Elevated Temperature Plasma Nitriding of CrMoV Tool Steel for the Enhancement of Hardness and Wear Resistance

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Elevated temperature plasma nitriding of Cr-Mo-V based tool steel was performed by varying the treatment time to enhance hardness and wear resistance. Steel samples after metallographic polishing were placed on the conducting substrate holder in the nitriding reactor and evacuated to 0.5 Pa pressure. The sample holder was then negatively biased at 250 V to accelerate the ions toward the surface of the samples. A gas mixture of N_2 and H_2 was then passed into the vacuum chamber to generate the plasma. After plasma generation nitriding was performed at variable temperatures 500°C and 550°C for 6 and 10 hrs. Then X-ray diffraction (XRD) and Scanning Electron Microscope/Electron Dispersive Spectroscopic (SEM/EDS) studies were followed to understand the structural modifications. XRD analysis predicted the presence of iron nitrides whereas SEM/EDS had shown the presence of N availability from the surface to the core of the steels. Following the structural characterization hardness and wear resistance were measured by using Vicker's microhardness tester and ball-on-plate method respectively. It was found that the hardness, case depth, and wear resistance of the steel were significantly enhanced mainly due to nitrogen solid solnution and nitride formation. Thus, it has been proved that a longer time or higher temperature of nitriding may be beneficial for such improvement.

Keywords: Plasma nitriding, 90CrMoV8 Tool Steel, Electron Microscopy, Wear, X-ray Diffraction.

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1. Introduction

Recently, tool industries realized the premature failure of tools due to electrochemical and mechanical degradation. Cutting tools encounter frequent frictional forces in the service conditions and thus causing damage to the surface. Especially wear and tear is the commonly found surface degradations that cause premature failure of the tools and thus challenge their longevity in the service life. To avoid the disruption of the industrial processes immediate replacement of the tools is necessitated. This leads to a huge loss of material and cost along with the loss of time and energy. In order to prevent premature failure of the tools and enhance their longevity the surface must be protected against these degradations. For the protection of the material surface, deposition of hard and corrosion-resistant layers by following physical and chemical vapour deposition had long been practiced (Ref. 1– 4). However, the delamination of these layers due to inadequate adhesion limits its widespread applications. It has also been realized that these processes require a high temperature and longer treatment time, use of corrosives, explosives, and toxic precursors which could be challenging to the safety of the workers and the environment.

Surface engineering of materials by following laser and plasma processing had been recognized as a better solution to overcome the problems due to layer deposition. It has been reported earlier that selective laser melting produced a duplex layer of Ti6Al4V on 316L stainless steel. The duplex structure so formed was then exposed to glow discharge plasma oxidation process at 650^{o}C and 750^{o}C for 1 and 4 hrs. It was shown that the hardness and wear resistance of the duplex structure were better than that of 316L stainless steel due to the formation of titanium oxide phases and diffusion zone depth (Ref. 5). Hilmi et al. (Ref.6) also worked on selective laser melting to form Ti6Al4V on 316L stainless steel and then followed oxidation in plasma atmosphere. TiO_2 layer was formed on the surface of the Ti6Al4V/316L duplex structure to several layer thicknesses. In this study, it was shown that the plasma oxidized layer has better corrosion resistance in simulated body fluid solution than that of 316L stainless steel. The improvement was better when oxidized at the higher temperature of 750^{o}C for 4 hrs.

The present study is focused on plasma processing to engineer the surface for improved hardness and wear resistance without employing any coating techniques like physical and chemical vapour deposition. Plasma nitriding as one of the plasma processing techniques is an eco-friendly and efficient process had been recognized as a better solution for the improvement of hardness and wear resistance properties (Ref. 7 -10). Recently, 90CrMoV8 alloy steel used for making cutting tools has drawn the attention of the tool industries. Though, this steel retains its mechanical properties over a wide range of temperatures, however not been accepted for wider applications. The service life of the parts/tools made up of this steel is severely affected in its applications in wood machining where the parts are exposed to an environment causing wear and corrosion. Wear and corrosion synergistically degrade the tools and reduce their service life. Hence for its widespread applications, the enhancement of wear and corrosion-resistant properties is highly desirable. It has already been shown by Manee et al. (Ref. 11) that the wear and corrosion resistance of 34CrNiMo6 low alloy steel can be highly improved by modifying the surface following plasma nitriding. Rad et al. (Ref. 12) had shown improved resistance to wear after plasma nitriding. Some other workers also had shown improved wear resistance after plasma nitriding (Ref. 13 – 17).

In the process of nitriding nitrogen diffuses into the near-surface region of the metallic materials resulting in the formation of hard and wear resistant nitrided layer without depositing the layer on the surface. It is possible by conventional gas nitriding or plasma-assisted nitriding. However, plasma nitriding has received more attention than conventional gas nitriding due to more controllability and cost-effectiveness. So far, various types of steel had been treated by plasma nitriding process for the achievement of desirable properties (Ref. 18 – 21). However, less is known about the nitriding of 90CrMoV8 steel and its effects on wear, corrosion, and fatigue resistance. Corinne et al. (Ref. 7) reported the hardness improvement after plasma nitriding of the same steel. In their work, the hardness of the steel was improved to around 1150 H_v but no significant improvement in corrosion resistance. This study was limited to plasma nitriding for the improvement of hardness only but its effect on wear resistance was left. Later Rao et al. (Ref. 22, 23) attempted nitriding of the same steel and showed an improvement in hardness and corrosion resistance after nitriding. Trinadh et al. (Ref. 24) and also Bhadraiah et al. (Ref. 25 – 27) realized the improvement of hardness and corrosion resistance of the same steel nitrided at the lower temperature of 450 and upto 500^{o}C.

As mentioned above the improvement of hardness of plasma nitrided 90CrMoV8 steel had been reported however, to our knowledge, so far there is no information regarding the improvement of wear resistance. Effects of elevated temperature plasma nitriding above 500^{o}C - 550^{o}C where the risk of tempering may deteriorate the hardness and wear resistance have not been studied much. Corinne et al. (Ref. 7) reported the plasma nitriding of this steel for the improvement of hardness but not the wear resistance. BOUZID et al. (Ref. 28) worked on the CrN deposition by following the magnetron sputtering method for the improvement of the wear resistance of the same steel. Aouadi et al. reported the wear resistance of 90CrMoV8 steel after coating with the CrN layer by following magnetron sputtering technique (Ref. 29).

Plasma nitriding modifies the surface with enhanced hardness and corrosion resistance with no risk of delaminations of layer as found in PVD and CVD processes hence it may be useful for the surface engineering of steel for its widespread applications. The present study was focused on elevated temperature plasma nitriding of 90CrMoV8 steel for the enhancement of hardness and wear resistance properties.

2. Materials and Methods

Samples of dimension 10 mm × 10 mm × 5 mm were cut from a big steel sheet after the hardening and tempering heat treatment processes. The compositional analysis can be presented in Table1 as below:

Table 1: **Chemical composition of 90CrMoV8 steel**

Elements	Cr	Si	Mo	Mn	C	V	Fe
Content (wt.%)	8.0	1	1.5	0.5	0.5	0.5	balance

Plasma Nitriding Processing

All the steel samples were placed on the sample holder in the reactor chamber after metallographic polishing and ultrasonic cleaning.

The sample holder was connected to a D.C. power supply for biasing it negatively. These samples were kept biased at -250V. To the sample holder, an external heater was connected for temperature control. For recording the temperature a thermocouple was connected to the sample holder. The reactor chamber was evacuated by using a combination of rotary and diffusion pumps. It was pumped down to 0.5 Pa pressure before feeding the plasma-generating gases. Then Ar gas was fed into the chamber and generated the Ar plasma. Ar+ ions from the plasma were bombarded on the surface of the samples for the removal of native oxide and dirt/greasy materials.

Ion bombardment and external heating raised the temperature of the samples to achieve the desired temperature. Once the desirable temperature was attained Ar+ bombardment was stopped and N_2 and H_2 (4:1) gases were filled up to 550 Pa working pressure. Plasma was then triggered and the nitriding cycle was initiated. At 500 and 550^{o}C, nitriding had been performed by varying the processing time between 6 and 10 h. Steel samples corresponding to treatment at 500 for 10 h, 550^{o}C for 6 and 10 h are represented hereafter as S31, S29, and S28 respectively. Plasma nitriding parameters are summarized and represented in Table 2.

Table 2: The parameters of plasma nitriding

Sample code	**S30**	**S28**	**S29**
N_2:H_2 Gas ratio	80:20	80:20	80:20
Initial Pressure (Pa)	0.5	0.5	0.5
Working Pressure (Pa)	550	550	550
Voltage (negative bias) (V)	250	250	250
Temperature (°C)	500	550	550
Time (h)	10	10	6

Characterization

To understand the structural modifications the bare and the nitrided steels were subjected to XRD studies (utilizing an *X-ray diffractometer* (XRD - INEL CPS 120) with a radiation source of Co-*kα* (λ = 0.17902 nm)). After XRD, all the steel samples were cut across the cross-section, mirror polished, and etched with Villela's reagent. Then subjected to SEM and EDS (SEM JEOL, JSM 5900) analyses for the microstructural characterization and elemental availability.

