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High Strengthening and Toughing of DLC Coating via Pretreated Stainless Steel Dies by Massive Nitrogen Supersaturation

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Abstract

A stainless steel die substrate was massively nitrogen-supersaturated (MNSed) to have nano-structured microstructure with high hardness of 1700 HV and nitrogen solute content of 4 mass%. This pretreated AISI420 martensitic stainless steel die was buffered by silicon and coated by the hydrogenated DLC (Diamond-Like Carbon). Hardness and scratch testing revealed that the interface through the (DLC coating layer) – (Si-based buffer layer) – (MNSed substrate), had sufficient strength and toughness enough to suppress the crack initiation and propagation under severe tribological conditions.

1 Introduction

DLC (Diamond Like Carbon) coating has been widely utilized as a tribofilm of moving mechanical elements (Mabuchi 2013), a protective coating of tools and dies (Dohda 2005, Shirzadian 2022), and, a thick die material for fine imprinting the micro-/nano-textures (Aizawa, 2018-September). In every case, the interfacial strength must be carefully designed to retard the crack initiation from surface and to protect the die material from delamination and crack propagation (Aizawa, 2022). As depicted in Fig. 1, there are three approaches to improve this interfacial strength in adaptive way to each application.

In Fig. 1a, the substrate surface is heat- or surface-treated to have adaptive interface to DLC coating; e.g., the crystallographic structure was controlled or modified to DLC coating (Haneef 2024). The interfacial delamination might well be prevented under mild stressing conditions. When the applied stresses increase more, there is a risk of crack initiation at the surface of DLC coating. A ceramic or metallic buffer layer is required to arrest this cracking by their strength or plastic deformation. In the duplex approach (Aizawa, 2012), several ten-nm thick buffer layer relaxes the stress state to stop crack propagation across this layer as depicted in Fig. 1b. In more severe tribological conditions where the

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applied normal and shear stresses exceed the critical limit of coatings, the substrate must be pretreated to improve the microstructural integrity across the buffer layer between coating and substrate in Fig. 1c (Farghali 2025).

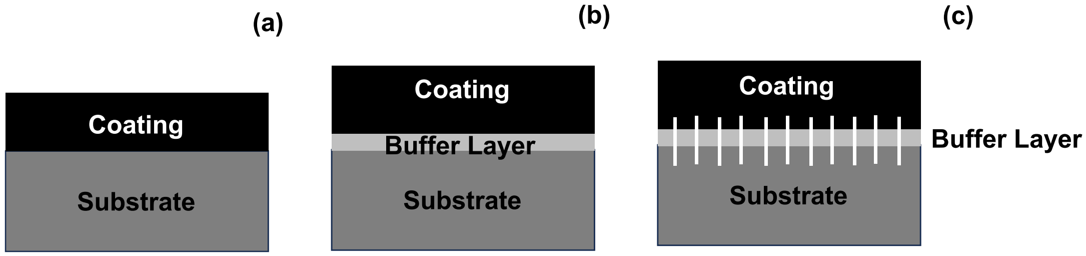

Figure 1: Three approaches to strengthen the surface coating against the applied stresses. a) Substrate surface treatment adaptive to each coating, b) duplex method by buffer layer formation, and, c) pretreatment of substrate for chemical bonding among the pretreated substrate, the buffer layer and the coating.

In the present paper, a role of pretreatment of die substrate by MNS (Massive Nitrogen Supersaturation) in the integrity of DLC coating system, is investigated by hardness and scratch tests. Two DLC coating systems on the AISI420 dis substrate were prepared with and without MNS treatment. As illustrated in Fig. 2, MNSed layer is formed into the AISI420 substrate with the specified thickness. The silicon buffer layer was deposited on this MNSed layer before DLC film coating. The hardness and scratching testing was utilized to evaluate the improvement of coating strength and toughness by this MNS treatment. Microstructure analysis proves that this significant strengthening and toughing comes from the mutual bonding state of interface among the nitrogen from the MNSed substrate, the silicon from the buffer layer and the carbon from the DLC coating.

