

Active Screen Plasma Nitriding of Austenitic Stainless Steel

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ABSTRACT

Active screen plasma nitriding (ASPN) is a novel surface engineering technique which provides many advantages over conventional DC plasma nitriding (DCPN). In this study the ASPN technique has been used to nitride the austenitic stainless steel (AISI 316). The morphology, composition and properties of the AS plasma nitrided layers have been characterised and compared with those of the normal DC plasma nitrided layers. It has been shown that ASPN can achieve similar hardening effects for austenitic stainless steel when compared to the conventional DCPN, but, the AS technique does not have the common problems associated with the DC technique such as the 'edging effect'. ASPN at lower temperature of 420°C can also produce a precipitation-free layer, named as S-phase, on the 316 stainless steel surface. The AS plasma nitrided S-phase exhibits not only high hardness and wear resistance but also very good corrosion resistance.

INTRODUCTION

Plasma nitriding using glow discharge technology has been accepted in industry over the past thirty years. This relatively new nitriding process is carried out in vacuum, where a high-voltage electrical potential is applied to the workpiece (cathode) and the furnace wall (anode) to form a plasma, through which the active nitriding species are transferred to the component surface [1]. It is well known that plasma nitriding offers many advantages over traditional gas nitriding and bath nitriding, particularly, in terms of reduced gas consumption, reduced energy consumption and the completely removal of any environmental hazard [2]. Nonetheless, the rapid development and the uptake of DC plasma nitriding technology into industrial surface engineering have been slowed down in recent years [3, 4]. This is because in the conventional DC system, the components to be treated are subject to a high cathodic potential, so that plasma forms directly on the component surface. Whilst this is efficient for heating and treating relatively simple shapes or small

loads, the normal DC technique has its inherent shortcomings, such as difficulties in maintaining a uniform chamber temperature, particularly in full workloads of components with varied dimensions, damage caused to parts by arcing, the "edging effect" and the "hollow cathode effect" [3, 5].

Efforts have been made in the past few years to overcome these common problems of DC plasma nitriding. A recent step forward in this direction was the invention and industrial acceptance of the Active Screen Plasma Nitriding (ASPN) technology [6]. In such a novel nitriding process, the entire workload is surrounded by a large screen or cage, on which, a high voltage cathodic potential is applied (hence the term Active Screen is used). As schematically shown in Fig. 1, the worktable and the parts to be treated are placed in a floating potential or subjected to a relative lower bias voltage, e.g. - 100 ~ - 200 V. Therefore, it is on the active screen, rather than on the component surface that the plasma forms. The plasma heats up the active screen, and radiation from the screen provides the heat that brings components to the required temperature for treatment. The plasma forms on the screen also contains a mixture of ions, electrons and other active nitriding species, which are then encouraged to flow through the screen and over the workload by a specially designed gas flow. As such, very complex shaped components can be treated and the active species can even enter blind holes, producing uniform modified layers on all parts of different geometry and size in a heavily loaded chamber [3, 7]. Since plasma is not formed on the component surface, the arcing damage and the "edge effect" can be eliminated.

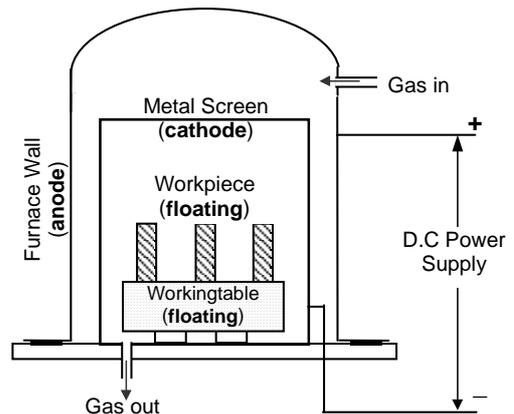


Fig. 1 Schematic diagram showing the principles of an AS plasma nitriding system

In this study, samples of AISI 316 austenitic stainless steel were plasma nitrided using the active screen plasma nitriding technology. The purpose of the work was to investigate the nitriding response of austenitic stainless steels under active screen plasma nitriding conditions, and to compare the morphology, the