After structural characterization, the hardness of all the nitrided steels along with the bare steel was measured by using a Vickers microhardness tester (LECO MST 210) at an applied load of 50 g. All the measurements were repeated 6 times to the accuracy level within ~ (±) 20 H_v and then the hardness vs. depth profile was plotted.

The wear study was performed with a ball-on-plate wear tester (TR-208-M1, Duccom Instruments Pvt. Ltd.) for 10 minutes each on the surface of the nitrided and bare steels. A dry sliding condition was employed for the wear test which was carried out with a 10 kg load and 15 rpm speed on a 4 mm track diameter resulting in a sliding speed of 3.14 mm/s. As the counter body, a diamond cone (Rockwell diamond geometry) was employed. Wear depth vs. sliding distance plots were obtained from the tests. For each sample, tribological tests were carried out twice and the deviation in the final wear depth was calculated in % of total wear depth. If the variation was less than 5% then the sliding wear vs. wear depth plot having lower noise was taken for the manuscript. For all the samples, two tests were sufficient due to less than 5% deviation. Moreover, the wear tracks of the samples whose data are provided were analyzed by SEM and EDS to understand the wear mechanism and to find any preferential chemical change due to the wear damage respectively.

3. Results and Discussion

3.1 X-ray diffraction analyses and phase formation

Nitrided steels were exposed to detailed XRD and SEM/EDS analyses to understand the phase formation. Diffraction patterns of the S0 (bare steel) revealed the Fe peaks ((110), (200), and (211)) as shown in Fig. 1. Steel nitrided at 550ºC for 10 h (S29) had shown the peaks of Fe-nitrides → Fe_4N (γ') and $Fe_{2\text{-}3}N$ (ε_N). Fe_4N (γ') and $Fe_{2\text{-}3}N$ are known to improve the hardness and wear resistance of the steel (Ref. 26, 27). Low-intensity peaks of Cr-nitrides also appeared after nitriding at a higher temperature. As the Cr concentration is 8.0% in the steel, it could be enough to produce the CrN phase after nitriding at the higher temperature of 550ºC. The presence of these nitrides is attributable to the improvement in the hardness of the steel.

Fig. 1 shows the intensity of γ' (Fe_4N) peak is lower than that of the εN peaks. It may also be observed that the peak intensities of εN and the γ' (Fe_4N) phases increased with the increase in nitriding temperature. Hence, it may be concluded that higher-temperature nitriding is beneficial more than nitriding at a lower temperature for enhancing wear resistance. A careful observation of Fe peaks indicates the dilation of Fe peaks. This could be due to the nitrogen over-saturation and hence stress generation in the crystal lattice leading to the improvement in the hardness and wear resistance.

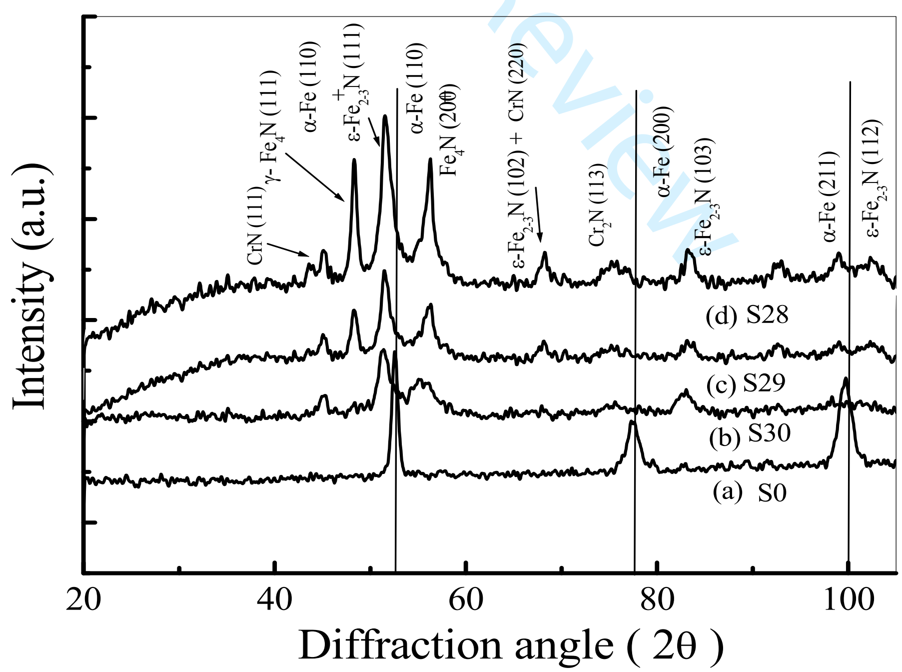

Fig. 1 XRD using *Co-K_α radiation* source unfolds the Fe peaks for (a) S0 (bare steel) and Fe – nitrides for the (b) S30, (c) S29, and (d) S28 nitrided steels.

In S29 steel, which was nitrided for 6 h at 550^{o}C, a shift of the Fe (100) peak from 52.6^{o} to 51.5^{o} was found (Fig. 2). S28 steel nitrided for a longer time of 10 h has also shown a shifting of Fe (100) peak to a lower angle. This peak shifting was earlier shown by Bhadraiah *et al.* (Ref. 23) for the steel nitrided at this process conditions. In the latter case, the peak has been shifted to 51.7^{o}. Though both the nitrided steels have shown the peak shifting to a lower angle, the extent of shifting is comparatively more but not significant for the steel S29 i.e. nitrided for a shorter duration of 6 h. The peak shifting indicates the stress generated could be due to the nitrogen inclusion in the crystal lattice. Nitriding for a shorter duration may thus lead to stress generation more than that after a longer duration of nitriding. This observation evidences the diffusion of nitrogen is more into the bulk of the steel after 10 h nitriding. Hence, nitrogen accumulation at the surface level is less thus causing lesser stress than shown by S29 steel treated for 6 h. In the latter one, nitrogen accumulation could be more at the surface level as diffusion of nitrogen is comparatively less.

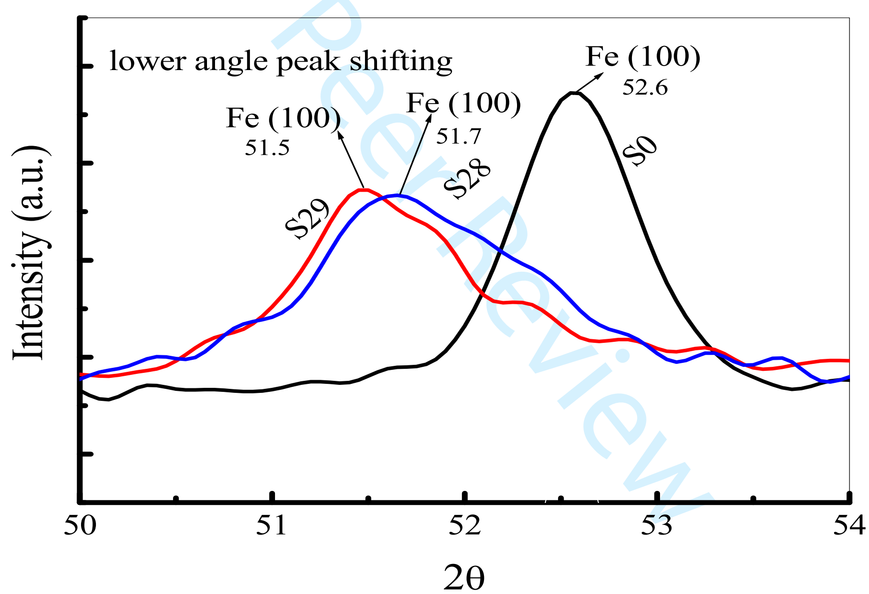

Fig. 2 Representation of shifting of Fe (100) peak of the bare steel S0 to lower angles after nitriding at 550^{o}C for 6 (S29), and 10 h S28 (Ref. 25).

Moreover, stress generation is known to influence fatigue, corrosion, and wear resistance properties. In Fig. 2, it is obvious that both the nitrided steels have higher stress when compared with the bare steel. Also, the S29 steel has more stress accumulation when compared to S28 steel. This means the retention of nitrogen concentration may be more which may lead to the generation of more nitrides also. It may be suggested here that the stress generated in the nitrided steels may be responsible for the improved wear resistance. When compared to S29 steel, the stress accumulation is less pronounced in S28 steel which could be the possible reason why S29 steel exhibited better resistance to wear. However, the idea of stress generation is yet to be confirmed by further experimental evidences. This part of the work is beyond the scope of the present studies and remains for future work.

3.2 Scanning Electron Microscopy (SEM) with Energy-Dispersive X-ray Spectroscopy (EDS)

One of the nitrided steels S28 had been selected for the microstructural and elemental characterization using SEM and EDS across the cross-section. After polishing and etching with Villela's reagent it was analyzed under SEM and EDS. It is seen from Fig. 3(a) that a very thin white layer has been formed at the top of the surface which may contribute to the corrosion resistance but maybe because of its brittle nature deteriorating the wear resistance.

From Fig. 3(b) it is clear that the N concentration is maximum at the top of the surface and gradually decreases towards the core of the steel. It is expected that more the nitrogen concentration more will be the Fe-nitride formation and also the stress generation. This may cause greater resistance to wear than that of steel with low nitrogen concentration in the solid solution. It has also been revealed from Fig. 3(b) that the layer with the nitrogen inclusion is more than 100 µm which indicates the range of case depth and in turn the protective layer.

