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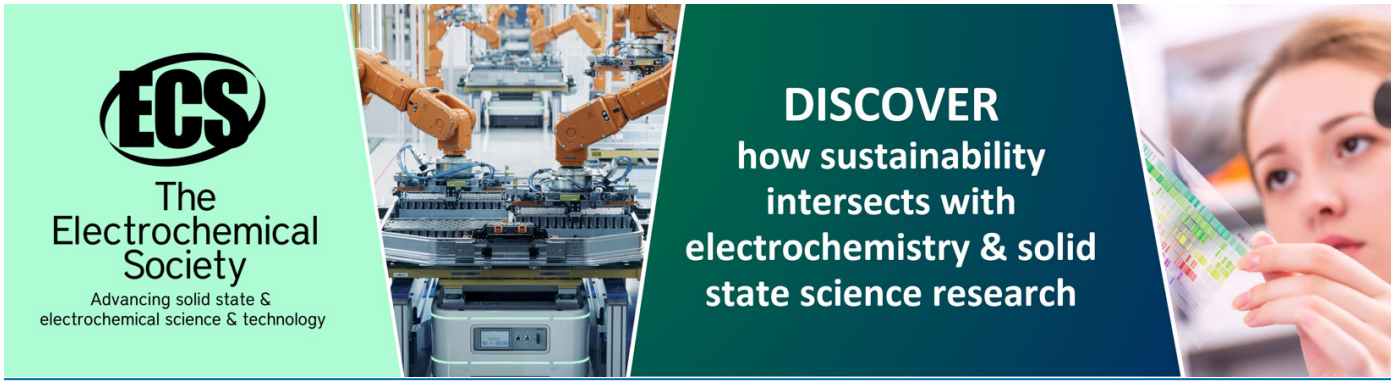

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The Role of Activated Nitrogen Species on Double-folded Screen Nitriding Process

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Abstract: As clean and energy saving surface hardening technology, plasma nitriding techniques have been evolved with object of higher performance in the last decades. Even though the diffusion of nitrogen inward to steel is occurred at the final step, solid diffusion from surface, energy transition from gas molecule of nitrogen to atomic or an activated state have many different steps depending on the plasma conditions, parameters and the design of each equipment. And this study made comparative on nitrogen sources transfer with conventional DC plasma nitriding and novel nitriding process using plasma diagnosis and metallurgical observation. With different vacuum pressure, gas ratio and new designed electrode (double-folded screen cathode electrode), it showed a different behavior of DC plasma nitriding including the nano-sized nitride on the outer surface of specimen due to nitrogen source of determining plasma species. In this study, plasma species was able to identify with optical emission spectroscopy (OES) studies. From these observations, we could understand better role of ions or neutral nitrogen species, like neutral nitrogen (N), N_2^+ and NH_x radicals in plasma nitriding process with different parameters. And cutting layers of nitride specimen were showed the results due to a different species gas flow ratio or plasma conditions.
Keyword: atomic nitrogen, neutral nitrogen, diffusion rate in steel, hollow cathode discharge (HCD) effect, plasma species in plasma nitriding process, optical emission spectroscopy (OES).

1. Introduction

Generally, plasma nitriding process has an excellent benefit in low deformation, energy saving, eco-friendly, can treat a selected area or parts, product reliability, and it has expectedly merits for economical process with low energy consumption and gases. And plasma nitriding process has been widely accepted in industry uses, for the applications to automobile parts, machinery, dies, and molds to enhance wear and anti-corrosion and fatigue properties.

Although plasma nitriding process has many above-mentioned advantages over conventional gas nitriding, it has still applied to the complicated shape product (especially products with deep hollows) and controlling of thickness of compound layer is relatively difficult in practice. During DC plasma nitriding process, nitrogen molecule is introduced to the product surface where nitrogen molecule is activated via glow discharge area in electric field. And nitrogen molecules should be dissociated to ionic species or several radicals for subsequent reactions and adsorption on steel surface and then atomic reacted nitrogen atoms can diffuse into interstitial sites of steel. At the same time, it has a different diffusion rate and hardness profile in dependence on the plasma condition, energy states, the kinds of activated species and mass transfer difference.