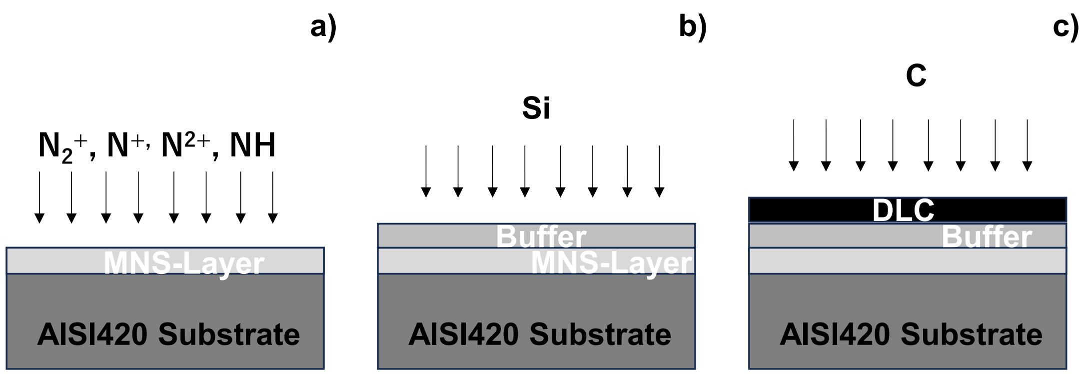

Figure 2: A surface treatment procedure for DLC coating. (a) Pretreatment of AISI420 substrate by MNS, (b) formation of silicon buffer layer, and (c) DLC coating.

2 Method and Materials

Massive nitrogen supersaturation (MNS) process was first explained on its feature of surface treatment. Buffer layer formation and DLC coating were stated as a standard approach. Hardness and scratching testing was also stated on the instrumentation to evaluate the strength and toughness of coating system.

2.1 Massive Nitrogen Supersaturation

A plasma nitriding immersion system (YS-Electric Co., Ltd.; Kofu, Japan) was utilized to make MNS treatment at 673 K for 16 ks under the highly intensified nitrogen ion and NH-radical conditions in the hollow cathode setup after the plasma diagnosis (Aizawa 2018-October). As stated in (Aizawa 2024), this MNS is characterized by nitrogen solid solution into the stainless steel substrates without precipitation synthesis of chromium and iron nitrides. This solid solution accompanies with the nano-structuring of crystallographic structure of substrate and the fast-rate nitrogen diffusion through the newly built nano-grain-boundaries.

2.2 DLC coating and buffer layer formation

DLC films were deposited by bipolar-type plasma-based ion implantation and deposition (PBII&D) technique (Hirata 2015). Precursor gases of Tetramethylsilane (TMS) and Toluene (C_7H_8) were used at ambient temperature. Positive and negative pulse voltages of +1.5 kV and -5 kV were regulated to generate plasma around the samples as illustrated in Fig. 3. All samples were degreased for 600 s before the deposition process, using the ultrasonic cleaner system with three different solvents of petroleum benzene, ethanol, and acetone. Samples were presputtered by argon ions for 3.6 ks to remove any residual contaminations. This presputtering was followed by formation of hydrogenated silicon carbide (a-SiCx:H) interlayer for 3.6 ks and by deposition of hydrogenated diamond-like carbon (H-DLC) for 7.2 ks. After both processes, all samples were cut and polished until a mirror-like surface was obtained in the cross-section surfaces with Silicon-Carbide (SiC) sandpaper from #280 to #4000 and alumina powder solution with aluminum oxide (Al_2O_3) particle sizes of 3, 0.3, and 0.05 µm.

