High-Density Plasma Nitriding Assisted Micro-Texturing onto Martensitic Stainless Steel Mold-Die

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Abstract *Martensitic stainless steels have been widely utilized as a mold-die material for injection molding and mold-stamping. In usual, heat treatments, including the case hardening methods are used to enhance the surface hardness of these molds and dies. As needed, the surface texturing is also employed to have the surface profile leather-touched or textile-patterned. In this traditional approach, chemical etching processes as well as fine machining are applied to dig a micro-hole and a micro-groove onto the mold-die surfaces. In the former, residuals of etching agents deteriorate the quality of mold-die materials. In the latter, preparation for CAM data often retards the leading time. In addition, these surface-textured mold-dies are easy to wear themselves in use even after heat treatment. The authors have developed a high density plasma nitriding for precipitation hardening of steels, titanium and aluminum alloys and for solid-solution hardening for stainless steels and tool steels. In particular, high content of nitrogen atoms up to 40 at % can be infiltrated in depth of AISI420 martensitic stainless steels down to 30 μm. This results in significant increase of hardness because of solid-solution strengthening process without any precipitation reactions to nitrides. In the present paper, initial micro-dot and micro-line patterns are first printed onto the surface of polished stainless steel mold by the dispenser. This masked specimen is nitrided at 693 K for 7.2 ks or 14.4 ks at 70 Pa by using the high density plasma nitriding system. The masked part is never nitrided to maintain the same hardness as the matrix; the unmasked parts are selectively nitrided to have higher hardness than 1000 Hv. That is, the initial masking pattern is transformed to hardness profile pattern on the mold surface. This hardness-patterned mold-die is mechanically blasted by brushing tools. Since the masked parts of mold-die surface are selectively removed by this blasting, the original mask pattern is dug or machined into the mold-die. This micro-textured mold-die geometry is analyzed by using the surface profilometer and SEM to demonstrate that this processed mold-die is utilized as a die unit for injection molding and mold-stamping.*

1. Introduction

Micro- and nano-textures on the metal and polymer surfaces of parts and components have functions to reduce the friction and wear and to improve the joining strength [1, 2]. As needed, the surface texturing is also employed to have the surface profile leather-touched or textile-patterned. In order to fabricate these micro- and nano-textured surface of products, the mold-die units for injection molding or stamping must have their original micro- and nano-textures on surface. When using the micro-milling or micro-EDM, huge amount of digital data has to be built in as CAM data before actual micro-milling or micro-EDM [3, 4]. In addition, practical operation time significantly increases with refinement of micro- and nano-pattern sizes and geometries. Consider that a micro-dot with the diameter of 40 μm is machined to have a pitch of 50 μm onto the 70 x 50 mm^2 surface of mold-die, for an example. Assuming that 10 seconds is needed for micro-milling a single micro-dot, this micro-dot texturing process requires for 3 x 10^7 seconds or 10^4 hours per a mold-die unit with 70 x 50 mm^2. This time consumption is much enhanced with complexity of unit-pattern geometry. Hence, traditional tooling with use of CAM data can never be used for micro-texturing into the mold-die units.

A plasma assisted nitriding provides a means to make various kinds of micro-textures onto the surface of stainless steels simultaneously [5, 6]. However, as reported in [5], the conventional SiO_2 hard masking by lithography is never suitable to original masking for nitriding-assisted micro-texturing. The authors [7, 8] have proposed the ink-jet printing method as an efficient masking for micro-texturing via high density plasma nitriding. In the present paper, this approach is expanded to print the micro-textures onto the stainless steel mold-die material by the dispenser, to make nitriding of this printed species and to machine the original micro-textures by removal of masked regions. First, the experimental procedure is introduced to explain the related procedure to this new micro-texturing. In particular, a high density plasma nitriding system is precisely stated to describe the importance of solid-solution hardening in the present micro-texturing. Two types of specimens with different masked patterns are employed for each experiment. Double-stripe patterned AISI420 type martensitic stainless steel plates are employed to prove that surface hardness profile is attained in corresponding to masked pattern by plasma nitriding and that these masked regions are selectively removed by blasting method. The AISI420 mold-die units are prepared for printing the micro-dot and micro-line patterns to demonstrate that a mold-die unit is fabricated to have the micro-dot shaped holes and micro-line shaped grooves through the present processing.