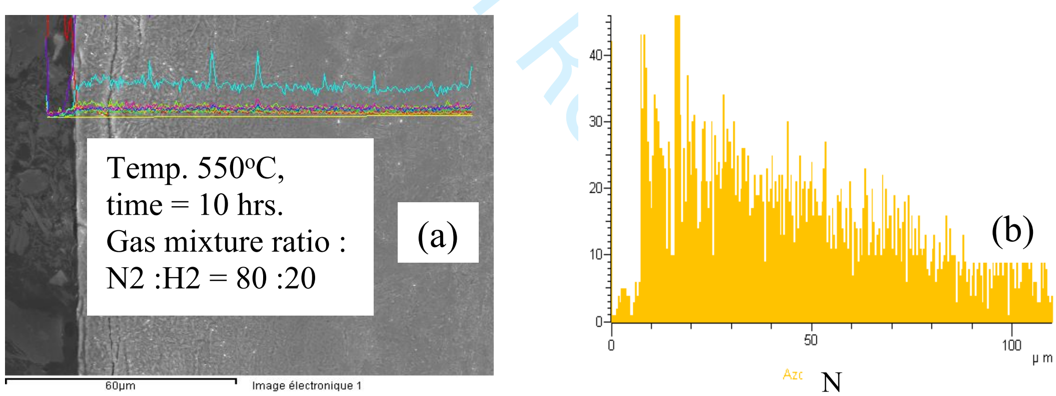

Fig. 3 Cross-section of S28 steel from the surface towards the core observed under SEM: (a) microstructure and line scan across the cross-section, and (b) the elemental availability of N from surface to the core.

3.3 Analysis of the surface hardness following microhardness measurements

To understand the effects on hardness, all the steel samples before and after nitriding were subjected to microhardness measurement. Fig. 4(a) represents the microhardness profiles of the S28 and S30 steels.

It is observed from Fig. 4(a) that the maximum hardness of S30 steel at the near-surface level is ~ 1260 ± 10 HV0.05 which is significantly higher than that of ~ 657 ± 20 HV0.05 of the bare steel. It can be observed that there is a fall of hardness from the surface toward the depth of the steel. At ~137 μm depth the hardness had fallen to ~ 707 HV0.05 which is ~ 50 HV0.05 more than that of the bare steel. However, with the rise in temperature to 550°C for the same duration of 10 h for S28 steel, the depth was increased to ~ 152 μm. The increase in temperature caused the nitrogen to diffuse more inside the core and thus resulting in the formation of a wider case depth. However, the treatment at the higher temperature of 550°C for a longer time may result in the tempering of the steel which reduces the hardness. This can be observed in Fig. 4(a), where the hardness profile of S28 steel goes below the base hardness to some extent (after a distance of around 160 μm from the surface). The tempering effect may also be the reason for a lower surface hardness of S28 than that of S30 steel.

Fig. 4(b) displays the microhardness *vs.* depth profiles of the steel nitrided at a fixed temperature of 550°C for different treatment times of 6 h (S29) and 10 h (S28). It is noticed that with the increase in treatment time a wider case depth has formed. It is revealed that ~ 121 μm case depth has formed after nitriding at 550°C for 6 h treatment. This case depth is lesser than the case depth ~ 137 μm formed after nitriding for a longer time of 10 h but at a lower temperature of 500°C (S30). Thus, it is concluded that nitriding at a higher temperature of 550°C for a shorter duration of 6 h can produce a case depth lesser than that produced after lower temperature nitriding at 500°C but for a longer duration of 10 h. Moreover, a wider nitrided layer can be seen after nitriding at the higher temperature of 550°C.

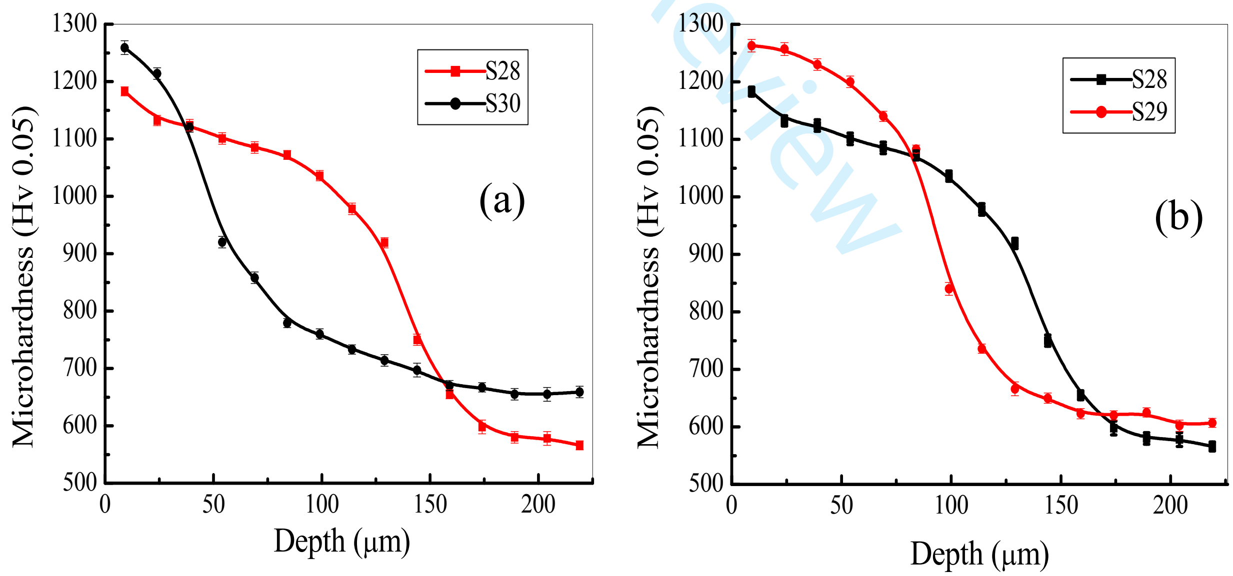

Fig. 4 Representation of microhardness *vs.* depth profiles of (a) S30 and S28 steels (similar to CM5510 as shown in (Ref. 25)), and the nitrided steels (b) S28 and S29 (HV0.05 for the bare steel (S0) is ~ 657 HV0.05).

The fall in the hardness is not that rapid in the case of S29 steel as can be seen in the S30 steel nitrided at 500^{o}C for 10 h. When the treatment time increased to 10 h at the higher temperature of 550^{o}C (S28) a further increase in the case depth was observed.

However, this is to be noted here that the maximum hardness at the near-surface region for the S28 steel is ~ 1184 HV0.05 which is lower than that found in S29 steel which is ~ 1265 HV0.05. This indicates that the increase in treatment time favours nitrogen diffusion more into the core and thus retains less concentration of nitrogen in the surface region. Nitrogen dissolution in the solid solution is more in S29 steel which has raised the compressive stress more than that found in the other steel S28 treated for a longer duration of 10 h. It may also be possible to generate more amount of Fe - nitrides resulting in an improvement in hardness. However, in support of compressive stress generation, further experimental evidence is needed.

3.4 Tests for Wear Resistance and analysis

Fig. 5 displays the sliding distance *vs*. wear depth of all the samples as obtained from the wear testing equipment. To compare the wear response of the samples (bare steel and nitrided at different conditions), these plots were smoothened and stacked in a single plot as displayed in Fig. 6(a).

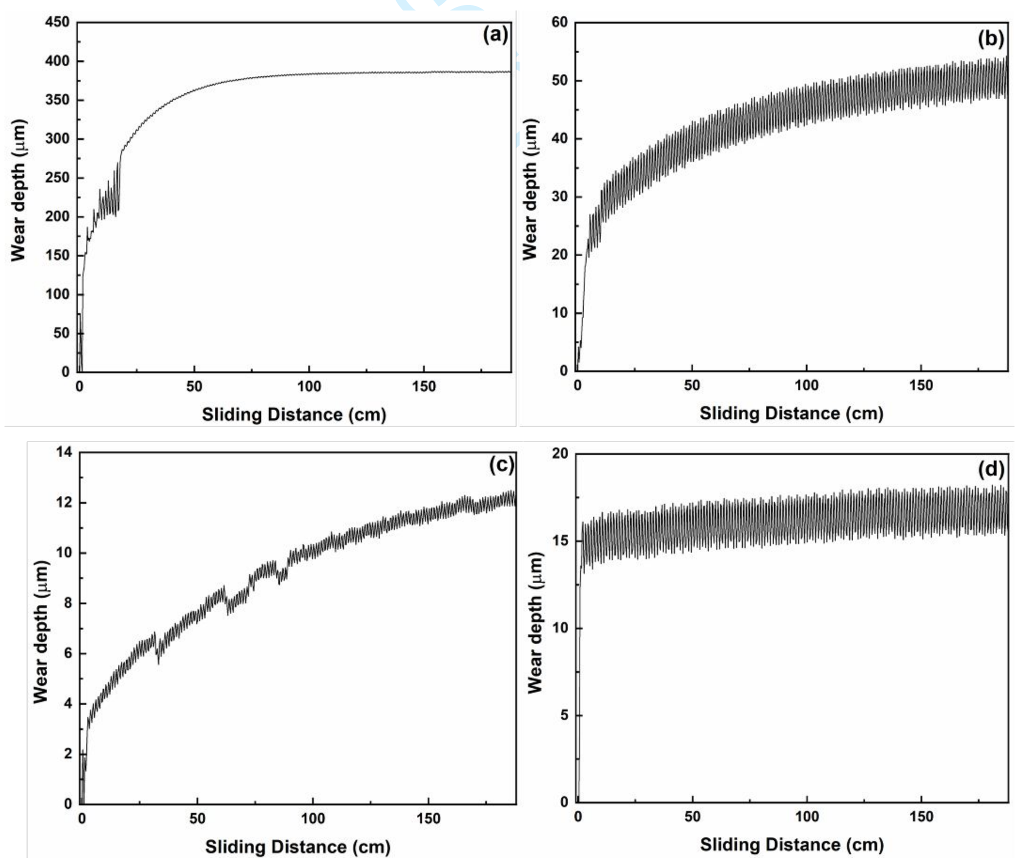

Fig. 5 Wear depth vs. sliding distance plots (raw data) of (a) S0, (b) S28, (c) S29 and (d) S30 steels.

