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Influence of duty cycle of pulse electrodeposition coated Ni-Al₂O₃ nanocomposites over surface roughness properties

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Abstract: This research presents the viability of duty cycle variation was explored as a potential 9 method to improve mechanical and surface roughness properties of Ni-Al₂O₃ nanocoatings through 10 pulse electrodeposition. Areal and surface roughness properties of nanocomposite pulse electro-11 deposition coated materials with varying duty cycle from 20% to 100% was studied, along with the 12 analysis of bearing area curve and power spectral densities. Results demonstrate that with decrease 13 in duty cycle, an enhancement in aerial roughness properties from 0.348 µm to 0.195 µm and surface 14 roughness properties from 0.779 µm to 0.245 µm was observed. The change in surface roughness 15 was due to grain size variation, resulting from the varying time intervals during pulse coatings. This 16 increase in grain size during change in duty cycle was confirmed with the scanning electron micro-17 scope. In addition to that, increase in grain size from 0.32 µm to 0.92 µm with increase in duty cycle 18 resulted in decrease in nanohardness from 4.21 GPa to 3.07 GPa. This work will provide a novel 19 method for obtaining Ni-Al₂O₃ nanocomposite coating with improved surface roughness and hard-20 ness properties for wider industrial applications. 21

Keywords: keyword 1; Pulse electrodeposition coating 2; nanocomposites 3; surface roughness 4; 22 Ni-Al₂O₃ 23

1. Introduction

Within the last decade, pulse electrodeposition coatings have been considered as a simple, 26 economic, and viable methodology for producing metal matrix composite (MMC) coating 27 exhibiting high mechanical, tribological properties and corrosion-resistant properties [1– 28 6]. Pulse electrodeposition is an augmentation of electrodeposition coating wherein vari-29 ous physical parameters including peak current density, duty cycle, frequency, pH and 30 bath composition of electrolyte can be precisely controlled for obtaining remarkable sur-31 face coatings [7–10]. Hard particles dispersed with pulse electrodeposition methods for 32 developing nanocomposite coatings and their resulting enhanced properties, have earned 33 wide acceptance in chemical, mechanical and electronic industries [3,11–13]. The advan-34 tageous properties of pulse electrodeposition coating such as low cost, easy design, re-35 duced grain size, high production rates and fever technological barriers results in the easy 36 conversion from laboratory state to industrial scale [7,14,15]. 37

Nickel-based nanocomposites exhibit outstanding properties and are therefore widely 38 used in various petrochemical, mechanical, electromechanical and tribological applica- 39 tions. It has been widely known that by supplementing ceramic nanoparticles such as 40 Al₂O₃, SiC, ZrO₂, MnO, ZrO, TiN, etc further improves coating surface characteristics. It 41 has been reported that Ni-Al₂O₃ composite coating, developed through pulse electrodep- 42 osition techniques, hardness and tribological properties are affected by both frequency 43

Citation: To be added by editorial staff during production.

Academic Editor: Firstname Lastname

Received: date Accepted: date Published: date

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Copyright: © 2022 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/license s/by/4.0/). and duty cycle [16]. It has been noticed that relatively low frequency and lower duty cycle 44 result in enhanced tribological properties including hardness. It was added that pulse 45 electrodeposition properties can have an influence on hardness and wear characteristics 46 of coating without any alterations in the bath composition. Jegan et al. [17] employed Watt 47 solution for Ni-Al₂O₃ nanocomposite coating by changing duty cycle, current density 48 and frequency during deposition of coatings. It was espied that duty cycle was a predom-49 inant factor which influences hardness of the specimen. Chen et al. [18] varied frequency 50 of pulse electrodeposition coating for Ni-Al2O3 and espied that increase in frequency re-51 sulted in decrease in hardness of composite coatings. Steinbach et al. [19] espied the lower 52 agglomeration of particles during coating for pulsed electrodeposition coating than direct 53 deposition coating. Along with this, smaller the particles used for coating more effective 54 will it be to pin grain boundaries which will help in improving hardness of the surface. 55 Ma et al. [20] fabricated Ni-Al₂O₃ coating with the help of ultrasonic-assisted electrodep-56 osition method. It was observed that ultrasonic power affected the number of particles 57 which had been incorporated on the surface in addition to their surface roughness. The 58 increase in the ultrasonic power resulted in a change in hardness of the coated surface. 59 The impact of current density on the pulse electrodeposition coating was studied by Gul 60 et al. [21] with Al₂O₃ nanoparticles embedded with Ni. Increase of Al₂O₃ deposition has 61 been observed with increasing current density, which resulted in increase of microhard-62 ness. During ON time, particles will be attached to surface due to the current provided 63 and during OFF time, particles which are loosely adsorbed will be detached. During OFF 64 state, loosely attached agglomerated particles will fall back to the electrolyte. With in-65 crease in current density, particles attached on to cathodic surface increases. It was con-66 cluded that microhardness enhancement has resulted from a decrease in the grain size 67 and increasing current density. Along with it, it was noted that pulsed electrodeposition 68 coating was having an improved properties compared to direct electrodeposition coating 69 in all the current densities. 70

