Investigation of the Damage Mechanism of CrN and Diamond-Like Carbon Coatings on Precipitation-Hardened and Duplex-Treated X42Cr13/W Tool Steel by 3D Scratch Testing

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The present work deals with the characterization of the scratch resistance of two different types of coatings, i.e., chromium nitride (CrN) and diamond-like carbon prepared on X42Cr13/W (1.2083) plastic mold tool steel by physical vapor deposition and plasma-enhanced chemical vapor deposition, respectively. Our study focuses on the influence of the duplex treatment, i.e., plasma nitriding + ceramic coating on the scratch resistance of the tool steel. An advanced 3D scratch testing methodology has been used to investigate the coating adhesion and damage mechanism during scratching. The scratch analysis is completed by ball cratering test and micro-Vickers test to determine the thickness and hardness of the coatings. The test results demonstrate that the applied duplex treatment is an unambiguously advantageous surface technological process which manifests itself in higher loadability and lower sensitivity for cracking of the duplex coatings, increasing the critical forces. The scratch resistance of the combined substrate/coating material system is enhanced by the harder substrate material, providing a better interfacial bonding for both types of the ceramic coatings without changing the basic damage mechanisms.

Keywords: CrN, DLC, duplex treatment, PECVD, PVD, 3D scratch test

1. Introduction

Surface coatings play an important role in improving the mechanical properties of engineering components. They provide effective and flexible solutions for the tribological problems occurring in engineering applications. Coatings modify the tribological performance in several ways, e.g., by inducing residual compressive stresses, altering the surface chemistry and surface roughness, increasing the surface hardness or the strength, and thereby providing better mechanical properties, as well as better resistance to wear or lower friction coefficient (Ref 1-3). In the present research, we deal with two different types of surface coatings, i.e., diamond-like carbon (DLC) and chromium nitride (CrN) deposited on the substrate made of X42Cr13/W tool steel in two different conditions. On the one hand, the coating is deposited on a precipitation-hardened steel substrate; on the other hand, the same steel substrate is additionally nitrided before the coating procedure.

The investigated two coating materials are widely used in industry today. The applied DLC coating belongs to the class of amorphous carbon materials that offer unique mechanical and tribological properties. It is a metastable form of carbon that consists of sp³ diamond bonds and sp² graphite bonds (Ref 4). The wide range of applications of DLC coatings in the automotive (Ref 5) and aerospace industry, or as a protective layer for cutting (Ref 6, 7) and forming tools (Ref 8) and as biomedical implants (Ref 9-11), is due to its high hardness, chemical inertness, wear resistance, corrosion resistance, excellent adhesion (Ref 12), and very low (0.05-0.20) friction coefficient in the different tribopair combinations (Ref 13). Wear-resistant DLC coatings are applied on hard disks, eyeglass frames, electronic devices, or optical devices (Ref 14) for infrared and visible light range due to their scratch resistance. The primary concern for DLC coating is realizing a strong adhesion to the substrate and the ability to withstand cracking under the influence of external load. The obstacle in the application of DLC coatings in automobile components is their insufficient thermal instability. Therefore, in order to improve the thermal stability, doping with non-metal/metal is a convenient way to improve the tribological properties of DLC coating. Due to the deposition process, these coatings may possess high compressive stress that is usually reduced by Si or WC doping, thereby reducing the hardness, as well (Ref 15-17). This internal stress makes it challenging for DLC to bond to the substrate for a long period of time. Thus, in order to have a reliable and durable coating, we should investigate the adhesion properties, damage mechanisms, and failure modes of the DLC coating.
CrN is an interstitial compound in which nitrogen atoms occupy the octahedral interstitial position in the chromium lattice. The physical elaboration of the properties of this coating has been reported, extensively (Ref 18, 19). It possesses high hardness, extreme corrosion resistance, low residual stresses, excellent abrasive wear resistance, and a low coefficient of friction with different tribopairs. This coating offers extremely strong adhesion, i.e., there exists a molecular bond to the substrate material. CrN coating is electrically conducting and non-oxidizing and non-toxic; it has a high chemical resistance and environment-friendly processing technology. Such coatings find wide applications in high-temperature loading conditions, and in the form of wear-resistant precision components, molds, and die (Ref 20), or automotive parts such as shafts. The primary objective of surface coating is to protect the material from wear and damage under high and extreme loading conditions. When the component having a thin coating is subjected to high loading, elastic and plastic deformations may occur that ultimately results in premature failure of the coating (Ref 21).