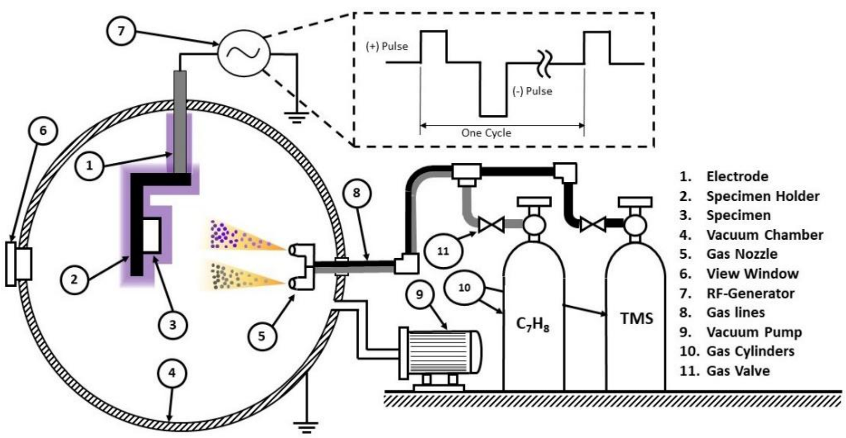

Figure 3: Plasma based implantation and deposition system for formation of silicon buffer and DLC coating onto the AISI420 substrates with and without pretreatment via MNS.

2.3 Materials Characterization

AISI SUS420-J2 martensite stainless steel with a chemical composition of Cr 14%, Ni 2%, Mn 1%, Si 1%, P 0.04%, C 0.15%, Si 0.03%, and Fe in balance was used as a substrate in this study.

The microstructural analyses on the surface and the cross-section were made using scanning electron microscope and energy dispersive spectroscopy (SEM-EDS; JSM-7500FA, JEOL Ltd.). MNSed surfaces were analyzed by X-ray diffractometer (XRD, SmartLab, Rigaku) with the monochromatic CuK_α radiation ($\lambda = 0.1542$ nm) and Bragg–Brentanno geometry (45 kV, 200 mA). The 2θ measurement ranged from 30° to 90° with the scanning speed of 4 deg/min and the step angle of 0.02°. H-DLC layers were characterized by Raman spectroscopy (Renishaw; Tokyo, Japan) within 900-1800 cm^{-1} range and 532 nm of laser source. The Gaussian curve fitting function was used to identify both D and G peaks. X-ray photoelectron spectroscopy (XPS, PHI 5000 Versa-Probe II, ULVAC-PHI Inc.) was employed to detect all types of chemical bonding state throughout and between each layer together with the depth profile of the element concentration. Al-K_α radiation was used with Ar^+ ions at 4 kV to sputter the sample surface with a sputtering rate of 13 nm/min.

2.4 Mechanical Characterization

Nanoindentation tester (ENT-NEXUS, Elionix Inc.) with Berkovich nano-indenter and a load of 9 mN was utilized to measure the hardness and Young's modulus of the H-DLC films. The microhardness testing machine (HM-200, Mitutoyo Co.) was used by applying the load of 0.1 N for surface measurements of AISI420J2 substrates after the plasma nitriding process. Tribological properties of H-DLC were evaluated by ball-on-disc tribometer (MTF-5000, Rtec instruments) with 10 mm diameter alumina (Al_2O_3) ball at 4 N load under the rotational speed of 240 rpm, the wear track radius of 3 mm, and, the total sliding distance of 500 m.

The adhesion between DLC films and steel substrate was tested using the Rockwell C indentation method (963-210 HR-110MR, Mitutoyo Co.; Kanagawa, Japan) by respectively applying the loads of 1471 N and 2719 N. In addition, Nanovea Macro Scratch Tester (Micro Photonics Inc.) equipped with an acoustic emission detector, was utilized to describe the effect of MNS pretreatment on the structural integrity of coating system. The diamond indenter had 200 μm radius. The load was applied from 1 N at the initial condition with the loading rate of 20 N/mm. The total scratch distance was varied to be 3 mm and 8 mm using the substrates without and with MCS treatment. The scratching tests were performed in three times.

