INFLUENCE OF PLASMA-NITRIDING ON THE ADHESION OF DLC FILMS

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Abstract

DLC films have special properties, which are of great interest in fields of tribology, e. g. the high hardness and the low coefficient of friction. These properties are limited because of shortcomings in adhesion of DLC films on steel. So far, metallic adhesive layers like titanium and chromium are established options for the improvement of the adhesion of DLC films on steel. However, it is hardly investigated how plasma nitrided surfaces increase the adhesion by itself.

Beginning for this research were the different surface modifications, which can occur through plasma nitriding. Three different surface modifications were investigated in detail: Compound layer-free (α), γ'-nitride compound layer and ε-nitride compound layer. These surface modifications differ in their composition, crystal structure, bond type, as well as their solubility and diffusion velocity of carbon. By means of a two-stage nitriding process, it was ensured that the hardness depth profile of all three surface modifications were similar. Thus, the "eggshell" effect should have no significant influence on the research. Afterwards, the nitrided specimens were DLC coated by PACVD. Tests, executed on a scratch test rig, indicate that plasma nitriding can improve the adhesion of DLC films. LC_2 values of up to 60 N could be achieved. Typical values of LC_2 DLC films with metallic adhesive layers are about 25 N. During the investigations, it became apparent that adhesion in this system is strongly influenced by other factors, such as environmental conditions and polishing processes.

Keywords: Plasma Nitriding, DLC films, adhesion, Surface modification

1. INTRODUCTION

1.1. DLC-Films

The technical potential of diamond-like carbon (DLC) films for tribological applications was recognized in the 1970s and 1980s by [1,2] and others. DLC films offer a rare combination of high hardness, chemical resistance, and high wear resistance with simultaneously low coefficients of friction. Thus, they open up a wide spectrum for various technical applications in industry. In this context, DLC films are used worldwide today in the automotive industry [3,4], in recording heads of hard disks [5,6], razor blades as well as cutting and forging tools [7,8], in the field of medical technology [9,10] and sensor technology [11].

A distinction is made between hydrogen-free DLC films with high proportions of tetrahedral C-C bond components (ta-C) and hydrogen-containing a-C:H films [12]. Today, low-pressure plasma processes are used for the production of a-C:H coatings, with a distinction being made between PVD (physical vapor deposition) and PACVD (plasma-assisted chemical vapor deposition).

During the development of DLC films, it soon became clear that their application possibilities were limited by insufficient adhesion to the base material and that adhesion improvement was essential for broad application. One of the first approaches to solve this problem involved the modification of DLC films with metals [14,15]. Through empirical studies, it became clear that metallic layers between DLC and the base material can further improve adhesion [16,17]. Experiments were conducted with aluminum [18] and various carbide builders. Meanwhile, metallic interlayers are used as a standard for adhesion improvement of DLC films [19-21]. Chromium and titanium are mainly used for this purpose. The mechanism underlying the adhesion improvement in this process has not yet been satisfactorily investigated.

Another element that can be used for adhesion improvement is silicon (Si). Si can be used in pure form as an adhesion layer [17,22] or the DLC film is doped with Si in the transition area (a-C:H:Si) [13]. The adhesion improvement by a-C:H:Si interlayers is mainly used when pure PACVD processes are used for DLC deposition, where the application of a metallic adhesion layer is not possible. Si-containing precursors, e.g. tetramethylsilane (TMS), are used for this purpose.

However, further increased loads in tribo-systems, e.g. in forging tools, still require improvements of the adhesive strengths. Experimental results show that the stability and adhesion strength of coatings can be significantly improved by surface hardening, e.g., nitriding treatment [23,24], but no distinction is made between the influence of the support effect and the adhesion effect.

Despite these efforts, insufficient adhesion is still the limiting factor in the application of DLC films. The acting adhesion mechanisms are not sufficiently understood, so that the potential of DLC films cannot be fully used.

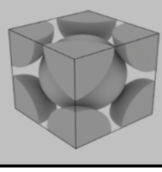
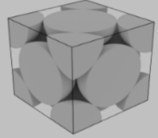
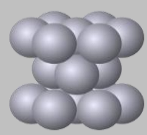
1.2. Plasma Nitriding

Nitriding is an established thermochemical process for the surface modification of metals (e.g. steel, titanium) in order to harden the surface layer and to reduce corrosion and wear on the surface [25]. A distinction is made between salt bath nitriding, gas nitriding and plasma nitriding [26].