2. Experimental Procedure

The present plasma-nitriding assisted micro-texturing method consists of three processes as shown in Fig. 1. At first, an original mask-pattern is printed on the surface of mold-die by using the dispenser or the ink-jet printer. Selection of plastic primer inks to endure in the nitriding condition becomes essential to make micro-patterning onto the surface of tools steel and stainless steel substrates. In second, the substrate materials are plasma-nitrided to have sufficient hardness without change in the contents of chromium and iron elements and with less damage onto the substrate material surface. Finally, this nitrided surface is mechanically polished to remove the un-nitrided patterns and the residual inks and to form a negative micro-texture against the initially printed micro-pattern. For an example, the printed micro-dots on the substrate changes themselves to the micro-dimple or micro-holes by the present method.

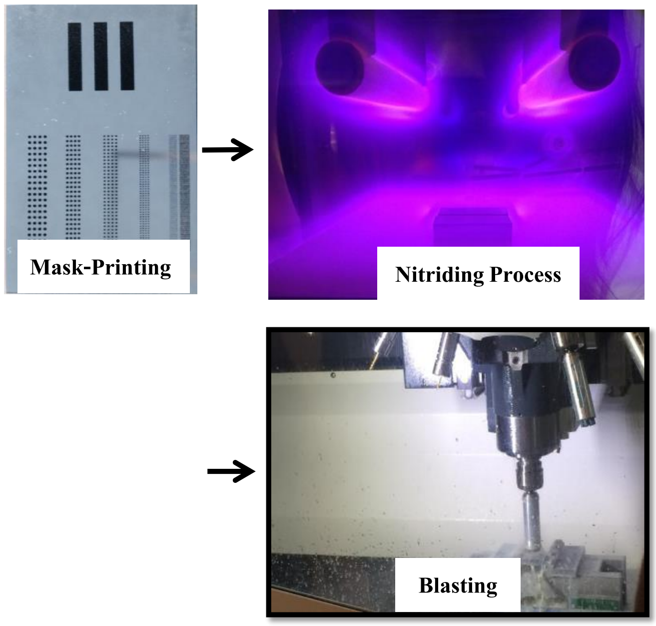

Fig. 1: A plasma-nitriding assisted micro-texturing process.

In the following, the dispenser (Musashi-Engineering, Co. Ltd.) was utilized to print the designed micro-patterns directly onto the substrates. The original CAD data for these micro-patterns were once exported into the drawing software “Illustrator”; CAD data was transformed to the sequence of drawing commands. Without any CAM data, the input micro-patterns were printed by this drawing process. Our developed high density plasma nitriding [9-10] was utilized for nitriding in Fig. 1. As explained in later, the low-temperature nitriding condition was selected to be free from formation of nitrides. The blasting tools were also employed as a means to mechanically remove the printed masks and to dig the masked patterns in Fig. 1.

2.1 High Density Plasma Nitriding System

High density plasma nitriding system was set-up for solid-solution hardening of steels. Different from the DC- or RF-plasma generators, where the plasmas are ignited and generated in the frequency of 13. 56 MHZ or its multiples, the present high density nitriding system has no mechanical matching box with slow response time of 1 s to 10 s to adjust the applied power. Since input and out powers are automatically matched by frequency adjustment around 2 MHz, the matching response time is only limited to 1 ms at most. This prompt power control provides to make full use of meso-plasma pressure range over 50 Pa. Figure 2 depicts the outlook of present nitriding system.

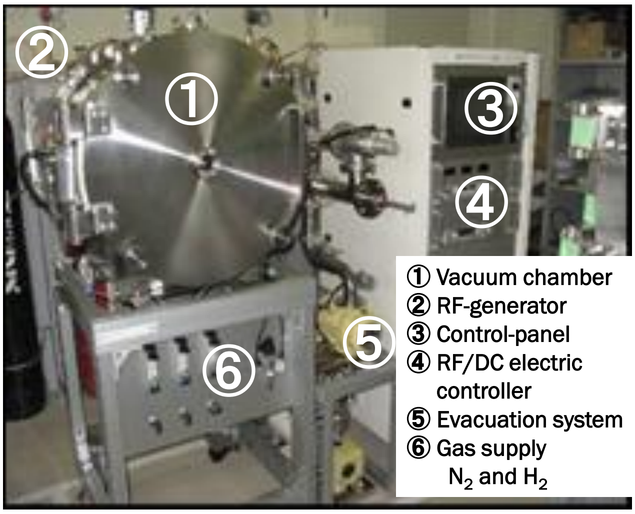

Fig. 2: High density plasma nitriding system for solid solution hardening of steel mold-dies.