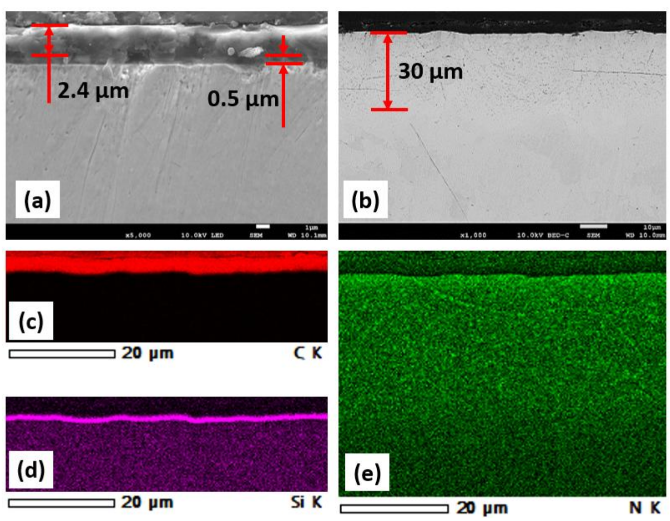

Figure 4. Comparison of the cross-sectional SEM image and element mapping between two specimens with and without MNS-treatment. (a) SEM cross-section micrograph of a-C:H and a-SiCx:H films deposited on DLC sample without MNS, (b) SEM image of the nitrided thickness of the DLC sample with MNS, (c, d) carbon and silicon mapping in the DLC sample without MNS, and (e) nitrogen mapping across the DLC sample with MNS.

3 Results

Two DLC-coated specimens were prepared with and without MNS pretreatment. SEM-EDS was utilized to describe the cross-sectional microstructure of DLC coating across the buffer layer. Its strength and toughness was mechanically characterized with aid of chemical bonding analysis.

3.1 MNS Treatment to AISI420 Die Substrate

XRD analysis was performed to describe the synthesized phases on the MNSed AISI420 substrate surface. The original martensitic peaks of α'(110) and α'(200) at $2\theta = 44.8^o$ and 65.04^o, shifted in the lower 2θ angles to 43.28^o and 63.76^o, respectively. This indicates a lattice expansion of approximately 3.6% due to the diffusion of nitrogen solutes into the martensitic BCC crystal structure and the transformation to expanded martensitic phases (α'_N). Formation of iron nitrides was only seen at the vicinity of surface; no chromium nitrides were detected even in trace level.

3.2 Multi-Layered System for Protective Coating

Through comparison of Raman spectra between two DLC coatings with and without MNS-pretreatment, no significant difference was noticed between two spectra except for sp3 to sp2 ratio. When using the MNS-pretreatment, nitrogen-rich top surface promotes more sp3 bonding formation. This sp3 ratio is estimated to be higher by 14% from (Ferrari 2000) based on I_D/I_G and G-peak position. The cross-sectional microstructure was analyzed by SEM-EDX. The DLC film (or a-C:H) and silicon buffer layer (a-SiCx:H) are formed onto the AISI420 substrate without and with MNS in Figs. 4a and 4b, respectively. After element mapping in Figs. 4c and 4d, carbon distributed only in a-C:H film while silicon is detected mainly in a-SiCx:H layer. As shown in Fig. 4e, nitrogen distributes mainly in the MNSed substrate but also in the DLC-coating and buffer layer.

