한국표면공학회지
J. Kor. Inst. Surf. Eng.
Vol. 38, No. 5, 2005.
<연구논문>

Effects of Gas Flow Ratio on the Properties of Tool Steel Treated by a Direct Current Plasma Nitriding Process

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(Received 16 September 2005 ; accepted 14 October 2005)

Abstract

Nitriding treatments were conducted on tool steel (SKD 61) at a temperature of 500°C for 5 hr using high vacuum direct current (DC) plasma, with ammonia and argon as source gases. The structural and compositional changes produced in the nitrided layers by applying different ratios of Ar to NH_3 (n_{Ar}/n_{NH3}) were investigated using glancing x-ray diffraction (GXRD), optical microscopy, atomic force microscopy (AFM), micro-Vickers hardness testing, and pin-on-disc type tribometer. Nitriding case depths of around of 50 μm were produced, varying slightly with different ratios of n_{Ar}/n_{NH3}. It was found that the specimen surface hardness was 1150 Hv with n_{Ar}/n_{NH3}=1, increasing to a maximum value of 1500 Hv with n_{Ar}/n_{NH3}=5. With a further increase in ratio to n_{Ar}/n_{NH3}=10, the surface hardness of the specimen reduced slightly to a value of 1370 Hv. These phenomena were caused by changes of the crystallographic structure of the nitride layers, i.e the γ'-Fe_4N phase only was observed in the sample treated with n_{Ar}/n_{NH3}=1, and the intensity of the γ'-Fe_4N phase were reduced but new phase of ε'-Fe_3N, which was known as a high hardness, with increasing n_{Ar}/n_{NH3}. Also, the relative weight loss of counterface of the pin-on-disc with unnitrided steel was 0.2. And that of nitrided steel at a gas mixture (n_{Ar}/n_{NH3}) of 1, 5, 7, and 10 was 0.4, 0.7, 0.6, and 0.5 mg, respectively. This means that the wear resistance of the nitrided samples could be increased by a factor of 2 at least than that of unnitrided steel.

Keywords : Plasma nitriding process, SKD 61, Hardness test, Wear test

1. Introduction

Several nitriding techniques have been used for a long time in industry to improve the thermal fatigue resistance and the tribomechanical properties of engineering components. The improvement of tribological properties and corrosion resistance of these materials have been studied for many years[1-3], essentially in several steel types. Some nitride procedures are described in the literature which show their different effects in the final products[4,5].

During nitriding, nitrogen is diffused into a steel surface where it combines with alloying nitrides. These precipitates strengthen the surface region and introduce beneficial compressive stresses at the surface[6]. The relatively low temperature of nitriding, usually in the range of 480-570°C allows fully stabilized, hardened and tempered components to be surface hardened with only minimal risk of distortion and dimensional variations. In comparison to traditional thermal and thermochemical surface treatments such as hardening and carburizing, nitriding allows the reduction or even elimination of the need for a subsequent expensive machining phase. Also, to avoid using the expensive high-vacuum pumps, low-vacuum plasma assisted nitriding techniques made by Brokman and Tuler was currently well employed[7,8].

However, although the structural properties of nitrided tool steel are highly important in obtaining a better understanding of their physical properties, they

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*Corresponding author. E-mail : hgjang@phya.yonsei.ac.kr have not yet been well investigated. Therefore, the purpose of this study was to obtain the structural properties of SKD 61 and their structural variation induced by the gas ratio of Ar to NH_3 (n_{Ar}/n_{NH3}). In the present study, we used the low-pressure direct current (DC) plasma technique for the treatment of tool steel (SKD 61) using ammonia and nitrogen source gases.

2. Experimental Procedure

Commercial tool steels (SKD 61) were used for this experiment and the specimen was cut into a disc type sample of $\phi 28 \times 15$ mm. The weight composition of tool steel used in this study was C (0.35%), Si (0.93%), Mn (0.48%), P (0.03%), S (0.03%), Cr (5.69%), Mo (1.23%), V (1.11%), and Fe (90.15%). The surfaces of the specimen to be treated were polished to a 1 mm diamond finish by conventional metallographic techniques. The specimen was subsequently cleaned with ultrasonic detergent, deionized water, alcohol, and dry nitrogen. All samples were kept in a dry oven at 60°C for 24 h to remove the residual mechanical stress and solvent. All samples were mounted to a copper plate inside of furnace for hardening to improve the hardness. To avoid modification of structure due to the hardening process, heat treating are carried out 3 step annealing such as shown in Fig. 1. The hardness of the heat treated samples was 500 Hv_{100}.