composition and properties of the AS plasma nitrided layers with those of the normal DC plasma nitrided layers. Earlier work with DC technique has shown that when the nitriding temperature is sufficiently low, precipitation of chromium nitrides can be suppressed and a hard and corrosion resistant layer, known as S phase, can be produced on austenitic stainless steel surface, thus achieving combined improvement in wear, fatigue and corrosion resistance [8, 9, 10]. Accordingly, it was also the purpose of the present study to investigate the possibility of producing an S-phase layer on austenitic stainless steel surface by using the novel AS plasma nitriding technology.

EXPERIMENT

Materials

The AISI 316 austenitic stainless steel used in this study had chemical compositions (in wt %) of 0.06%C – 19.23%Cr – 11.26%Ni – 2.67%Mo – 1.86%Mn – Fe. Samples were cut from hot rolled bars 25.4 mm diameter to discs of 8 mm thick. The flat surfaces of the discs were wet ground using SiC papers from 240 grit down to 1200 grit. The samples were cleaned in soapy water and then acetone before nitriding.

Plasma nitriding experiment

Nitriding experiment was carried out in a DC plasma nitriding unit (40 kw Klöckner), which comprises a sealed chamber, a vacuum system, a DC power supply system, a gas supply system, and a temperature measurement and control system. For DC nitriding, the samples to be treated were directly placed on the cathodic working table as normal. The furnace wall was connected to the DC source as the anode. Temperatures were measured by a thermocouple inserted into a hole of 3 mm diameter in a dummy sample. Processing began by evacuating the chamber, back filling with treatment gases, heating the samples to treatment temperature using the plasma formed on the sample surface, keeping the temperature for a set time, and finally cooling down to room temperature in the furnace.

Active Screen (AS) plasma nitriding was carried out in the same DC nitriding furnace (40 kw Klöckner) but with the addition of a laboratory ASPN set-up using the working principle as shown in Fig. 1. A mesh cylinder of 120 mm diameter and 130 mm height, with a removable top lid, was used as the active screen. They were made of 0.7 mm thick perforated austenitic stainless steel sheet, which had uniformly distributed round holes of 6 mm diameter. The cylinder was placed on the DC nitriding worktable and connected to the cathodic potential. Before the nitriding experiments, all the screen was ultrasonically cleaned in soapy water and then acetone. Afterwards, it was further sputtering cleaned and pre-nitrided inside the nitriding chamber to eliminate residual contaminants

on the screen surface.

A sample table of 100 mm diameter was placed inside the screen but isolated from the cathode potential. As a result, the samples on this table were not subject to any applied electrical potential, and thus, there was no plasma formed directly on the sample surface. The distance between the sample (flat) surface and the top lid was 12 mm. The nearest distance from the cylinder to the sample edge was about 30 mm. Heating was achieved by radiation from the active screen. Temperature was measured on a dummy sample which was also isolated and placed on the table in a symmetrical position as the sample to be treated.

The AS nitriding procedures were the same as DC nitriding. Both processes were carried out at temperatures of 420°C, 460°C and 500°C for 20 hours. Samples were identified accordingly as AS420, AS460, AS500, DC420, DC460 and DC500, with the initial letters indicating the treatment method, and the numbers suggesting the treatment temperature. The nitriding gas was a mixture of 25%N₂ + 75%H₂, and the working pressure was 500 Pa.

Characterisation of plasma nitrided samples

Various techniques were used to characterise the structures and properties of the plasma nitrided samples. These include metallographic analysis for morphology and microstructure examination, glow discharge spectrometry (GDS) analysis for chemical composition determination, X-ray diffraction analysis for phase identification, and indentation tests for micro hardness and load bearing capacity measurement.

