

The Effect of Methane and Nitrogen Ratio on the Mechanical and Tribological Properties of Plasma Carbonitrided Stainless Steel

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Abstract: *In this work, commercial stainless steel AISI 316 substrates were plasma carbonitrided using a microwave-plasma-enhanced chemical vapour deposition (MPECVD) system. The substrates were subjected to four different methane, nitrogen and hydrogen ratios while other deposition parameters, such as microwave power, chamber pressure and substrate temperature were held constant throughout the study. The hardness and the friction coefficient of the treated layers were measured using a Micro Vicker hardness tester and a pin-on-disc tribometer, respectively. The morphology and elemental analysis of the carbonitrided layers were observed using a field-emission scanning electron microscope (FESEM) and energy dispersive X-ray (EDX) spectroscopy, respectively. The test results show the following phenomena: (a) the hardness of the plasma carbonitrided layer increases with increasing methane gas content in the methane, nitrogen and hydrogen mixtures; (b) the friction coefficient decreases with increasing methane gas content; and (c) the surface roughness increases with increasing methane gas content in the methane, nitrogen and hydrogen mixtures. These phenomena could be due to the diffusion of N and C atoms into the substrate, which resulted in the formation of carbonitrides and nitrides of iron and chromium in the stainless steel substrate. The test results also show that a nitrogen-methane-hydrogen ratio of 87:3:10 gives the best mechanical and tribological characteristics in carbonitrided specimens.*

Keywords: carbonitriding AISI 316, MPECVD, microstructure, tribology, hardness

1. INTRODUCTION

Stainless steel is widely used in the food, chemical, medical and vacuum-moulding tool industries due to its excellent corrosion and oxidation resistance at high temperature. However, stainless steel has low wear resistance and hardness, and poor tribological characteristics, which limit its usage in some engineering component applications. Plasma nitriding and carbonitriding processes are used

to improve mechanical and chemical properties such as hardness, wear resistance and anti-scuffing characteristics.¹ Plasma carbonitriding is a thermochemical processes in which methane and nitrogen are introduced into the deposition chamber under vacuum to generate a gradient of C and N in the surface region of metallic samples. Plasma nitriding and carbonitriding processes introduce more and faster nitrogen and carbon diffusion into substrates, thus allowing for shorter diffusion times and lower processing temperatures.

Carbonitriding at temperatures above 450 °C can result in the formation of CrN or CrC on the substrate surface, which binds chromium from the solid solution and thus lowers the corrosion resistance of the sample.² Introducing a large amount of hydrogen or a small amount of acetylene during the plasma process can reduce chromium precipitation, thus improving the corrosion resistance.¹ Carbonitride processing is more useful than carburisation for steel subject to wear³ and also exhibits a better corrosion resistance than that of pure nitrided and carburised layers.⁴ Blawert and his co-workers found that the carbide phases are responsible for the significant increase in microhardness as well as carbon-expanded austenite through plasma carburisation.⁵ The objective of this study was to investigate and discuss the effect of the methane and nitrogen ratios on the mechanical and tribological properties of carbonitrided stainless steel samples.

2. EXPERIMENTAL

In this work, carbonitrided samples were prepared by microwave-plasma-enhanced chemical vapour deposition (MPECVD). A commercial stainless steel sample with the following composition (wt%) was used in this study: C, 0.7; P, 0.03; S, 0.05; Mn, 1.38; Cr, 15.48; Mo, 1.79; V, 0.09; Si, 0.39; Ni, 9.68; and the remainder was Fe. Samples were marked A, B, C and D, corresponding to different methane and nitrogen contents. Other process parameters were held constant as shown in Table 1. A coin-shaped sample with a diameter of 30 mm and thickness of 5 mm was polished to a surface finish of 6 µm using SiC emery paper and emery cloth with diamond paste. Prior to the deposition process, the substrate was ultrasonically cleaned with acetone for 30 minutes to remove any contaminations on the substrate surfaces. The samples were then placed in the deposition chamber of a MPECVD system for carbonitriding.

Table 1: Plasma carbonitriding process parameters.