The cylindrical vacuum chamber had a diameter of 1.0 m and a height of 1.6 m. The base plate, 0.7 m in diameter, onto which the steel to be nitrided was mounted, was connected to the DC voltage-controlled generator. In addition to plasma heating, heater was fitted into the walls of the chamber, and the substrate temperature was measured using a thermocouple. To control the pressure, a regulating valve was placed between the pump and chamber. The process gases, NH_3 and Ar, which were controlled by mass-flow controllers, were introduced into the chamber from the top through a shower head.

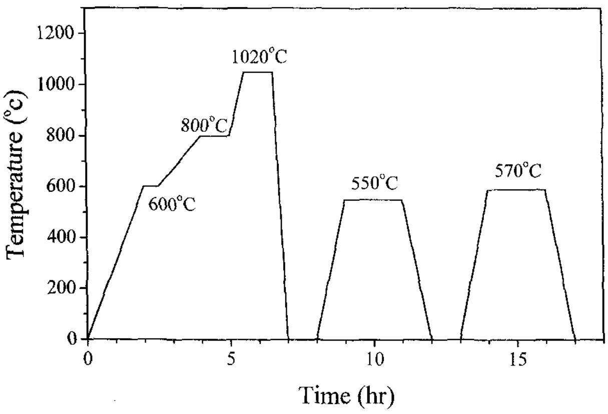

Fig. 1. Annealing temperature of the tool steel as a function of annealing time.

Four steel samples were treated at 500°C with various gas ratio of NH_3 to Ar (n_{Ar}/n_{NH3}) at a fixed discharge voltage of 500 and the substrate bias of 0 V. The source gas used was ammonia (99.98%) and argon (99.9995%) and total flow rate was 1000 sccm. The chamber was evacuated with an 8-in-diam. root pump with pump speed of 5,400 l/min. Initial base pressure was typically 1×10^{-3} Torr in the chamber and working pressure during nitriding was 2-5 Torr. All samples were treated for 5 h while the n_{Ar}/n_{NH3} ranged from 1 to 10.

The specimens were investigated by several techniques including scanning electron microscopy (SEM); glancing angle X-ray diffraction (GXRD) using Cu K α 1 radiation. An AFM (PSI Co.) was used to study the surface morphology of the nitrided surface and to measure the root-mean-square (rms) surface roughness. The microhardness measurements (Micro-Vickers hardness Tester, Future tech. Co.) were taken on the nitrided surface and were carried out using the load dependence of the residual penetration depth of the indenter – calculated from the geometry of the Vickers pyramid imprint. Ball-on-disk type wear tests were performed at room temperature. Applied load was 5 N and the sliding distance was 1,000 m with a linear velocity of 4 mm s^{-1}. A bearing ball (SUJ2) with 6 mm in diameter was used as counterface ball and the relative humidity was 25%.

3. Results and Discussion

Fig. 2(a)-(e) shows the AFM surface images of the tool steel as a function of n_{Ar}/n_{NH3}. A significant difference is observed in their surface morphology. Surface roughness of the steel nitrided for 5 hr was higher than that of the unnitrided steel. To get reliable surface roughness data, five different areas of each sample were scanned. The rms surface roughness of the unnitrided steel and the steels nitrided at $n_{Ar}/n_{NH3}=1$, $n_{Ar}/n_{NH3}=5$, $n_{Ar}/n_{NH3}=7$, and $n_{Ar}/n_{NH3}=10$ was 21.6, 45.6, 101, 118 and 149 nm, respectively. The rms surface roughness of the nitrided steel increased with increasing n_{Ar}/n_{NH3}. As shown in Fig. 2, the surface of the bare steel was smooth, but the surface of the steel nitrided at $n_{Ar}/n_{NH3}=5$ became like a

