples.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/lubricants11010019/s1>, Figure S1: Loading-unloading curves of micro-hardness test carried out on (a) m-CrN_PN50; (b) m-CrN_PN200; (c) m-AlTiN_PN50; (d) m-AlTiN_PN200. Figure S2: Optical images (taken at $50\times$ mag.) of wear craters (240 s) for PN50 samples after thermal fatigue TF100, TF300, and TF500. Figure S3: Optical images (taken at $50\times$ mag.) of wear craters (240 s) for PN200 samples after thermal fatigue TF100, TF300, and TF500.

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and D.K.; supervision, U.M. and D.K. All authors have read and agreed to the published version of the manuscript.

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References

1. Kovačević, L.; Terek, P.; Miletić, A.; Kukuruzović, D.; Škorić, B.; Panjan, P. Industrial Evaluation of Duplex PVD Hard Coatings for HPDC. *J. Braz. Soc. Mech. Sci. Eng.* **2018**, *40*, 271. [\[CrossRef\]](#)
2. Mitterer, C.; Holler, F.; Üstel, F.; Heim, D. Application of Hard Coatings in Aluminium Die Casting—Soldering, Erosion and Thermal Fatigue Behaviour. *Surf. Coat. Technol.* **2000**, *125*, 233–239. [\[CrossRef\]](#)
3. Sundqvist, M.; Hogmark, S. Effects of Liquid Aluminium on Hot-Work Tool Steel. *Tribol. Int.* **1993**, *26*, 129–134. [\[CrossRef\]](#)
4. Liu, B.; Wang, B.; Yang, X.; Zhao, X.; Qin, M.; Gu, J. Thermal Fatigue Evaluation of AISI H13 Steels Surface Modified by Gas Nitriding with Pre- and Post-Shot Peening. *Appl. Surf. Sci.* **2019**, *483*, 45–51. [\[CrossRef\]](#)
5. Wang, B.; Zhao, X.; Li, W.; Qin, M.; Gu, J. Effect of Nitrided-Layer Microstructure Control on Wear Behavior of AISI H13 Hot Work Die Steel. *Appl. Surf. Sci.* **2018**, *431*, 39–43. [\[CrossRef\]](#)
6. Legg, K.O.; Graham, M.; Chang, P.; Rastagar, F.; Gonzales, A.; Sartwell, B. The Replacement of Electroplating. *Surf. Coat. Technol.* **1996**, *81*, 99–105. [\[CrossRef\]](#)
7. Paiva, J.M.; Fox-Rabinovich, G.; Junior, E.L.; Stolf, P.; Ahmed, Y.S.; Martins, M.M.; Bork, C.; Veldhuis, S. Tribological and Wear Performance of Nanocomposite PVD Hard Coatings Deposited on Aluminum Die Casting Tool. *Materials* **2018**, *11*, 358. [\[CrossRef\]](#)
8. Peng, J.; Zhu, Z.; Su, D. Sliding Wear of Nitrided and Duplex Coated H13 Steel against Aluminium Alloy. *Tribol. Int.* **2019**, *129*, 232–238. [\[CrossRef\]](#)
9. Wang, B.; Bourne, G.R.; Korenyi-Both, A.L.; Monroe, A.K.; Midson, S.P.; Kaufman, M.J. Method to Evaluate the Adhesion Behavior of Aluminum-Based Alloys on Various Materials and Coatings for Lube-Free Die Casting. *J. Mater. Process. Technol.* **2016**, *237*, 386–393. [\[CrossRef\]](#)
10. Li, G.; Li, X.; Wu, J. Study of the Thermal Fatigue Crack Initial Life of H13 and H21 Steels. *J. Mater. Process. Technol.* **1998**, *74*, 23–26. [\[CrossRef\]](#)
11. Siddiqui, S.A.; Mária, M.B. Wear Behaviour of Duplex (PN+PVD) Treated Layers Produced on X42CR13 Steel. *Multidiscip. Tudományok* **2019**, *9*, 3–11. [\[CrossRef\]](#)