Tribology tests

Tribological properties were evaluated using a pin-on-disc tribometer, in which the 316 steel sample (disc) was rotating against a stationary WC/Co ball 8 mm diameter at a speed of 66 r.p.m (0.031m/s), for a total sliding distance of 500 m. The normal contact load was 10 N, which produced an initial maximum Hertzian contact stress of 1500 MPa on the untreated 316 steel surface. All tests were conducted in air and without lubrication.

A stylus profilometer was used to determine the 2-D profile of a wear track. By integrating the area across the track profile, and then, multiplying by the circumference length of the track, wear volume loss was obtained. Three measurements were performed for each wear track and the average value used. Wear rate is expressed as volume loss per unit sliding distance per unit contacting load (mm³ N⁻¹ m⁻¹).

RESULTS

Morphology and microstructure

Visual examination of the nitrided samples revealed

that DC nitriding produced a non-uniform surface. An example in Fig. 2 a) shows that the edge of the DC nitrided sample has different colours as compared to the central area. This phenomenon, generally known as 'edge effect', is one of the common problem for DC plasma nitriding as mentioned. It has been explained in terms of the non-uniform sputtering and deposition during nitriding process [11]. The 'edge effect' was found to become more apparent with increasing nitriding temperature. In comparison, AS nitriding produced a uniform matt-grey surface throughout the sample, regardless of the nitriding temperature, Fig. 2 b). From an aesthetic point of view, AS technique produced a much better nitriding effect.

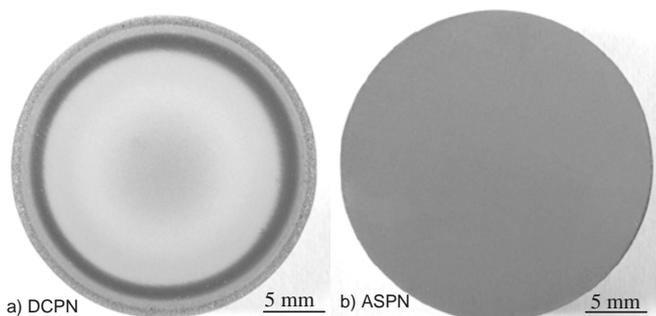


Fig. 2 Surface morphologies of a) DC plasma nitrided and b) AS plasma nitrided 316 steel samples

The nitrided samples were cross-sectioned, polished and then etched in a 50% HCl + 25% HNO₃ + 25% H₂O solution. The resultant microstructures are shown in Fig. 3. Three pictures in the right (AS420, AS460 and AS500) represent the 420°C, 460°C and 500°C AS nitrided samples; and three pictures in the left represent the corresponding DC nitrided samples. It can be seen that, under all the nitriding conditions used in this study, a nitrided layer was produced on the 316 stainless steel surface. Although the thickness and morphology of the nitrided layer are strongly influenced by the nitriding temperature, the nitriding method seems to have very little influence. AS nitriding and DC nitriding produced virtually identical microstructures. These include an 'unetched' layer produced at 420°C, a mixed 'unetched' and 'black' layer at 460°C and a 'black' layer at 500°C.

Such a microstructure and its evolution with temperature in DC plasma nitriding has been studied by many investigators [9, 12, 13, 14]. It has been well established that the unetched white layer produced at lower temperature (420°C) is a single phase supersaturated with nitrogen, and is normally referred to as S-phase. The DC nitrided S-phase layer has very high hardness, and more importantly, it has superior corrosion resistance so that it can resist the attacks by several corrosive reagent, including the solution of 50%HCl + 25% HNO₃ + 25% H₂O used in this study. When the nitriding temperature is higher

than a threshold value, precipitation of chromium nitride would occur which depleted the free chromium from the substrate. As a result, the corrosion resistance of the stainless steel will become deteriorated [9, 15, 16]. This has lead to the 'dark' phases in the 460°C nitrided surface, and the completely 'dark' layer in the 500°C nitrided surface.