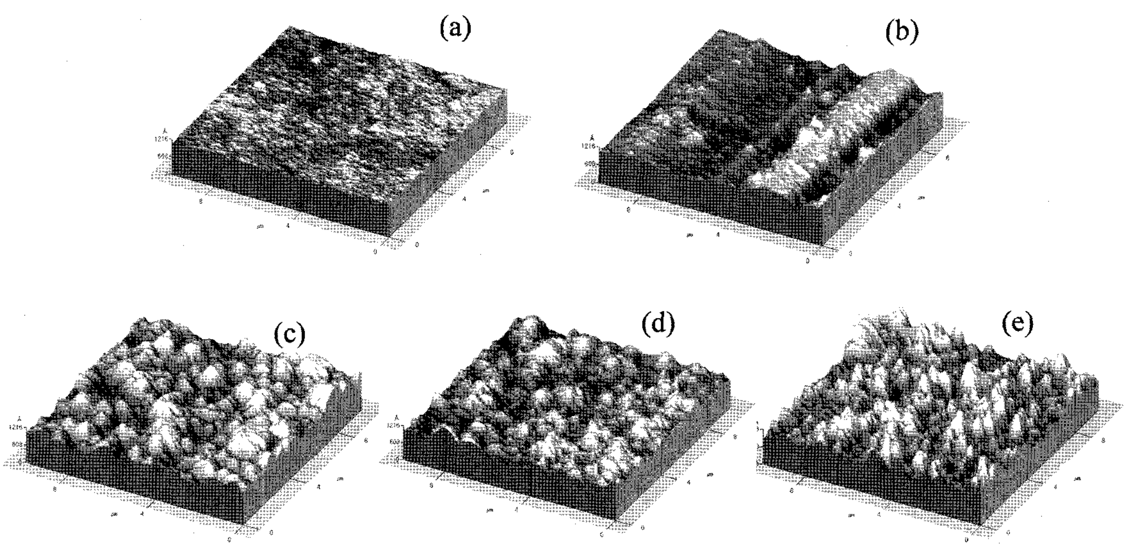

Fig. 2. AFM surface image of the tool steel as a function of relative gas flow rate: (a) bare steel, (b) $n_{Ar}/n_{Ar\ NH3}=1$, (c) $n_{Ar}/n_{Ar\ NH3}=5$, (d) $n_{Ar}/n_{Ar\ NH3}=7$, (e) $n_{Ar}/n_{Ar\ NH3}=10$.

conical and or pyramid structure, due to the difference of sputtering yield in a localized area[9]. And the diameter of the conical structure were ranged from 0.5 to 1.53 μm and their height ranged from 18 to 43 nm. While the steel nitrided at $n_{Ar}/n_{NH3}=10$, the number of small conical structure at the steel surface were increased (refer to Fig. 2(e)). Their size was slightly decreased to 0.4-0.8 μm, but the height of the conical structure greatly increased to 0.06-0.13 μm. The difference of the surface morphology may be due to the different differential cross section and the ionization energy between argon and ammonia. The differential cross section of ammonia is smaller than that of argon and the ionization energy of Ar (15.75 eV)[10] is larger than that of ammonia (11.2 eV)[11], so that the flux of the incident ions to the surface may be increased with increasing n_{Ar}/n_{NH3}.

Fig. 3 shows the optical microstructure of cross-

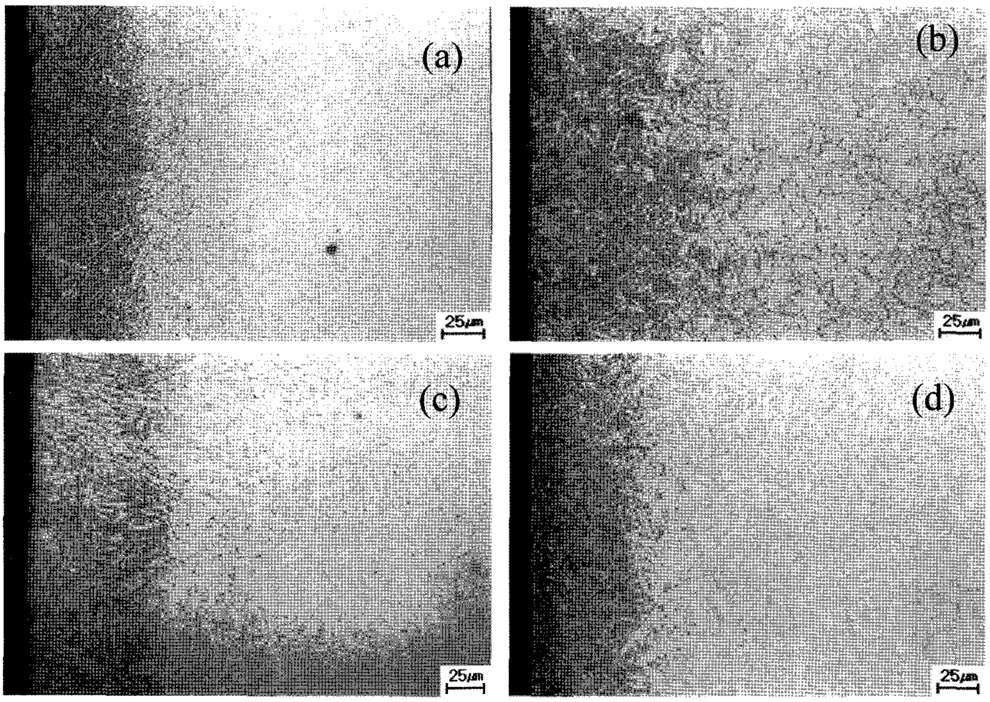

Fig. 3. Cross-sectional photograph of the plasma nitrided SKD61 steel as a function of relative gas flow rate: (a) $n_{Ar}/n_{Ar\ NH3}=1$, (b) $n_{Ar}/n_{Ar\ NH3}=5$, (c) $n_{Ar}/n_{Ar\ NH3}=7$, (d) $n_{Ar}/n_{Ar\ NH3}=10$.