Different from the conventional processes, the vacuum chamber is electrically neutral so that RF-power and DC-bias should be controlled independently from each other. A dipole electrode is utilized to generate RF-plasma; DC bias is directly applied to the specimens. Heating unit is located under this DC-biased cathode plate. The emissive light spectroscopy (PMA-11, Hamamatsu, Co. Ltd.) as well as the Langmuir probe system (ALP System, Impedans, Co. Ltd.), are instrumented to the present plasma nitriding system to make quantitative diagnosis on the generated nitrogen plasmas. Through the preliminary studies, the nitriding conditions were optimized as listed in Table 1.

Table 1: Optimal nitriding conditions for solid solution hardening via the high density plasma nitriding processes.

Process	Parameters
Pre-sputtering	DC(500V) Nitrogen (75 Pa) at 693 K for 1.8 ks
Nitriding	RF(250V), DC(300V) Nitrogen (100 ml/min) Hydrogen (20 ml/min) 75 Pa at 693 K for 7.2 ks and 14.4 ks

In the following nitriding experiments, the specimens are located on the cathode table before evacuation down to the base pressure of 0.1 Pa. Then, nitrogen gas is first introduced as a carrier gas for heating. After heating to the specified holding temperature, nitrogen pre-sputtering is started at the constant pressure. After pre-sputtering, hydrogen gas was added to nitrogen gas with the specified partial pressure ratio. Both pressure (P) and temperature (T) controls were automatically performed with the tolerance of $\Delta P < 1$ Pa in deviation of partial pressure and $\Delta T < 1$ K in temperature fluctuation.

2.2 Mask-Pattern Formation

Two types of masking were employed to make initial patterns onto the specimens. First, the carbon-tape was used to make line patterns; no nitrogen atoms can infiltrate into the masked regions through this carbon-tape. Next, the dispenser was utilized to print the micro-line and micro-dot patterns onto the specimen. The average thickness of printed patterns was 10 μm. The minimum diameter of micro-dot pattern was 100 μm in diameter. In order that the printed patterns are free from damage during nitriding at 693 K, the primer was optimized in the preliminary study. A typical printed pattern onto the surface of specimen is shown in Fig. 3.

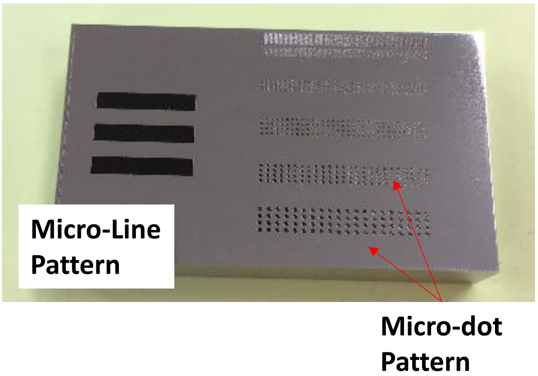

Fig. 3: A typical printed micro-texture onto the polished surface of steel mold-die block.

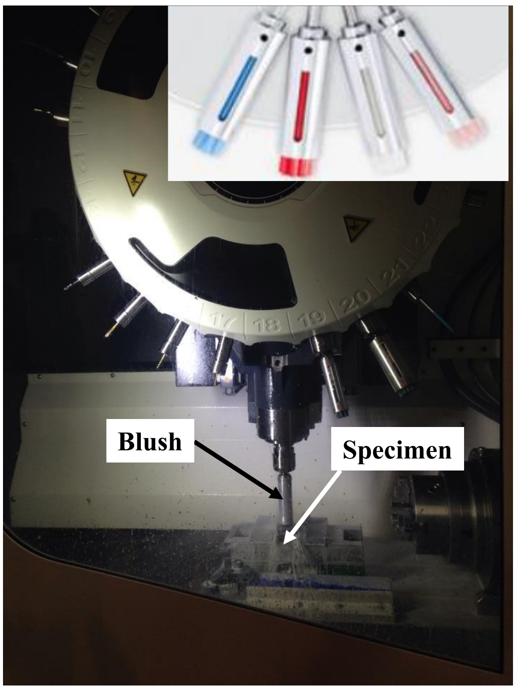

Fig. 4: Blasting process with use of ceramic fiber blushes.