12. Candido Recco, A.A.; Tschiptschin, A.P. Structural and Mechanical Characterization of Duplex Multilayer Coatings Deposited onto H13 Tool Steel. *J. Mater. Res. Technol.* **2012**, *1*, 182–188. [\[CrossRef\]](#)
13. Yang, S.; Cooke, K.; Sun, H.; Li, X.; Lin, K.; Dong, H. Development of Advanced Duplex Surface Systems by Combining CrAlN Multilayer Coatings with Plasma Nitrided Steel Substrates. *Surf. Coat. Technol.* **2013**, *236*, 2–7. [\[CrossRef\]](#)
14. La Vecchia, G.M.; Lecis, N. Impact Test and Tribological Behaviour of Duplex-Treated Low-Alloy Steel. *Surf. Coat. Technol.* **2010**, *205*, 614–619. [\[CrossRef\]](#)
15. Tillmann, W.; Vogli, E.; Momeni, S. Mechanical and Tribological Properties of Ti/TiAlN Duplex Coatings on High and Low Alloy Tool Steels. *Vacuum* **2009**, *84*, 387–392. [\[CrossRef\]](#)
16. Batista, J.C.A.; Godoy, C.; Buono, V.T.L.; Matthews, A. Characterisation of Duplex and Non-Duplex (Ti, Al)N and Cr-N PVD Coatings. *Mater. Sci. Eng. A* **2002**, *336*, 39–51. [\[CrossRef\]](#)
17. Batista, J.C.A.; Joseph, M.C.; Godoy, C.; Matthews, A. Micro-Abrasion Wear Testing of PVD TiN Coatings on Untreated and Plasma Nitrided AISI H13 Steel. *Wear* **2001**, *249*, 971–979. [\[CrossRef\]](#)
18. Azzi, M.; Benkahoul, M.; Klemberg-Sapieha, J.E.; Martinu, L. Corrosion and Mechanical Properties of Duplex-Treated 301 Stainless Steel. *Surf. Coat. Technol.* **2010**, *205*, 1557–1563. [\[CrossRef\]](#)
19. Kalss, W.; Reiter, A.; Derflinger, V.; Gey, C.; Endrino, J.L. Modern Coatings in High Performance Cutting Applications. *Int. J. Refract. Met. Hard Mater.* **2006**, *24*, 399–404. [\[CrossRef\]](#)
20. Kale, A.N.; Ravindranath, K.; Kothari, D.C.; Raole, P.M. Tribological Properties (Ti,Al) N Coatings Deposited at Different Bias Voltage Using the Cathodic Arc Technique. *Surf. Coat. Technol.* **2001**, *145*, 60–70. [\[CrossRef\]](#)
21. Kothari, D.C.; Kale, A.N. Recent Trends in Surface Engineering Using Cathodic Arc Technique. *Surf. Coat. Technol.* **2002**, *158*–159, 174–179. [\[CrossRef\]](#)
22. Tien, S.K.; Duh, J.G.; Lee, J.W. Oxidation Behavior of Sputtered CrN/AlN Multilayer Coatings during Heat Treatment. *Surf. Coat. Technol.* **2007**, *201*, 5138–5142. [\[CrossRef\]](#)
23. Kovalev, A.I.; Wainstein, D.L.; Rashkovskiy, A.Y.; Fox-Rabinovich, G.S.; Yamamoto, K.; Veldhuis, S.; Aguirre, M.; Beake, B.D. Impact of Al and Cr Alloying in TiN-Based PVD Coatings on Cutting Performance during Machining of Hard to Cut Materials. *Vacuum* **2009**, *84*, 184–187. [\[CrossRef\]](#)

24. Polcar, T.; Martinez, R.; Vítů, T.; Kopecký, L.; Rodriguez, R.; Cavaleiro, A. High Temperature Tribology of CrN and Multilayered Cr/CrN Coatings. *Surf. Coat. Technol.* **2009**, *203*, 3254–3259. [[CrossRef](#)]
25. Bouamerene, M.S.; Nouveau, C.; Aknouche, H.; Atmani, T.D.; Challali, M.O. A Study of Cr/CrN and Cr/CrN/CrAlN Multilayer Coatings for Permanent Mold Castings of Aluminum Alloys: Wear and Soldering Tendency. *J. Mater. Eng. Struct.* **2021**, *8*, 83–94.