The S0 (bare steel) exhibits maximum wear depth or the least wear resistance due to its soft nature compared to hard nitrided layers. The improvement in wear resistance is remarkable after plasma nitriding of the steel. All the nitrided steels show similar wear depth. However, S29 steel displays the best wear-resistant properties among these tested steels. This is due to high hardness and the reason is already discussed in the hardness section.

S29 and S30 steel samples have shown similar wear depth and wear plots. It is worth mentioning here that S30 and S29 steels had shown similar hardness. Though these two samples are different in terms of nitriding time and temperatures, their nitrogen intake may be the same because diffusion distance depends on diffusion time and temperature. Compared to these nitrided steels, S28 shows marginally lower wear resistance. This trend has also been observed in hardness profiles (Fig. 4(a,b)). This could be due to longer nitriding time allowing longer time for nitrogen diffusion and thus resulting in wider nitrogen distributed region. Moreover, a longer heating time at the elevated temperature caused the tempering of the steel mentioned earlier.

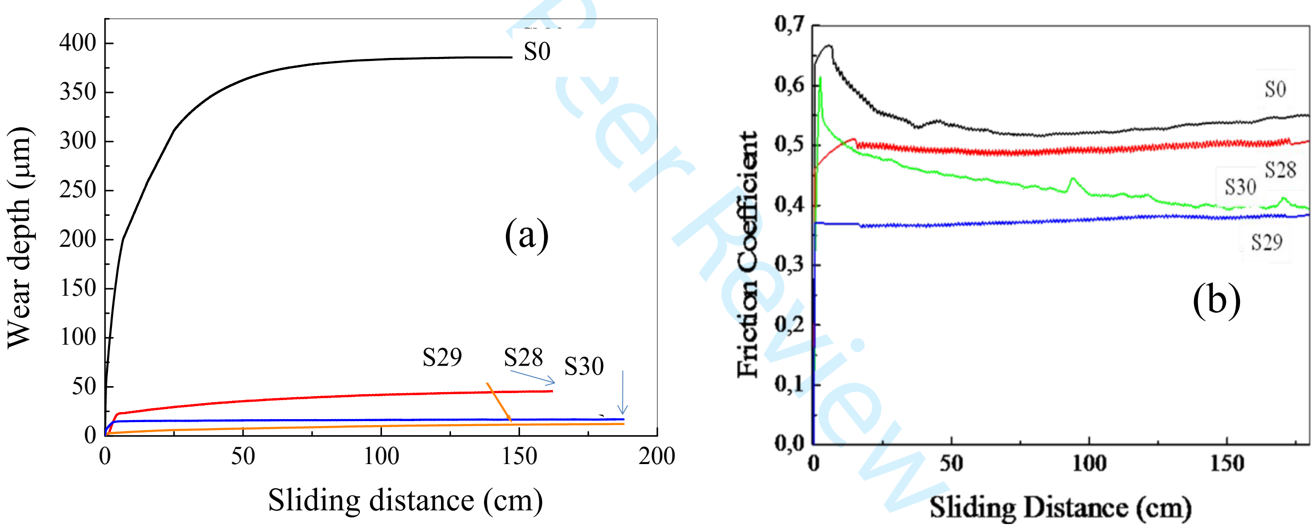

Fig. 6 (a) Smoothened wear depth *vs*. sliding distance wear plot and (b) friction coefficient *vs*. sliding distance plot of all the samples.

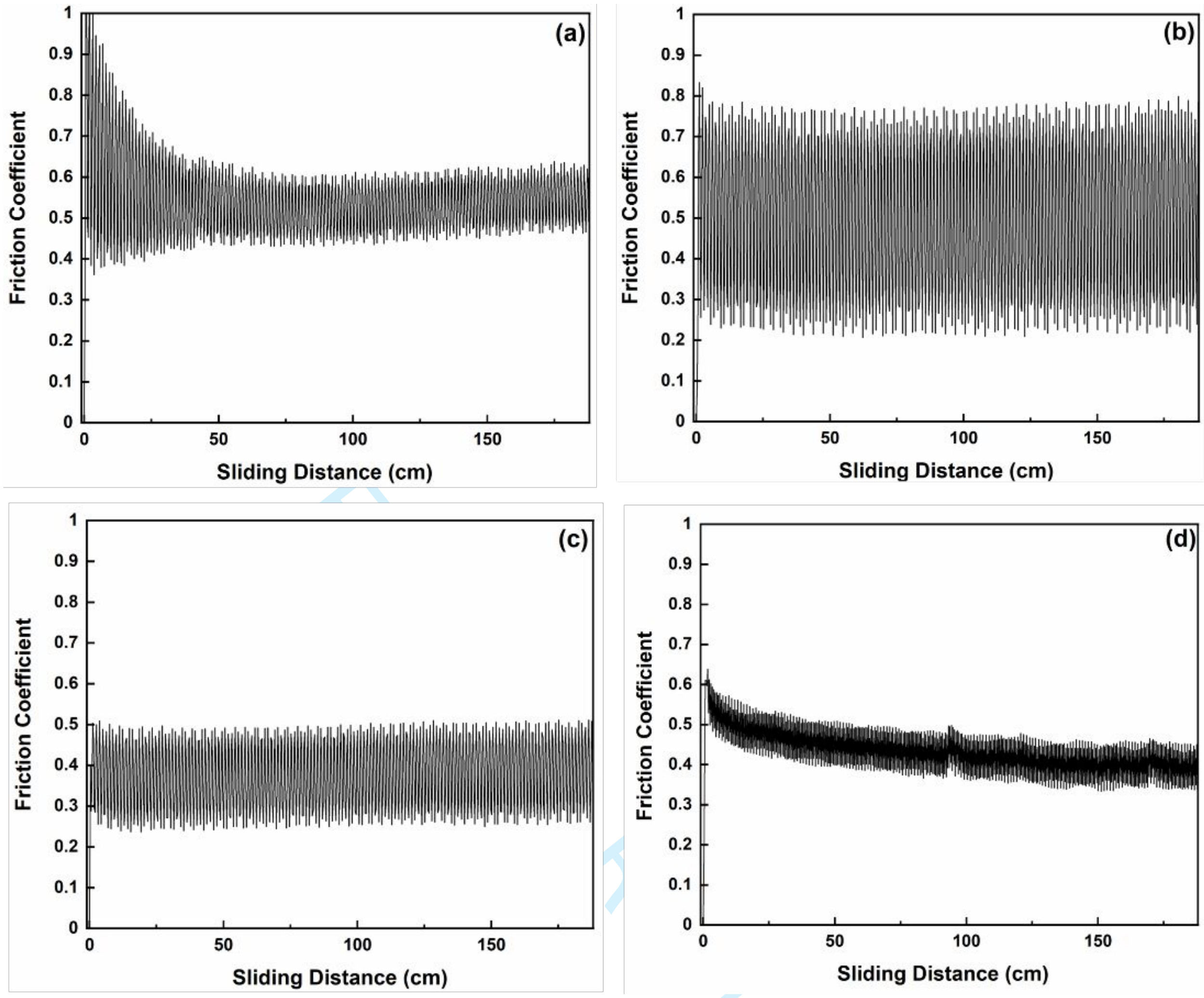

Fig. 7 Friction coefficient vs. sliding distance plots (raw data) of (a) S0, (b) S28, (c) S29 and (d) S30 steels.

Fig. 7 displays the friction coefficient values during the entire sliding path of all the samples ((a) S0, (b) S28, (c) S29 and (d) S30). It is worth mentioning that the noise band of friction coefficient of S29 and S30 are the most stable and minimum among all the samples. This also reflects their superior wear response. Fig. 6(b) displays the smoothened friction coefficient plot of all the samples together for easy comparison. A comparison of these values may conclude that bare steel has the highest friction coefficient compared to nitrided steel. Higher friction is dealt with as a negative aspect in tribology as it can increase the wear rate/damage of the surface. On the other hand, S30 and S29 have almost the same steady-state value of friction coefficient different from S28 steel with marginally higher than these two steels.