Deposition parameters	A	B	C	D
CH ₄ :N ₂ :H ₂ (%)	1:89:10	2:88:10	3:87:10	4:86:10
Microwave power (kW)	1.5	1.5	1.5	1.5
Frequency (GHz)	2.45	2.45	2.45	2.45
Substrate temperature (°C)	450	450	450	450
Chamber pressure (torr)	1×10^{-4}	1×10^{-4}	1×10^{-4}	1×10^{-4}

After the carbonitriding process, the sample was subjected to microhardness measurement, friction tests, AFM observations and microstructural examinations. A Vickers microhardness tester model AKASHI MVK-E was used to measure the hardness of the sample. The measurement was conducted using a 25-g load with a diamond tip. The tribological characteristics of the sample were evaluated using a pin-on-disc tribometer model CSEM at a sliding speed of 3.50 cm/s over a distance of 300 m with a load of 10 N under dry friction conditions. An alumina ball 6 mm in diameter was used as a static partner in this test. The friction coefficient versus sliding distance was recorded and then examined to determine the frictional characteristics of the sample.

The carbonitrided samples were subjected to friction tests, microhardness tests, AFM observations and microstructural examinations. The tribological properties of the treated samples were evaluated using a pin-on-disc tribometer model CSEM at a sliding speed of 3.50 cm/s over a distance of 300 m with a load of 10 N under dry conditions. An alumina ball 6 mm in diameter was used as a static partner in this test. The friction coefficient versus sliding distance was recorded and then examined to determine the frictional characteristics of the samples. A Vickers microhardness tester model AKASHI MVK-E was used to measure the hardness of the samples. The measurement was conducted using a 25-g load with a diamond tip and Knoop indenter.

Samples for AFM measurement were cut to a size of 10 mm × 10 mm × 5 mm and then ultrasonically cleaned using ethanol for 15 minutes. AFM measurement analysis was performed using AFM Shimadzu equipment. Samples for surface examination were ultrasonically cleaned for 30 minutes using ethanol. Samples for subsurface examination were cut, sectioned, mounted and polished to a surface finish of 1 μm and finally etched with Adler etchant. The microstructure of the carbonitrided layer was analysed by field-emission scanning electron microscopy (FESEM, LEO 1525) with an energy dispersive X-ray analyser attachment.

3. RESULTS AND DISCUSSION

3.1 Microstructure

Microstructural examination revealed that N and C were mainly incorporated into the existing iron lattice as interstitial atoms or as a finely dispersed alloy precipitate in the diffusion layer, as shown in Figure 1. It was observed that smaller nitride and carbide grain precipitates were deposited onto the substrate surface when a methane and nitrogen ratio of 1:89 was introduced into the chamber (Figure 1a). As the methane gas content increased to 2%, the agglomerated nitride and carbide precipitates formed on the substrate surface.

