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On the combination of plasma nitrided surfaces and LIPSS

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Abstract

LIPSS are subjected to excessive wear when exposed to direct contact in tribological applications. Therefore, precautions must be taken to increase LIPSS' hardness and wear resistance while simultaneously preserving their properties like superhydrophilicity. This work shows that a firstly plasma nitrided and subsequently structured surface results in LIPSS of high nano-hardness (14.88 GPa ± 1.05 GPa) who show a super hydrophilic wetting behavior (contact angle of 7°). The results indicate that a previous nitriding could bring LIPSS into tribological applications.

Keywords: Laser micro machining, Surface modification, Steel, LIPSS

1 Introduction

Sheet metal processes such as deep drawing are highly efficient due to high material utilization while simultaneously being subjected to friction. This friction is reduced using mostly conventional, mineral oil-based lubricants. But due to the increasing environmental awareness, the application of alternative lubricants is of great interest. A great step towards this objective would be the utilization of deionized water in forming applications. One major obstacle is its low viscosity that provides water from staying where it is needed like the contact zones between the die and the blank. This obstacle could be overcome using surface structures like laser induced periodic surface structures (LIPSS) that alter surface properties making surfaces i.e., hydrophile. The problem is that these nanostructures wear off in direct tribological contact. Therefore, processes are needed to increase the hardness as well as the wear resistance of the LIPSS or even to protect them from direct contact. Previously investigated solutions included laser hardening [1], the combination of LIPSS and PVD hard coatings [2], and the use of hierarchical structures [3]. To provide further possibilities for preparing surface structures for tribological applications, this work combines plasma nitrided surfaces with different surface structures. It is shown that this combination leads to an increased hardness of LIPSS while preserving their hydrophilic behavior at the same time.

2 Methodology

As substrates hardened and tempered cylindrical disks made of 1.2379 with diameters of 32 mm, thicknesses of 4 mm, and an initial hardness of 62 ± 2 HRC were used. Each disk was polished to a mean arithmetic height of smaller than 6 nm. Subsequently, plasma nitriding processes by varying the gas compositions and treatment durations were carried out on all disks in a plasma nitriding device of type Eltropuls. The nitriding parameters are shown in Tab. 1. At a gas flow rate ratio of 1:7 (6/43 l/h N_2/H_2) no hard and brittle compound layers (CL) are formed. When increasing the N_2/H_2 ratio to 1:1 the formation of CL takes place. Since all other nitriding parameters were kept constant, both the depth of the diffusion layers (DL) and the thicknesses of the compound layers only depend on the nitriding durations. Further information is provided in [4, 5, 6]. According to the test setting of Tab. 1, not only the mechanical properties of the near-surface regions are significantly influenced. This refers to the surface hardness, the hardness depth curve, and thus the mechanical supporting function, which have a direct impact on the achievable tribological properties. In addition, the chemical surface

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properties are influenced by the gas composition and plasma nitriding duration resulting in different phase proportions such as formed martensites, Fe_3C or $Cr_{26}C_6$ measured by X-ray diffraction (XRD). Plasma nitriding affects the amounts of formed nitrides such as γ'-Fe_4N and ε-Fe_3N, see Tab. 1. The different gas flow ratios and nitriding duration results in different nitriding hardness depths (NHD) and compound layer thicknesses (CLT) which can also be taken from Tab. 1.

Tab. 1: Plasma nitriding parameters and resulting nitriding hardness depths (NHD), compound layer thicknesses (CLT) and quantitative phase proportions of γ'-Fe_4N and ε-Fe_3N nitrides.