Fig. 8 displays the low-magnification SEM images of the wear tracks of S0, S28 and S29 steels, and these figures also provide an idea of the wear resistance properties of the samples. This figure also gives a quantitative explanation of the wear track width that can be used as a parameter to judge wear damage. Fig. 8(a) displays the wear track of the S0 steel and this wear track is the widest here. This observation is obviously due to its lower hardness and poor wear resistance compared to nitrided steel. S28 steel shows a comparatively lower wear track width (160 µm), but the value is higher than that of S29 (100 µm). The observation again conforms to the trend displayed in Fig. 6(a).

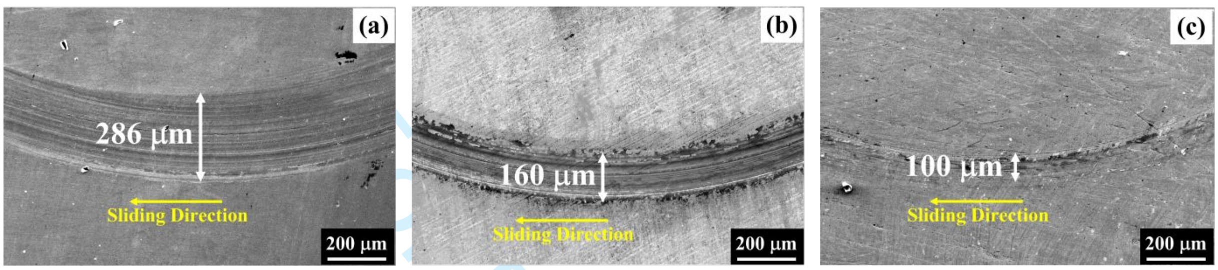

Fig. 8 SEM images of the wear tracks: (a) S0, (b) S28, and (c) S29 steels.

For a better understanding of the damage caused by the sliding wear test, SEM images of all the above-mentioned samples at higher magnifications are displayed in Fig. 9. In all three figures (Fig. 9a, b, and c), the tracks are predominantly a result of an abrasive wear mechanism. The following two reasons can explain the mechanism. One of the reasons could be the mechanism of wear. There is a low possibility of wear by the adhesive mechanism as the counter body used here is a diamond indenter with a metallic body. The second reason is that all the bare and nitrided steels are hard and brittle (the hardness of bare steel is also about ~ 657 HV0.05) and responsive to the non-adhesive wear mechanism. In Fig. 9(a), severe damages occurred as rubbing marks and plowing. Moreover, there is the presence of a deep groove also caused as a result of severe plowing. Severe damage is natural due to the comparatively softer nature of the base steel. In the case of the S28 steel (Fig. 9(b)), rubbing marks and plowing signatures are less damaging than Fig. 9(a) as the sample has experienced hardening due to the nitriding process. The presence of flakes is also visible in this figure. But, in the case of S29 steel, the wear features presented in Fig. 9(c) are less pronounced. Only mild rubbing marks are visible, confirming the lowest wear attack as observed in Fig. 6(a) plot. No large-scale debris has been present in any of the wear micrographs.

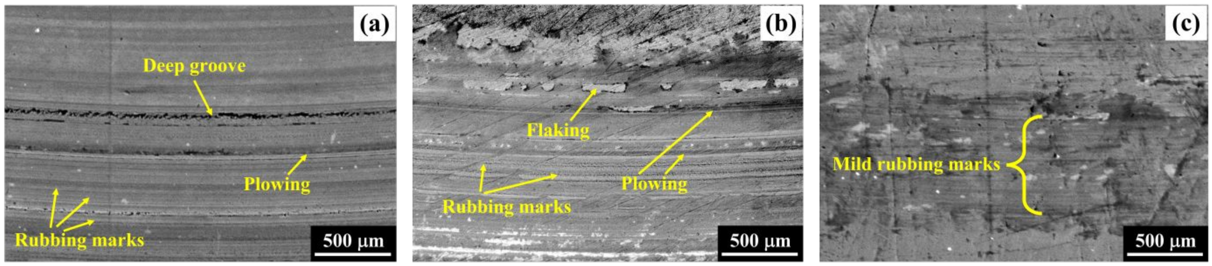

Fig. 9 SEM images of the wear track with higher magnification: (a) S0, (b) S28, and (c) S29 steels

It is also important to mention that in this study the wear test was done under a fixed load, as, in an earlier study (Ref. 30) on nitriding the wear response was the same irrespective of the load level. In the case of nitriding, the hardness gradually falls toward the bulk over a large depth and so the load variation does not impart significant variation in wear. Moreover, specimens tested below 10 kg load did not reveal visible wear tracks due to the high hardness of the samples.

For the investigation of any preferential removal of any phase/elements during the wear test, the wear tracks were analyzed under SEM/EDS. Here are EDS line scan plots for the elemental availability across the wear tracks captured. Results are displayed in Fig. 10 for samples (a) S0, (b) S28, and (c) S29. The plots superimposed on the wear tracks may conclude that there was no preferential wear attack/damage. Moreover, this can also rule out the possibility of oxidative wear mechanisms. So, the wear mechanisms were predominantly abrasive in type due to the hard nature of the samples (including the base material).

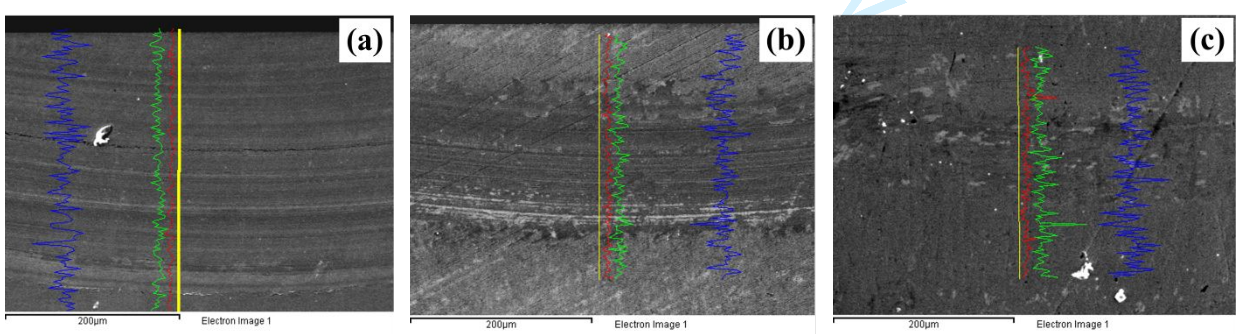

Fig. 10 EDS line scan across wear track of (a) S0, (b) S28, and (c) S29 steels.

Hence, the conclusion may be drawn that wear resistance has also been increased manyfold by nitriding the steel-like hardness. Based on the nitriding parameters, there are visible effects on the tribological properties. XRD analyses presented in the above sections suggest that there could be stress generation in the S28 and S29 steels (Fig. 2) which is beneficial for enhancing the wear resistance property.

It is clear that the shorter duration treatment of 6 h at 550°C (S29) has a slightly higher stress value when compared to that of S28 steel (for a longer time of 10h at the same temperature). From XRD it is observed that the nitride steels possess mainly the Fe-nitrides → Fe_4N (γ') and $Fe_{2-3}N$ responsible for the improvement of the wear resistance (Ref. 31, 32). The shifting of the Fe peak as shown in Fig.2 could be due to the stress generation caused by nitrogen inclusion in the solid solution. It may improve the hardness. However, this is speculation only, which needs further confirmation by more experimental evidence. Hence, the determination of stress generation after plasma nitriding will be the focus of future work. Future work will focus on the gradient layer deposition of TiC on the surface of this steel. The hard and gradient layers may further improve the hardness and wear resistance of this steel. The deposited layer may be adherent to the substrate surface with comparatively less compressive stress than the directly deposited layer. This work remains for future studies.

4. Conclusions

The following conclusions may be drawn from the present study of elevated temperature plasma nitriding of Cr-Mo-V- based tool steel at varying treatment conditions:

- Nitrided samples show peak shifts in XRD due to nitrogen incorporation in the iron lattice. XRD also exhibits the formation of nitride phases. However, the actual nitride phase and peak intensity changes with nitriding parameters.
- Nitrogen incorporation was also evident from the EDS profile of the nitrogen across the cross-section showing a gradual decrease in nitrogen content away from the surface.
- Nitriding at elevated temperatures is responsible for a significant improvement in hardness due to nitrogen solid solution and nitride formation mainly.
- All the nitrided steels possess better resistance to wear than the bare steel in terms of wear depth and friction co-efficient values. Wear mechanisms were found to be predominantly abrasive in nature.
- Finally, the nitriding conditions in the present studies which are higher temperature and shorter duration (S29 steel nitrided at 550°C for 6 h) and lower temperature but longer duration (S30 steel nitrided at 500°C for 10 h), both are beneficial for the improvement of the hardness and wear resistance significantly.

Acknowledgments

For the support and encouragement and for granting the permission to present this work, the authors thankfully acknowledge GITAM (Deemed to be University), Visakhapatnam. Technical support extended by ENSAM, Paris Tech. France is gratefully acknowledged.