2.3 Blasting by brushing tools

Among several blasting media, a brushing tool with alumina-fiber bundles was employed to mechanically blast the masked part of steel mold-dies. As depicted in Fig. 4, this brushing tool was directly fixed into a tooling set at the machining center. Hence, the same CAM programs as tool selection and control, were available to select the tool number to this brush, to control the brushing tool position and to make brushing as designed.

In the following mechanical blasting process, this brushing tool is controlled to move in the lateral direction across the specimen in Fig. 5 with rotation under water-solution lubricating oils. The feed depth of tool was fixed to be around 1 μm. Since the brushing operation was done in the one-way direction, the feeding into depth was controlled by increasing the number of passes (N). This single motion of brushing was counted as a single pass or N = 1. Then, deeper micro-textures were expected to be formed with increasing N.

2.4 Specimen

Martensitic stainless steel of type AISI420 (abbreviated by AISI-SUS420) was employed as a mold-die test-piece. Two types of test-pieces were prepared for experiments: 20 x 20 x 5 mm^3 plate and 70 x 50 x 20 mm^3 block. The former was used for hardness testing and blasting tests. The latter was utilized for printing test and blasting tests.

2.5 Observation and Measurement

Optical microscope and SEM (scanning electron microscope) were employed to make fine observation of specimens. Micro-Vickers hardness tester (Mitsutoyo, Co. Ltd.) was used for precise hardness testing. Surface profilometer (Keyence, Co. Ltd.) and surface roughness profilometer (Mitsutoyo, Co. Ltd.) were used to measure the surface profile change by blasting.

3. EXPERIMENTAL RESULTS

Two types of specimen are utilized in the present micro-texturing experiments. Double-stripe patterned AISI-SUS420 specimen is employed to describe the hardening and blasting behavior in the present method. Fine-patterned AISI-SUS420 mold-units are utilized to prove that fine concave micro-textures are machined into the mold-die substrate.

3.1 Hardening by High Density Plasma Nitriding

The double-stripe patterned AISI-SUS420 plate specimen was plasma nitrided for 7.2 ks under the conditions in Table 1. Its matrix hardness is 200 Hv. Figure 5 depicts the nitrided specimen after peeling out the masking tape. Plasma nitriding took place selectively on the un-masked regions. Hence, this selective nitriding reflects onto the hardness profile across the line-A in Fig. 5.

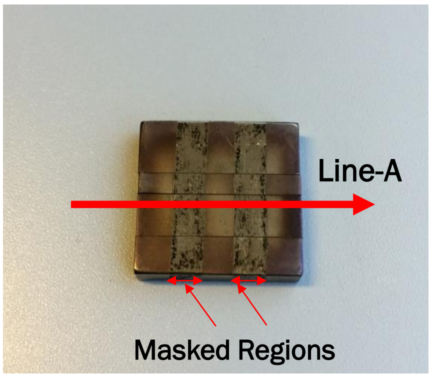

Fig. 5: A plsma-nitided AISI-SUS420 plate specimen after peeling

Hardness was measured five times to calculate the average hardness at each position along the Line-A. Figure 6 shows the hardness profile along this line. The measured hardness in the masked region is equivalent to the matrix hardness of 200 Hv. In the un-masked regions, the measured hardness is increased up to 1400 Hv, seven times higher than the matrix hardness. To be discussed in later, the reference hardness data [9] for plasma-nitrided low chromium steels of SKD61 by the commercial nitriding systems ranged from 1000 Hv to 1200 Hv. Then, hardness by the present nitriding must be driven by the different mechanism from the conventional nitriding process.

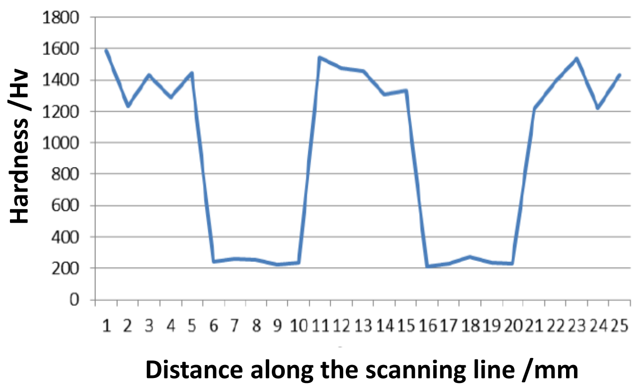

Fig. 6: Hardness profile along the line-A in Fig. 5.

