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Imprinting of Micro-/Nano-Textures onto Metals and Alloys with Use of the Laser-Printed DLC-Die

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Abstract. This paper focused a two-step procedure to imprint the tailored emblems, patterns, symbols and codes onto the metallic and polymer product surfaces. The laser printing was first used to form these tailored micro-/nano-textures onto a Diamond-Like Carbon (DLC) coating die. The DLC film with the thickness of 20 µm and the hardness of 22 GPa was utilized as a mother die. Femtosecond laser printing was used to shape the tailored micro-/nano-textures on this die. Seven emblems such as a star-patterned texture with the maximum depth of 4 µm were just cut into the DLC-die to have color-grating by micro-texturing and surface plasmonic brilliance by nanotexturing. In second, Computer Numerical Control (CNC) - stamping was used to imprint these textures onto the aluminum alloy plate with the thickness of 1 mm. Scanning Electron Microscopy (SEM) and three dimensional profilometer were used to investigate the geometric accuracy in this two-step printing procedure. The constituent micro-/nano-textures of each emblem was accurately imprinted onto the aluminum work. The optical properties were also duplicated together with this geometric imprinting.

Introduction

Holography and color-grating techniques have been widely utilized for copy-proof of originally designed sheets and films. A typical example of this surface decoration is noticed in a newly designed 10,000 Yen paper billets [1]. In addition to the accurately printed portrait of late Mr. E. Shibusawa, the famous founder of enterprising in Japan, a few holographic symbols are also imprinted onto this billet to be free from forgery. Besides for this copy-proof technique, the color-grating with surface plasmonic design is used to decorate the polymer surface [2] and to modify the original surface properties [3]. In the mass production of papers and metals with holographic emblems, a mother die is first prepared by mechanical machining, grinding and finishing to print those emblems onto plastic and metallic thin films, and to cut and join them onto the paper films and metallic sheets [4]. This traditional procedure often suffers from the loss of capacity to follow the flexible design and from the difficulty to print them onto various polymer and metallic products with the enough proof of geometric accuracy and optical properties.

In recent, the femtosecond laser micro-/nano-texturing method was highlighted not only to make surface property modification of metallic and alloyed parts [5-8] but also to fabricate the mother die to imprint various textures onto the metallic and polymer products [9-11]. In particular, the nanotextures by Laser-Induced Periodic Surface Structuring (LIPSS) were formed onto the hardened die and the DLC-coating die together with the microtextures. As stated in [7-8, 10], the well-designed surface with micro-/nano-textures has higher fractal dimension than 2.2; owing to this fractal surface geometry with its high spatial frequency ratio, this surface has super-hydrophobicity with its contact angle higher than 170°. In addition, the LIPSS-nanostructured surface has surface plasmonic brilliance together with color-grating by microstructures. With the use of CNC – stamping, these micro-/nano-textures on the punch and die are also reproduced on the metallic and polymer work surfaces [10-12]. Hence, various micro-/nano-textures are designed and duplicated onto the work material surfaces by using the femtosecond laser printing and the CNC-stamping.

In the present paper, this two-step procedure is utilized to describe the dimensional accuracy in the femtosecond laser printing and the CNC-imprinting. In particular, two metallic plates are employed to investigate the influence of their flow stress on the CNC-imprinting behavior; e.g., aluminum alloy plate and pure tin sheet. In addition, the loading sequence is also controlled to discuss the effect of microscopic plastic flow on the filling process into the concave micro-/nano-textures on the DLC-die during imprinting.