Temperature in °C	Duration in h	N_2-flow in l/h	H_2-flow in l/h	NHD in mm	CLT in µm	γ': Fe_4N in %	ε: Fe_3N in %
480	8	6	43	0.07	0	9,6	8,1
480	25	6	43	0.10	0	5,6	9,1
480	100	6	43	0.22	0	19,1	10,1
480	8	25	25	0.09	4	9,3	53,5
480	25	25	25	0.17	7	13,0	56,3
480	100	25	25	0.26	13	17,4	58,9

As surface treatment these disks were structured with LIPSS and none-periodic structures (NPS) which result due to different laser fluences. As laser source, the pulsed fiber laser TruMicro 5050 by Trumpf was used. The pulse energy was set to 200 µJ for LIPSS and 225 µJ for NPS at a repetition rate of 50 kHz and a single path cycle. The laser spot size on the substrate was set to 46 µm. The path trajectory consisted of parallel, equidistant lines. The LIPSS emerged at a path distance of 36.8 µm, while the distance was set to 2.3 µm for the NPS. The overview images of the resulting structures were taken using SEM (EVO MA10 microscope by Zeiss) at 14 k fold magnification for the LIPSS and 2 k-fold for the NPS. The mean distance between two peaks of the NPS respectively the periodicity of the LIPSS as well as the height and width were measured via CLSM images and evaluated via VK-X 3000 MultiFileAnalyzer by Keyence. The indentation tests were performed on a universal micro-hardness (UMH) tester Fischerscope H100C made by Helmut Fischer GmbH. The indentation hardness H_{IT} as well as the elastic indentation modulus E_{IT} were measured according to DIN EN 14577. A detailed description is to be found in [2]. The wetting behavior of the firstly plasma nitrided and subsequently structured substrates was determined via Sessile Drop tests. During these tests, a single droplet of deionized water was applied to the substrates' surfaces and the resulting contact angles (CA) were measured. Contact angles greater than 90° indicate a hydrophobic surface, contact angles smaller than 90° indicate a hydrophilic surface and contact angles smaller than 30° indicate a super hydrophilic surface. A detailed description is provided in [2].

3 Results

Consequently, the plasma nitrided surface was exposed to different thermal loads. Fig. 1 and Fig. 2 depict the different types of structures.

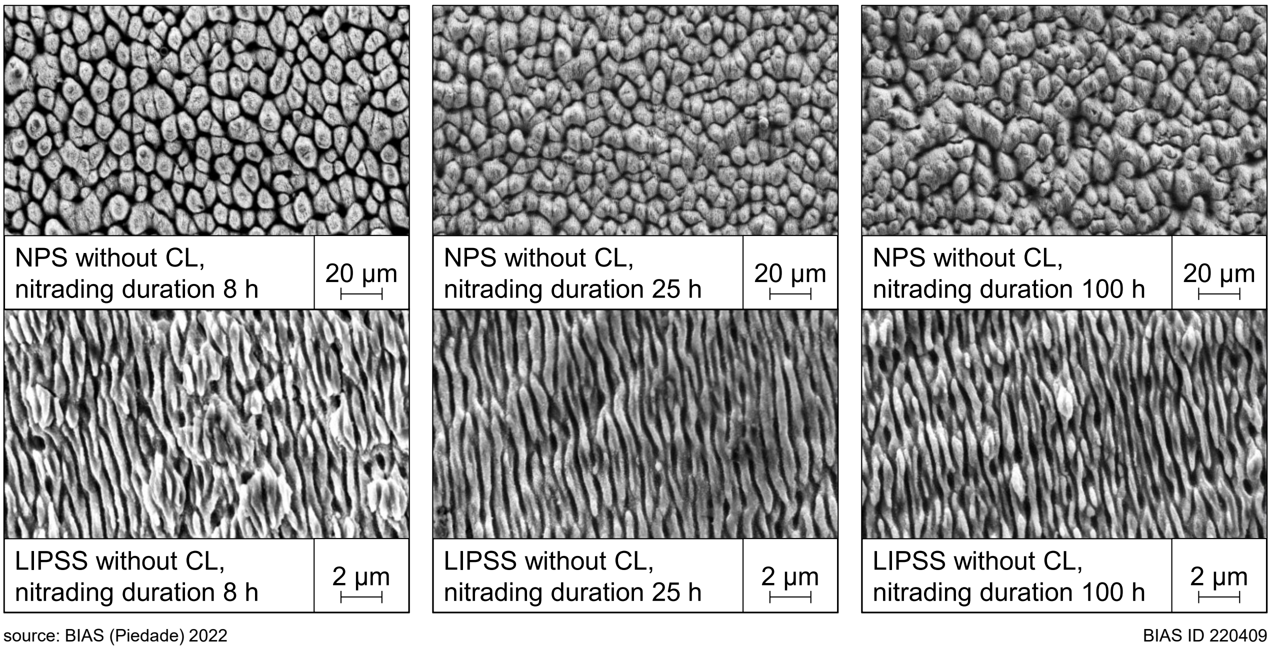

Fig. 1: NPS and LIPSS after structuring of plasma nitrided steels substrates without CL.