3.2 Micro-Texturing by Blasting

In case of mechanical blasting by the alumina fibers, the softer parts than the hardness of alumina are selectively removed through the brushing process and flashed out together with the lubricating solution in the machining center. On the other hand, the nitrided regions have sufficient hardness against the mechanical impact in this brushing process. Then, the flat surface of specimen shown in Fig. 5 is expected to have a stepwise microtetxure, the depth of which increases by blasting.

The alumina-fiber bundle tool was moved along the line-A in Fig. 5 with rotating motion. The number of passes (N) was also controlled to be N = 1, 5 and 20, respectively. Figure 7 depicts the measured surface profile when N = 20.

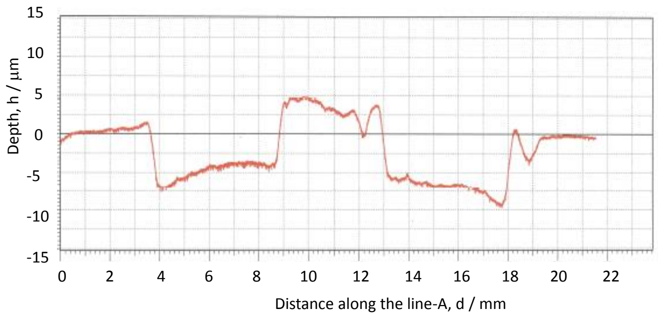

Fig. 7: Measured surface profile after mechanical blasting by N = 20.

To be compared with the double-stripe masked regions in Fig. 5 and with the high hardness sections in Fig. 6, the masked regions or double-strip masked regions are selectively polished and removed to change the original flat surface to the stepwise surface with two grooves. Their average depth is around 9 µm. This proves that the same micro-textures as the initially printed micro-patterns on the substrate are precisely machined into the same substrate by using the present method.

The nitrided layer thickness has a significant influence on the micro-texture formation behavior by the present blasting. If the hardness profile in Fig. 6 has nothing to do with the digging process by the blasting, the machined depth of masked region increases monotonically with the blasting. The blasted depth at d = 3.5 mm in Fig. 7 is selected as a parameter (H) to vary with the number of passes (N) in this blasting. Figure 8 depicts the variation of H with N.

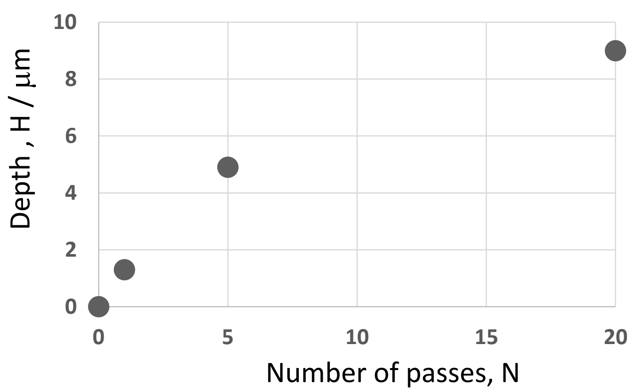

Fig. 8: Variation of the groove depth, H with increasing the number of passes (N) in the present blasting process.

The groove depth increases monotonically up to 5 µm in proportion with N. This implies that hardness profile even when H = 5 µm is nearly equal to that in Fig. 6; the nitrided regions have sufficiently high hardness against the brushing process by alumina-fiber bundles. When H > 6 µm, the blasting rate is significantly retarded since the hardness of nitrided regions gradually decreases.

3.3 Micro-Texturing into Specimens

As shown in Fig. 3, five stripes as well as micro-dots with different diameters were printed as a micro-pattern on the specimen surface. Using the same processing conditions as listed in Table 1, this micro-patterned specimen was also plasma-nitrided for 14.4 ks. The nitrided specimen was further subjected to blasting process with use of the ceramic-fiber bundle brush.