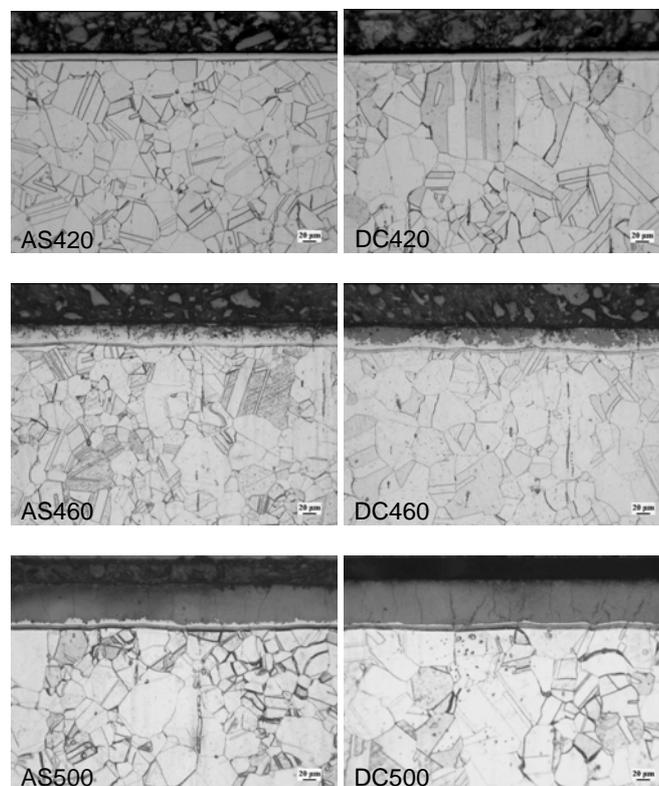


Fig. 3 Optical microstructures of the AS nitrided (AS420, AS460, AS500) and DC nitrided (DC420, DC460, DC500) AISI 316 austenitic stainless steel

The similarity of microstructures as shown in Fig. 3 has led us to believe that AS technique used in this study has produced a similar nitriding effect on the 316 steel surface as the conventional DC plasma nitriding. The unetched white layer on the 420°C AS nitrided surface is also a single phase (S-phase) which has a very good corrosion resistant, so that it can withstand the attack from the corrosive reagent of 50%HCl + 25% HNO₃ + 25% H₂O. The 'dark' phase and the 'dark' layer in the higher temperature nitrided layers (AS460, AS500) are related to the chromium nitride precipitation. These presumptions are supported by more evidence derived from characteristic studies of the nitrided layer with variety analytical methods, as shown below.

Nitrogen distribution

Chemical compositions in the nitrided surface were measured with a glow discharge spectrometer (Leco GDS 750). The nitrogen depth profiles, Fig. 4, indicate

that AS nitriding at a lower temperature of 420°C introduced nitrogen of up to 15 wt % into the 316 steel surface. Such a high amount of nitrogen has exceeded the theoretical solubility of the austenite lattice. Therefore, the AS nitrided layer should also be nitrogen-supersaturated austenite as the lower temperature DC nitrided layer. Increasing the nitriding temperature from 420°C to 460°C further increased the nitrogen concentration in the nitrided layer and produced a deeper case depth.

Due to the depth limitation of the GDS machine, only the nitrogen concentration of up to a depth of about 65 μm was obtained from the 500°C AS nitrided samples. Nonetheless, the incomplete nitrogen profile shown in Fig. 4 indicates that AS nitriding at 500°C introduced a much higher amount of nitrogen into the steel surface and produced a much deeper case depth.

In conjunction with the microstructure examinations, the thickness of the nitrided layer was estimated to be about 10 μm , 30 μm and 75 μm respectively for the 420°C, 460°C and 500°C AS nitrided sample.