Plasma nitriding offers the advantage that the formation of the nitriding zone can be adjusted in wide limits. With the support of a plasma, a nitrogen-hydrogen atmosphere is generated and atomic nitrogen is made available to the material surface, which diffuses into the workpiece [27]. In the workpiece, the nitrogen (N) causes a transformation of the original tool surface by forming a nitriding zone. This can consist of a compound layer (CL) on the surface and a diffusion zone (DZ). The formation of a CL can be prevented by selecting suitable process parameters [28].

In steels, a complete transformation of the original material surface takes place in the CL with the formation of iron nitrides. After the nitriding process, γ' (Fe_4N)- and ε ($Fe_{2-3}N$)-nitrides have been detected so far [29,30]. These differ from the original ferritic iron surface in terms of their structural, chemical, physical and mechanical properties (**Table 1**). They have a ceramic character with increased hardness and brittleness [31].

Table 1 Crystal structure, C-solubility and diffusion rate of the possible phases formed during plasma nitriding at the surface and in the near-surface region

Properties	Ferrite (α)	γ'-Nitride	ε-Nitride
Crystal structure [32]	BCC 	FCC 	HCP 
Maximum Carbon solubility [26, 29]	0.003 %	0.2 %	3.6 %
Carbon diffusion rate [26]	high	middle	Very low

In contrast to CL, no complete transformation of the material takes place in the DZ. Depending on the alloy content and composition of the steel, nitride precipitates are formed [26]. Since the diffusion zone has no influence in the investigations presented, a more in-depth description is omitted. Another effect of N in the nitriding zone is the redistribution of carbon (C), since the N is able to convert existing carbides into nitrides, with the release of C [33]. Due to the decarbonizing effect of the hydrogen-containing atmosphere [34], some of the released C effuses and the DZ becomes depleted of C [35]. Some of the C is also displaced from the diffusion front of the N into the interior of the workpiece during the nitriding process [35]. It is assumed that the different material modifications affect the adhesion of the DLC film. In particular, it is assumed that the different carbon solubility and diffusion rates have an influence on the adhesion of the DLC film.

By combining a coating with a previous plasma nitriding in so-called duplex processes, the coating adhesion can be improved. These duplex processes have already been successfully used in the case of nitride coatings such as TiN, CrN and TiBN [36 to 39]. Mostly, the adhesion improvement is attributed to a better supporting effect [23]. Duplex processes lead to better coating adhesion than purely thermal surface hardening [24], which is attributed to the gradual transition of hardness between the coating and the base material. Further investigations prove that the enhanced adhesion with these coatings goes beyond the pure support effect and that the formation of the surface during nitriding strongly influences the result [37,38,40,41]. In individual scientific paper [42], positive results have already been obtained with regard to duplex processes with DLC films. However, tests with duplex processes in industrial practice were discontinued due to the strongly fluctuating results and the associated low process reliability.

1.3. Own preliminary work

At the IOT, in cooperation with the Fraunhofer IST, a series of preliminary work to improve the adhesion of DLC films to steel surfaces by prior plasma nitriding was done. Initial approaches have already been described in [39,43-45]. Independently of this, there have been extensive experiments on the specific adjustment of the interface boundary surface of tool steels by plasma nitriding treatment, although the focus has not been on the combination with DLC films. The results were combined and form the basis for the present work.

This preliminary work shows that duplex processes can be used to improve the adhesion of DLC films. However, it also proved that the results were difficult to reproduce. Nitriding with the same hardness depth profile did not automatically lead to good adhesion. This indicates, that in addition to the supporting effect, there must be other adhesion-enhancing mechanisms caused by plasma nitriding. However, the resulting surface modifications and their influence on adhesion were not investigated in the studies carried out at that time.

Furthermore, the possibilities of selectively adjusting boundary surfaces by plasma nitriding had already been researched at the IOT in collaboration with the Fraunhofer IST in connection with the treatment of forging dies [28,40,46]. In this context it was possible to selectively adjust the type of compound layer (γ'- or ε-nitride).