First, variation of micro-dot patterns with plasma nitriding and blasting was investigated by high resolution optical microscope. Figure 9 compares the micro-dot pattern before and after nitriding, and after blasting.

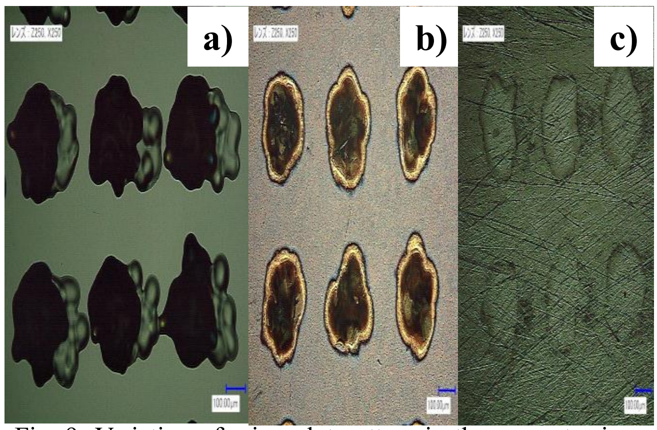

Fig. 9: Variation of micro-dot pattern in the present micro-texturing. a) Just printed pattern on the specimen surface, b) After plasma-nitriding, and, c) After blasting.

The residual primer plastic inks in Fig. 9 a) were removed in the plasma nitriding process; the original thick micro-dot patters were left as a masked region in Fig. 9 b). Figure 9 c) shows the blasted specimen surface by N = 5. Less scratches were seen in the un-masked or nitrided region; many scratched traces were seen in the masked region. This proves that the original micro-dots are left as a micro-dimple with the same geometry as the original micro-dot pattern.

Next, variation of five stripe patterns by brush-blasting process was investigated to describe the micro-texturing behavior into the mold-die. Figure 10 depicts the plasma-nitrided specimen with five-stripe pattern. Besides some spiky noises during measurement, the nitrided regions have low surface roughness; while, the masked or un-nitrided regions have siginicant rough surface. This might be because the soft plastic inks printed on the surface are subjected to nitrogen ion bombardment during the plasma nitriding. The average roughness (Ra) was measured to be 0.097 µm and the maximum roughness (Rz), 0. 94 µm, respectively.

Figure 11 describes the digging process of masked regions on the nitride surface of specimen with increasing the number of steps (N). When N = 1, the masked or un-nitrided regions are selectively removed by the present brushing as shown in Fig. 11 a). When increasing N up to N = 5, the micro-groove patterns are formed to have the same geometry and size as the original five-stripe pattern in Fig. 3. Both Ra and Rz become nearly constant by Ra = 0.04 μm and Rz = 0.4 μm, irrespective to N. This implies that the originally printed micro-patterns onto the specimen surface could be cut-in or micro-textured by the brush-blasting into the specimen without surface roughing.

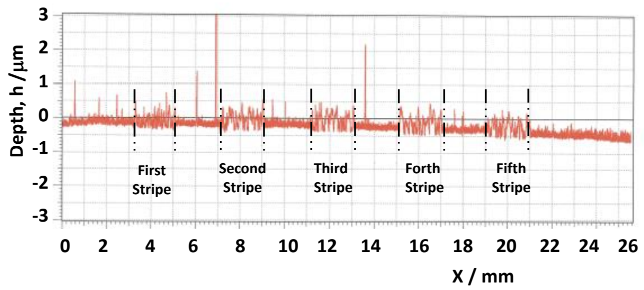

Fig. 10: Surface profile of the plasma-nitrided specimen before brush-blasting.