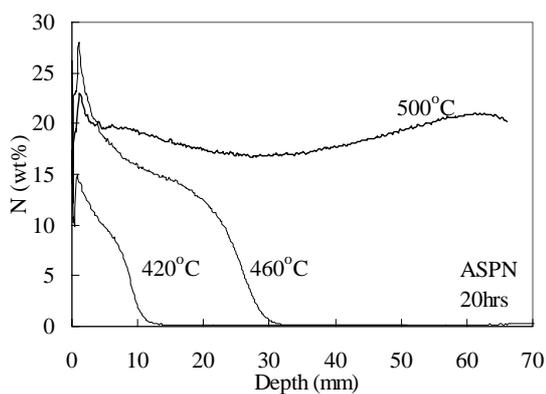


Fig. 4 Nitrogen concentration profiles measured by GDS in AS nitrided 316 steel sample surface

Phase structure of the AS nitrided layer

XRD analysis was performed on the untreated and plasma nitrided 316 steel surface with a Philips X-Ray Diffractometer using $\text{Cu-K}\alpha$ radiation ($\lambda=0.154 \text{ nm}$). The scanning angle (2θ) was from 30 to 100° and the scanning rate was 0.02° per second. Both DC and AS nitrided samples were analysed.

Fig. 5 shows that the untreated 316 steel produced two major diffraction peaks of γ (111) and γ (200) in the range of 35 - 55°, confirming the f.c.c structured austenitic substrate.

The lower temperature (420°C) AS nitrided sample produced a similar peak patterns to those of the untreated steel, but all the corresponding peaks were shifted to lower angles. Two major peaks, S1 and S2 as shown in Fig. 5, are broad and well defined. They could not be identified according to the existing ASTM

X-ray Diffraction Index. However, they possess all the characteristics of the nitrogen S-phase formed in DC plasma nitriding [15, 17]. It is thus concluded that nitrogen S phase has indeed been produced on the austenitic stainless steel surface by the active screen plasma nitriding. Using the established theories for DC nitriding, the XRD results shown in Fig. 5 for AS nitriding can be explained. The peak shift at lower temperature was caused by the solution of nitrogen, which expanded the f.c.c lattice structure of the substrate. With increasing nitriding temperature to 460°C, more nitrogen was dissolved in the lattice; causing increased lattice expansion. Thus, the peaks of S1 and S2 further shifted to the left. At a temperature of 500°C, both S1 and S2 shifted back to the higher angle due to the precipitation of chromium nitride. The formation of chromium nitride has deteriorated the corrosion resistance of the steel.

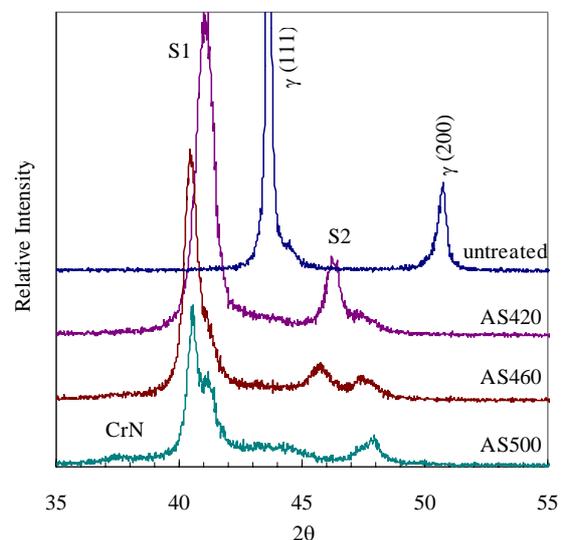


Fig. 5 X-ray diffraction patterns of untreated and AS plasma nitrided 316 steel

Indentation properties

Vickers indentation tests were performed on the nitrided surface using a Mitutoyo MVK-H tester under loads ranging from 0.025 kg to 1 kg. Fig. 6 shows the variation of surface hardness (HV) with testing load for untreated and nitrided samples produced at various temperature as indicated. Considering the similarities of microstructure, chemical composition and phase constituents of a AS nitrided layer and a DC nitrided layer as shown before, it is not surprise to see that the 'hardness vs. load' profiles for a AS nitrided sample at the same temperature as the DC nitrided sample are almost exactly the same within the testing error. Both AS nitriding and DC nitriding produced a significant improvement in surface hardness and load bearing capacity.