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The properties of pulse electrodeposited coatings can easily be altered with the help of various parameters for example current density, duty cycle, deposition duration or time, pH of the electrolytic solution, etc. By changing time period at which the pulses are imposed, duty cycle of the coating can be varied which will change duty cycle of the coating phenomenon. The relation between the time intervals and duty cycle is given as 76

$$\gamma = \frac{T_{ON}}{T_{ON} + T_{OFF}}$$
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Where γ is the duty cycle, ToN is the time where the pulses are imposed and ToFF is the 79 relaxation time. Yang et al. [22] observed that with the surge in duty cycle the grain struc-80 ture became coarser along with which the decrease in hardness and decrease in particle 81 incorporation was observed. Similar observations were recorded by Lajevardi et al. [23] 82 during the coating of Ni-TiO₂. A decrease in microhardness and TiO₂ deposition was ob-83 served with increase in duty cycles. However, researchers have only focussed on the ef-84 fects of electrodeposition factors on the morphology, microstructure, hardness, corrosion 85 and anti-wear properties and not much focus was provided for surface roughness prop-86 erties. 87

The roughness parameters of a surface can be calculated by two methods: two dimensional (2D) or three dimensional (3D). The majority of engineering and scientific investigations have used 2D roughness analysis. Three-dimensional surface roughness, 90 however, has become more important recently [24,25]. 2D parameters include Ra, Rq, Rt, 91 Rpm, Rvm, and Rz. Ra represents arithmetic average height or centre line average is the 92 frequently used roughness parameter for quality purposes. It represents average absolute 93 deviation from profile mean height. However, Ra cannot be deemed for the roughness, as 94 it shows only the average of peaks and valleys. Rq is root mean square deviation from 95 profile mean line, which is more sensitive than Ra. Rq can be more precise than Ra within 96 the context of roughness of surfaces. The interdistance of highest peak and lowest valley 97 over the sampling line is denoted by Rt. Rpm and Rvm embodies mean of maximum 98 peaks and valleys in sampling length. Rz is a ten-point average or in other words it is 99 calculated by averaging 5 x highest peaks and 5 x lowest valleys over sampling distance. 100 Peaks are a subset of summits, which are places that are higher than their eight closest 101 neighbours. A peak height must be greater than 5% of the surface's ten-point height in 102 order for it to be considered a summit. All these parameters represent over the 2D plane. 103 3D roughness parameters include Sa, Sq, St, Spm, Svm, and Sz, which represents rough-104 ness parameters over the 3D surface. The terms are synonymous with that of 2D rough-105 ness parameters. Development of Ni-Al2O3 nanocoatings have been achieved in this study 106 by varying duty cycle parameters between 20% to 100%. A modified Watts bath has been 107 employed to contain pulse electrodeposition coating electrolyte. The microstructural 108 properties of coated surface was evaluated using an SEM and EDS for the elemental anal-109 ysis. Several studies have been conducted to assess both tribological and mechanical prop-110 erties of Ni-Al₂O₃ pulse electrodeposition coating, a comprehensive study over the rough-111 ness parameters have yet to be conducted. In this work, an extensive analysis of the sur-112 face roughness properties was done for coating surface at various duty cycles from 20% 113 to 100%. The nano hardness of the coated surface was studied with the help of a nano 114 indenter. 115

2. Materials and Methods

This study presents as to how pulse electrodeposition has been employed as a coating technique. EN1A steel was employed as cathode while pure Nickel has been employed as 118 anode. Considering the adhesive properties, availability, and cost, EN1A was made as the 119 substrate. The cathode has been produced circular shape having 30 mm diameter and 3.5 120 mm height or thickness, as in disc shaped. Nickel, the anode, was rectangular with a thick-121 ness of 2 mm. The samples were polished with grit papers 220, 600, 800, and 1200 and 122 roughness was made below 0.05 µm. After that, samples were conditioned by using ace-123 tone contained in an ultrasonic agitator for five minutes to get rid of any surface contaminants.