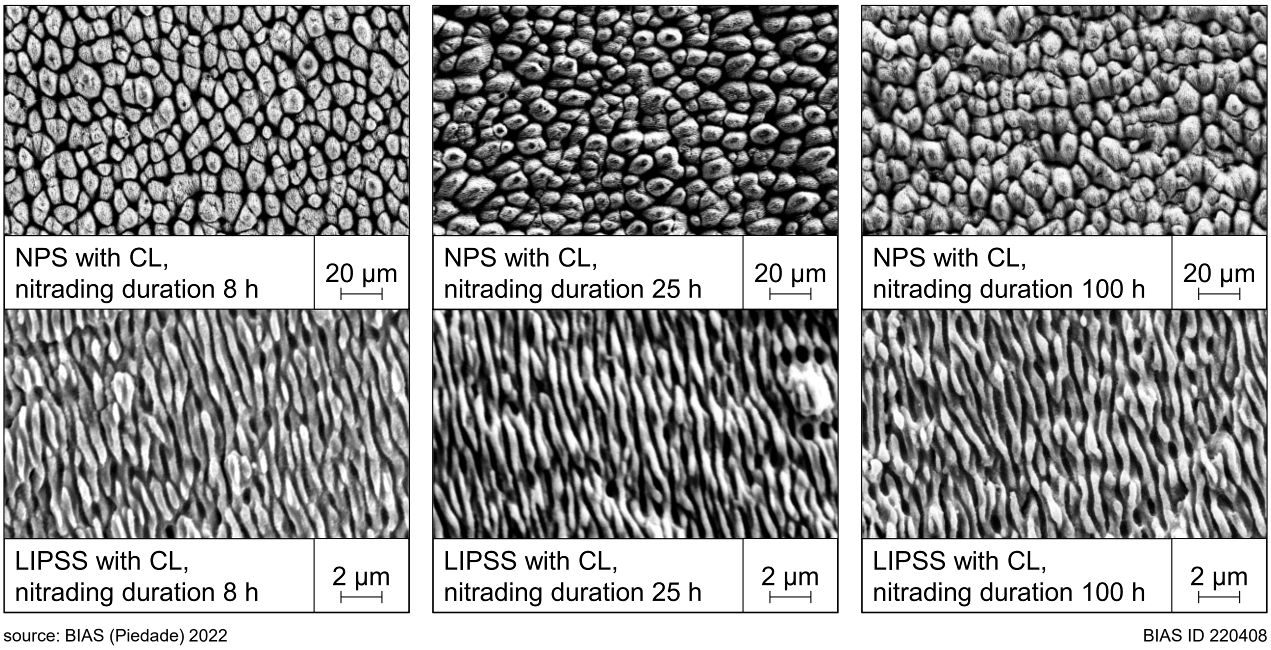

Fig. 2: NPS and LIPSS after structuring of plasma nitrided steels substrates with CL.

As the Fig. 1 and Fig. 2 depict, the formation of brittle compound layers with increased amounts of ε-Fe_3N has no visual effect on the emerging structures whether LIPSS or NPS and compared to the nitriding states without CL's. In case of the LIPSS, homogeneous and ditch-like structures occur while in case of NPS island-like structures cover the substrates' surfaces independent of the formed nitrides (γ'-Fe_4N and ε-Fe_3N).

The geometrical properties are summarized in Fig. 3. Since the NPS do not form homogeneous ditch-like structures, the mean distance between two peaks substitutes the periodicity in case of the NPS. As Fig. 3 depicts there is no influence on the geometric properties whether a CL is used or not. But there is an influence of the nitriding conditions on the mean distance between two peaks if NPS are applied. With increasing nitriding duration expressed through the nitriding depth, the distance between two peaks decreases slightly.