26. Chim, Y.C.; Ding, X.Z.; Zeng, X.T.; Zhang, S. Oxidation Resistance of TiN, CrN, TiAlN and CrAlN Coatings Deposited by Lateral Rotating Cathode Arc. *Thin Solid Film.* **2009**, *517*, 4845–4849. [[CrossRef](#)]
27. Conde, A.; Cristóbal, A.B.; Fuentes, G.; Tate, T.; de Damborenea, J. Surface Analysis of Electrochemically Stripped CrN Coatings. *Surf. Coat. Technol.* **2006**, *201*, 3588–3595. [[CrossRef](#)]
28. Wu, Z.T.; Qi, Z.B.; Zhu, F.P.; Liu, B.; Wang, Z.C. Influences of Y Addition on Mechanical Properties and Oxidation Resistance of CrN Coating. *Phys. Procedia* **2013**, *50*, 150–155. [[CrossRef](#)]
29. Barshilia, H.C.; Jain, A.; Rajam, K.S. Structure, Hardness and Thermal Stability of Nanolayered TiN/CrN Multilayer Coatings. *Vacuum* **2003**, *72*, 241–248. [[CrossRef](#)]
30. Thorat, N.; Mundotia, R.; Varma, R.; Kale, A.; Mhatre, U.; Patel, N. Structural & Oxidation Behavior of TiN & Al_xTi_{1-x}N Coatings Deposited by CA-PVD Technique. In *AIP Conference Proceedings 2018*; AIP Publishing LLC: Melville, NY, USA, 2018; Volume 1942, p. 080041. [[CrossRef](#)]
31. Galindo, R.E.; Endrino, J.L.; Martínez, R.; Albella, J.M. Improving the Oxidation Resistance of AlCrN Coatings by Tailoring Chromium Out-Diffusion. *Spectrochim. Acta-Part B At. Spectrosc.* **2010**, *65*, 950–958. [[CrossRef](#)]
32. Feng, Y.P.; Zhang, L.; Ke, R.X.; Wan, Q.L.; Wang, Z.; Lu, Z.H. Thermal Stability and Oxidation Behavior of AlTiN, AlCrN and AlCrSiWN Coatings. *Int. J. Refract. Met. Hard Mater.* **2014**, *43*, 241–249. [[CrossRef](#)]
33. Fox-Rabinovich, G.S.; Beake, B.D.; Endrino, J.L.; Veldhuis, S.C.; Parkinson, R.; Shuster, L.S.; Miganov, M.S. Effect of Mechanical Properties Measured at Room and Elevated Temperatures on the Wear Resistance of Cutting Tools with TiAlN and AlCrN Coatings. *Surf. Coat. Technol.* **2006**, *200*, 5738–5742. [[CrossRef](#)]
34. Fox-Rabinovich, G.S.; Weatherly, G.C.; Dodonov, A.I.; Kovalev, A.I.; Shuster, L.S.; Veldhuis, S.C.; Dosbaeva, G.K.; Wainstein, D.L.; Miganov, M.S. Nano-Crystalline Filtered Arc Deposited (FAD) TiAlN PVD Coatings for High-Speed Machining Applications. *Surf. Coat. Technol.* **2004**, *177–178*, 800–811. [[CrossRef](#)]
35. Gaitan, G.B.; Caicedo, J.C.; Balogh, A.G.; Gottschalk, S. Cutting Tools Performance Enhancement by Using a TiN/TiAlN Multilayer Coating System. *Phys. Status Solidi Curr. Top. Solid State Phys.* **2007**, *4*, 4260–4266. [[CrossRef](#)]
36. Bayón, R.; Igartua, A.; Fernández, X.; Martínez, R.; Rodríguez, R.J.; García, J.A.; de Frutos, A.; Arenas, M.A.; de Damborenea, J. Corrosion-Wear Behaviour of PVD Cr/CrN Multilayer Coatings for Gear Applications. *Tribol. Int.* **2009**, *42*, 591–599. [[CrossRef](#)]
