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## Improved Adhesion of DLC Films by using a Nitriding Layer on AISI H13 Substrate

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### Abstract

Diamond-like carbon (DLC) is difficult to achieve sufficient adhesion because of weak bonding between DLC film and the substrate. The purpose of this study is to improve the adhesion between substrate and DLC film. DLC film was deposited on AISI H13 using linear ion source. To improve adhesion, the substrate was treated by dual post plasma nitriding. In order to define the mechanism of the improvement in adhesive strength, the gradient layer between substrate and DLC film was analyzed by Glow Discharge Spectrometer (GDS) and Scanning Electron Microscope (SEM). The microstructure of the DLC film was analyzed using a micro Raman spectrometer. Mechanical properties were measured by nano-indentation, micro vickers hardness tester and tribology tester. The characteristic of adhesion was observed by scratch test. The adhesion of the DLC film was enhanced by active screen plasma nitriding layer.

*Keywords* : DLC Coating, Plasma nitriding, Adhesion, Active screen

## 1. Introduction

Diamond-like carbon (DLC) coating has a unique combination of excellent mechanical and chemical properties such as low friction, high wear resistance and corrosion resistance. Therefore, it has been applied to various applications such as cutting tools, VLSI packaging tools, dies, sliding parts, automotive engine parts, hard disks, electronic components, infrared optical windows, machining drills and bio-medical parts. However, it is difficult to apply

to most substrates materials because of low adhesion. This poor adhesion is mainly due to high residual compressive stress of the films and instability of the carbon-carbon bonds, which reduce the chemical cohesion to different substrate materials.[1] The high residual stress in the fabricated DLC film causes failure of interaction between the DLC film and the substrate. Reduction of residual stress of the DLC coating is an important issue in obtaining good adhesion to metallic substrates. Also, when this material is applied on soft materials like low alloy steel, plastic deformation of the substrates used results in poor durability of the DLC coating.[2-4] J. Jiang et al. investigated the tribological prop-

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erties of DLC films with various substrates to determine the effect of the mechanical properties of the substrates. They demonstrated that substrates with lower elasticity and higher yield strength were desirable for improvement of adhesion.[5] Therefore, including nitriding metal into the substrates is good for improving the adhesion strength at the film-substrate interaction. To prevent the DLC thin film from being cracked and fractured, the plasma nitriding process is used as a pre-treatment process before DLC thin film deposition, because this process increases the hardness of the metal substrate and suppresses the plastic deformation of the base metal.[2,6,7,15] On the other hand, the local heating of substrates by ion collision is known to relax the compressive residual stress in DLC films. Then, if the entire surface is heated by dual-post plasma nitriding heating, the residual stress in the DLC films will be improved. The active screen plasma nitriding and deposition system is a relatively new method used for DLC film deposition. Plasma nitriding has potential for use as a pre-treatment technique during DLC deposition on steel substrates, as it helps in preventing DLC coating failure by hardening the substrate and retarding plastic deformation of the substrate.[6-8]

In this paper, an active screen plasma nitriding and deposition system was used to improve adhesion. DLC films were prepared on nitrided and non-nitrided AISI H13 substrates. In order to clarify the mechanism of the improvement in adhesive strength, the nitrided layer between the substrate and the DLC film was investigated by glow discharge spectrometer (GDS) and scanning electron microscope (SEM). The characteristics of adhesion were observed by scratch tester. Furthermore, the microstructure of the DLC

film was analyzed using a micro-Raman spectrometer. Nano-indentation was used to measure the mechanical properties. The characteristics of the improved adhesion were observed by scratch tester. A method to determine the adhesion strength of the DLC films was suggested from these results, and the effect of the active screen plasma nitriding on the improvement of the adhesion of the DLC films was evaluated quantitatively.

## 2. Experimental procedure

AISI H13 combines good hardness and abrasion resistance with the ability to resist heat checking. AISI H13 (Seah, South Korea) is a tool steel for high working temperatures and is the most widely used steel for aluminum and zinc die casting dies. It is also popular for extrusion press tooling because of its ability to withstand drastic cooling from high operating temperatures. The chemical composition of AISI H13 is shown in Table 1. The specimens were in the form of round disks with diameters of 20 mm and thicknesses of 10 mm. Specimens were polished with sand paper of grit no. 200, 320, 600 and 1200 before final polishing with 1 and 3  $\mu\text{m}$  diamond suspension. Then, to remove any chemical residues or impurities, the specimens were cleaned in trichloroethylene (Daejin chemical, South Korea), acetone (Daejin chemical, South Korea), and 2-propanol (Daejin chemical, South Korea), in that order, for 5 min each in an ultrasonic bath.