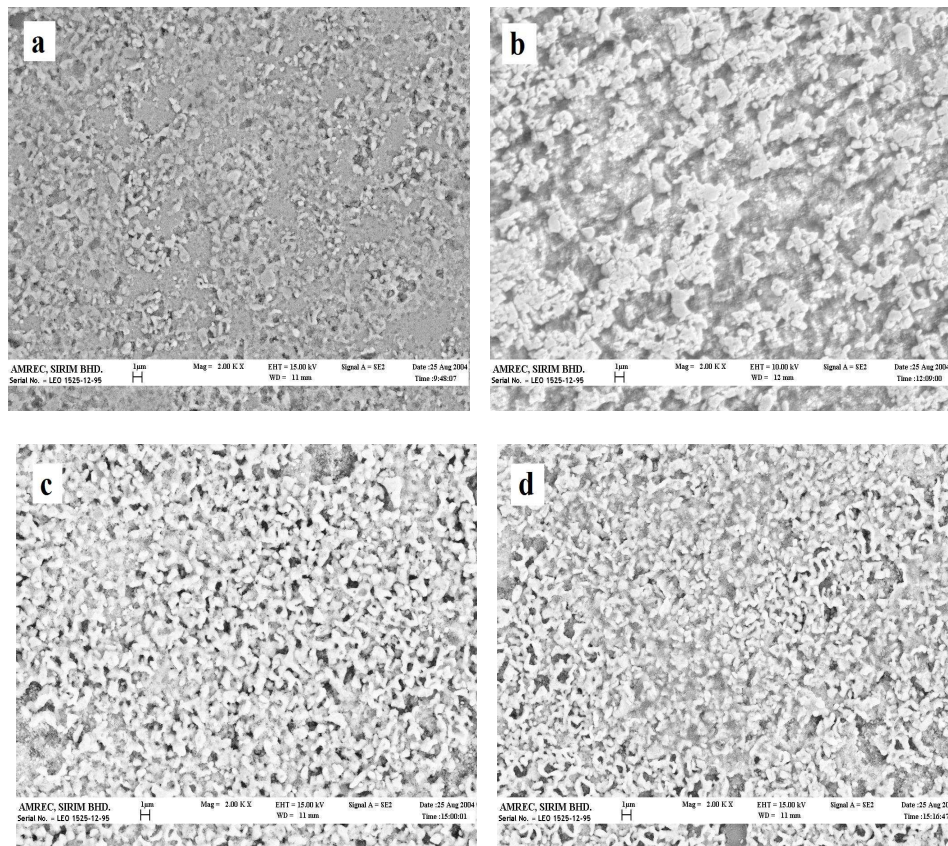


Figure 1: SEM surface morphology of the carbonitrided samples: (a) sample A, (b) Sample B, (c) Sample C, (d) Sample D.

Subsequently, when the methane content was increased to 3%, the solubility limit of nitrogen and carbon in the ferritic matrix was reached. Finally, coherent nitride and carbide precipitates were formed on the carbonitrided layer, covering the substrate surface with pores, as shown in Figure 1c. At a methane content of 4%, the formation of nitride and carbide was saturated, resulting in the formation of a smooth carbonitrided layer (Figure 1d).

Figure 2 shows that the carbonitrided layer was dense and uniformly diffused into the substrate material. The diffused carbonitrided layers increased with increasing methane percentage up to 3% and then decreased as the methane content increased to 4%. The decrease in the carbonitrided layer thickness is thought to be a result of the saturated formation of metal nitride and carbide as the methane content increased to 4% (Figure 1d).

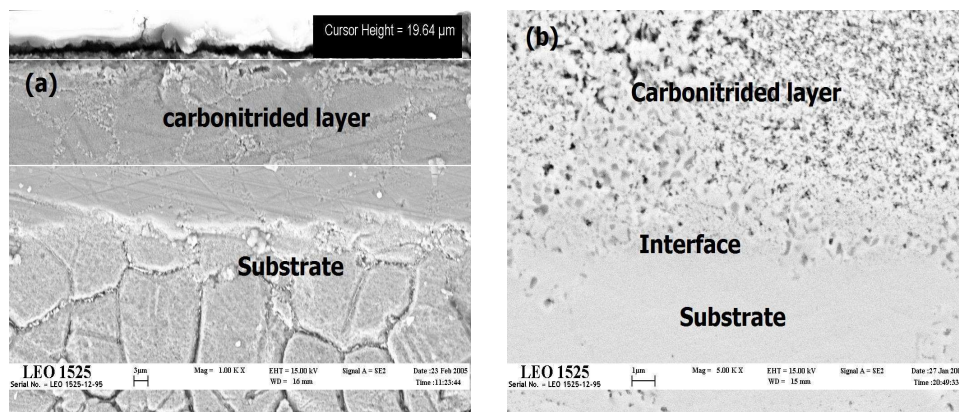


Figure 2: SEM cross-section morphology: (a) sample C ($\times 1k$), (b) close-up view at the interface ($\times 5k$).

Figure 3 shows the energy dispersive spectroscopy line profiles of the carbonitriding layer. It can be seen that carbon and nitrogen were observed to have diffused into the subsurface of the stainless steel substrate. This resulted in the formation of nitrides and carbides of iron and chromium in the stainless steel substrate, leading to the higher hardness and wear resistance of the carbonitrided samples.