37. Ducros, C.; Sanchette, F. Multilayered and Nanolayered Hard Nitride Thin Films Deposited by Cathodic Arc Evaporation. Part 2: Mechanical Properties and Cutting Performances. *Surf. Coat. Technol.* **2006**, *201*, 1045–1052. [[CrossRef](#)]
38. Wilczek, A.; Morgiel, J.; Rogal, Ł.; Maziarz, W.; Smolik, J. Microstructure and Wear of (CrN/CrAlN)/(CrAlN/VN) and (CrN/TiAlN)/(TiAlN/VN) Coatings for Molds Used in High Pressure Casting of Aluminum. *Coatings* **2020**, *10*, 261. [[CrossRef](#)]
39. Deng, Y.; Tan, C.; Wang, Y.; Chen, L.; Cai, P.; Kuang, T.; Lei, S.; Zhou, K. Effects of Tailored Nitriding Layers on Comprehensive Properties of Duplex Plasma-Treated AlTiN Coatings. *Ceram. Int.* **2017**, *43*, 8721–8729. [[CrossRef](#)]
40. Rousseau, A.F.; Partridge, J.G.; Mayes, E.L.H.; Toton, J.T.; Kracica, M.; McCulloch, D.G.; Doyle, E.D. Microstructural and Tribological Characterisation of a Nitriding/TiAlN PVD Coating Duplex Treatment Applied to M2 High Speed Steel Tools. *Surf. Coat. Technol.* **2015**, *272*, 403–408. [[CrossRef](#)]
41. Mundotia, R.; Ghorude, T.; Kale, A.; Mhatre, U. Study of Multilayer and Multi-Component Coatings Deposited Using Cathodic Arc Technique on H-13 Hot Work Steel for Die-Casting Applications. *Int. J. Nano Dimens.* **2020**, *11*, 177–187.
42. Mundotia, R.; Ghorude, T.; Kothari, D.C.C.; Kale, A.; Thorat, N. Tuning Bilayer Period of AlN/CrN Superlattice Coatings Deposited Using Cathodic Arc Technique for Superior Mechanical Properties and Thermal Stability. *Appl. Surf. Sci. Adv.* **2022**, *7*, 100205. [[CrossRef](#)]
43. Rutherford, K.L.; Hutchings, I.M. A Micro-Abrasive Wear Test, with Particular Application to Coated Systems. *Surf. Coat. Technol.* **1996**, *79*, 231–239. [[CrossRef](#)]
44. Pharr, G.M.; Oliver, W.C. Measurement of Thin Film Mechanical Properties Using Nanoindentation. *MRS Bull.* **1992**, *17*, 28–33. [[CrossRef](#)]
45. Oliver, W.C.; Pharr, G.M. Measurement of Hardness and Elastic Modulus by Instrumented Indentation: Advances in Understanding and Refinements to Methodology. *J. Mater. Res.* **2004**, *19*, 3–20. [[CrossRef](#)]
46. Oliver, W.C.; Pharr, G.M. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *J. Mater. Res.* **1992**, *7*, 1564–1583. [[CrossRef](#)]
47. Mundotia, R.; Thorat, N.J.; Kale, A.; Mhatre, U.; Kothari, D.C.; Kovacs, T.; Ghorude, T. Study of Corrosion Properties of CrN and Multilayer CrN/Cr Coating at Different Electrolyte Temperatures Deposited on Stainless Steel by Vacuum Arc Process. In *AIP Conference Proceedings 2019*; AIP Publishing LLC: Melville, NY, USA, 2019; Volume 2115, p. 030313.