Fig. 1 provides a schematic of the active screen plasma nitriding system. The active screen plasma nitriding system was used for nitriding on steel tool dies (SKD61 (Seah, South Korea) or AISI H13) before deposition of DLC coating. Samples are placed on the base plate

Table. 1. Chemical compositions (wt.%) of AISI H13.

| C         | Si        | Mn    | P     | S     | Cr        | Mo        | V         |
|-----------|-----------|-------|-------|-------|-----------|-----------|-----------|
| 0.32/0.42 | 0.08/1.20 | <0.50 | <0.03 | <0.03 | 4.50/5.50 | 1.00/1.50 | 0.80/1.50 |

Balance Fe.

Table. 2. Conditions for active screen plasma nitriding.

| Process       | Process time (min) | treatment pressure (Torr) | Temperature (°C) | N <sub>2</sub> gas (sccm) | H <sub>2</sub> gas (sccm) | DC bias (A) | pulse bias (A) |
|---------------|--------------------|---------------------------|------------------|---------------------------|---------------------------|-------------|----------------|
| 1. Heating I  | 60                 | 0.3                       | 225              | 500                       | -                         | -           | -              |
| 2. Heating II | 60                 | 0.3                       | 450              | -                         | 500                       | -           | -              |
| 3. Cleaning   | 30                 | 0.1                       | 450              | 500                       | 500                       |             | 7              |
| 4. Nitriding  | 240                | 0.1                       | 450              | 300                       | 900                       | 20          |                |

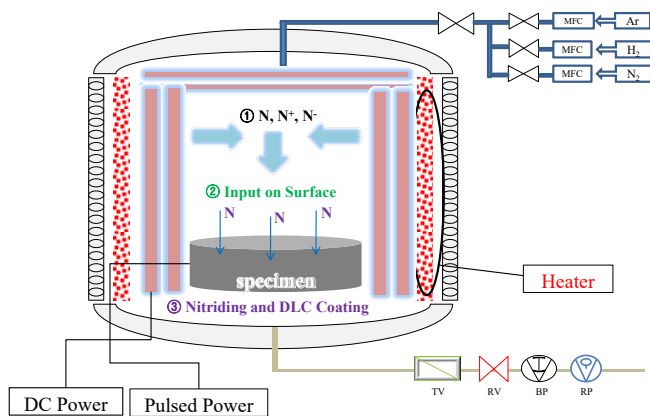


Fig. 1. Schematic diagram of active screen plasma nitriding system.

which is enclosed by the large metal active screen made from expanded mesh called active screen. The base plate and AISI H13 to be treated are then allowed to float without pulsed power. The rationale behind this innovation was the claim that the active species in plasma nitriding were highly energetic neutrals rather than ions and so there is no need to form the plasma directly onto the parts to be treated.[9] The parameters of the active screen plasma nitriding treatment, such as pulsed DC power, DC bias voltage, working pressure, nitriding processing time, and type of precursor gas used, were varied as shown in Table. 2. The hardness of the nitrided AISI H13 substrates was measured by a micro-Vickers hardness tester (Mitutoyo, HM-220A, Japan) under an indentation load of 1.0 N. The thickness of the nitriding layer was measured by SEM depth profile analysis. GDS (Horiba, JY10000RF, Japan) depth profile analysis was performed to determine the nitrided chemical compound.

DLC films were deposited on the nitrided AISI H13 substrates using a linear ion source (LIS). Fig. 2 shows a schematic of the LIS system. The distance between the LIS and the substrate holder was about 150 mm. A DC power supply was applied to the substrate holder, which can be rotated at the desired speed of 3.33 rpm. Before DLC deposition, the substrates were initially cleaned for 50 min with an Ar ion beam with a current of 0.6 A, voltage of  $-1400$  V and substrate bias voltage of  $-100$  V. After Ar cleaning, substrates were treated with chromium (Cr) sputter by Ar gas at 80 sccm, target current of 5 A, and substrate bias voltage of  $-100$  V. The Ar plasma cleaning conditions and Cr sputtering