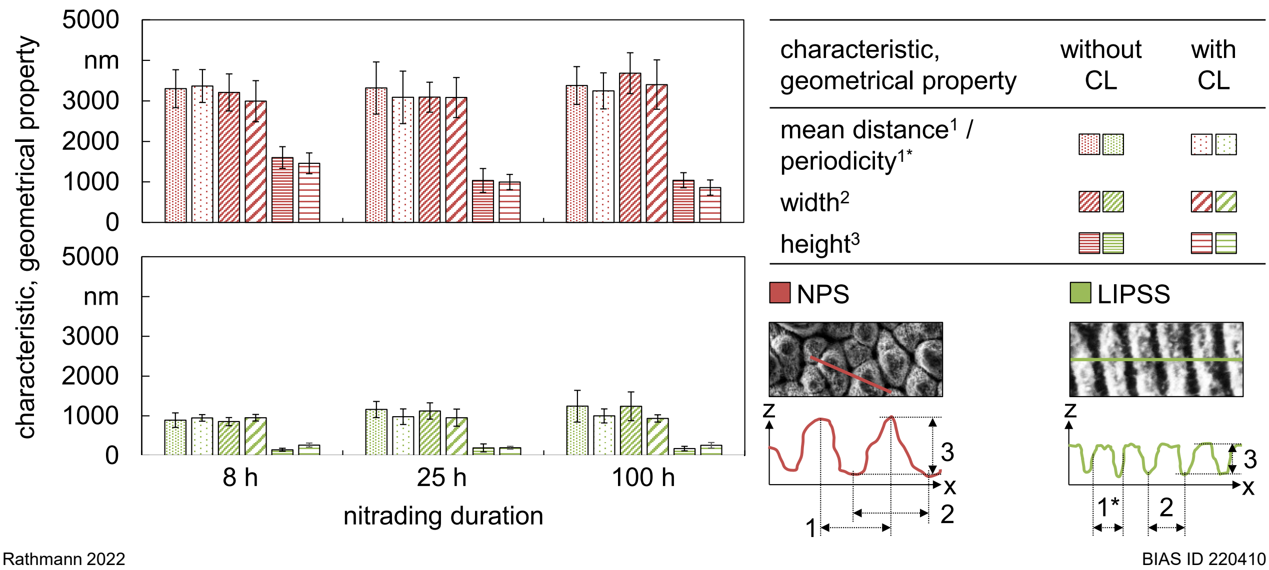

Fig. 3: Characteristic and geometrical properties of the processed structures in dependency of the nitriding duration and with and without the CL.

With these geometric prerequisites, the structured substrates were examined regarding their wetting behavior. The results of the Sessile-Drop-Tests carried out are summarized in Fig. 4. The contact angle reveals that the processed surfaces covered with LIPSS have a super hydrophilic (CA < 30°) behavior regardless of the prior nitriding conditions. Contrasting, the initial polished surface has a hydrophobic behavior according to a CA greater than 90°.

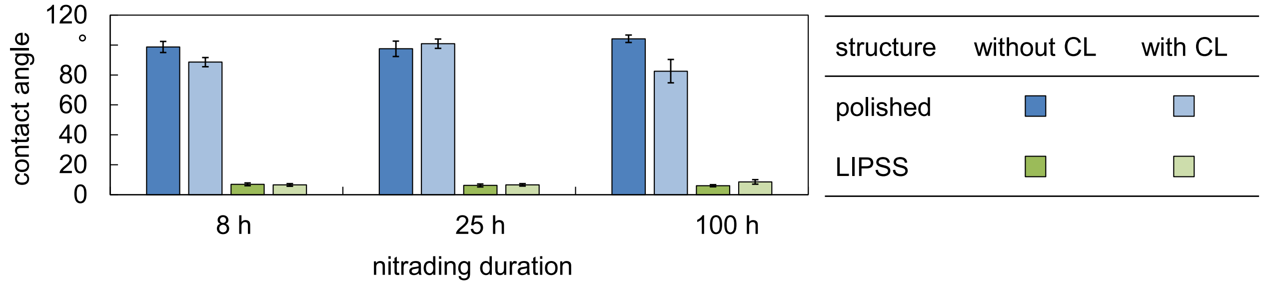

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Fig. 4: Contact angle on NPS and LIPSS structured in dependency of nitriding duration and with and without the CL.