Fig. 7 shows hardness (HK0.01) profiles measured on the cross section of the nitrided samples. Again, the

similar hardening effect produced by AS nitriding and DC nitriding is demonstrated.

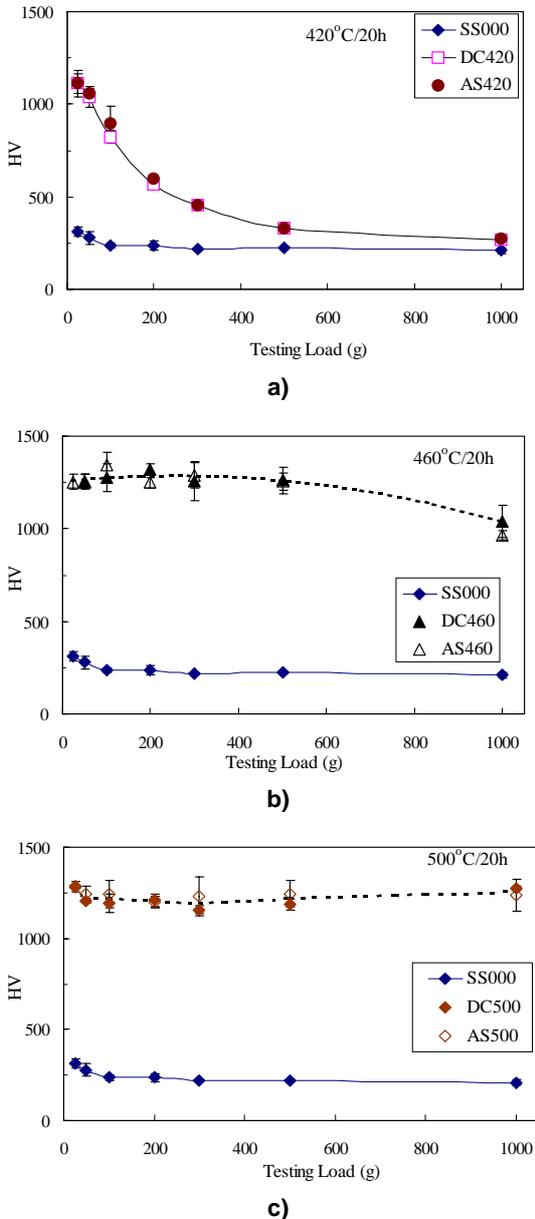


Fig. 6 Variation of Vickers hardness with testing load on the surfaces of untreated (SS000) and various temperature plasma nitrided 316 steel samples.

However, differences were indeed observed during indentation tests of the lower temperature (420°C) nitrided surface. It was found that cracks would start to appear around and/or inside the Vickers indentation mark when the testing load was increased to a critical value. Further increasing the testing load increased the quantity and length of the cracks. For the DC nitrided sample, this critical load was 0.2 kg, and for the AS nitrided sample, it was 0.5 kg. This difference in crack initiating load could suggest that the lower temperature (420°C) AS nitrided layer has better ductility and higher load bearing capacity.

The difference in ductility, if it indeed exists, could be attributed to the different outer surface morphologies produced by AS nitriding and DC nitriding. Detailed examinations of the nitrided surface under a high resolution FEG - SEM revealed that the DC nitrided surface, Fig. 8 b), consists of 'cones' of irregular sizes and distributions, probably due to the sputtering effect. In contrast, the AS nitrided surface, Fig. 8 a), consists of multiple particles with well defined boundaries, most likely, due to the deposition effect as described elsewhere [4].