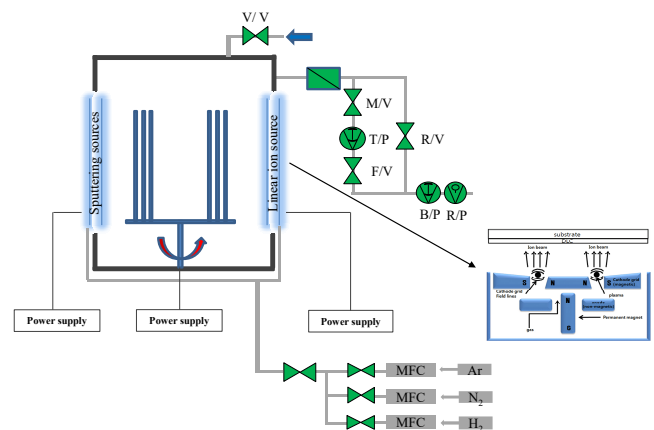


Fig. 2. Schematic diagram of hybrid deposition system for DLC deposition process.

Table. 3. Conditions for DLC film deposition.

|   |            |      |
|---|------------|------|
| Process time (min)                                | 70         |      |
| Bias (V)  | -100       |      |
| Ion beam C <sub>2</sub> H <sub>2</sub> gas (sccm) | 80         |      |
| Power Supply                                      | Current(A) | 0.6  |
|   | Voltage(V) | 1400 |

were selected to obtain sufficient adhesion without significant surface damage. Table. 3. shows the conditions for DLC film deposition. The microstructure of the DLC films was analyzed using a micro-Raman spectrometer (Bruker, Vertex 80V, Germany). The microstructure of the interface between the DLC films and the substrates was examined in detail by SEM (Hitachi, S-4800, Japan) observation. Mechanical properties were measured by nano-indentation (Anton Paar, NHT-T-AE-0000, Swiss) with the continuous stiffness method (CSM) mode. In order to minimize the effects of the substrates, nano-indentation was set to 0~500 nm depth. Indentation depth was measured at 25 locations in the range of 0~500 nm. The adhesion strength between the DLC films and the substrates was observed by scratch tester (J&L Tech Co., Ltd., JLST022, South Korea). A sharp diamond tip of 200  $\mu\text{m}$  radius was used for scratching. The load speed increased uniformly from 0 to 50 N for a distance of 8 mm at a scratching speed of 0.2 mm/s. The scratched path was then observed in an optical microscope mounted on the scratch tester. During the scratch test, friction forces were continuously monitored.

### 3. Results and Discussion

#### 3.1. Nitriding

Fig. 3 shows a cross-sectional SEM image of nitride AISI H13. The compound layer formed to a depth of 35  $\mu\text{m}$  on the substrate. It is observed that the microstructure consists of an internal nucleus of a nitride layer on the sample. The nitride layer consists of an  $\text{N}_2$  diffusion zone with fine precipitated nitride plates and an oxide compound layer in the counterpart.[10] Then the nitride layer was formed by a penetration and diffusion reaction of  $\text{N}_2$  ion. GDS analysis was used for analyzing the nitride layers, because it is difficult to use SEM imaging to determine

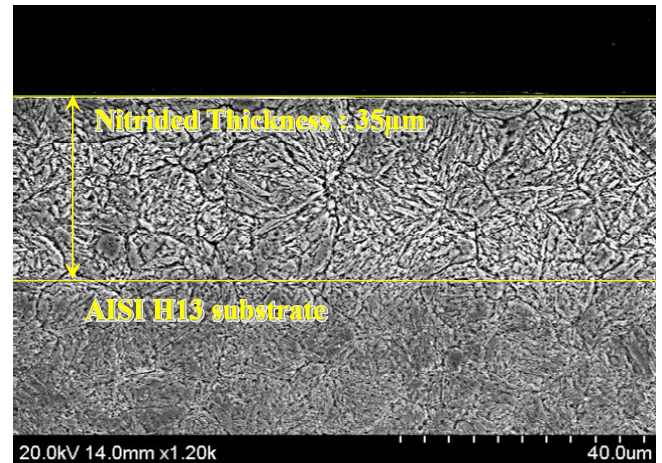


Fig. 3. Cross-sectional SEM image of nitrided AISI H13 substrate.

nitride.