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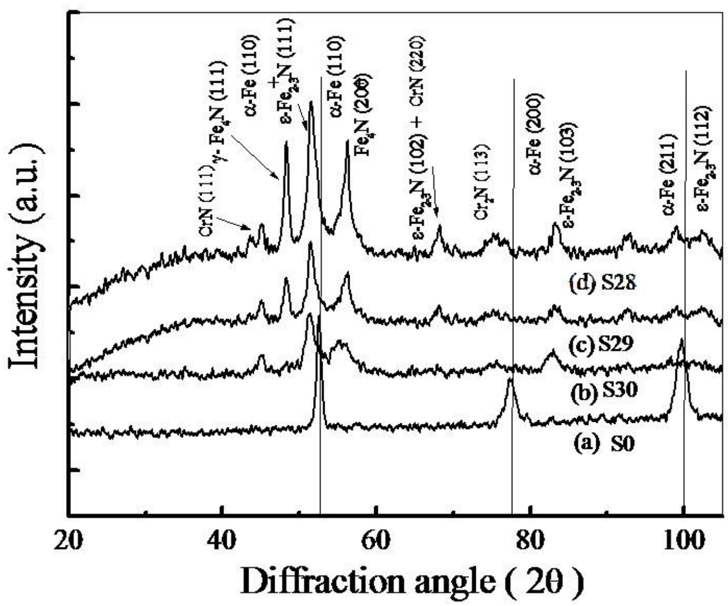

Fig. 1 XRD using Co-Kα radiation source unfolds the Fe peaks for (a) S0 (bare steel) and Fe – nitrides for the (b) S30, (c) S29, and (d) S28 nitrided steels.

254x190mm (96 x 96 DPI)

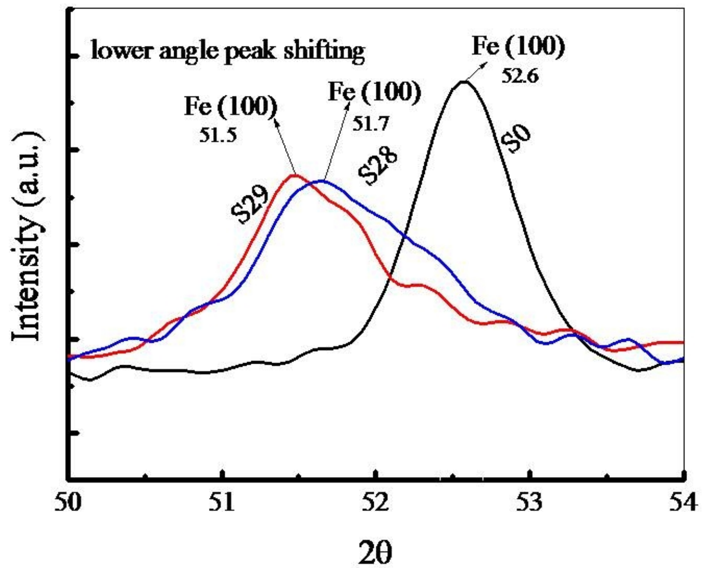

Fig. 2 Representation of shifting of Fe (100) peak of the bare steel S0 to lower angles after nitriding at 550oC for 6 (S29), and 10 h S28 (Ref. 25).

254x190mm (96 x 96 DPI)

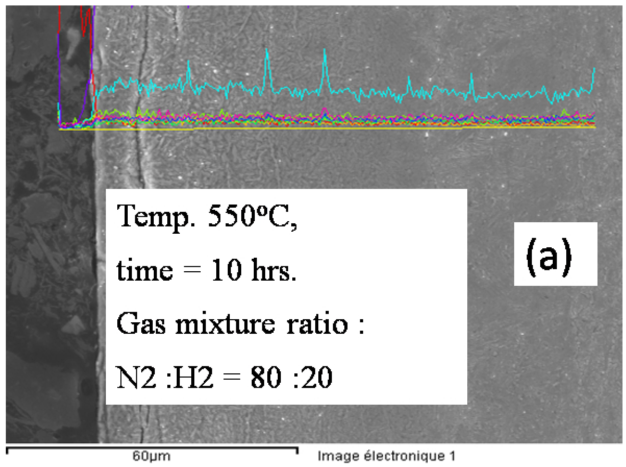

Fig. 3 Cross-section of S28 steel from the surface towards the core observed under SEM: (a) microstructure and line scan across the cross-section, and (b) the elemental availability of N from surface to the core.

254x190mm (96 x 96 DPI)

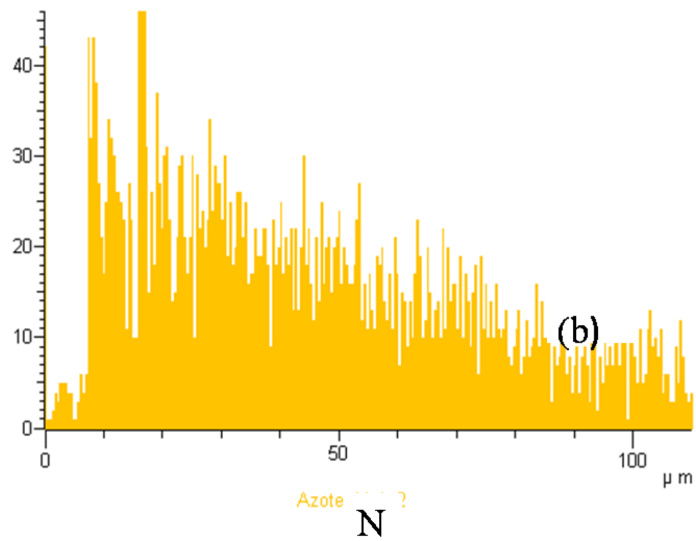

Fig. 3 Cross-section of S28 steel from the surface towards the core observed under SEM: (a) microstructure and line scan across the cross-section, and (b) the elemental availability of N from surface to the core.

254x190mm (96 x 96 DPI)

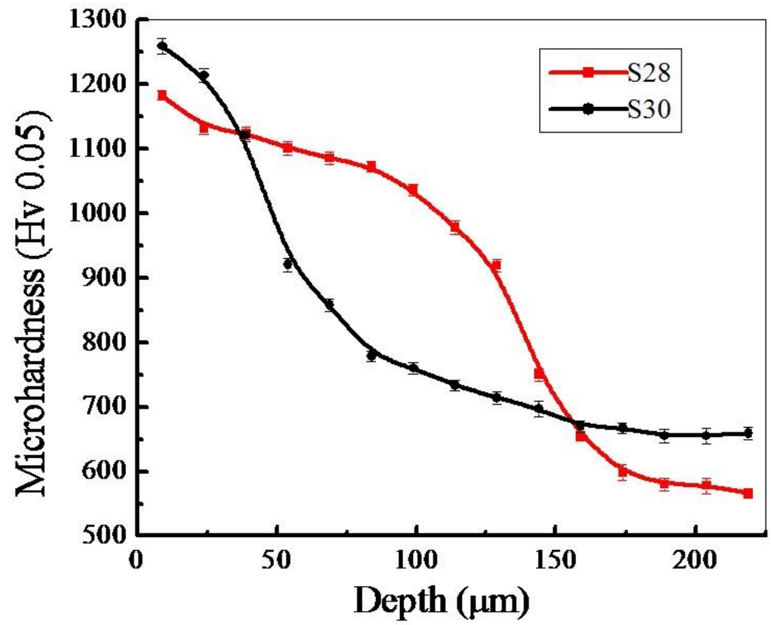

Fig. 4 Representation of microhardness vs. depth profiles of (a) S30 and S28 steels (similar to CM5510 as shown in (Ref. 25)), and the nitrided steels (b) S28 and S29 (HV0.05 for the bare steel (S0) is ~ 657 HV0.05).

254x190mm (96 x 96 DPI)

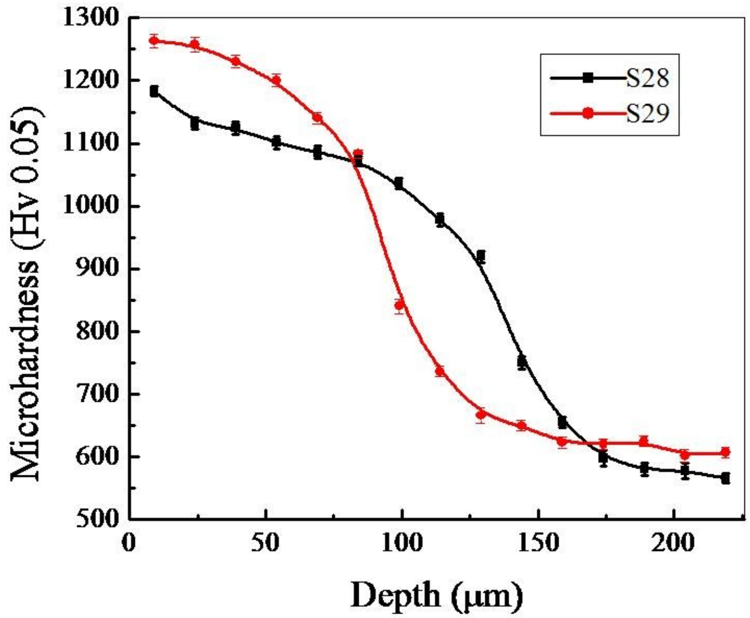

Fig. 4 Representation of microhardness vs. depth profiles of (a) S30 and S28 steels (similar to CM5510 as shown in (Ref. 25)), and the nitrided steels (b) S28 and S29 (HV0.05 for the bare steel (S0) is ~ 657 HV0.05).