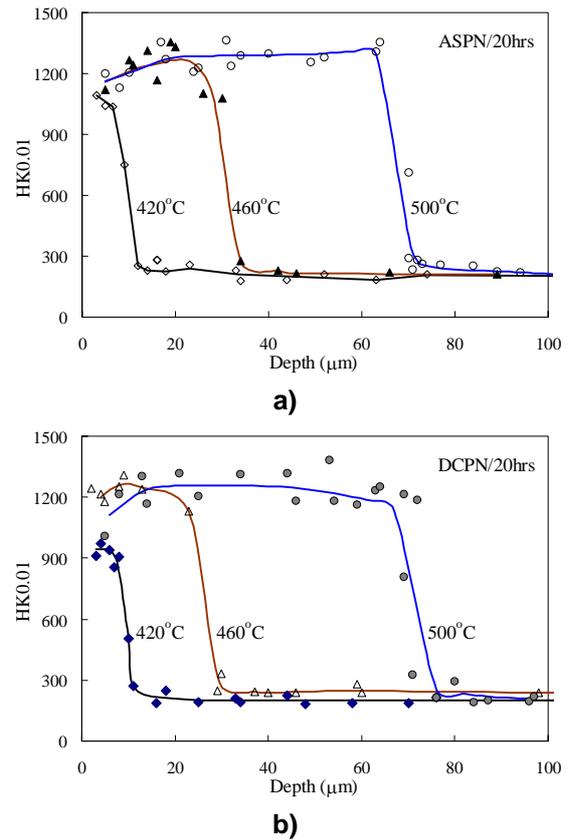


Fig. 7 Hardness profiles measured on the cross section of a) AS nitrided and b) DC nitrided 316 stainless steel samples

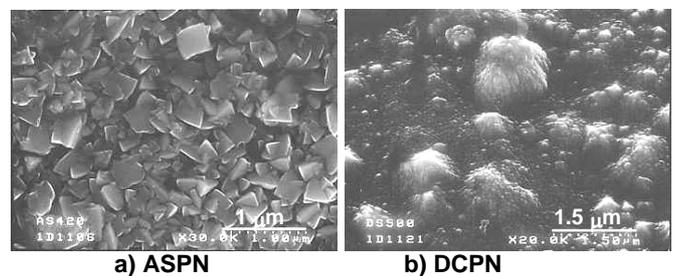


Fig. 8 FEG-SEM images of a) AS plasma nitrided and b) DC plasma nitrided 316 steel surface.

Tribological properties

Tribological properties of untreated and plasma

nitrided 316 steel were evaluated with a pin-on-disc tribometer. Fig. 8 shows the wear rate ($\text{mm}^3 \text{m}^{-1} \text{N}^{-1}$) measured after a sliding distance of 500 meters under a contact load of 10 N. It shows that the wear rates of the nitrided samples vary slightly with the nitriding temperature, and thus, with the composition, the thickness and the hardness of the surface layer. However, all the nitrided samples exhibited a considerably reduced wear rate as compared to the untreated ones. The wear rate of the nitrided samples is two orders of magnitude less than the untreated samples under the present testing conditions.

The significantly improved wear performance by plasma nitriding can also be revealed by visual examinations of the worn surfaces. It was found that the wear track on the untreated surface was wide and deep. Grooves, both on a macro and micro scales, were observed inside the track, which signified the occurrence of abrasive wear. On the other hand, wear tracks on the AS nitrided samples were shallow and superficial. This can be clearly seen in Fig. 10.

However, under present testing conditions, no clear difference in wear resistance was found between AS nitrided samples and DC nitrided samples.