Experimental Procedure

Femtosecond laser printing system. A femtosecond laser system (FEM-1; LPS-Works, Co., Ltd., Tokyo, Japan) was used to print the tailored spatial textures directly onto the DLC coating surface. The wavelength (λ) of the laser was 515 nm, with the pulse width of 200 fs and the pulse repetition rate of 400 kHz. The maximum average power was 40 W, and the maximum pulse energy was 50 μ J. The working area was 300 mm x 300 mm. In practical operation, a working plate with the size of 280 mm x 150 mm was placed on the work-table. The irradiation power of a single pulse is estimated to be 0.25 GW. This high power irradiation in the 200 fs interval drives a well-defined ablation into the targeting materials. The femtosecond laser machining process was controlled by the Computer Aided Manufacturing (CAM) data. In this experiment, each microtexture is represented by the assembly of line segments. Nanotexture is cut into each micro-texture by the LIPSS effects. In this LIPSS, each nano-groove is formed by the nonlinear optical interaction between the controlled incidental laser beam and the traveling beam on the surface. Depending on the laser irradiation parameters and the surface condition, the nano-groove depth (d_L) is uniquely determined; in this case, $d_L \sim 400$ nm. On the other hand, the LIPSS-period (Λ) or the nano-groove width is also determined by the laser processing conditions. In this case, $\Lambda \sim 300$ nm.

CNC-stamping system. The laser printed DLC coating punch was fixed into the upper die set. Both the upper and lower dies sets were respectively fixed to the upper and lower bolsters of CNC (ZEN90; Hoden-Seimitsu, Co., Ltd., Kanagawa, Japan) – stamper with the maximum loading capacity by 50 kN. In the following experiments, the upper bolster was incrementally lowered to imprint the micro-/nano-textures onto the aluminum work after the starting position in contact of the DLC coating punch to the work surface. The stroke velocity was constant by 0.05 mm/s. The upsetting was performed until the total stroke became 150 µm by the applied load of 3 kN. As stated in [12], the programmable loading sequence in this CNC stamping was also utilized to investigate its influence on the imprinting behavior of the mother micro-/nano-textures onto the metallic plates.

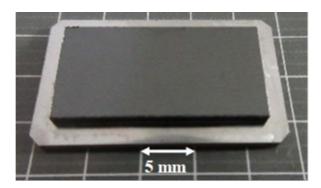


Figure 1. DLC-die coated onto the SKD11 substrate.

Die and work materials. A SKD11 substrate with 100 mm x 100 mm was DLC-coated by Medium Frequency (MF) – Plasma Enhanced Chemical Vapor Deposition (PECVD) method as reported in [13-14]. The DLC-coating die was cut from this mother plate and finished to a die shape. The DLC coating thickness was $20~\mu m$. A pure AA1060 aluminum plate was utilized as a standard work material to describe the imprinting process. A pure tin plate with the purity of 99.99% and the thickness of 1 mm was also used to investigate the effect of work flow stress on the imprinting behavior.

Experimental Results and Discussion

A DLC-die was prepared as a mother die for femtosecond laser printing of micro-/nano-textures. This printed DLC-die was fixed into the CNC-stamper for imprinting the tailored textures onto the work materials. SEM analysis and three dimensional surface profilometer were utilized to discuss the geometric accuracy in the laser printing and the CNC-imprinting.

Fabrication of DLC-Die. The DLC-coated SKD11 punch with the size of 10 mm x 20 mm x 4 mm was prepared for femtosecond laser printing, as depicted in Figure 1. Since the DLC coating thickness was 20 μm, every microtexture with the shallow depths can be laser-printed only into the amorphous carbon layer. This DLC coating die has a smooth surface enough to be utilized for stamping without further grinding and polishing. In addition, this DLC die has sufficiently higher hardness than 20 GPa. In general, a thick DLC film has a risk of inhomogeneity in its inside. As stated in [15], various defects were induced into DLC films during PVD (Physical Vapor Deposition) and CVD processes. In the present study, MF-PECVD was utilized to synthesize the thick DLC film with much less amount of defects [13-14]. To demonstrate the homogeneity of MF-PECVD DLC coating, the coating process under the pressures of 2.5 Pa and 3 Pa was stopped to prepare each growing DLC films for hardness testing. Figure 2 summarizes the whole measured hardness of DLC films with various thickness. The measured hardness is constant by 22 GPa; this proves that MF-PECVD DLC films have sufficiently homogeneous structure enough to be used as a punch and a die. The average surface roughness was much less than 0.1 μm.

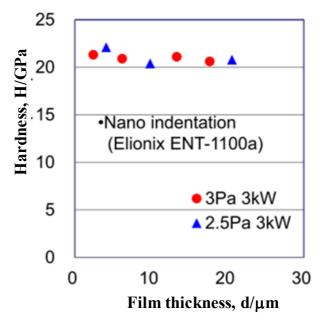


Figure 2. Hardness of DLC coating die material, invariant to the coating thickness and to the plasma processing condition.