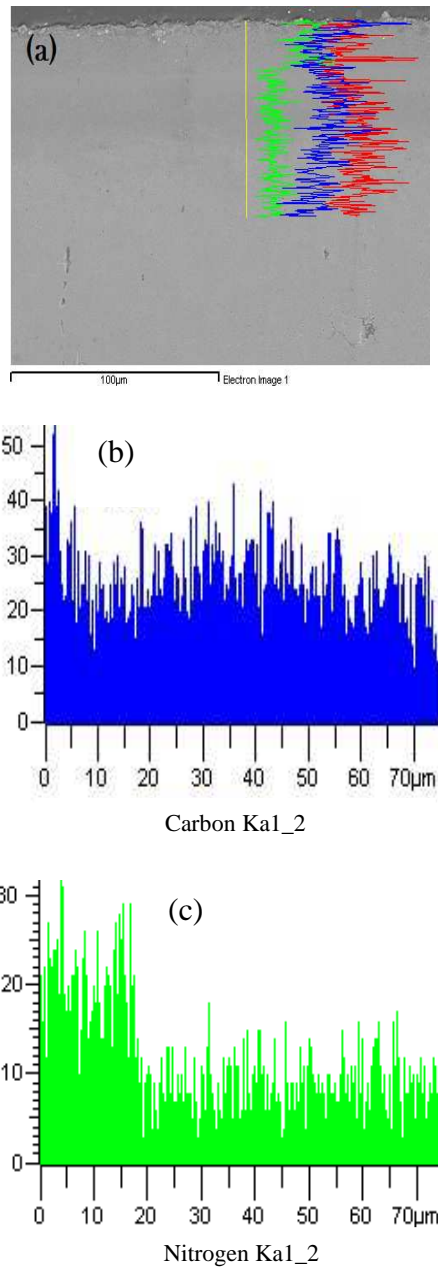


Figure 3: EDS analysis on the carbonitriding layer of sample D: (a) cross-section line scan, (b) EDS Spectrum of carbon, (c) EDS Spectrum of nitrogen.

3.2 Microhardness

Figure 4 shows the microhardness of a carbonitrided sample at a load of 25 g. The test results show that the plasma carbonitriding process increased the microhardness of the sample depending on the nitrogen-methane-hydrogen ratio. The hardness of the untreated commercial stainless steel substrate was 207.9 HV_{0.025}. Sample C, which featured 3% methane gas, was the hardest, with a reading of 752.2 HV, whereas Sample A, which used 1% methane gas, showed the lowest hardness value of 600.4 HV. The microhardness increased with increasing methane gas content up to 3%, reaching a maximum hardness of 752.2 HV, which was then reduced to 642.8 HV when the methane gas content increased to 4%. In this process, the carbonitriding reaction not only occurs at the surface but also in the subsurface region of the specimen owing to the diffusion of N and C atoms into the substrate. This phenomenon resulted in the formation of carbonitrides and nitrides of iron, chromium, etc., in the stainless steel substrate, thus greatly enhancing the surface hardness of the treated sample.

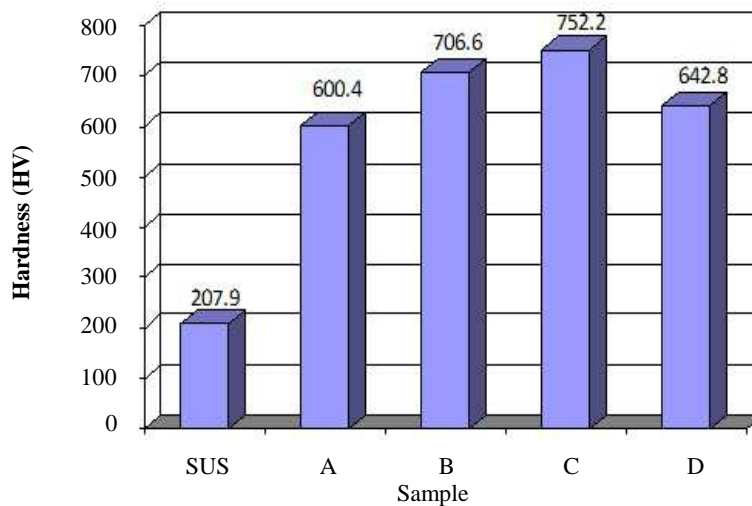


Figure 4: Hardness of untreated and carbonitrided stainless steel coupon.

Knoop indentation produces a smaller indentation than Vickers hardness testing; thus, the hardness profile of a cross-section of the carbonitrided layer can be observed. The load used for this measurement was 50 g, and measurements were taken at intervals of 10 microns. It can be seen from Figure 5 that the hardness of the near-surface region, about 10 microns from the surface, recorded the highest reading, which subsequently decreased as the distance from the surface increased. This hardness profile can be used to monitor the depth of

carbon and nitrogen diffusion into the titanium substrate. For the sample carbonitrided with 2 and 3% methane, the diffusion layer was estimated to be about 150 microns from the surface (Figure 9). For the sample carbonitrided with 1% methane, the diffusion layer was estimated to be about 100 microns from the surface. This shows that the diffusion depth of Sample A is lower compared to the sample carbonitrided at a higher methane gas content.