]	Г аble 1. Elec	trolytic Corr	position			
Chemical composition		Quantity	(g/L)	Function		
Nickel Sulphate Hexahydrate (N	iSO ₄ .6H ₂ O)	265	265		Nickel Source	
Nickel (II) Chloride (NiCl ₂ .6	6H ₂ O)	48	Со	Conductivity and Nickel Sour		
Boric Acid (H ₃ BO ₃)		31	Bu	uffering agent a	nd Stabilizer	
Aluminium Oxide (Al ₂ O	l,)	10		Reinforcing	agent	
Ta	able 2. Test o	conditions fo	r coatings			
Ta	able 2. Test of	conditions fo	or coatings	Darameter /	Parameter 5	
Ta	able 2. Test o Parameter 1	conditions fo Parameter 2	Parameter 3	Parameter 4	Parameter 5	
Ta Current Density (A/dm ²)	able 2. Test of Parameter 1	conditions fo Parameter 2	Parameter 3	Parameter 4	Parameter 5	
Ta Current Density (A/dm²) Duty Cycle (%)	able 2. Test of Parameter 1	conditions fo Parameter 2 40	Parameter 3 3 60	Parameter 4 80	Parameter 5	
Ta Current Density (A/dm²) Duty Cycle (%) Frequency (kHz)	able 2. Test of Parameter 1	conditions fo Parameter 2 40	Parameter 3 3 60 10	Parameter 4 80	Parameter 5	
Ta Current Density (A/dm²) Duty Cycle (%) Frequency (kHz) Time (min)	able 2. Test of Parameter 1 20	conditions fo Parameter 2 40	Parameter 3 3 60 10 60	Parameter 4 80	Parameter 5	
Ta Current Density (A/dm²) Duty Cycle (%) Frequency (kHz) Time (min) pH	able 2. Test of Parameter 1 20	conditions fo Parameter 2 40	Parameter 3 3 60 10 60 4.2 ± 0.2	Parameter 4	Parameter 5	
Ta Current Density (A/dm²) Duty Cycle (%) Frequency (kHz) Time (min) pH Temperature (°C)	able 2. Test of Parameter 1 20	conditions fo Parameter 2 40	Parameter 3 3 60 10 60 4.2 ± 0.2 60 ± 5	Parameter 4	Parameter 5	
Ta Current Density (A/dm ²) Duty Cycle (%) Frequency (kHz) Time (min) pH Temperature (°C) Anode	able 2. Test of Parameter 1 20	conditions fo Parameter 2 40	Parameter 3 3 60 10 60 4.2 ± 0.2 60 ± 5 Nickel Plate	Parameter 4	Parameter 5	

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A modified Watts Solution was used as electrolytic bath. The electrolytic chemical 133 composition of the modified Watt Solution with their properties is shown in Table 1. Al₂O₃ 134 with a particle size less than 50 nm (Sigma-Aldrich, Gillingham, UK) was the reinforcing 135 material used. The constituents were magnetically stirred for 24 hours and an additional 136 ultrasonic agitation at a frequency of 10 kHz was provided for 4 hrs. Appropriate blending 137 and dispersion of nanoparticles in their respective electrolytes were established by mag-138 netic agitation and ultrasonic stirring. The electrolytic solution is heated to 60 °C in final 139 phase. 140



Figure 1. Schematic Diagram of Pulse electrodeposition coating

A pulse power generator was used for pulse electrodeposition coating technique. For 145 the pulse electrodeposition coating, duty cycle was the only varying factor. All other pa-146 rameters, current density, frequency, pH of electrolyte, stir speed and electrolyte temper-147 ature were kept constant. The range of the duty cycle and various other parameters were 148established from previous research and trials [26–31]. An increase of duty cycle from 20% 149 to 100% has been achieved incrementally by 20%. Frequency was fixed at 10 kHz and pH 150 was maintained at 4.2±0.2 and 3 A/dm² constant current density. The pulse electrodeposi-151 tion was conducted at solution temperature of 60°C along with continuous magnetic stir-152 ring and ultrasonic agitation throughout the process. The coating process was set to 1 hour. After coating, distilled water was used to condition samples followed by acetone conditioning in an ultrasonic bath to remove all chemicals attached to surface. Each coat-155 ing was performed 3 times to check its repeatability of the coating. 156