Laser Printing. Two types of DLC coating dies were laser printed to have different microtextures. Seven emblems were printed into the first DLC die to describe the laser printing procedure and the imprinting behavior onto aluminum plate. A star-shaped emblem was only printed to analyze the geometric accuracy in laser printing and the imprinting capacity into aluminum and tin.

Figure 3a depicts the seven emblems, laser-printed onto the DLC coating die from a star-shaped texture M_1 to a circular texture M_7 . Each microtexture consists of polygonal segments including the nano-grooves with their tailored orientations. Each segment is distinguished by its own color-grating and its surface plasmonic brilliance. In the laser machining operation, the whole DLC surface was ground down to 7 μ m except seven square areas with the size of 4 mm x 4mm. Each microtexture was formed onto each square area to build up an alignment of seven micro-textures on the DLC

coating punch. The M_1 emblem was only cut into the DLC punch with the size of 6 mm x 6 mm in Figure 3b.

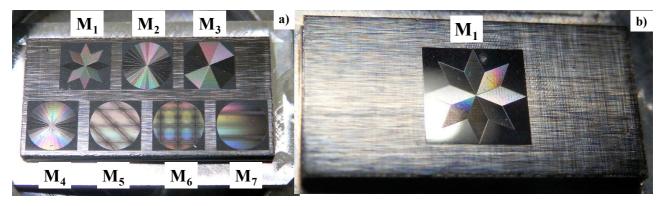


Figure 3. Laser printing of microtextures into the DLC coating die. a) Seven emblem microtextures from a star-shaped microtexture, M_1 to a circular microtexture, M_7 , and b) a star-shaped microtexture, M_1 at the center.

Since the DLC film thickness coated by MF-CVD reaches to 20 μ m, each microtexture and nanotexture is cut into the maximum depth of 4 μ m in this DLC film to form steep edges and edge corners. In addition to its higher hardness of this DLC coatings than 20 GPa, its surface smoothness is preferable to a die and punch material to imprint micro- and nano-textures with sufficient accuracy in geometry. Furthermore, the amorphous carbon structure such as Glassy Carbon (GC) and DLC are suitable to fast-rate, homogeneous ablation by the short-pulse laser machining. Different from the diamond coating, various kinds of substrate geometry can be employed as a forming tool by using this thick DLC coating. The curved surfaces and inner surfaces of parts and members can be also coated by DLC via MF-CVD process. This suggests that the rolling process with the micro-/nano-textured DLC-coated rolls enables to make large-area imprinting onto the metallic sheet, and that the extrusion and drawing processes are also useful to imprint the micro-/nano-textures onto the external surfaces of bars and wires and onto the inner surfaces of pipes, respectively.

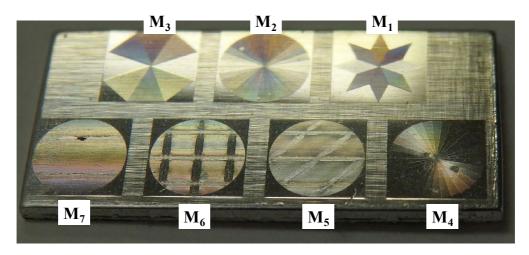


Figure 4. CNC-imprinting of seven emblem microtextures (M₁, M₂ ... M₇) onto the as-rolled AA1060 aluminum alloy plate with its thickness of 1.0 mm.

CNC-Imprinting. The laser printed DLC coating die was used for fine stamping to imprint these micro-textures onto the metallic and polymer works. AA1060 aluminum alloy plate with the thickness of 1 mm and the as-rolled surface roughness, was utilized as a work for imprinting. Figure 4 shows seven microtexture replicas which are imprinted by coining the microtextured DLC punch in Figure 3a. Seven replicas in Figure 4 correspond to seven microtextures in Figure 3a in a mirror-

refelection image. In parallel with the geometric imprinting from the microtextures on the DLC punch to the plate, the color-grating properties are also duplicated on this aluminum work.