Fig. 4 shows the chemical composition depth profile of the AISI H13 nitrided by GDS. The relative wt.% values of Fe, Cr, and N are plotted as a line scan, taking into account the sensitivity factors for the stated elements. The surface of AISI H13 contained N ions to a depth of 35  $\mu\text{m}$  because N ions penetrated into AISI H13. In particular, electron irradiation performed by applying a positive voltage is effective at increasing the substrate temperature,[11] which is easy for the diffusion of N atoms on the substrate. In addition, the  $\text{N}_2$  wt.% dropped significantly by about 35  $\mu\text{m}$  and was consistent with the case depth measured using SEM. Therefore, it can be seen that the nitride layer formed on the surface of AISI H13.

Fig. 5 shows the cross-sectional hardness of AISI H13. The cross-sectional hardness values of

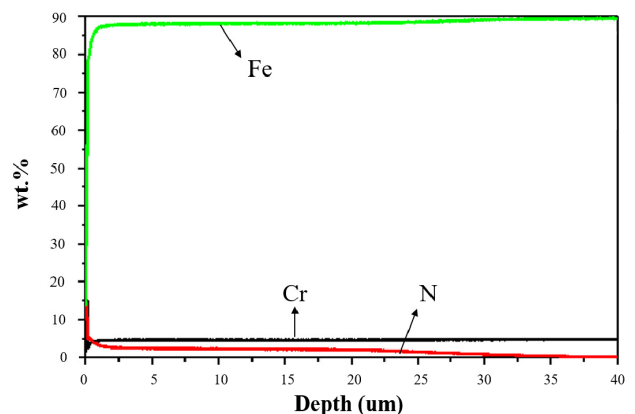


Fig. 4. Chemical composition depth profile of the nitrided AISI H13, measured by GDS.

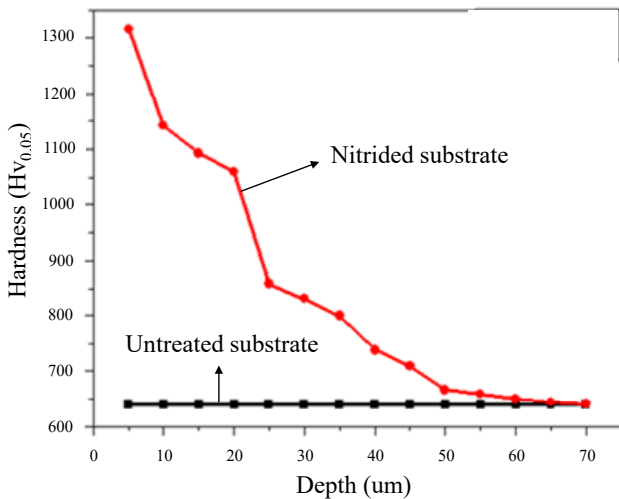


Fig. 5. Micro-hardness Vickers depth profile of nitrided AISI H13 substrate.

nitrided and non-nitrided AISI H13 were measured per 5  $\mu\text{m}$  at 50 g load using a micro-Vickers hardness tester. We have compared the hardness values of the nitrided and non-nitrided AISI H13. After nitriding at 450°C. for 4 hours, a nitride layer having a surface hardness of 1315 Hv was obtained, which is more than double than the hardness of non-nitrided AISI H13. The surface hardness sharply decreased within the case depth up to  $\sim 35 \mu\text{m}$ ; at this depth the hardness of the nitrided layer was similar to that of the non-nitrided AISI H13. It was found that AISI H13 was nitrided to a depth of 35  $\mu\text{m}$ .

### 3.2. DLC deposition

Fig. 6 shows a cross-sectional SEM image of a DLC coating layer and Cr buffer layer. The thickness was 1.34  $\mu\text{m}$  for the DLC film and 0.3  $\mu\text{m}$  for the Cr buffer layer. The DLC film was deposited by acetylene gas using a LIS. And Cr buffer layer to enhanced adhesion of DLC film was deposited using a sputtering by Cr target. The DLC film, that was deposited by LIS on nitrided AISI H13 is high density due to its high ion energy.[12] Therefore, defects like cracks and pinholes were not observed.