The samples were studied under a non-contact 3D optical profilometer and various 157 parameters including Ra, Rq, Rt, Sa, Sq, St, Kurtosis, and Skewness were analysed along 158 with power spectral density (PSD) and bearing area curve (BAC). Nanohardness of sur-159 faces have been obtained by utilising nano indenter. Berkovich, 3-faced pyramidal, in-160 denter was used for the study. A total of 15 indentations have been conducted on the 161 coatings and results were analysed. 162

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The microstructure of coating was obtained with the help of a Scanning Electron Mi-163 croscope (JEOL). The grain size of coated materials was obtained with ImageJ, an open 164 license software. 165

3. Results and Discussions

3.1. Surface Morphology

Fig. 2 is showing surface morphology of samples at various duty cycles. An increase 168 in grain-size is seen with a rise in duty cycles. The electrodeposition coating with a duty 169 cycle 20% exhibited smoothest surface. As duty cycle increases, size of particles increased. 170 The change in grain size can be confirmed by the free energy of nucleation for new grains [32]. During Ton of pulse electrodeposition coating, the nanoparticles present in the electrolyte solution will be pulled towards the cathode surface and will be embedded in them. During TOFF, while current supply is cut out, loosely embedded and agglomerated particles will be detached from cathode surface and will return to electrolytic solution. This 175 process will be repeated henceforth. With decrease in duty cycle, TOFF time will be in-176 creased, as a result of which agglomeration of the particles will decrease, and grains will 177 become finer. Once duty cycle is increased (decrease in TOFF and increase in TON) particle 178 embedding will increase resulting in more agglomerated particles. This results in decrease of nucleation rate and causes increase in grain growth [33].



Figure 2. Scanning Electron Microscope images of coated samples at varying duty cycles (a) 20% 183 (b) 40% (c) 60% (d) 80% and (e) 100%. 184

3.2. Roughness Analysis

Fig 3 show profilometer images of samples at various duty cycles. Areal roughness 187 parameters and surface roughness parameters of all samples were analysed. Various Ar-188 eal roughness parameters including Ra, Rq, Rz, Rpm, Rvm, Rt and Rz of samples at vary-189 ing duty cycle is shown in Table 3. At a duty cycle of 20% Ra value was observed as 0.195 190 μ m. Ra increased with an increase of duty cycle. Ra values were observed as 0.175 μ m, 191 0.214 µm, 0.234 µm and 0.348 µm when duty cycles were 40%, 60%, 80% and 100% respec-192 tively. For getting more accurate Areal roughness parameters, Rq was analysed. Rq values 193 also increased when the duty cycle has increased from 20%, 40%, 60%, 80% to 100% as 194 0.271 μm, 0.253 μm, 0.299 μm, 0.326 μm, 0.541 μm respectively. 195

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Figure 3. Profilometer images of duty cycle (a) 20%, (b) 40%, (c) 60%, (d) 80% and (e) 100% 199 200

Table 3. Areal Roughness of samples with different duty cycles	
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Areal Roughness paramters (μm)						
Duty Cycle	Ra	Rq	Rpm	Rvm	Rtm	Rz
20	0.195	0.271	0.781	1.043	2.125	0.752
40	0.175	0.253	0.972	1.084	1.495	0.967
60	0.214	0.299	1.244	1.155	2.549	1.998
80	0.234	0.326	1.267	1.368	2.635	2.107
100	0.348	0.541	2.748	1.550	4.299	2.857

Table 4. Surface Roughness of samples with different duty cycles							
	Surface Roughness (μm)						
Duty Cycle	Sa	Sq	Spm	Svm	Stm	Sz	
20	0.245	0.529	14.161	7.830	19.560	15.612	
40	0.277	0.682	15.865	5.345	22.212	15.974	
60	0.334	0.728	16.427	3.631	22.559	16.436	
80	0.371	0.742	18.948	3.531	27.479	16.687	
100	0.779	1.714	23.046	4.350	27.396	16.339	