SEM was first utilized to make comparison on the microtexture geometry between the original DLC microtextures and the imprinted replica on the aluminum work plate. Two segments from a star-shaped emblem in Figures 3 and 4 were employed for SEM analysis. Figure 5a depicts two neighboring segments of A and B across the intersegmental edge in M₁ on the DLC die. Each segment consists of an alternative alignment of micro-edge and concave terrace. On the other hand, two segments of A' and B' on the imprinted aluminum plate is made of the alignment of micro-groove and convex terraces. This mirror-image inversion between Figures 5a and 5b reveals that the microtextures on the DLC die are accurately imprinted onto the aluminum alloy plate.

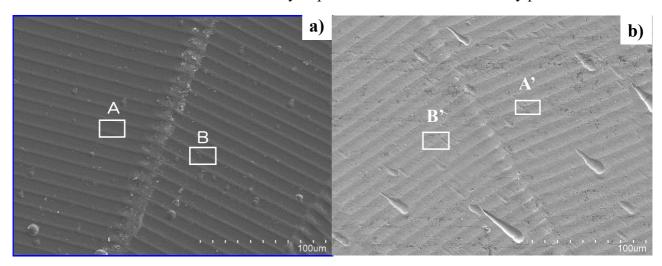


Figure 5. Topological comparison of two segments in the star-shaped emblem microtexture between two SEM images on the laser-printed DLC punch and on the CNC-imprinted aluminum alloy plate.

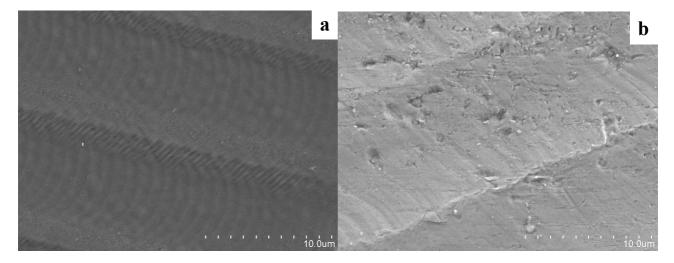


Figure 6. Comparison of high resolution SEM images between the nanotextured DLC punch surface and the imprinted replica on the pure aluminum plate. a) Nanotextures in the region-A in Figure 5a, and b) nanotexture replica in the region-A' in Figure 5b.

High resolution SEM was utilized to investigate the accuracy in imprinting of nanotextures from the DLC punch to the aluminum plate. As depicted in Figure 6a, the LIPSS-ripples are formed on the concave terraces, and, the micro-edges with the period of 300 nm. On the imprinted replicas in Figure 6b, these nanostructured textures are vaguely formed even on the convex terraces and the micro-grooves, respectively. The present micro-/nano-texturing in the laser printing and the CNC-impriniting is characterized by this hierarchical structure

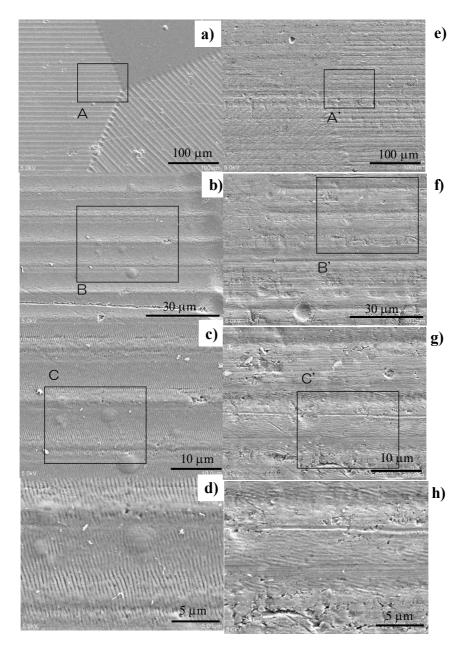


Figure 7. Multidimensional SEM images on the femtosecond-laser printed star-shaped textures onto the DLC punch and the CNC-imprinted replicas onto the aluminum plate. a) to d): Micro-/nano-textures which are laser-printed onto the original mother die, and e) to h): micro-/nano-texture which are imprinted onto the rolled aluminum plate surface.