2. METHODOLOGICAL BASES

As sample material, the ferritic-martensitic cold work tool steel 1.2379 (X155CrVMo12-1) was used. The samples were round samples with a diameter of 35 mm and a thickness of 4 mm. Before the tests, the round specimens were prepared to a polishing level with 0,05 µm Ra. The experiments were performed in a hot-wall plasma nitriding system. A DC pulse plasma generator was used. The coating with DLC was done on a PACVD system, the plasma activation was done by high frequency activation. The composition of the compound layer was determined by X-ray diffraction (Siemens D9000 XRD). The measurement was performed in Detector Scan at a fixed angle of 5 ° and were taken between 20 ° and 100 ° with an increment of 0.2 ° and a scan speed of 5 s per increment. As adhesion tests the scratch test was used. The measuring distance was 5 mm and a linear force increase from 1 to 50 N was used. The main criterion was LC_2, i.e. the force at which the layer was debonded.

3. EXPERIMENTAL PART

Before performing the scratch tests, the samples were nitrided in a two-step process. This was necessary to ensure that all samples have a similar hardness depth profile and thus the support effect has no influence on the results. Different process parameters are required to produce the different surface modifications, resulting in different hardness depth profiles. The exact process parameters of the individual nitriding processes are given in (**Figure 1**). First all samples received the nitriding for the γ'-surface and in a second nitriding process each of the other two surface modifications were adjusted. To generate the compound-free surface, named α in the following, the samples were annealed at 560 °C without plasma. For the ε-surface, the samples were nitrided again at 480 °C. After nitriding, XRD was used to check whether the desired surface modifications were present. The nitriding of the samples resulted in a roughening of the surface. This is in the range of 0.2 µm Ra. Since it could not be excluded that this roughness would have an effect on the adhesion of the DLC film, some of the samples were polished again before the coating process until they had an Ra value of less than 0.01 µm. These samples are referred to as "nitrided with intermediate polish" or "polished". XRD measurements were also taken to ensure that the samples have the appropriate surface modifications after re-polishing.

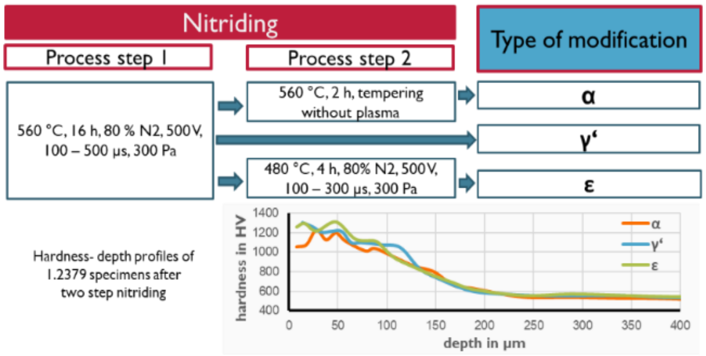


Figure 1 Scheme for setting the different surfaces and hardness-depth profiles of the samples with different modifications

Subsequently, the samples were coated with a pure DLC film by PACVD. There were two different coatings applied. Firstly, the DLC film was applied directly to the surfaces, and in the second coating, an adhesive layer was added between the surface and the DLC film. This adhesive layer consists of a DLC film heavily enriched with silicon. The process parameters for the DLC coating were: 20 sccm Ar + 60 sccm C_2H_2, 1 Pa, BIAS 400 V, 1 h. The process parameters for the adhesive layer coating were: 20 sccm Ar + 20 sccm TMS, 1 Pa, BIAS 400 V, 10 min. In both cases, the total layer thickness was about 3 µm and a layer hardness of about 1800 HV was achieved.

Due to the small size of the nitriding system, only a limited number of samples could be produced simultaneously. Since there was a high number of surfaces to be evaluated (12), it was decided to produce all surfaces in small quantities per batch and to produce a sufficient number of identical surfaces for statistical confidence by making several batches. A total of 4 batches were produced.

After the coating the adhesion was investigated by scratch test focusing on the LC_2 value. The reason for this was that reading the LC_1 value, at which point cracks start to form in the coating, could not be recorded because of the rough surfaces. For each sample, 3 scratch tests were carried out and an average value for the LC_2 value was determined.