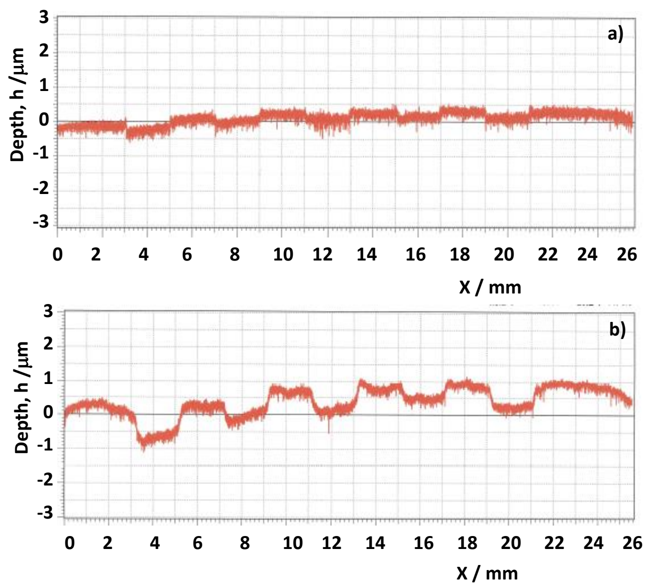

Fig. 11: Variation of surface roughness with increasing N during the brush-blasting process. a) N = 1, and, b) N = 5.

4. DISCUSSION

As pointed out in [8, 11], the hardening process via the plasma nitriding is classified into two categories on its dependency of processing temperature time: i.e. precipitation hardening and nitrogen solid-solution hardening processes. For an example, when the processing time is fixed to be 14.4 ks, 733 K or 460 °C might be a critical temperature (Tc) to delineate these two processes; when T > Tc, CrN precipitates in the stainless steel matrix while no nitrides are formed when T < Tc.

In this study, the nitriding temperature was fixed to be 693 K or 420 °C; then, the whole hardening behavior via the present high density plasma nitriding is governed by the solid-solution hardening process. In fact, the micro-Vickers hardness was measured to be 1400 Hv at the unmasked area in Fig. 6; the surface hardness was less than 1200 Hv in case of plasma nitriding at 753 K or 480 °C in [9]. In case of the precipitation hardening process, the hardness or strength of nitrided stainless steels is governed by the size and volume fraction of nitride precipitates. On the other hand, the hardness or strength is promoted by the concentration of unbound nitrogen solute in the crystalline structure of stainless steels in case of the nitrogen solid-solution hardening.

In application of the present micro-texturing, the sharp-edged surface profile becomes a key to fabricate the micro-textured molds and dies for imprinting the micro-patterns onto plastic and metallic parts. As shown in Figs. 7 and 11, a step-wise surface profile was wrought into the nitrided stainless steel substrate only by digging the masked regions. For an example, the depth change at X = 3 μm in Fig. 11 b) became 1 μm for ΔX = 100 μm. The head profile of ceramic fiber brush used for blasting has a little angulation suitable to polishing the metallic part surfaces. The edge-sharpness in the above mechanical removal must be improved by the ceramic fiber bundle shape and surface asperity.

As partially discussed in [8], the average nitrogen content detected by EDX-analysis is around 5 mass% or 20 at% even at the depth of 5 μm in the plasma nitrided regions of specimen in Fig. 5. This assures that the surface hardness map in Fig. 6 remains itself even in the depth of specimen to drive the mechanical removal process by brush-blasting. As shown in Fig. 7, the micro-groove depth by N = 20 reached to 9 to 10 μm in depth. This suggests that the nitriding affected layer thickness must be much deeper than 10 μm. In fact, the measured hardness in the cross-section of nitrided specimen in Fig. 5 is more than 800 Hv; high concentration of nitrogen is also detected by EDX. This implies that inner nitriding process or nitrogen solute diffusion has unique characteristics different from the classical theory, which was adaptive to the high temperature plasma nitriding behavior [9].

The edge-sharpness of microtextures dug into matrix by brush blasting suggests that nitrogen solute diffuses only into the depth of unmasked regions without scattering into the depth of substrate. This anisotropy in nitrogen solute diffusion is not only effective to micro-texturing for fabrication of molds and dies but also challenging to materials science to describe the low temperature diffusion of nitrogen atoms and to investigate the nano-heterogeneous structures via the nitriding in the inside of stainless steels.

5. CONCLUSION

A non-traditional micro-texturing method onto the mold-die is proposed with aid of high density plasma nitriding as one of the most cost-competitive processing to fabricate the micro-textured molds and dies. The originally designed micro-patterns are first printed onto the surface of mold-die material. Its bare surfaces other than the printed masks are selectively nitrided to have much higher hardness than the original matrix hardness. Then, the printed micro-patterns are only mechanically removed by brushing tool because of little removal on the hardened mold material surface. This selective removal of masked micro-patterns provides much deeper micro-textures into the stainless steel molds and dies by optimization of the brush tooth profiles for brush-blasting and by control of unbound nitrogen solute content for hardening.

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