Fig. 7 shows the chemical composition depth profile of the DLC film on nitrided AISI H13 by GDS normalized without Fe. C ions were

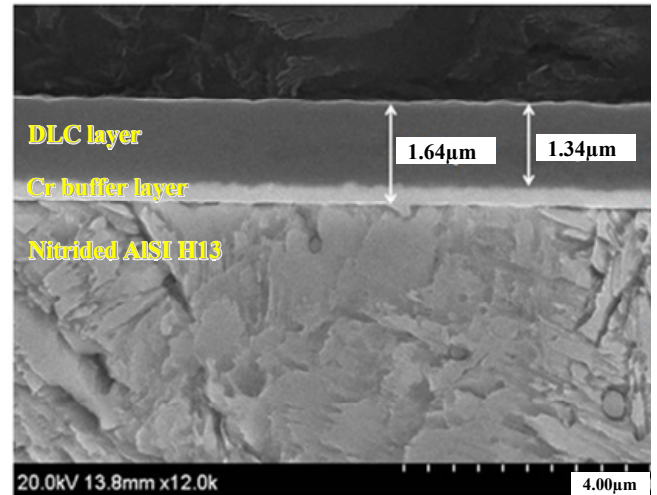


Fig. 6 Cross-sectional SEM images of DLC film and nitrided AISI H13 substrate.

added after DLC coating despite the addition of N ions, as shown in Fig. 7. The surface of AISI H13 contained carbon ions to a depth of

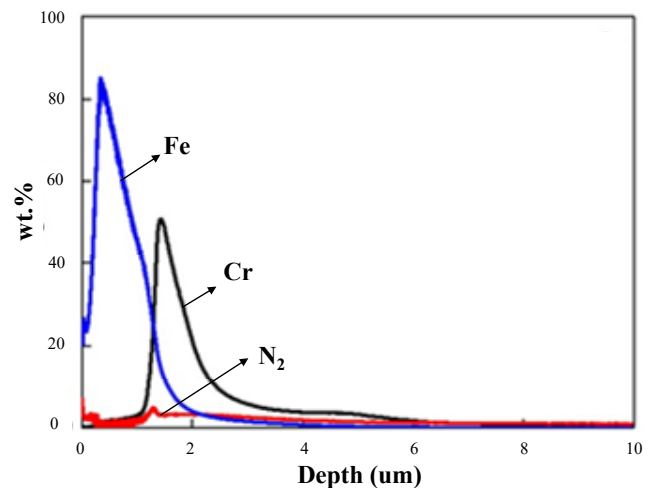


Fig. 7. Chemical composition depth profile of DLC film, measured by GDS.

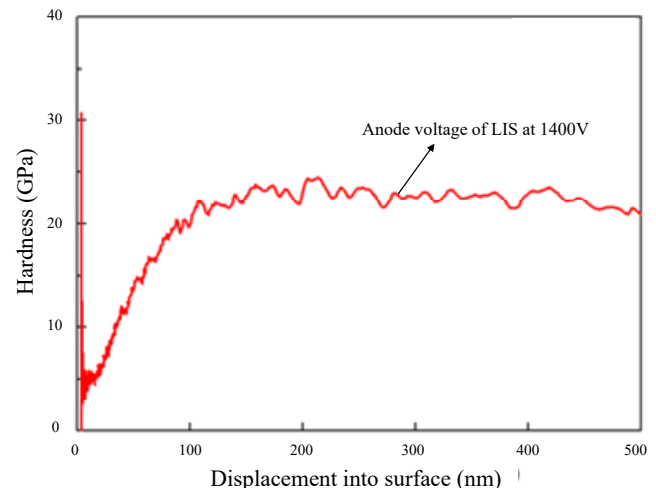


Fig. 8. Surface hardness of the DLC film, measured by Nano-indentation.



3  $\mu\text{m}$ . C and Cr ions were measured more effectively by GDS analysis than by SEM imaging: GDS analysis revealed that AISI H13 contains carbon ions of 0.34~0.42 wt.% and Cr ions of 4.52~5.50 wt.%. The hardness of the DLC films can be seen in Fig. 8. The values of the DLC films are found to be 20~25 GPa.

Fig. 9 shows the micro-Raman spectra of the deposited DLC films. It can be seen that there are two main peaks with broad shoulders on the 1590  $\text{cm}^{-1}$  and 1365  $\text{cm}^{-1}$  spectra. All spectra are typical of hydrogenated amorphous carbon (a-C:H), characterized by a G-peak near 1540  $\text{cm}^{-1}$  with a broad D-peak shoulder near 1365  $\text{cm}^{-1}$ . [13] The G-peak was induced by the lattice vibration in the graphite-like hexagonal ring; the D-peak is known to be associated with the existence of graphitic clusters with a short range of crystallinity. [14] Using two Gaussian curves, the micro-Raman spectra were deconvoluted into D- and G-peaks. [15]