Several models for the plasma nitriding processes have been proposed in the part to explain the mass transfer mechanism in plasma nitriding process, example sputtering model, and role of dominant plasma species etc[1].

Recently, plasma-assisted nitriding technology[1-6], and screen nitriding process and its applications[7-9] that utilizes nitrogen atom with auxiliary electrode has been deeply studied because they are able to produce compound-layer-free nitriding layers on steel alloys and thick nitriding layers on non-ferrous metals.

During the conventional plasma process, nitrogen molecule is introduced to product a surface on which some nitrogen gases are ionized in glow discharge area with high current. Since nitrogen molecules are to dissociate as ions or atoms for subsequent reactions, a high ionizing rate can beneficially affect the properties of surface coatings or nitriding layers by the plasma process.

Therefore, many studies have focused on solving such problems by adopting auxiliary electrodes or post plasma technique in a plasma nitriding system.

The novel nitriding process was conceptionally designed and scale-up to generate a high-density neutral atom including others activated ionic species utilizing trapped electron and ions collisions between double folded-cathodic electrodes with enlarged mean free path under higher vacuum range than general plasma nitriding. Although the novel nitriding process utilized high vacuum, high plasma density was achievable from restricted electrons in the magnetic field between negatively charged screens. Fig. 1 shows and summarizes the simple concept and principles of the novel nitriding process.

In particular, after the novel nitriding process has showed a bright mirror surface without compound layer on the specimen surface.

The novel nitriding process, so called by ATONA process, can describe a brief three step reaction of plasma nitriding procedure from ionic source to diffusion couple in the vacuum chamber.

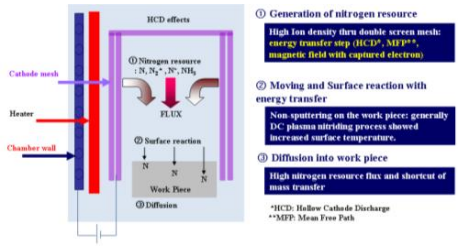


Fig. 1 The concept and a brief of the novel nitriding (ATONA) process.

2. Experimentals procedure

The specimen was a S45C carbon steel. Specimen of S45C was prepared with quenching at 1143K and tempering at 433K and SKD11 mold steel was prepared with quenching at 1303K and tempering at 773K. It was polished with SiC paper followed by fine polishing with 1 μm diamond pastes. Polished S45C carbon steel and SKD11 mold steel specimens were ultrasonically cleaned in acetone.

With the plasma nitriding system, both the novel nitriding and DC plasma nitriding were carried out at the same chamber by applying DC power on the screen and on the jig, for each process, respectively. Base pressures for both the novel nitriding and DC plasma nitriding process were 5×10^{-3} Torr. The temperatures for the novel nitriding and DC plasma nitriding were 500℃, respectively. Before the main process, specimen was ion bombardment with Ar and H_2 gas at a pressure of 5×10^{-2} Torr for 30 minute. During the ion cleaning, a cathode voltage of about -800 V was applied on the jig. After the ion cleaning, N_2 and H_2 gases were backfilled to the nitriding chamber and 10 - 20 KW of power was applied on the screen for the novel nitriding process and on the stage for the DC plasma nitriding process. The working pressure was 0.1 Torr for the novel nitriding and about 2 Torr for DC plasma nitriding process. The ratio of N_2 to H_2 was 1:3 and 3:1 (Fig. 2).

Plasma species was analyzed with optical emission spectroscopy (OES, AVANTE AvaSpec-3648). Microstructure was observed by scanning electron microscope (SEM, HITACH S-4300). The surface hardness and the case depth profiles were determined with a micro-Vickers hardness tester (Future Tech FM-7). An indentation cracking test was carried out with a Rockwell hardness tester (Matsuzawa DXT-3).

3. Results and discussions

Fig. 3 showed results of OES analysis at DC plasma nitriding process with a changing parameters, 1 Torr, 673K, N_2:H_2 = 1:3 about 650V DC power. It has almost same intensity of peak with position of plasma species.