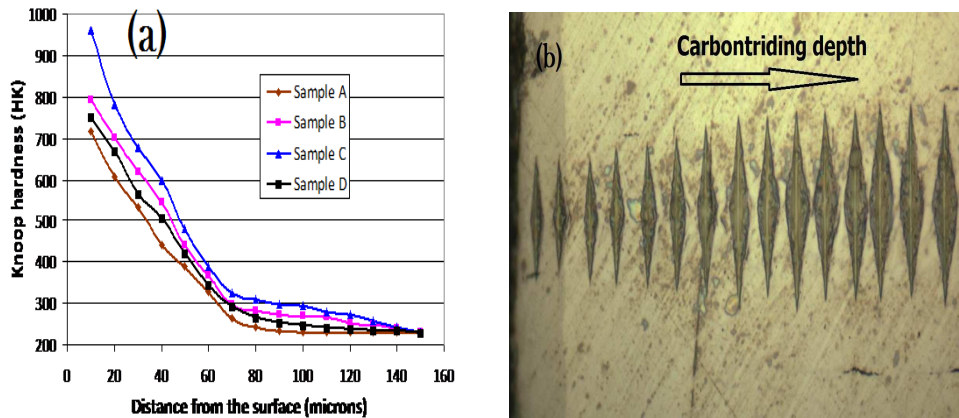


Figure 5: Knoop microhardness: (a) microhardness profile, (b) microhardness indentation on sample C.

3.3 Surface Roughness

Figure 6 shows a 3D surface model of the carbonitrided surface obtained by atomic force microscopy under different nitrogen-methane-hydrogen ratios. When a methane-nitrogen-hydrogen ratio of 1:89:10 was introduced into the chamber (Figure 6a), nitrogen and carbon atoms condensed into suitable nuclei sites. A strong substrate/coating atom interaction resulted in low adatom mobility and a high density of nuclei, producing smaller grain sizes in the carbonitrided layer and a smoother surface. As the methane content increased up to 3%, high adatom mobility and the ease with which nuclei spread laterally increased the formation of pores at the interface (Figure 6c). This phenomenon resulted in an increase in the surface roughness of the carbonitrided layer, as shown Figure 7. At a methane content of 4%, the carbonitrided layer became smoother as a result of the saturation of nitride and carbide formation.