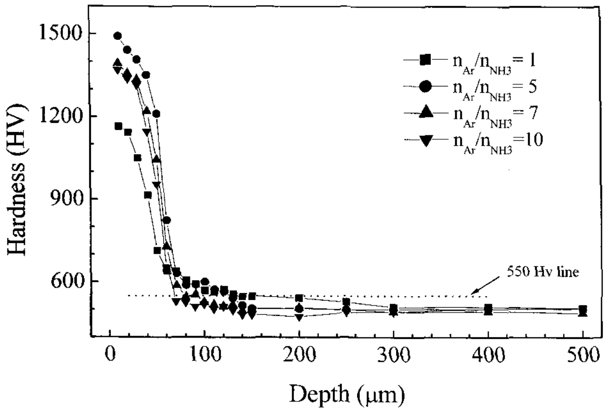

Fig. 4. The microhardness depth profiles obtained from the cross-section of nitrided samples as the function of relative gas flow rate: (a) $n_{Ar}/n_{Ar\ NH3}$=1, (b) $n_{Ar}/n_{Ar\ NH3}$=5, (c) $n_{Ar}/n_{Ar\ NH3}$=7, (d) $n_{Ar}/n_{Ar\ NH3}$=10.

sections plasma-nitrided specimens as a function of n_{Ar}/n_{NH3}. During nitriding, nitrogen diffuses into the steel surface and combines with alloying elements to form a diffusion zone containing a fine dispersion of nitride precipitates. It can be seen that distinct nitride layer is observed on the nitrided surface. Fig. 4 displays the microhardness depth profiles obtained from the cross-section of nitrided samples. As shown in Fig. 4, the micro-Vickers hardness of the surface nitrided at a gas mixture (n_{Ar}/n_{NH3}) of 1, 5, 7, and 10 was 1165, 1492, 1394, and 1390 Hv, respectively. This means that the hardness of the nitrided samples could be increased by a factor of 2. From this type of grape, we have estimated the penetration depth of the indenter for a microhardness 100% greater than the initial value of the unnitrided steel plus 50 Hv. The obtained values are considered to be representative of, but not necessarily equal to, the thickness of the nitrided layer. The values of this representative depth for a gas mixture (n_{Ar}/n_{NH3}) of 1, 5, 7, and 10 were 130, 125, 90, and 70 μm, respectively. The decrease of the representative depth with increasing n_{Ar}/n_{NH3} may be explained as follows; as increasing n_{Ar}/n_{NH3}, amount of Ar^+ ions in plasma should be increased. And the mass of Ar^+ is heavier than that of NH_3^+ so the projected range of Ar^+ ions with 500 V incidented on tool steel is shorter than that of NH_3^+ ions. Also, the projected Ar^+ ions in tool steel are very inert so that a fine dispersion of nitride precipitates could not formed in tool steel.

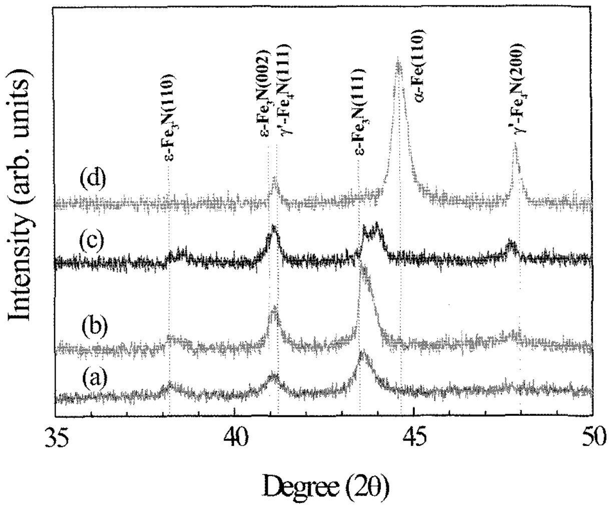

Fig. 5. XRD spectrum of the plasma nitrided SKD61 steel as the function of relative gas flow rate: (a) $n_{Ar}/n_{Ar\ NH3}$=1, (b) $n_{Ar}/n_{Ar\ NH3}$=5, (c) $n_{Ar}/n_{Ar\ NH3}$=7, (d) $n_{Ar}/n_{Ar\ NH3}$=10.