48. Abusuilik, S.B. Pre-, Intermediate, and Post-Treatment of Hard Coatings to Improve Their Performance for Forming and Cutting Tools. *Surf. Coat. Technol.* **2015**, *284*, 384–395. [[CrossRef](#)]
49. Ebrahimzadeh, I.; Ashrafzadeh, F. High Temperature Wear and Frictional Properties of Duplex-Treated Tool Steel Sliding against a Two Phase Brass. *Ceram. Int.* **2014**, *40*, 16429–16439. [[CrossRef](#)]

50. Bujak, J.; Walkowicz, J.; Kusiński, J. Influence of the Nitrogen Pressure on the Structure and Properties of (Ti,Al)N Coatings Deposited by Cathodic Vacuum Arc PVD Process. *Surf. Coat. Technol.* **2004**, *180–181*, 150–157. [\[CrossRef\]](#)
51. Bonu, V.; Jeevitha, M.; Praveen Kumar, V.; Barshilia, H.C. Nanolayered Multilayer Ti/TiN Coatings: Role of Bi-Layer Thickness and Annealing on Solid Particle Erosion Behaviour at Elevated Temperature. *Surf. Coat. Technol.* **2019**, *357*, 204–211. [\[CrossRef\]](#)
52. Teng, Y.; Guo, Y.Y.; Zhang, M.; Yang, Y.J.; Huang, Z.; Zhou, Y.W.; Wu, F.Y.; Liang, Y.S. Effect of Cr/CrN x Transition Layer on Mechanical Properties of CrN Coatings Deposited on Plasma Nitrided Austenitic Stainless Steel. *Surf. Coat. Technol.* **2019**, *367*, 100–107. [\[CrossRef\]](#)
53. Wicinski, P.; Smolik, J.; Garbacz, H.; Kurzydowski, K.J. Microstructure and Mechanical Properties of Nanostructure Multilayer CrN/Cr Coatings on Titanium Alloy. *Thin Solid Film.* **2011**, *519*, 4069–4073. [\[CrossRef\]](#)
54. Krella, A. Resistance of PVD Coatings to Erosive and Wear Processes: A Review. *Coatings* **2020**, *10*, 921. [\[CrossRef\]](#)
55. William Grips, V.K.; Barshilia, H.C.; Selvi, V.E.; Kalavati; Rajam, K.S. Electrochemical Behavior of Single Layer CrN, TiN, TiAlN Coatings and Nanolayered TiAlN/CrN Multilayer Coatings Prepared by Reactive Direct Current Magnetron Sputtering. *Thin Solid Film.* **2006**, *514*, 204–211. [\[CrossRef\]](#)
56. Cruz, M.R.; Nachez, L.; Gomez, B.J.; Nosei, L.; Feugeas, J.N.; Staia, M.H. Ion Nitrided AISI H13 Tool Steel Part I—Microstructural Aspects. *Surf. Eng.* **2006**, *22*, 359–366. [\[CrossRef\]](#)
57. Bull, S.J.; Berasetegui, E.G. An Overview of the Potential of Quantitative Coating Adhesion Measurement by Scratch Testing. *Tribol. Int.* **2006**, *39*, 99–114. [\[CrossRef\]](#)
58. Brooks, J.; Davidson, J.; Forder, S.; Münz, W.-D.; Larsson, M. A Mössbauer Spectroscopy Study of Ti-Fe Interfaces Produced by the PVD Process. *Thin Solid Films* **1997**, *308–309*, 351–357. [\[CrossRef\]](#)
59. Salas, O.; Oseguera, J.; Garcí, N.; Figueroa, U. Nitriding of an H13 Die Steel in a Dual Plasma Reactor. *J. Mater. Eng. Perform.* **2001**, *10*, 649–655. [\[CrossRef\]](#)
60. Ahmad, F.; Zhang, L.; Zheng, J.; Sidra, I.; Zhang, S. Characterization of AlCrN and AlCrON Coatings Deposited on Plasma Nitrided AISI H13 Steels Using Ion-Source-Enhanced Arc Ion Plating. *Coatings* **2020**, *10*, 306. [\[CrossRef\]](#)
61. Navinšek, B.; Panjan, P.; Gorenjak, F. Improvement of Hot Forging Manufacturing with PVD and DUPLEX Coatings. *Surf. Coat. Technol.* **2001**, *137*, 255–264. [\[CrossRef\]](#)
62. Soković, M.; Panjan, P.; Kirn, R. Possibilities of Improvement of Dies Casting Tools with Duplex Treatment. *J. Mater. Process. Technol.* **2004**, *157–158*, 613–616. [\[CrossRef\]](#)

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