The average peaks and valleys of Areal surface were also analysed. The average Ar-209 eal peak height of samples increases when duty cycle increased. The 100% duty cycle sam-210 ples were having the highest peak of 2.748 µm and decreased when duty cycle decreased. 211 The peak height of 80%, 60%, 40%, and 20% was 1.267 μm , 1.244 μm , 0.972 μm , and 0.781 212 µm respectively. Similarly, Areal valley height of samples was analysed. The valley height 213 increased from -1.043 μ m to -1.084 μ m from duty cycle 20% to 40%. Thereafter a slight 214 decrease in height was observed as -1.155 µm at 60% duty cycle which further increased 215 to -1.368 µm and -1.550 µm at 80% and 100% respectively. The Rt has been observed to 216 increase when duty cycle increased from 2.125 µm to 4.299 µm at 20% and 100% duty 217 cycles respectively. 218

The Rz values were analysed for obtaining a comprehensive knowledge of the average ten-point height of the profile in the sampling length. At 20% duty cycle, the Rz was observed as 0.752μ m, which increased to 0.967μ m, 1.998μ m, 2.107μ m, and 2.857μ m for 221

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duty cycles 40%, 60%, 80%, and 100%. Therefore, it is reasonable to conclude that, with an 222 increase in duty cycle, average maximum height difference of surface increases. 223



Figure 4. Areal and Surface Roughness parameters for different Duty Cycles

Surface roughness parameters have been analysed to understand roughness charac-229 teristics in the entire surface and are shown in Table 4. The surface roughness parameter 230 calculates roughness of the whole surface whereas Areal roughness parameter will calcu-231 late roughness of the singular plane. Sa value of 20% was 0.245 µm. The Sa values in-232 creased correspondingly with duty cycle. For 40%, 60%, 80% and 100% the values were 233 0.277 µm, 0.334 µm, 0.371 µm, and 0.779 µm respectively. A similar increase was observed 234 for the Sq values of 0.529 μ m, 0.682 μ m, 0.728 μ m, 0.742 μ m, and 1.714 μ m for DC from 235 20% to 100% respectively. The average peak and average valley heights were also noted 236 and were having a similar trend as that of the Areal roughness parameters with height 237 increasing when duty cycle increased. Similarly for St and Sz a trend matching to that of 238 aerial roughness properties were observed. The maximum peak height will influence the 239 tribological properties of the surface as the peaks will restrict the complete contact of the 240 counter surface to the material [34]. Similarly, the increase in valley height will help in the 241 increased retention of lubricant, which will help in an improved tribological properties of 242 the surface [34]. 243

able 5. Skewness and Kurtosis for various duty cycles							
Skewness and Kurtosis							
Duty Cycle	Ssk	Sku					
20	8.404	124.368					
40	8.566	118.789					
60	7.171	82.631					
80	7.365	51.362					
100	5.698	46.365					

The variation of skewness and kurtosis with change in duty cycle was also analysed 248 and shown in Table 5. The skewness parameter reacts strongly to isolated deep dips or 249 extreme peaks. In the present pulse electrodeposition coating all the Ssk values are posi-250 tive which implies that the surface is skewed downward relative to the mean line. The 251 lower duty cycle samples, 20%, tends to have more peaks and filled valleys. With the rise 252 in duty cycle from 20% to 100%, skewness decreases, which implies that the number of 253 peaks in the surface decreases. 254

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The measure of sharpness of peaks on a surface can be defined as kurtosis or Sku. 255 The sharper peaks and heavier tails project positive kurtosis. The same positive kurtosis 256 can be observed in all duty cycle samples, pointing towards the relatively high peaks and 257 broader valleys at the surface. It can also be observed that with decline in duty cycle an 258 growth in kurtosis value is observed. The positive excess kurtosis value projects distribu-259 tion of more peaks and fatter valleys. That is, the distribution is having peaks close to the 260 mean value and valleys which are extremely frequent than the normal distributions. These 261 distributions are also known as leptokurtic or leptokurtotic, which will help in improving 262 the tribological properties, by helping the lubricant to retain more on the surface [35]. The 263 positive value of skewness and kurtosis values greater than 3, provides the insight that 264 samples can have better tribological properties. To substantiate these findings, bearing 265 area curves were explored and analysed. However, hardness of coating plays a similar 266 role in tribology and has to be analysed. 267