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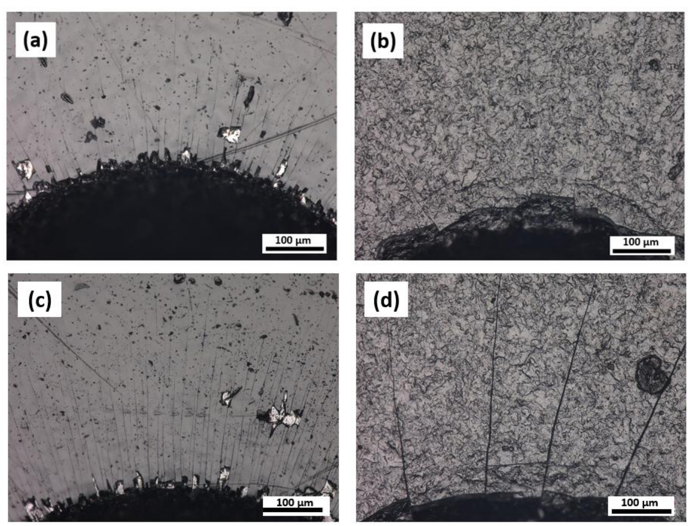

Figure 5. Hardness testing by Rockwell indentation. a) and b): DLC coating without MNS by W = 1471 N and 2719 N, and, c) and d): DLC coating with MNS by W = 1471 N and 2719 N, respectively.

3.3 Hardness Testing

The Rockwell C indentation was performed to describe the interfacial strength of two samples without and with MNS-pretreatment. When applying the load (W) of 1471 N, many radial microcracks and small-sized delaminated areas are spotted around the indented region of DLC sample without MNS as shown in Fig. 5a. These failures are classified as a HF2 type of acceptable failures according to the VDI 3198 indentation test (Verein 1991; Vidakis 2003). On the other hand, hardly visible few microcracks are spread out of the imprint of the PN-DLC sample which can be classified as HF1 as seen in Fig5b. When further indentation up to W = 2719 N, severe cracking and damages were seen in Fig. 5c while no delamination occurred under the same HF1 classification for DLC coating with MNS, as shown in Fig. 5d.

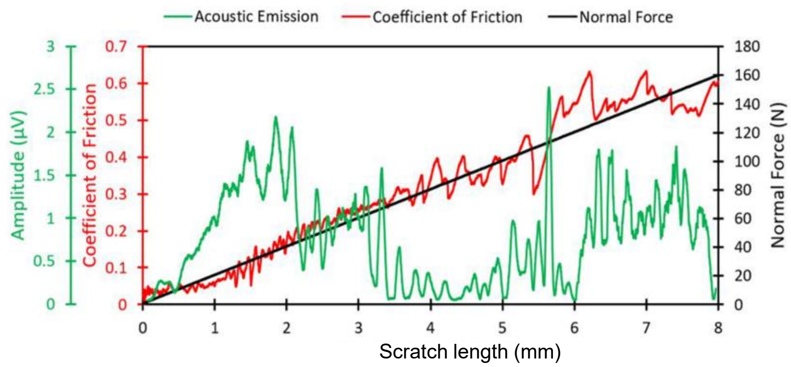

Figure 6. Variation of the coefficient of friction and measured amplitude in acoustic emission with increasing the scratch length and normal force for the a-C:H coating onto the MNSed AISI420 substrate.

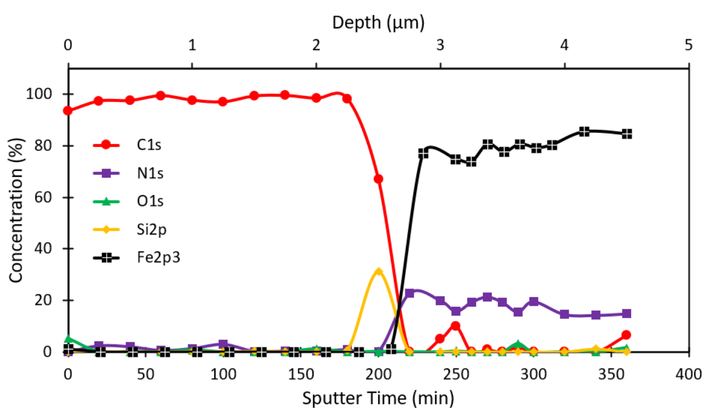

Figure 7. Depth profiles of C1s, N1s, O1s, Si2p and Fe2p3 contents from the surface of a-C:H coating across the buffer layer to the MNSed layer.