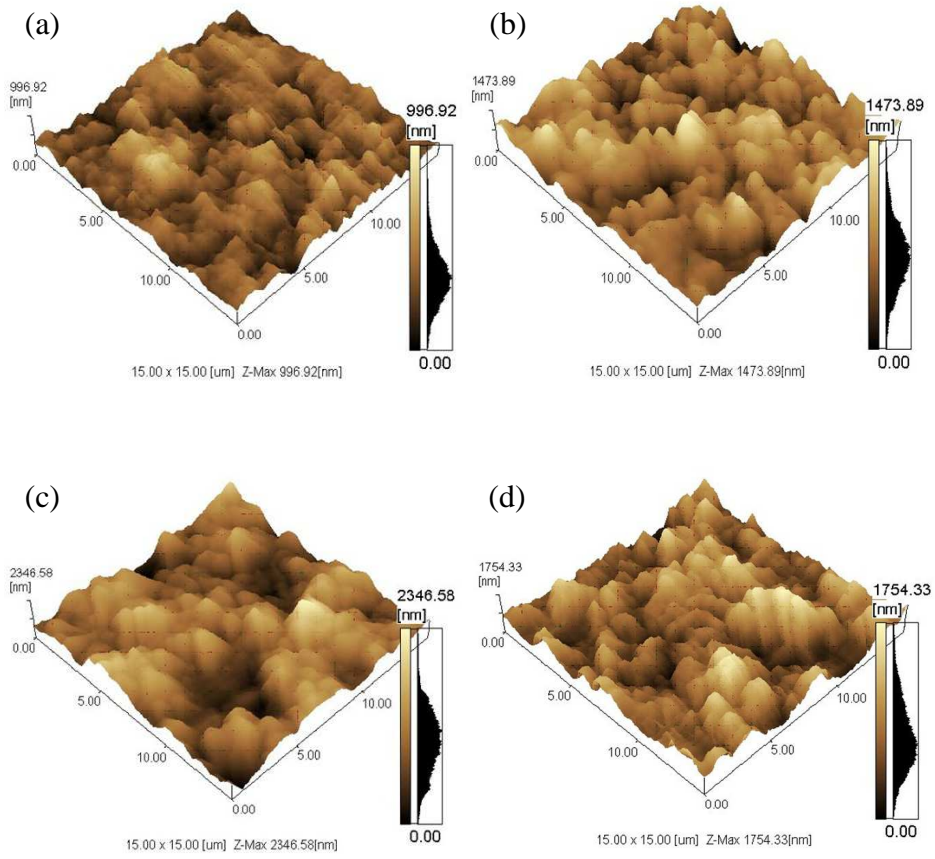


Figure 6: Surface roughness of the carbonitrided surface.

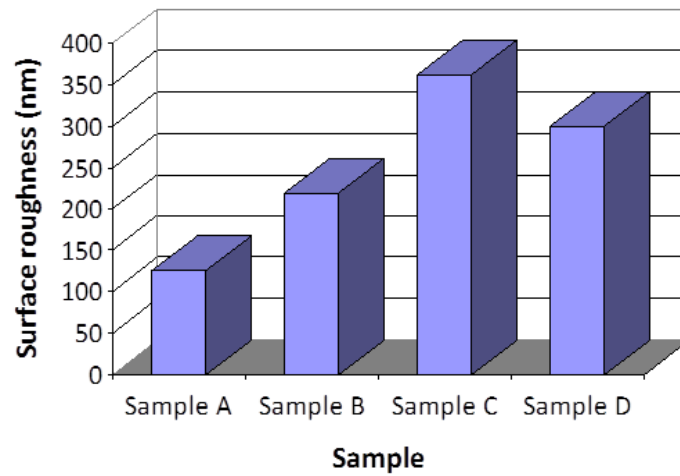


Figure 7: Surface roughness of the carbonitrided surface.

3.4 Friction and Wear

Figure 8 shows that all carbonitrided samples exhibited lower coefficients of friction (COF) compared with the untreated sample; in addition, the COF was observed to depend on the methane content introduced into the deposition chamber. It was observed that the decrease in the COF with increasing methane content may be due to the diffusion of an excess amount of carbon as shown in Figure 8. The higher the methane gas content that was introduced into the chamber, the higher the amount of carbon that diffused into the substrate became, which eventually reduced the friction coefficient due to the formation of graphite as a solid lubricant.

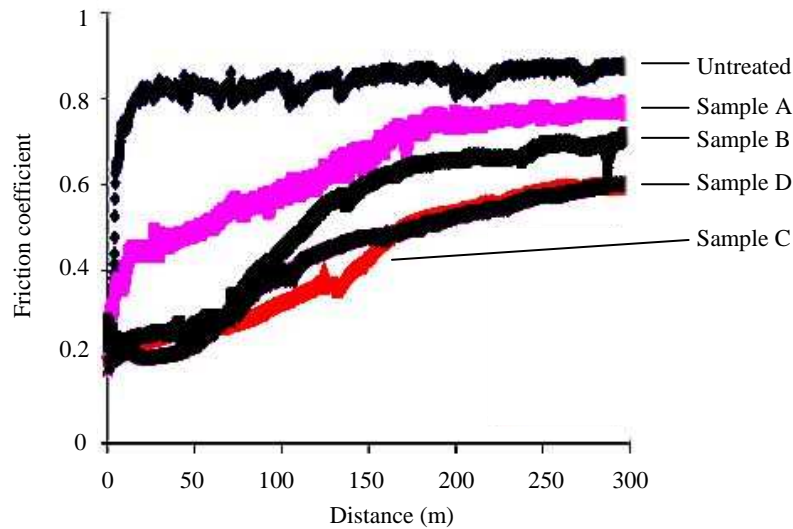


Figure 8: Graph of Friction Coefficient against Sliding Distance.

In the early stage of sliding, a static alumina ball was observed to slide along the carbonitrided layer with a COF of 0.2. As the sliding progressed, the carbonitrided layer started to deteriorate, thus increasing the friction coefficient value depending on the methane and nitrogen contents. The higher the methane content that was introduced into the chamber, the lower the COF became. Figure 8 also shows that the COF of the carbonitrided samples were still lower than the COF of the uncoated sample, even after a distance of 300 metres. This shows that the carbonitrided layer of the carbonitrided samples remained undamaged. If the carbonitrided layer had been damaged and exposed the untreated surface, the friction coefficient reading would have been approximately 0.8, which was the COF reading of the untreated sample. This indicates that the carbonitrided layer supported good adhesion between the carbonitrided/substrate interface and, at the same time, reduced the friction coefficient.