3.3. Bearing area Curve

A broad-spectrum view of roughness variation can be obtained with the help of the 269 bearing area curves which is provided in Fig 5. The variations peak-valley and the basic 270 roughness of samples with different duty cycles can be analysed with the help of the Bearing Area Curve (BAC). Percentages of peaks, MR1 and percentages of valleys, MR2 can 272 be obtained from the BAC. Furthermore, reduced valley-height, Svk, reduced-peak 273 height, Spk, and core or basic roughness, Sk can be acquired from the BAC. 274



Figure 5. Bearing area curves for different Duty Cycles

From Fig 5, it can be seen that number of peaks were maximum for samples with a 280 100% duty cycle. When an increase in the duty cycle takes place it scores reduced number 281 of peaks. The increased Rpk values imply that the surface is composed of a higher number 282 of peaks. The high peaks provide a lower contact area during the tribo testing, which will 283 result in increased contact stress. Lower surface contact area contributes to a reduction in 284 friction and wear properties during the running in stage of tribo testing. On the other 285 hand, the decrease in the Svk values represents the increased number of valleys in the 286 surface below the core surface Sk. With increasing amount of valley, the lubrication 287 retention capacity will increase. The increase in the lubrication retention capacity will help 288 reduce inter surfaces wear and friction values. Ratios of Spk/Sk and Svk/Sk is analysed to 289 simplify the process. The Spk/Sk and Svk/Sk analysis will help to acknowledge whether 290 the surface is dominated by peaks or valleys and the values are shown in Table 6. The 291 Spk/Sk values dominate the Svk/Sk for all duty cycles. The Spk/Sk values are seen to in-292 crease with increasing duty cycle; 20% having a value of 2.03. The value increases when 293 the duty cycle increases as 40%, 60%, 80% and 100% having a ratio of 2.77, 2.38, 2.24, 5.79 294 respectively. Increased number of peaks help reduce the contact area which contributes 295 to enhancing tribological properties of interfaces. Similarly, the Svk/Sk values decreases 296 when duty cycle increased. The values were 0.89 for 20% duty cycle which decreases to 297 0.54 for a duty cycle of 100% [34]. 298

Table 6. Bearing area parameters for different duty cycles									
				Bearin	g Area Para	ameters			
Duty Cycle	Rk (nm)	Rpk (nm)	Rvk (nm)	Rpk/Rk	Rvk/Rk	Mr1 (%)	Mr2 (%)	V1 (x 1013 nm3)	V2 (x 1013 nm3)
20	422.495	858.300	376.515	2.032	0.891	16.74	82.885	1.920	0.769
40	423.675	1174.255	380.045	2.772	0.897	17.97	82.910	2.525	0.7865
60	567.250	1348.270	314.545	2.377	0.555	18.49	84.415	2.820	0.576
80	685.720	1535.510	364.475	2.239	0.532	19.215	90.980	3.185	0.393
100	697.960	4040.490	376.69	5.789	0.540	19.73	92.080	9.670	0.545
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Figure 6. Bearing area parameters for different Duty Cycles

The V1 and V2 represent the material deposition profile peak area and lubricants 306 filled profile valley area, respectively. The V1 value for 20% duty cycle was 1.92 x 10¹³ nm³, 307 which increased to 2.52 x 1013 nm3 for duty cycle 40%. A steep increase in the V1 value was 308 observed at 100%, 9.67 x 10¹³ nm³. It can be concluded that the amount of the peak volume increased duty cycle increased. Whereas least amount of peak was observed at a lower duty cycle. Similar observations were seen in V2 as well. Decrease in V2 is seen when duty 311 cycle increased. The V2 was 0.76×10^{13} nm³ for 20% duty cycle which increased to 0.79 x 312 1013 nm3 at 40% duty cycle. A decrease in value was observed at 60% and 80% duty cycle 313 as 0.57×10^{13} nm³ and 0.39×10^{13} nm³ which finally increased to 0.54×10^{13} nm³ for 100% 314 duty cycle. In lieu of the surface roughness parameters, hardness values are also expected 315 to be higher for the lower duty cycle samples. 316