4. RESULTS

The results of the nitrided samples with intermediate polish have shown the most consistent results. For these samples there is little variation between the different batches with the exception of batch 4, which shows significantly better adhesion results than the other batches for all surfaces. As can be seen in (**Figure 2**) and (**Figure 3**), there is no significant difference in the LC_2 values of pure DLC films and DLC films with adhesion layer. The surface without compound layer (α) performs the worst and the surfaces with compound layer show a significantly improved LC_2 value, with no difference between γ' and ε. This can also be observed, despite the higher absolute values, for batch 4. In the case of a compound layer, an LC_2 value of about 30 N can be expected, while batch 4 reaches values up to 46 N.

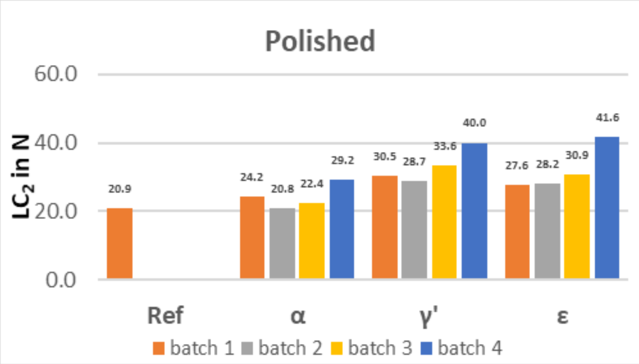


Figure 2 Comparison of LC_2 values between the different surfaces and batches with nitrided and polished surfaces.

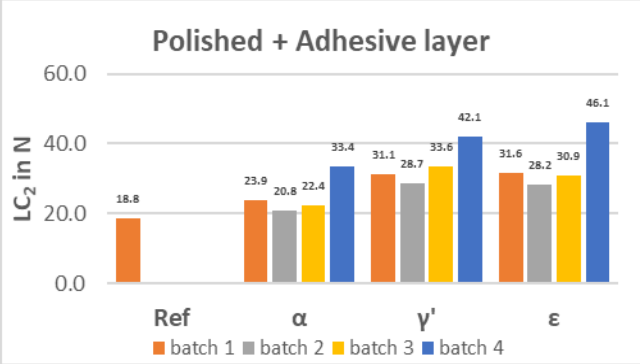


Figure 3 Comparison of LC_2 values between the different surfaces and batches for nitrided and polished surface with adhesive layer

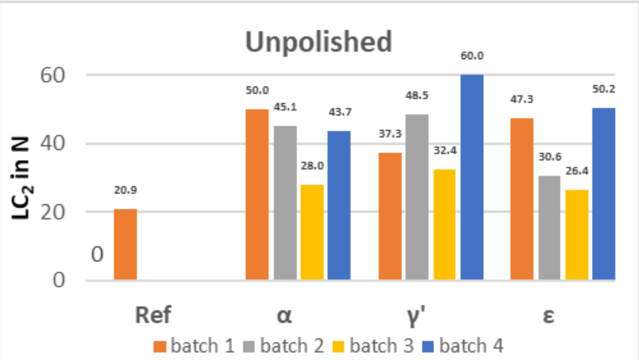


Figure 4 Comparison of LC_2 values between the different surfaces and batches with nitrided unpolished surface

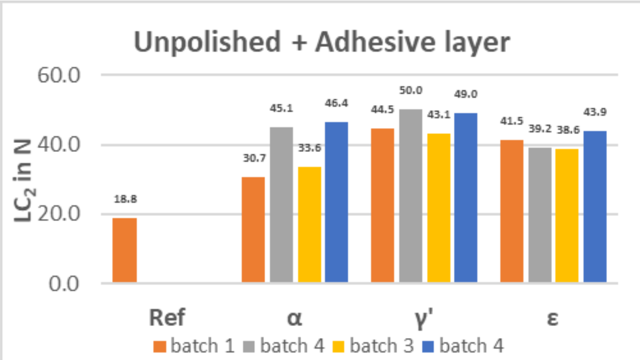


Figure 5 Comparison of LC_2 values between the different surfaces and batches for nitrided and unpolished surface with adhesive layer

For the samples without intermediate polish, the results of the scratch tests are not as consistent. There are large differences in the LC_2 value between the batches, especially for the samples without an adhesive layer, as can be seen in (**Figure 4**). For samples with adhesive layer, the differences between the batches are much smaller with the exception of the α modification see (**Figure 5**). In general, it is noticeable that significantly higher adhesion values are achieved without intermediate polish than with intermediate polish. This seems to be largely independent of the type of surface, since adhesion values of up to 50 N could be achieved with all modifications. In batch 4, even 60 N could be achieved with γ'. Here, the adhesive layer does not seem to have a significant influence on the maximum LC_2 value.