254x190mm (96 x 96 DPI)

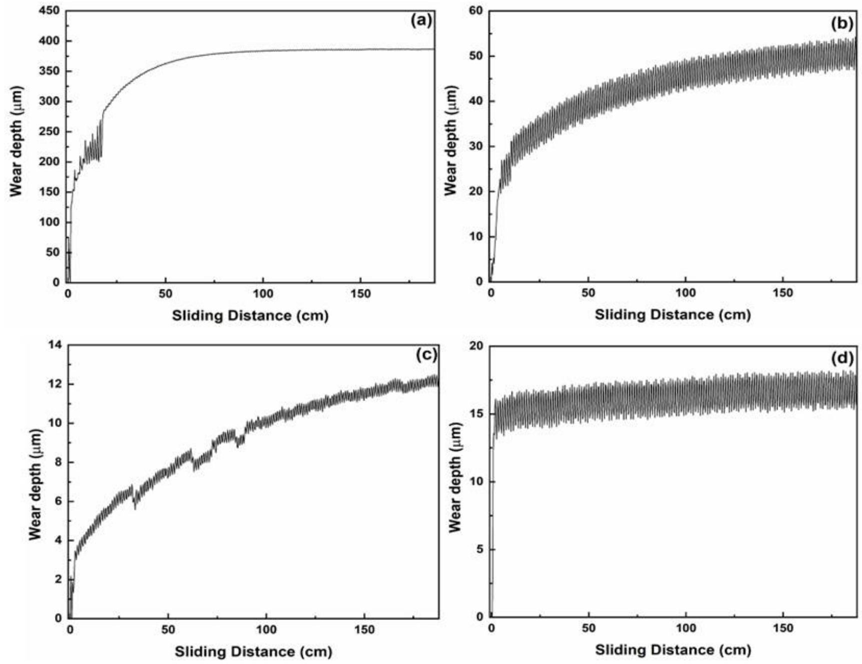

Fig. 5 Wear depth vs. sliding distance plots (raw data) of (a) S0, (b) S28, (c) S29 and (d) S30 steels.

254x190mm (96 x 96 DPI)

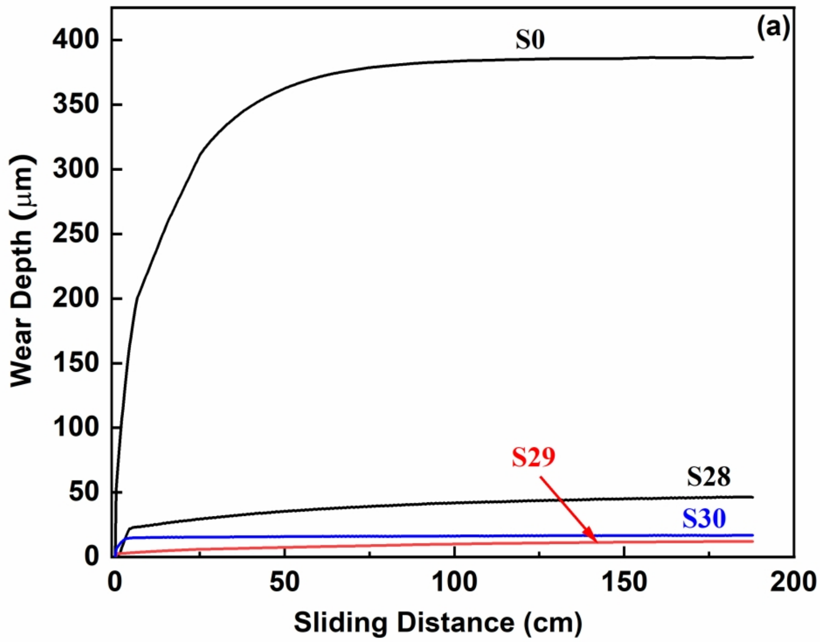

Fig. 6 (a) Smoothened wear depth vs. sliding distance wear plot and (b) friction coefficient vs. sliding distance plot of all the samples.

272x208mm (300 x 300 DPI)

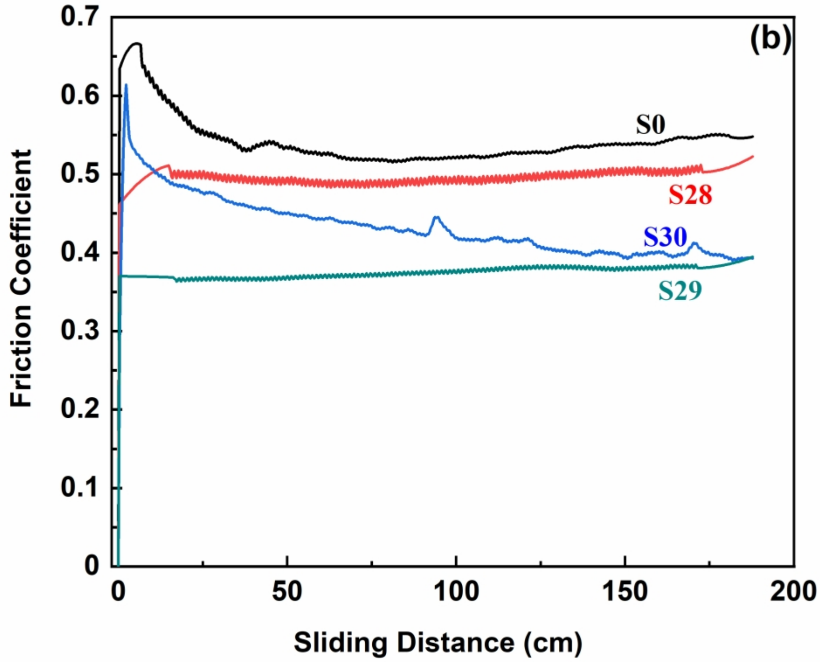

Fig. 6 (a) Smoothened wear depth vs. sliding distance wear plot and (b) friction coefficient vs. sliding distance plot of all the samples.

272x208mm (300 x 300 DPI)

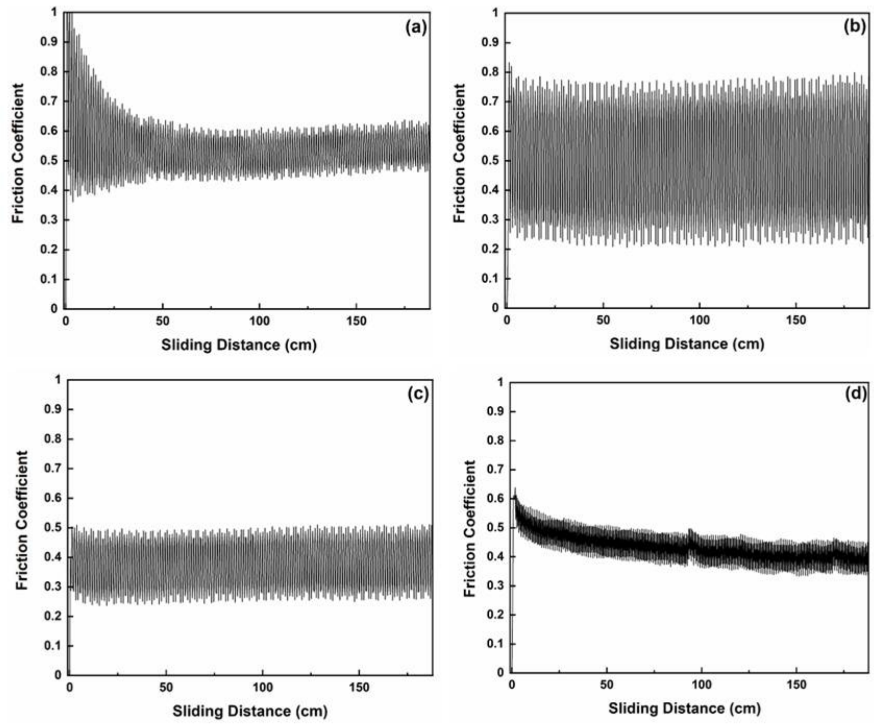

Fig. 7 Friction coefficient vs. sliding distance plots (raw data) of (a) S0, (b) S28, (c) S29 and (d) S30 steels.

254x190mm (96 x 96 DPI)

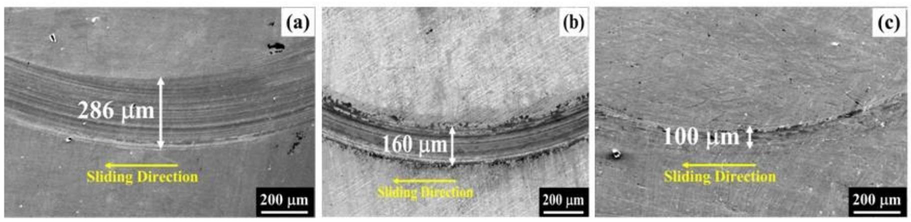

Fig. 8 SEM images of the wear tracks: (a) S0, (b) S28, and (c) S29 steels.