Fig. 4 were showed results of OES analysis of the novel nitriding process with changed parameters, (a) 0.1 Torr, 673K, N_2:H_2 = 1:3, (b) 0.1 Torr, 673K, N_2:H_2 = 3:1, and (c) 1 Torr, 673K, N_2:H_2 = 1:3 12KW DC power on the double-folded screen. In the result of OES analysis of DC plasma nitriding process showed a dominant plasma species with N_2^*, N_2^+.

However, in Fig. 4 (a), Fig. 4(b) and (c) have shown higher intensity of spectra than DC plasma nitriding with some parameters for temperature, gas ratio and pressure.

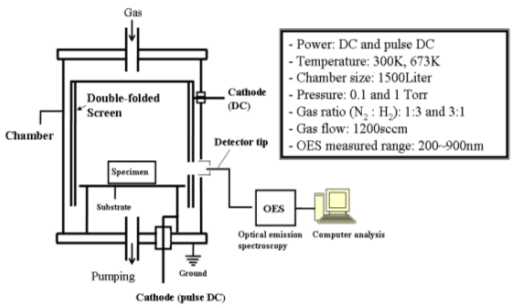


Fig. 2 The parameters of DC plasma nitriding and the novel nitriding process with schematic diagram.

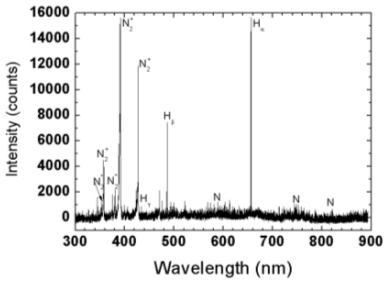


Fig. 3 The results of OES analysis for DC plasma nitriding process at 1 Torr, 673K and gas ratio N_2:H_2 = 1:3.

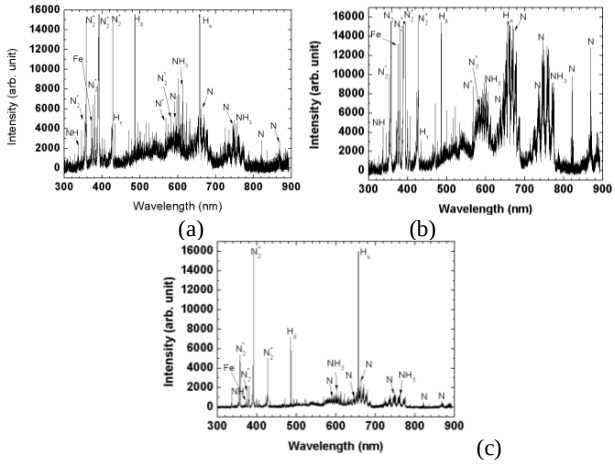
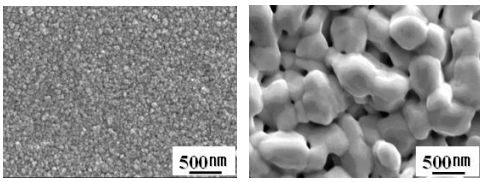


Fig. 4 The results of OES analysis for the novel nitriding process with experimental parameters: (a) 0.1Torr, 673 K, and N_2:H_2 = 1:3, (b) 0.1Torr, 673 K, and N_2:H_2 = 3:1, and (c) 1 Torr, 673 K, and N_2:H_2 = 1:3.

Especially, in the case of the condition of the high nitrogen gas ratio, Fig. 4 (b) showed a peak of high intensity with complicated species, N_2^*, N_2^+, N^+, N, NH_3. It can understand that new concepts and designs for the novel nitriding process, and possibility of high density plasma in higher vacuum chamber and composed auxiliary electrode within double screens. When the N_2 gas flow can make to an increasing plasma species from the crashed N_2 molecules in the double-folded screen, it is summarized of a dominant species in the plasma environment each process in Table 1.