Let us consider what determines the dimensional accuracy of CNC-imprinting process. As demonstrated in Figures 5b and 6b, the experimental setup for stamping is properly adequate to drive the plastic flow of work materials into to the micro- and nano-meter scaled die cavities. This correlation by SEM analysis between the original microtextures on the DLC die and their replicas on the work plate, proves that micro-meter scaled imprinting homogeneously takes place to duplicate the original textures but that nano-meter scaled imprinting process becomes heterogeneous by the difference of microscopic plastic flow of work materials in local.

The multi-dimensional SEM analysis is utilized to precisely compare the micro-/nano-imprinted replica-structure onto the aluminum plate with the original textures on the DLC die. Figure 7 shows the variation of SEM images on the adjacent two segments in the star-shaped M_1 -emblem with increasing the resolution in analysis. Figures 7a to 7d depict the focusing views on the micro-/nano-textures of laser-printed DLC punch from sub-mm range to μm size. As seen in Figures 7a to 7b, each segment of M1 emblem is composed of micro-edges and concave terraces with regular alignment by

the pitch of $10 \mu m$. Under high resolution in Figures 7c and 7d, the nano-textured LIPSS-ripples are regularly cut into these micro-edges and terraces. These Figures 7a to 7d with Figures 5a and 5b, reveals the multi-dimensional structure of micro-/nano-textures on the laser-printed die. Each tailored emblem is sculptured as a regular alignment of micro-edged segments together with the nanotextured LIPSS ripples.

Figures 7e to 7h also depict the variation of SEM images on the CNC-imprinted aluminum plate surface with increasing the resolution in analysis. As discussed in comparison between micro-edges on DLC punch and micro-grooves on aluminum work in Figure 5, the microtextures in Figures 7e to 7f are corresponding to those in Figures 7a to 7b in the mirror-image inversion. Through the simultaneous CNC-imprinting of all the micro-edges onto the aluminum work surface, the aluminum plate is surface-decorated by the micro-textured emblem.

As shown in Figures 7g and 7h, the nanotextures are noticed both on the micro-grooves and their adjacent convex terraces. They are vaguely formed on the micro-grooves and terraces, and aligned in parallel to the micro-grooves. As had been analyzed in [9, 12], the nanotextures with the orientation of +30° on the nitrided punch was duplicated in the mirror-image inversion to those with the orientation of -30°. After that normal imprinting behavior of nanotextures in [9, 12], the nanogrooves in Figures 7c and 7d were thought to be imprinted onto the aluminum plate in their mirror-image inversion. The nano-texture misorentation in Figure 7h from the prediction, reveals that the microscopic plastic flow is sensitive to the meso-scopic plastic flow when imprinting the DLC microedges.

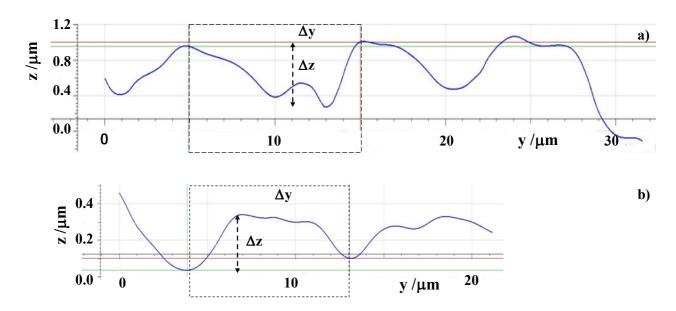


Figure 8. Comparison of the cross-sectional profile across the microtextures between the A-region in Figure 7a and the A'-region in Figure 7e. a) Cross-sectional profile of textures in the A-region of star-shaped emblem laser-printed onto the DLC punch, and b) cross-sectional profile of textures in the A'-region of replica CNC-imprinted onto the aluminum plate.

Three dimensional profilometer was utilized to investigate this imprinting behavior of micro-edges in the DLC punch to the aluminum plate. Figure 8 compares the cross-sectional profiles across the micro-edges of DLC die and across the micro-grooves of aluminum replica. As depicted in Figure 8a, the pitch (Δy) of DLC micro-edges in the segment is 10.1 μ m and their average depth (Δz) is 0.7 μ m. On the other hand, $\Delta y = 9.2 \mu$ m and $\Delta z = 0.3 \mu$ m in Figure 8b. This difference of Δy and Δz between the DLC micro-edge textures and the aluminum micro-groove ones, reveals that the concave terrace between the adjacent DLC micro-edges is only filled in partial by aluminum work and that nanotextures on the DLC concave terraces are coined onto aluminum only near the DLC micro-edges.