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3.4. Power Spectral Density

Fig 7 illustrates the plots exhibiting the disparity of Power Spectral Density (PSD) 320 with spatial frequency for duty cycles 20%, 40%, 60%, 80% and 100% for x-axis and y-axis. 321 Spatially dependent surface profiles of samples with various duty cycles, 20%, 40%, 60%, 322 80% and 100% were analysed in the present PSD analysis. A Fourier series decomposes 323 input surface profile's roughness frequency (spatial frequency). Each roughness fre-324 quency's power spectral densities are recorded and averaged for PSD function calculation. 325 Fig 7 shows results of these analyses with spatial frequency on x-axis and average rough-326 ness the RMS values on y-axis. It is evident from Fig 7 a and b that power density is high 327

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for duty cycle 100% at lower frequency range, 0-25 /mm. For the same range, 0-25 /mm 328 density decreases with decrease in duty cycle, with 20% having least roughness profile 329 variation. In both cases, amplitude is seen to decrease with increase in spatial frequency. 330 This espies that the dominating surface roughness is from mid-range and lower spatial 331 frequencies. The power spectrum is nearly smooth in all the duty cycles after a spatial 332 frequency of 60 /mm. the roughness frequency is independent of the flat portions with the 333 same average roughness values [36]. 334



Figure 7. Power Spectral analysis for different Duty Cycles samples in (a) X-axis and (b) **Y-Axis**

3.5. Nanohardness

Fig 8 shows hardness pattern influenced by changes in duty cycle. It shows that the 342 nano hardness reduced with increase in duty cycle. A significant impact was observed in 343 nano hardness with change in the duty cycle. Maximum nano hardness was observed at a duty cycle of 20% with 4.21 GPa. For duty cycles, 40%, 60%, 80% and 100% the nano hardness was observed as 3.90 GPa, 3.86 GPa, 3.19 GPa and 3.07 GPa respectively. Results indicate that duty cycle has an impact on hardness of coating.



Figure 8. (a) Nanoindentation hardness for Ni-Al₂O₃ coating at different duty cycles (b) Grain size of coatings at various duty cycles

The change in hardness can be explained by the Hall-Patch equation, relating hardness and grain size.

$$HV = HV_0 + \frac{\kappa}{\sqrt{d}}$$
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Where hardness is denoted by HV, whereas HV_0 and K are both constants, and d356represents grain size. Coatings hardness is affected by the grains size. The increase in grain357size with increasing duty cycle has already been observed earlier (Fig 2) and the grain size358is calculated using an open software ImageJ. The variation of grain size with change in359duty cycle is plotted in Fig 8 (b). The decrease in hardness with increase in duty cycle can360be attributed to Hall Patch relationship. The higher value of nano hardness was observed361for duty cycle 20% which will provide a better wear properties.362

4. Conclusions

In this study electrodeposition with varying duty cycles from 20% to 100% has been 364 employed for developing Ni-Al2O3 nanocomposite. Various Areal and surface roughness 365 properties of nanocomposite coatings have been analysed. It was observed that the rough-366 ness values increased when duty cycle increased. Both the skewness and kurtosis values 367 of surfaces were analysed and were observed that skewness decreased with increased 368 duty cycle. Similarly, with an increase in duty cycle, kurtosis was also seen to decrease. 369 However, all duty cycle were having kurtosis greater than 3 and positive skewness. Posi-370 tive skewness and higher kurtosis will help in reduction of friction, which points that 20% 371 duty cycle has the best wear properties. The nano hardness of samples was analysed and 372 was observed that lower duty cycle was having higher hardness, which helps to improve 373 tribological properties of surface. Decrease in nano hardness at higher duty cycle was due 374 to increase in grain size resulting from shorter OFF time. 375

376 Author Contributions: For research articles with several authors, a short paragraph specifying their 377 individual contributions must be provided. The following statements should be used "Conceptual-378 ization, AJ; methodology, AJ and ZK; software, AJ; validation, AJ; formal analysis, AJ; investigation, 379 ZK; resources, AJ; data curation, AJ; writing—original draft preparation, AJ, AS and ZK; writing— 380 review and editing, AJ; visualization, AS and ZK; supervision, ZK; project administration, ZK; fund-381 ing acquisition, All authors have read and agreed to the published version of the manuscript. 382 Funding: No funding has been received to conduct this research. 383 Informed Consent Statement: The authors declare no conflict of interest. 384 385 Acknowledgments: The authors would like to acknowledge Mr George Foot ASMPT SMT UK Ltd 386 for their in-kind support. 387 Conflicts of Interest: The authors declare no conflict of interest 388 389

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