Table 1 Summarize of dominant plasma species of DC plasma nitriding and the novel nitriding process

	DC plasma nitriding	the novel nitriding	
		Low	High
Vacuum	H_2 activity decrease Dominant species : N_2^*, N_2^+	~Torr	10^{-2} ~10^{-1}
		Decreasing H_2 activity	Increasing H_2 activity
Temperature	No affected	300K	673K ~
		H_2 and $N_2^{*(1st, 2nd)}$, N_2^+ activity	H_α, H_β and $N_2^{*(1st, 2nd)}$ N_2^+
Gas ratio (10^{-1} Torr, N_2/H_2)	H_2 activity decrease	$N_2^{*(1st, 2nd)}$, N_2^+, NH_x and N^+	Same left but more higher intensity

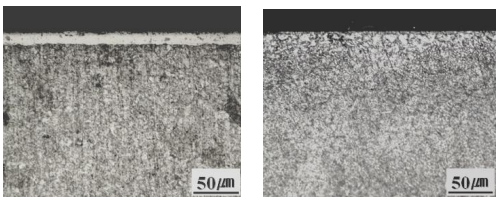


(a) (b)

Fig. 5 The scanning electron micrographs of S45C carbon steel after 2 hr treatment of (a) the novel nitriding and (b) DC plasma nitriding process.

As shown in the secondary electron image of Fig. 5 (b), 2 hr of the novel nitriding process resulted in the formation of nano-sized grains on the S45C carbon steel. The grain size ranged from 30 to 100 nm. On the other hand, 2 hr of DC plasma nitriding yielded 1 - 2 μm grains on the surface of S45C carbon steel, as shown in Fig. 5 (a). Fig. 6 (a) and 6 (b) shows cross-sectional micrographs of the S45C carbon steel after 2 hr of DC plasma nitriding (a) and the novel nitriding (b) treatments.

Generally, most surface of nitrided-steel has a compound layer composed of γ′-(Fe_4N) and/or ε-($Fe_{2-3}N$) phases.



(a) (b)

Fig. 6 Cross-sectional optical microscopy images of S45C carbon steel after 2 hr treatment of (a) DC plasma nitriding and (b) the novel nitriding process.

As shown in Fig. 6 (b), excess thickness of the compound layer does not occur in the novel nitriding treated S45C steel. On the other hand, the thickness of the compound layer of the DC plasma nitriding specimen was about 20 μm during same process time and temperature.

Fig. 7 shows the micro-hardness profiles of DC plasma nitriding and the novel nitriding of S45C steel. At the time, surface hardness of the novel nitrided S45C (black line) steel was very hard indeed about 850 HV. Fig. 8 shows X-ray pattern of the novel nitrided S45C steel. It was composed of γ′-Fe_4N and α-Fe. However it was difficultly distinguished this phase from optical microscopy. Therefore we are supposed to precipitate of γ′-Fe_4N with very small size. And nitrogen content of the nano-sized surface was about 40 atomic percent (Fig. 9). The surface hardness of the novel nitrided S45C carbon steel was about 850 Hv, which was higher than that of DC plasma nitrided S45C carbon steel.

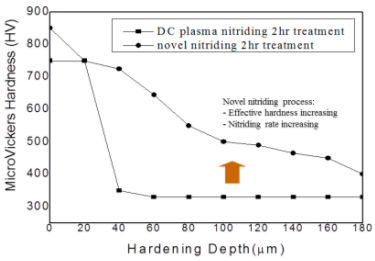


Fig. 7 The competition of micro-hardness profiles of S45C carbon steels of the novel nitrided (square) and DC plasma nitrided (filled circle) process.

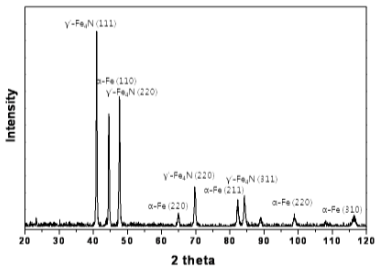


Fig. 8 The X-ray diffraction result of the novel nitrided S45C steel after 2 hr treatment.

To investigate the failure and appearance of the surface of the compound layer, an indentation cracking test was carried out, as shown in Fig. 10. After the indentation cracking test of the DC plasma nitriding specimen Fig. 10 (a), extended cracks were found near the circular indentation. On the other hand, no crack with a mirror

surface was found near an indentation in the novel nitriding specimen Fig. 10 (b). These results indicated that mechanical failure did not occur with the novel nitriding specimen because it had a very thin compound layer. Since the compound layer of the novel nitriding specimen was not thick, failure may have not been as severe as I was for the DC plasma nitriding specimen.