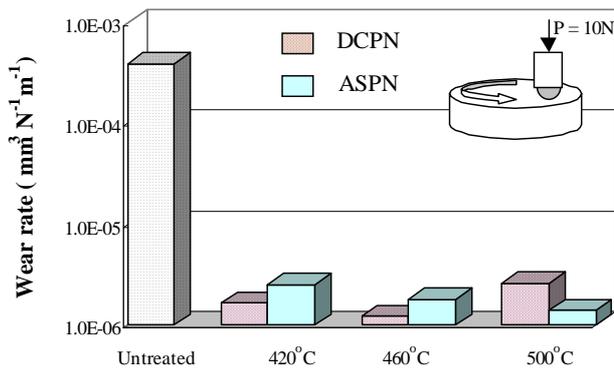


Fig. 9 Wear rate of untreated and plasma nitrided 316 stainless steel.

DISCUSSIONS

Austenitic stainless steel has a native surface oxide layer (Cr_2O_3) that protects the metal matrix from corrosion. The oxide layer has been regarded as one of the major problems for surface engineering of austenitic stainless steel [18, 19]. In nitriding, it would act as a barrier for diffusional nitrogen transport [20, 21, 22]. It is generally believed that during DC plasma nitriding, the sputtering of energetic positive ions can effectively remove the oxide film (Cr_2O_3) on the surface and thus accelerate nitrogen mass transfer. In an industrial AS plasma nitriding furnace, an auxiliary voltage can be applied to the parts to be treated at the beginning of a nitriding process to

depassivate the stainless steel surface [7].

However, in the present tests, the sample was placed at a floating potential, and there was no sputtering on the sample surface throughout the whole nitriding period. Yet, nitriding was successfully performed. The AS nitriding has achieved a very similar hardening effect as the normal DC nitriding. This would raise an issue with regard to the role of the oxide layer in nitriding. Probably, the hindering effect of oxide layer to nitrogen diffusion was not as strong as has been claimed, or the hydrogen containing gases used in this study have depassivated the stainless steel surface at the nitriding temperature. Alternatively, the samples were 'freshly' ground before nitriding in this study, and therefore, the oxide layer on the surface could be very thin, and thus, its deleterious effect is limited. Detailed studies are to be conducted to clarify this.

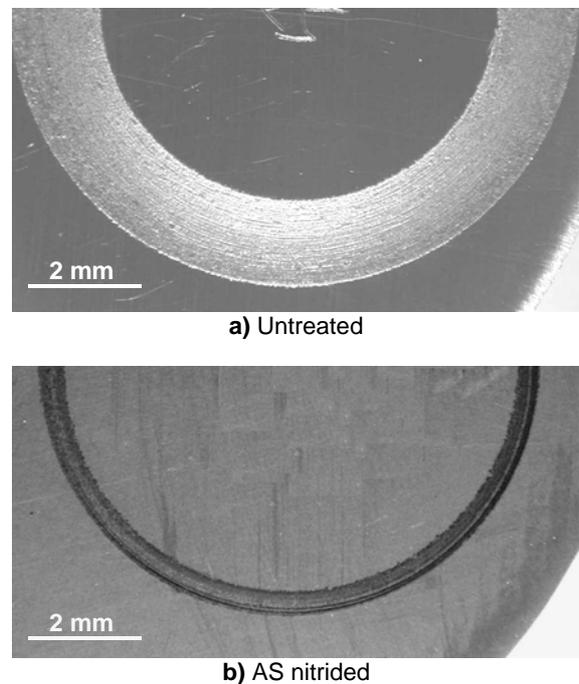


Fig. 10 Wear tracks on the untreated and 420°C active screen plasma nitrided 316 steel sample surface. Contact load 10 N, sliding distance 500 m.

CONCLUSIONS

In summary, active screen (AS) plasma nitriding can achieve similar hardening effect for austenitic stainless steel (AISI 316) as conventional DC plasma nitriding. However, the AS technique does not have the common problems associated with the DC technique such as the 'edging effect'. AS nitriding at a lower temperature, e.g. 420°C, can also produce an S-phase on the austenitic stainless steel surface which exhibits not only high hardness and high wear resistance but also good corrosion resistance.

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