Fig. 5 shows the glancing angle X-ray diffraction pattern as a function of n_{Ar}/n_{NH3}. The XRD measurements revealed that the formation of high nitrogen ε-Fe_3N, and γ'-Fe_4N phase on the outer surface, although a continuous nitride layer was not clearly observed by microscopy. ε-Fe_2N phase which contains higher nitrogen was not observed in the sample nitrided regardless of n_{Ar}/n_{NH3}. A few peaks corresponding to Fe_xN phase also were observed. In view of limited number of peaks, it was not possible to identify the phase precisely. Comparing Fig. 3 with the results of XRD, nitrided layer of the sample nitrided at n_{Ar}/n_{NH3}=1 was very shallow and ε-Fe_3N, and γ'-Fe_4N phase were coexisted. But increasing with the n_{Ar}/n_{NH3}=7, the intensity of ε-Fe_3N peak was decreased. The precipitation of α-Fe was showed in the nitrided layer at n_{Ar}/n_{NH3}=10, and it caused the reduced hardness of the nitrided layer. It was well known that the hardness effect on the nitrided samples is

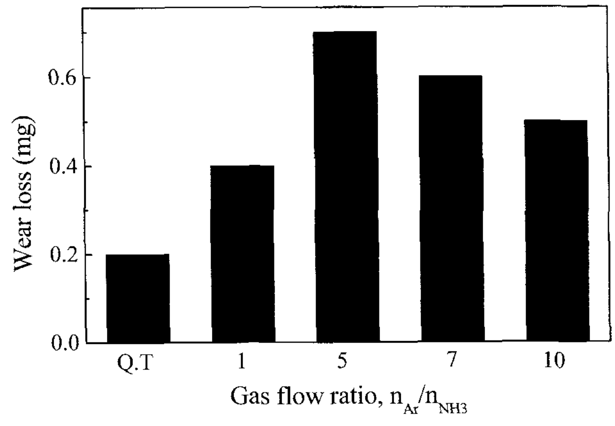

Fig. 6. Relative weight loss of the pin-on-disc as the function of relative gas flow rate: (a) $n_{Ar}/n_{Ar\ NH3}$=1, (b) $n_{Ar}/n_{Ar\ NH3}$=5, (c) $n_{Ar}/n_{Ar\ NH3}$=7, (d) $n_{Ar}/n_{Ar\ NH3}$=10.

dependent of the formation of nitride on the outer surface, and nitrogen containing martensite in the matrix.

Fig. 6 shows the relative weight loss of counterface of the pin-on-disc as a function of gas flow ratio, n_{Ar}/n_{NH3}. The plotted data are the average of results obtained from four tests after 1000 m sliding distance for each samples. As shown in Fig. 6, the relative weight loss of the pin-on-disc with unnitrided and nitrided at n_{Ar}/n_{NH3} of 1, 5, 7, and 10 was 0.2, 0.4, 0.7, 0.6, and 0.5 mg, respectively. This means that the hardness of the nitrided samples could be increased by a factor of 2 at least. These wear loss well accord with the results of the microhardness profile and the XRD analysis. When the phases of ε-Fe_3N and γ'-Fe_4N in nitrided layer was formed with maximum ratio, the nitrided layer became the maximum hardness and wear resistance.

4. Conclusions

Plasma nitriding into commercial tool steels (SKD61) at a process temperature of 500°C for nitriding time of 5 h produced high nitrogen ε-Fe_3N, and γ'-Fe_4N phase on the outer surface. ε-Fe_3N phase of the nitrided layer decreased with increasing n_{Ar}/n_{NH3}. The microhardness of the nitrided layer was above 1165 HV and the maximum microhardness is 1492 HV with $n_{Ar}/n_{NH3}=5$. The values of this representative depth for a gas mixture (n_{Ar}/n_{NH3}) of 1, 5, 7, and 10 were 130, 125, 90, and 70 μm, respectively.

The relative weight loss of the countface of the pin-on-disc with unnitrided and nitrided at n_{Ar}/n_{NH3} of 1, 5, 7, and 10 was 0.2, 0.4, 0.7, 0.6, and 0.5 mg, respectively. This means that the hardness of the nitrided samples could be increased by a factor of 2 at least. It was found that the nitrided layer had the maximum hardness and wear resistance, when the phases of ε-Fe_3N and γ'-Fe_4N in nitrided layer were formed with maximum ratio.

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