A key property to increase LIPSS' wear resistance is their hardness. Accordingly, the nitrided substrate should maintain its initial hardness during laser structuring. Therefore, the indentation hardness H_{IT} and the elastic indentation modulus E_{IT} of LIPSS were measured via nano-indentation and the results are presented in Fig. 5 and Fig. 6 in dependency of the nitrading duration and with and without CL.

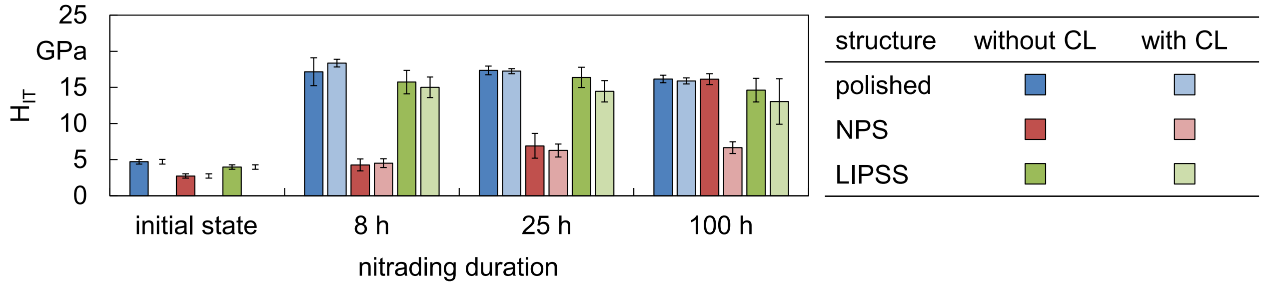

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Fig. 5: Indentation hardness H_{IT} in dependency of the and nitriding duration and with and without the CL.

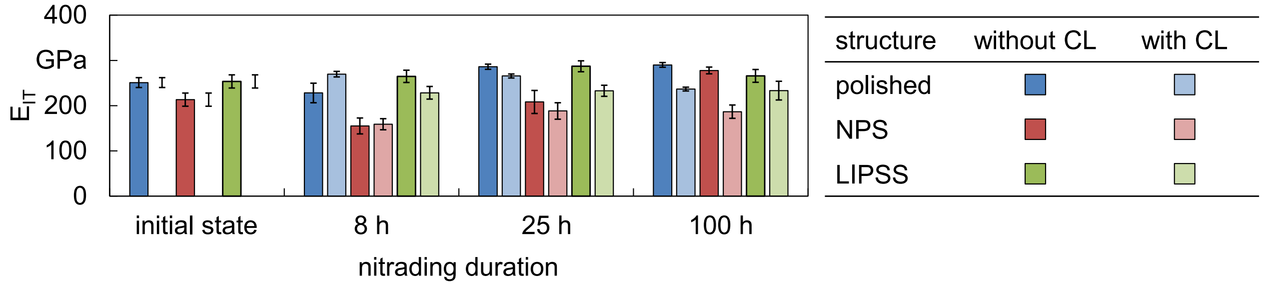

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Fig. 6: Elastic indentation modulus E_{IT} in dependency of the nitriding duration and with and without the CL.

The results of the indentation hardness in Fig. 5 depict that using NPS lead to an indentation hardness near the initial hardness of the hardened and tempered steel substrate independent of the usage of CL with one exception. At a nitriding duration of 100 h and without CL the indentation hardness of NPS is like the hardness of LIPSS and the polished and nitrided reference substrate. In contrast to the NPS, the appliance of LIPSS leads only to a negligible decrease in the indentation hardness compared to the polished and nitrided reference substrate independent of the usage of CL. The indentation modulus shows an influence of the CL with increasing nitriding depth. At durations of 8 h no influence can be seen. But at durations of 100 h, the formed CL leads to lower elastic indentation moduli. Overall nitriding depths, substrates structured with LIPSS lead to higher moduli compared to NPS-structured substrates. Those moduli achieved with LIPSS lie in the range of those moduli of hardened and tempered substrates without any surface structure.