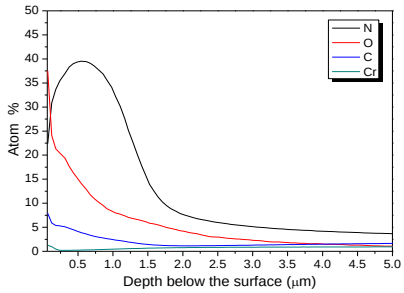
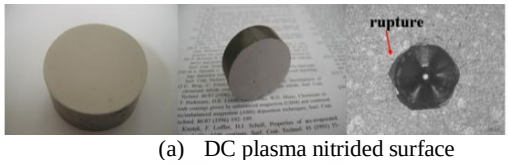


Fig. 9 The result of GDS analysis of the novel nitrided S45C steel.

The novel nitriding process also enhanced the nitrogen diffusion rate of the matrix (Fig. 11). Immediately below the compound layer, a diffusion layer (or diffusion zone) is formed by nitrogen diffusion. The diffused nitrogen atoms are interstitially locating in iron matrix, or forming nitrides with active nitriding elements at grain boundaries, or in grain. This diffusion zone, however, cannot be clearly observed with a microscope.



(a) DC plasma nitrided surface

(b) the novel nitrided surface

Fig. 10 Indentation cracking test results of (a) the novel nitrided S45C carbon steel specimen and (b) DC plasma nitrided S45C carbon steel specimen.

This high hardness of the novel nitrided specimen has shown a result from fast nitrogen diffusion to the matrix. Such fast nitrogen diffusion, compared with DC plasma nitriding, may have been due to the surface nano-grains and thin compound layer.

The adsorption of nitrogen may have increased due to the large portion of grain boundaries at the nano-structured nitride layer since chemical affinity was increased by the long grain boundaries.

The novel nitrided iron has composed with a nano-sized nitride (Fig. 11) on surface, α-Fe and precipitation γ'-Fe_4N phase almost (the result of X-ray diffraction in Fig. 8). The diffusivity of γ'-Fe_4N ($D_{N\gamma'} = 3.2 \times 10^{-12}$ cm^2/s) and ε-$Fe_{2-3}N$ ($D_{N\varepsilon} = 9.8 \times 10^{-11}$ cm^2/s) were slower than α-Fe ($D_{N\alpha} = 1.48 \times 10^{-2}$ cm^2/s) matrix's that at 723K.

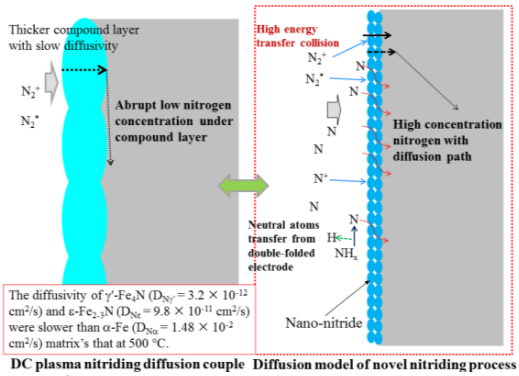


Fig. 11 The diffusion models of DC plasma nitriding and the novel nitriding (ATONA) treated specimen.

Therefore, the amount of adsorbed nitrogen may have been much higher on the novel nitrided specimen than on the DC plasma nitriding treated specimen which caused a high concentration gradient of nitrogen. In our case, the high concentration layer was under 500 nm of the novel nitrided surface, which was at least 4 times lower than that of the DC plasma nitriding treatment. And the nitrogen diffusion rate on the novel nitrided S45C carbon steel was much higher than that on the DC plasma nitriding treated S45C carbon steel.

In particular, plasma nitriding process can make easily the compound layer determined most slowly a diffusion couples via N_2^+, N_2^* at final step of solid diffusion. The compound layer is composed with ε-$Fe_{2\text{-}3}N$ and γ′-Fe_4N phase that has constant chemical concentration with 6.6 ~ 11.2wt. % of nitrogen within diffusion couples. In this case, the novel nitriding process can understand three steps with crashing neutral nitrogen atom and gas diffusion into the vacuum chamber and adsorption on the cold and electric floated specimen surface as following concepts.