This insufficient metal flow into the DLC concave terraces, drives the vague imprinting of nanotextures in Figure 6 and the nanotexture-imprinting with misorientation in Figure 7h.

Flow Stress Effect on the Imprinting Behavior.

A pure tin plate is employed to describe how the flow stress of work materials influences on the imprinting behavior. As shown in Figure 9, seven micro-textured emblems are distinctly duplicated onto the tin sheet. Each constituent segment in each polygonal emblem is distinguished by the colorgrating together with the surface plasmonic brilliance. This proves that the nanotextures on the DLC micro-edges and concave terraces are regularly imprinted onto the micro-grooves and convex terraces as a replica on the tin plate.

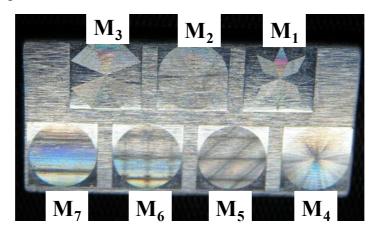


Figure 9. CNC-imprinting of seven emblem microtextures (M1, M2 ... M7) onto the as-rolled pure tin plate with its thickness of 0.5 mm.

This improvement in the micro-filling process by exchanging the work materials from aluminum to tin reveals that the microscopic flow is enhanced by using the low flow stress work materials.

Geometric Characterization.

The stroke speed in CNC-stamping was constant by 0.05 mm/s in the above experiments, where the local plastic flow is rather difficult to be controlled. When using the CNC-stamping system for imprinting, various loading sequence programs are available to control this plastic flow. Among them, the incremental imprinting with loading and unloading steps was suitable to make micropunching into the aluminum sheet [17]. This also suggests that the accuracy in imprinting the micro-nano-textures must be improved by the programed loading sequence in CNC-stamping.

Conclusions

A thicker amorphous carbon film than 20 μ m with the hardness of 22 GPa and the low surface roughness, provides a new die substrate material for impriting the micro-/nano-textures. Although the fine mechanical milling and machining is difficult to cut them into the hard and bridtle DLC films, the femtosecond laser printing becomes an effective tool to form the micro-/nano-textures onto the thick DLC coating die. Seven emblems are accurately cut into this DLC coating die with the maximum depth of 4 μ m. Each symbol consists of the polygonal segments; each segment is composed of the micro-edges and concave terraces. The oriented nanotestures with the ripple period of 300 nm are also formed onto the micro-edges and terraces. Owing to the significantly low surface roughness and high hardness of DLC, the mother micro-textures are accurately imprinted onto the asrolled aluminum alloy plate. The DLC micro-edges with the maximum depth of 4 μ m and the pitch of 10 μ m are embossed into the aluminum plate; the micro-edges sculpture the micro-grooves. The polygonal emblem on the DLC die duplicates its mirror image onto the work. Precise SEM analyses

and three dimensional profilometer reveal that the microscopic metal flow must be controlled to make full-filling into DLC concave terraces in order to imprint the nano-textures onto aluminum alloy plate.

When using the pure tine plate, the nanotextures are distictly imprinted to the plate together with the micro-texture emblems. This proves that the flow stress of work materials influences on the geometric accuracy in CNC-imprinting the nanotextures. The microscopic plastic flow goverens this full-filling process into the DLC nanotextures. The loading sequence by CNC-stamping also has influence on the microscopic imprinting behavior as well as the optical properties of imprinted emblems onto the metallic products.

This two-step procedure is suitable even to mass-production of micro-/nano-textured products without loss of flexibility to CAD of textures. Especially, the thick DLC coating works as a long-life die substrate with contribution to the carbon-neutral manufacturing. The metallic die-substrate is recycled for its next usage by ashing the used DLC coating die [18]. The total materials efficiency is promoted by using this DLC special tool.

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