4 Discussion

Concerning the elastic indentation modulus in Fig. 6, it is observed that except the combination of NPS and a nitriding depth of 0.05 mm no significant deviation from the initial indentation modulus of the hardened and tempered steel substrate is to be recognized. Since there is no significant deviation of the indentation hardness in terms of LIPSS for different nitriding depths, these hardnesses are averaged to a mean indentation hardness of 14.88 GPa ± 1.05 GPa. Compared to those hardnesses achieved by different processes like combing PVD hard coatings with LIPSS (DLC: 6.24 GPa ± 1.05 GPa, TiN_x: 4.94 GPa ± 0.94 GPa) [2] and laser hardening of LIPSS (5.66 GPa ± 1.93) [3], it becomes clear that the combination of firstly nitriding a surface and subsequently structuring with LIPSS leads to a three times higher indentation hardness. Simultaneously, the hydrophilic and even super hydrophilic property of with LIPSS structured surfaces could be maintained. A nitrided surface structured with LIPSS has a 22 times respectively 21 times lower contact angle than a DLC (155° ± 2) respectively a TiN_x coating (146° ± 2°) structured with LIPSS [2] or a 9 times lower contact angle than laser hardened LIPSS (62 ± 2°) [3]. This work thus demonstrates the suitability of firstly nitrided and subsequently with LIPSS structured substrates in principle for tribological applications. This is because, on the one hand, a high nano-hardness is present in the case of LIPSS and, on the other hand, the hydrophilic behavior is retained. In the following, wear tests will be carried out to further quantify their suitability.

5 Conclusion

In this work were firstly nitrided surfaces combined with LIPSS and NPS to obtain hard and simultaneously hydrophile surface structures for tribological applications. As the results indicate, LIPSS maintain the hardness of the nitrided substrate and the hydrophilicity in contrast to NPS. Therefore, it is concluded that a previous nitriding could bring LIPSS into tribological applications since it settles the right prerequisites regarding nano-hardness and wetting behavior.

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References

[1] L. Rathmann, T. Radel: Influence of laser hardening on laser induced periodic surface structures on steel substrates. IOP Conference Series: Materials Science and Engineering 1135 (2021) 0120245. https://doi.org/10.1088/1757-899X/1135/1/012024

[2] L. Rathmann, T. Rusche, H. Hasselbruch, A. Mehner, T. Radel: Friction and wear characterization of LIPSS and TiN / DLC variants. Applied Surface Science 584 (2022) 152654. https://doi.org/10.1016/j.apsusc.2022.152654

[3] L. Rathmann, T. Radel: On the use of LIPSS in single- and multi-scale laser-structured tool surfaces under lubricated conditions. Journal of Manufacturing Processes 77 (2022) 819-830. https://doi.org/10.1016/j.jmapro.2022.03.049

[4] H. Hasselbruch, A. Mehner, H.-W. Zoch: Influence of plasma nitriding parameters and subsequent surface finishing on the adhesion strength of tungsten doped PVD a-C:H coatings. In: THE "A" Coatings in Manufacturing Engineering (Ed.): Proceedings of the 13th International Conference of THE"A" Coatings, (2017) 169-179.

[5] H. Hasselbruch, A. Mehner, H.-W. Zoch: Einfluss der Plasmanitrierparameter und anschließenden Oberflächenveredelung auf die Haftfestigkeit von Wolfram dotierten PVD-a-C:H-Schichtsystemen. In: Gesellschaft für Tribologie e.V. (GfT) (Ed.): 58. Tribologie-Fachtagung (2017) 1-11.

[6] H. Hasselbruch, M. Herrmann, J. Heidhoff, et al.: Strukturierte und DUPLEX behandelte Werkzeuge für die Trockenbearbeitung beim Rundkneten. Dry Metal Forming OAJ FMT 5 (2019) 31-38.