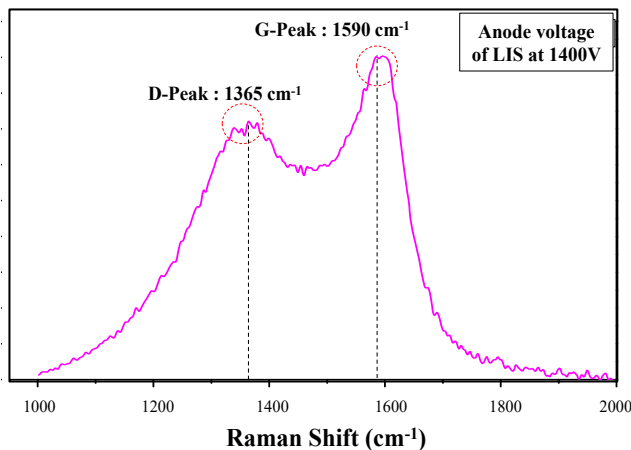


Fig. 9. Microstructure of DLC film by micro-Raman analysis.

### 3.3. Scratch test

Fig. 10 provides optical micrographs of the scratch tracks around the starting point (left) and final failure point (right) for the DLC films on the nitrided and non-nitrided AISI H13. DLC films on softer substrates are easily broken by strong local loads because of deformation of the substrates. Therefore, it is found that harder substrates enhance the adhesion of DLC films. [16] As shown in Fig. 10, in the case of the specimen without the nitride layer (a), the delamination of the DLC film occurred at 12.5 N from the starting point of the scratch test. On the other hand, the DLC film on the nitride layer, specimen (b), was pressed into the substrate without cracking or flaking, indicating sufficient adhesion between the DLC film and the substrate. It is found in Fig. 10 (b) that the width of the scratch track in specimen (b) was slightly narrower around the starting point of the scratch test, and the final failure load at which the DLC film was stripped perfectly from the substrate was slightly larger in specimen (a) than in specimen (b). These results indicate that the adhesion of specimen (b) is superior to the adhesion of specimen (a). The adhesion strength of the DLC film on nitride AISI H13 (b) was 25 N, which was higher than that on non-nitride AISI H13 (a). From these results, it can be seen that the adhesion strength of the DLC film on nitride AISI H13 is improved by the formation of a nitride layer.

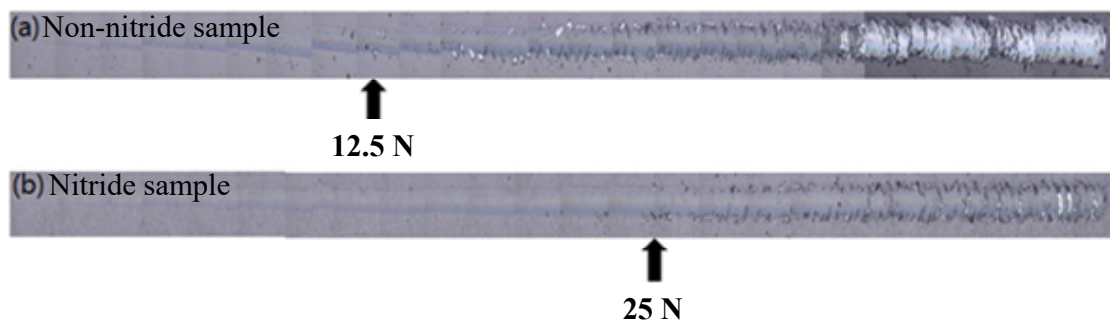


Fig. 10. Optical micrographs of scratch tracks around the starting point (left) and final failure point (right) of DLC films on (a) non-nitrided and (b) nitrided AISI H13 substrate.

## 4. Conclusions

The most outstanding result is the intimate relationship between the DLC film and the nitride layer. The DLC film was deposited on nitrided AISI H13 by LIS. Adhesion of DLC film, evaluated by scratch testing, was remarkably increased by the formation of a nitride layer by active screen plasma nitriding system. DLC films on the non-nitrided and nitrided AISI H13 were broken at 12.5 N, and 25 N, whereas, because of large deformation, the DLC film on the softer substrate was broken easily by local loads. The DLC film on the harder substrate was not broken until 25 N. It was found that the nitride layer improved the adhesion of the DLC film on AISI H13 and that a harder interlayer was more effective at improving the adhesion. As a result of this study, it was found that the nitriding treatment increases the adhesion between the surface of the material and the DLC film; at the same time, the hardening effect of the material surface further increases the adhesion.

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