Scratch tests were also carried out on samples that had been artificially roughened so that they had a similar roughness to the nitrided samples (0.2 µm Ra). The samples were roughened by grinding or by blasting with glass pearls. As can be seen in (**Figure 6**) roughening the polished surfaces of the non-nitrided specimen and subsequently roughening the nitrided specimens with intermediate polishing does not lead to a higher LC_2 value. For both surfaces, artificial roughening leads to a

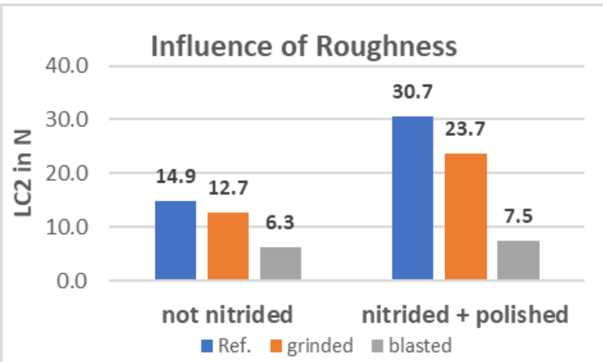


Figure 6 Comparison of LC_2 values between non-nitrided and nitrided polished surfaces at different roughnesses

degradation of the LC_2 value. Blasting the surface seems to have a stronger negative effect on adhesion than grinding the surface.

5. DISCUSSION

The results of the adhesion tests are very different. If the nitrided samples with intermediate polish are considered, it is clear that a bonding layer contributes to adhesion improvement. For all batches can be seen that the α surface has the poorest adhesion and the specimens with compound layer achieve a significantly higher LC_2 value. It is irrelevant whether the compound layer consists of γ' or ε. The adhesive layer also does not seem to have a significant effect on the LC_2 value of nitrided surfaces. Batch 4 shows higher absolute values, but the trend is comparable to the other batches. It can be assumed that for the polished samples the differences are mainly due to the different hardness of the surfaces. Thus, the main reason for the better adhesion values in the samples with interlayer is the better supporting effect.

For the nitrided samples without intermediate polish, the test results are not as consistent. Especially for the specimens without adhesion layer, the LC_2 values vary considerably between the different batches with the same modifications. With an adhesive layer, the results are clearly more consistent. Nevertheless, it is noticeable that significantly higher LC_2 values were achieved without intermediate polish than in the samples with intermediate polish. In these samples, it cannot be seen that any of the three surface modifications investigated has an influence on the LC_2 value. LC_2 values of up to 50 N can be found for all surfaces. Only batch 4 showed higher LC_2 values with 60 N for the γ'-sample.

It could be assumed that the rougher surface due to mechanical interlocking is responsible for the higher adhesion values for the unpolished nitrided samples. However, further scratch tests, on artificially roughened samples, showed that a rougher surface does not lead to higher LC_2 values for PACVD DLC films. The subsequently roughened non-nitrided samples and nitrided samples with intermediate polish, on the other hand, show lower LC_2 values. Thus, the rougher surface of the unpolished nitrided samples cannot be the main reason for the better performance of these samples. Therefore, no explanation for this adhesion behavior can be given in this paper. Nor is there any explanation why a blasted surface exhibits significantly poorer adhesion values than a ground surface, even though they have similar Ra values.

6. CONCLUSION

The investigations carried out were intended to determine whether similar or better adhesion values can be achieved for DLC films by nitriding without an additional metallic adhesive layer. For this purpose, different surface modifications that can occur during plasma nitriding were investigated in detail: Compound layer-free (α), γ'-nitride compound layer and ε-nitride compound layer.

It can be concluded that the adhesion of PACVD DLC films on steel samples can be significantly improved by nitriding. LC_2 values of up to 60 N have been achieved without an adhesion layer.

The adhesion results for samples with intermediate polish are consistent, but with 30 N they do not reach the maximum adhesion values of nitrided samples without intermediate polish with values of 50 N independent of the surface modification.

There is currently no explanation for the partially very good adhesion results for these specimens. However, the type of surface modification does not seem to play a role. The higher roughness of the non-polished specimens also does not seem to be an influencing factor.

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