254x190mm (96 x 96 DPI)

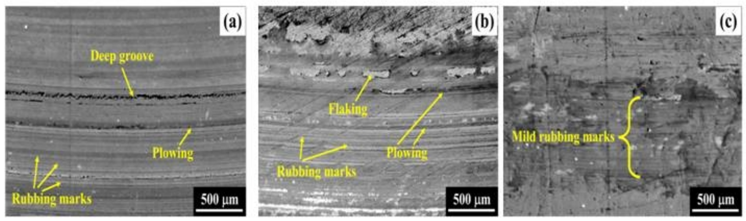

Fig. 9 SEM images of the wear track with higher magnification: (a) S0, (b) S28, and (c) S29 steels

254x190mm (96 x 96 DPI)

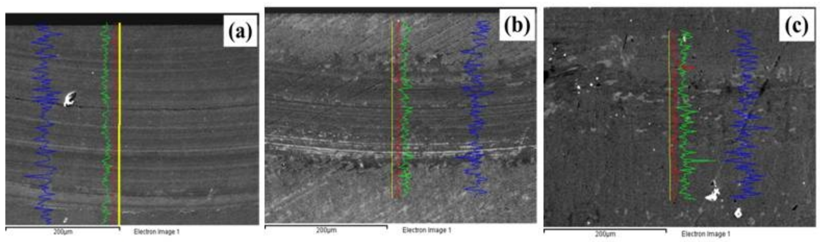

Fig. 10 EDS line scan across wear track of (a) S0, (b) S28, and (c) S29 steels.

254x190mm (96 x 96 DPI)

Table 1 :

Elements	Cr	Si	Mo	Mn	C	V	Fe
Content (wt.%)	8.0	1	1.5	0.5	0.5	0.5	Balance

Table 1: Chemical composition of 90CrMoV8 steel

254x190mm (96 x 96 DPI)

Table 1 :

Sample code	S30	S28	S29
N_2:H_2 Gas ratio	80:20	80:20	80:20
Initial Pressure (Pa)	0.5	0.5	0.5
Working Pressure (Pa)	550	550	550
Voltage (negative bias) (V)	250	250	250
Temperature (ºC)	500	550	550
Time (h)	10	10	6

Table 2: The parameters of plasma nitriding

254x190mm (96 x 96 DPI)

REPLYTOREVIEWERS'COMMENTS

Title:Elevated Temperature Plasma Nitriding of CrMoV Tool Steel for the Enhancement of Hardness and Wear Resistance

Authors:P.JanardhanaKiran,V.Srinivas,A.Basu,CorinneNouveau,K.RamMohanRao

Ref. No. JMEP-22-07-28880.R1

We sincerely appreciate the reviewers and associate editor for their criticalcomments on our work. In response to review comments, modification of the manuscript hasbeen carried out to the best of our capacity to improve its quality. All the modifications in therevised manuscript are marked in blue. The responses to all the comments are appendedbelow.

Reviewer: 1

(i) The authors should insert the following at an appropriate location either under introduction or experimental procedure to justify why load variation was not used:

"The wear test was done under a fixed load as in an earlier study [Ref...] on nitriding, the wear response was the same irrespective of the load level [Ref. A. Basu et al, "Plasma nitriding of a low alloy - high carbon steel", Trans IIM, 2007, 60(5), pp.471-479]. Because hardness gradually falls toward the bulk over a large depth, load variation does not impart significant variation in wear. Moreover, specimens tested below 10 kg load by the present authors did not reveal visible wear tracks due to the high hardness of the samples."

Reply: The above-mention information has been incorporated in the modified manuscript after descriptions of the wear tracks.

(ii) The authors' response to comment of Reviewer: 3 is not satisfactory. Fig. 5 should include the actual data points and not just smoothed out curves for wear. The raw wear data plots as well as the trend lines should be incorporated in the main body and not just in a supplementary file.

Reply: Thank you for the suggestion. The raw figures have been incorporated in the modified manuscript.

Reviewer: 2

There is little effort to contextualize the introduction with other similar studies. The quality of the figures and tables is below the recommended. There exist a lot of grammar errors or typing errors. I do not recommend publication of this work without extensive revision of grammar errors or formatting errors. Detailed comments are below.

1. Abstract:
- In the last sentence of the introduction it would be interesting to show the factors that contributed to the mentioned improvements.

Reply: The last sentence of the abstract is modified accordingly (It was found that the hardness, case depth, and wear resistance of the steel were enhanced significantly after nitriding at elevated temperatures mainly due to nitrogen solid solution and nitride formation, and a longer time or higher temperature of nitriding may be beneficial for such improvement).

2. Page 2, line 41, Keywords: nitriding, plasma, steel, wear, X-ray diffraction
- Has the potential to be improved.
Suggestion: Plasma nitriding, 90CrMoV8 Tool Steel, Electron Microscopy, Wear, X-ray Diffraction.

Reply: Modification has been incorporated in the latest manuscript file.

3. Introduction:
The initial contextualization part of the introduction is very generic. The authors should do a more focused review on tool steels and plasma nitriding treatments as this is the main focus of this study.
There exist a lot of grammar errors or formatting errors, please carefully check the introduction and revise them.
- Page 3, line 45, "The present study is focused on plasma processing to engineer the surface for improved hardness and wear resistance with no layer deposition….."; Page 4, line 41, "The present work is focused on the wear resistance of 90CrMoV8 steel….."
I suggest modifying the structure of one of these sentences to avoid repetitive information.
- Page 4, line 47, "Corinne et al. in 2011 (Ref. 7) reported…."
Remove "in 2011".

Reply: Overall modification and point-wise corrections have been incorporated in the manuscript either by changing the marked sentence or the previous sentence.

4. Materials and Methods:
- How many repetitions of the tribological tests were performed for each condition? (the question was answered but the information was not included in the manuscript).
- There exist a lot of grammar errors or formatting errors, please carefully check the materials and methods and revise them.
For example: Page 5, line 10, centimetroscubicos???; Page 5, line 12, lack of space in table 1.; Page 6, line 11-12, format the sentence "Characterization of the Plasma Nitrided Steels"; Page 6, line 28, remove the space in "(LECO MST 210)."; Page 6, line 51, remove the space in "SEM / EDS"; Page 6, line 55, remove the space in "(S 29)".

Reply: Point-wise corrections have been incorporated into the manuscript. Other parts are also modified for improvement.

5. Results and Discussion:
- Page 7, line 51. "In S29 steel, which was nitrided for 6 h at 555o0C,"... have a typing error.
- Page 9. Correct formatting errors in the legend of Fig. 3(a). The source of Figs. 3(a, b) are too small;
- Page 10. Put the mean and standard deviation in Fig. 4(a, b). Use the same scale in the graph in Fig. 4(a) and 4(b).
- Page 11. "Fig. 5 represents the smoothened wear and friction plots of all three nitrided and bare steels. Raw wear depth vs. sliding distance plots from which Fig. 5"... Identify the letter in Fig. 5.
- Page 11. Fig. 5(b) has errors. replace vertical axis comma with dot, and also is missing parentheses in identification b. The source of Figs. 5(a, b) are too small.
- Page 12, line 1. "This trend has also been observed in hardness profiles (Fig. 4)." Fig 4(a, b).
- Page 12, line 17. "Fig. 6 displays..." Identify the letter in Fig. 6;
- Page 12, line 45. "magnifications are displayed in Fig. 7.". Identify the letter in Fig. 7.
- Page 13, line 1. "....the S28 steel (Fig. (b))". Fig. number is missing.
- Page 13, line 25. "Results displayed in Fig. 8 for samples". Identify the letter in Fig. 8.
- Page 13, line 32. the dot at the end of the sentence is missing.
- There exist a lot of grammar errors or formatting errors, please carefully check the results and discussion and revise them.
For example: Page 7, line 5-6, "γ' (Fe4N)"; Page 7, line 7, "εN"; Page 7, line 10, "wear resistance.. A careful observation"; Page 7, line 45, "Fig. 1 XRD using Co-kα radiation source"; Page 8, line 41-42, "....for 10 h S28 (Ref. 25))."; Page 9, line 8, "....is obvious from Fig.3 (a)"; Page 9, line 14, "....From Fig. 3 (b) it is obvious that"; Page 9, line 51, "Vickers microindentation method. Fig. 4 (a).."; Page 9, line 55, "It is obvious from Fig. 4 (a) that.."; Page 10, line 9. "The same can be observed in Fig. 4 (a),"; Page 10, line 15. "Fig. 4 (b) shows the"; Page 11, line 22, "supplementary file for ready reference. Fig. 5 (a)"; Page 11, line 22 ", "hardness as observed in Fig. 5 (b)."; Page 12, line 7. "Fig 5 (b) displays"; Page 12, line 15. "...damage as observed in Fig. 5 (a)."; Page 12, line 19. "previously shown in Fig. 5 (a)."; Page 13, line 60. "Fe4N (γ') and"; Page 14, line 1. "Fe2-3N responsible";

Reply: All suggestions/error corrections have been incorporated in the modified manuscript.

6. Conclusions:
Conclusions could be shortened and presented in topic forms.
There exist a lot of grammar errors or formatting errors, please carefully check the conclusions and revise them.

Reply: The conclusion section has been modified.

7. References
- Page 16, see line 9 and 10.
Reply: The error has been corrected in the modified manuscript.

8. Comments: The Figures in the annex (Page 18 to 33) are all outside the standard

established by the journal, and are different from the figures that were presented in the text. The quality of the figures and tables is below the recommended.

Reply: The quality of the tables and some of the figures have been modified in the revised manuscript.