3.4 Scratch Testing

In the scratch testing of a-C:H coating onto the bare AISI420 substrate, the coefficient of friction (μ) abruptly increases at the initial stage where the normal load (P) = 2 N and L = 0.1mm. The conformal cracking occurs in the a-C:H film. When the scratch length (L) reaches 0.18, the amplitude in the acoustic emission also rises up abruptly. After ASTM C1624 standard (ASTM 2015), this signal indicates that buckling spallation occurs where the whole a-C:H film fractures to ashes. On the other hand, the crack initiation is significantly retarded in the scratching test of a-C:H coating onto the MNSed substrate. As see in Fig. 6, μ remains constant by 0.05 even when L = 1 mm. This proves that a-C:H coating has no damages and remains the same as before scratching. Although the side cracks were observed when L = 8.0 mm but no spallation occurred. This significant difference in toughness during scratching proves that the interfacial integrity of DLC coating system on the MNSed substrate across the buffer layer is enough to arrest the crack propagation to fatal fracture of DLC coating.

3.5 Interfacial Chemical Bonding

XPS was utilized to describe the chemical bonding state from the DLC coating across the buffer layer to the MNSed substrate. As shown in Fig. 7, three elements (carbon from DLC, silicon from buffer, and nitrogen from MNSed substrate) coexist in the buffer layer having mutual bonding states. To be noticed, no oxygen is detected in the whole depth. To be proved by the chemical binding state analyses via XPS, the carbon atoms in the DLC coating, the silicon atoms in the buffer layer, and the nitrogen solutes in the MNSed substrate have mutual bindings by C-Si, Si-N and N-C in addition to C-C, Si-Si, N-N and N-Fe. This chemically structured buffer layer is responsible for enhancement of strength and ductility in this new duplex method.

4 Discussion

Hardness and scratching testing reveals that MNS plays a role to make cross-over strengthening and toughing of DLC coating system. Crack initiation was retarded, and, crack propagation was arrested to prevent the coating system from partial delamination from substrate and fatal failure. This high wear toughing and crack arresting capability comes from the cross-over bonding structure among nitrogen (N) from substrate, silicon (Si) from buffer layer and carbon (C) from DLC. This complex binding state among N-Si-C is advanced to promote the heat resistance of DLC coating system.

The scratching behavior in the early stage demonstrates that low frictional state original to DLC coating is preserved until the normal load reaches 40 to 50 N, where most of DLC coating start to fracture without pretreatment via MNS. This suppression of crack initiation and propagation is preferable in application of DLC coating to moving mechanical elements and protective coating of tools and dies. The total engineering durability of this coating system is much improved by using the nano-laminated DLC coating with high toughness (Aizawa, 2019 and 2022). Especially, this protective coating is well suitable to micromanufacturing tools and micro-machines, where the tiny surface damage has a risk to induce the fatal failure (Usman 2025).

A pointwise XPS analyses provide the information on the chemical bonding ratio among C-Si, Si-N and N-C in Fig. 7. Nitrogen solid solution content might well be controlled to increase the bonding ratio of Si-N and N-C and to improve the interfacial strength and toughness in adaptive way to applications. The curved or inner surfaces of stainless steel products can be MNSed and DLC-coated by the present approach to improve their toughness and strength.

5 Conclusion

Pretreatment of stainless steel substrates by MNS significantly improves the wear toughness of DLC base protective coating without loss of its low friction. This strengthening and toughing is attributed to high interfacial integrity by cross-over chemical bonding state among the nitrogen from the MNSed substrate, the silicon from the buffer layer and the carbon from the DLC coating. This MNS-treatment of stainless steel dies is not only useful to metal forming in dry and cold but also effective for warm and hot mold-stamping of optical glass works.

Acknowledgments

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