At the first step, the generation of neutral nitrogen resource at Fig. 12, nitrogen molecules transferred activated and ionized species extremely by auxiliary electrode between double-folded electrodes with hollow cathode discharge under high vacuum chamber relatively general plasma nitriding process.

Especially, Fig. 12 was showed the captured electron motion in the double-folded screen that it has energetic motion of several effective collisions with higher vacuum state.

In the Fig. 4 (a) and (b) was showed and understood easily for activated species in the novel nitriding process due to nitrogen source of species for DC plasma nitriding, H_α, H_β, H_γ, and including N_2^+, N_2^* with neutral nitrogen and ammonia group in the novel plasma nitriding process [10-13].

And the second step, the motion of activated species has enlarged and moved to specimen surface with mean free path (MFP) via higher vacuum range than general plasma nitriding process.

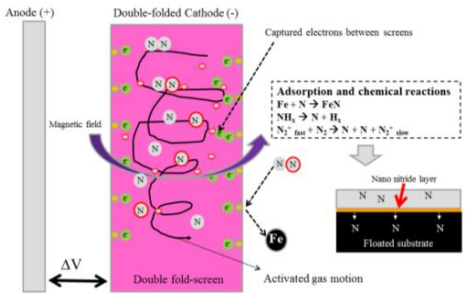


Fig. 12 Behaviors of captured electrons in the double-folded screen electrode and chemical reaction model of plasma species.

At third step, the surface of specimen has homogeneous temperature with an external heating elements, it can sustain a nano-sized nitride without grain growth even though it is composed with the sputtered iron atom from electrode with activated nitrogen species, and after nitriding treatment has a brighten surface. Finally, the enlarged surface area has composed with a high concentration nitrogen atom by nano-sized nitride enhanced high adsorption rate without formation of a compound layer and diffuse into the solid steel surface due to high concentration of neutral nitrogen atom.

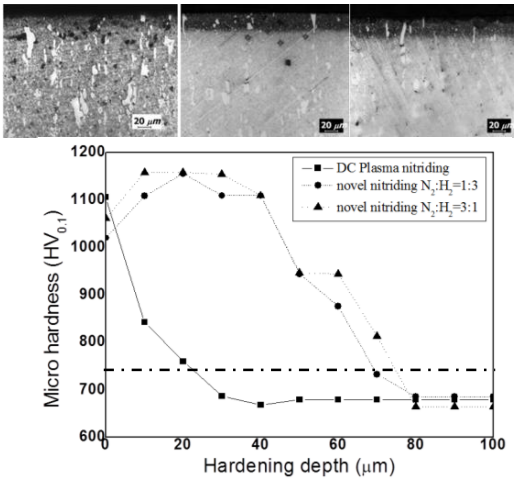


Fig. 13 It has shown a summarizing of analyzed results for the each process with parameter of DC plasma nitriding and the novel nitriding process on SKD 11 mold steel.

4. Conclusions

From the above comparative studies with different pressures and temperature and gas ratio, we could understand different mechanisms of mass transfer depending on the energy and position of glow source. Newly developed the novel nitriding process has the advantage for the treatment of complicated parts with high density plasma using auxiliary electrode in the chamber.

Definitely, the novel nitriding process distinguish with DC plasma nitriding process at dominant reactive species in the reaction chamber by OES analysis that the novel nitriding showed high energized neutral nitrogen atoms, activated nitrogen molecules, N_2^*, N_2^+, and NH_3 but DC plasma nitriding showed dominantly N_2^+ molecule. It can be shown distinguish of the depth profile each nitriding processes after treatment at Fig. 13.

Therefore, the novel nitriding shows a brighten mirror image with nano-sized nitride surface without compound layer even it has shown more deep hardening and high hardness profile than DC plasma nitriding process with same treating time. Exactly, the speed of the novel nitriding process is much faster than that of general plasma nitriding due to fast diffusion at least.

Whatever it is, the novel nitriding system can be used to easily get to the S-phase on austenitic stainless steel, in addition to the interlayer of PVD coatings. Besides this kinds process, as we know, is very useful in surface hardening of pre-hardening mold steel for the plastic forming tools that they have to have super cleaned surface with submicron ordered surface roughness.

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