Figure 9 shows that the wear track of Sample C had the shortest wear track width, compared to the other samples. This shows that Sample C is superior in terms of wear resistance. This can be attributed to its higher surface hardness (Figure 4) and lower friction coefficient (Figure 8). When the methane content was increased to 4%, the wear track width was observed to become larger, which was thought to be due to the saturation of nitride and carbide formation on the surface (Figure 1d and 6d); this subsequently reduced the surface hardness (Figure 7). Based on the above observations, it could be concluded that Sample C, with a methane-nitrogen-hydrogen ratio of 3:87:10, provided the optimum results.

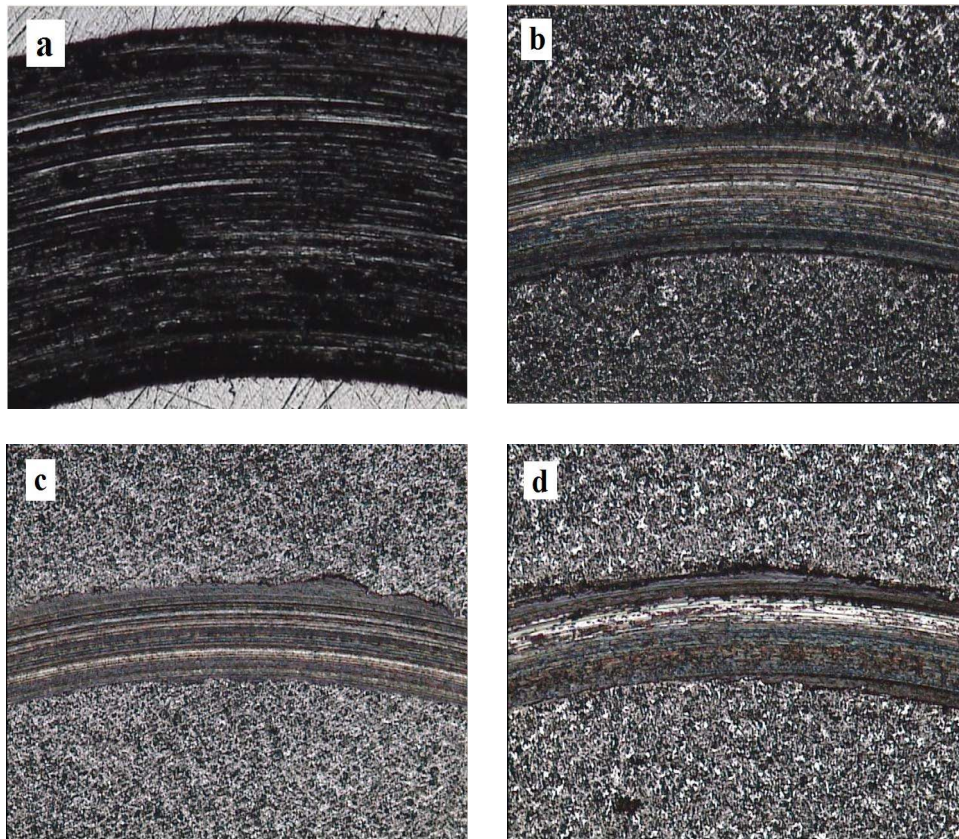


Figure 9: Optical micrographs of worn surfaces (x 20); (a) untreated, (b) sample A, (c) sample C, (d) sample D.

4. CONCLUSION

A carbonitriding layer was successfully deposited onto a stainless steel substrate using MPECVD system. Test results show that the surface hardness and wear resistance of the carbonitriding layer increases with increasing methane content up to 3% and then is slightly reduced when the methane content increases to 4%. A methane content of 4% results in the saturation of metal carbide and nitride formation. It was also observed that the formation of a carbonitriding layer reduces the COF, though the rate of reduction depends on the gas mixture ratio. The higher the methane gas content introduced into the deposition chamber is, the lower the COF will become. Based on the optimum mechanical and tribological results, it could be postulated that the optimum methane-nitrogen-hydrogen ratio is 3:87:10.

5. ACKNOWLEDGEMENT

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6. REFERENCES

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