In order to obtain excellent adhesion properties and to avoid the so-called eggshell effect, we have to provide appropriate mechanical support for the coating by pre-treating (e.g., precipitation hardening) the substrate. Hardening the substrate before the coating deposition helps to form a milder hardness gradient which ensures better adhesion and tribological properties. Applying an additional plasma nitriding to the precipitation hardened substrate helps to further improve the load carrying capacity and strengthen the mechanical support to the hard and brittle coatings. This combined method is called duplex surface engineering, involving the combination of two different techniques, e.g., plasma nitriding and surface coating, to build a two- or multilayer composite surface structure on any arbitrary substrate material with the purpose of improving the loadability and durability of the component surface (Ref 22-25).

For evaluating the adhesion properties of a coating, the standardized testing methodology adopted is the instrumented scratch test. The technique is widely recognized and used by the coating industries and the research laboratories as an important tool for quality assessment and analysis of the damage mechanism and failure modes under scratch loading. The test is performed by applying either a progressive (linearly increasing) or a constant load to create a scratch on the tested surface. Progressive load scratch tests have been extensively reported relating to coatings (Ref 26-31). Test results, such as the critical normal load \( L_{\text{cr}} \) leading to the coating failure or the friction coefficient \( \mu \), that is the normal loading force divided by the tangential force that works against scratching, can be determined to analyze the adhesion behavior of the coating.

Cracks initiate preferentially at defect sites of the coating and/or coating–substrate interface. When such a crack begins to propagate, it results in coating failure (Ref 32-35). The two major types of failure are the cohesive failure and the adhesive failure.

Cohesive failure occurs due to the tensile stress behind the stylus (through-thickness cracking) and exhibits the strength of the coating and is often represented by the force denoted by \( L_{\text{C1}} \).

Adhesive failure is caused by the compressive stress developing in the coating ahead the stylus. The related stress shows the strength of the bond between the deposited coating and the underlying substrate and is represented by \( L_{\text{C2}} \). The coating delaminates from the substrate either partially by cracking (lifting, buckling) or by full separation (spallation, chipping). The lowest critical load at which the coating delaminates from the substrate is known as the scratch adhesion force of the coating given by \( L_{\text{C3}} \). When scratch test is performed, there are several modes of failure that can be evaluated by optical microscopic analysis of the scratch groove. There are a great variety of possible failure modes depending on the substrate/coating combinations, and their identification is possible based on the suggestions of the standard ASTM C1624 (Ref 36). The coating adhesion characterizes the mechanical resistance of the interface between the coating and the substrate material.

The current study aims at elucidating the scratch resistance and damage mechanisms of the simply deposited and the duplex-treated CrN and multilayer DLC coatings using the instrumented scratch test, in addition, comparing their characteristic failure mechanisms. The basic objective is to have an insight into the effect of the applied duplex coating and evaluate its efficiency regarding the scratch resistance of the hard ceramic coatings on the investigated tool steel.

2. Experimental Work

2.1 Materials and Methods

The nominal chemical composition of the X42Cr13/W (1.2083) substrate material in wt.% is as follows:

- \( C = 0.38–0.45 \), \( \text{Si} \leq 1.0 \), \( \text{Mn} \leq 1.0 \), \( P \leq 0.030 \), \( S \leq 0.030 \), \( \text{Cr} = 12.00–13.50 \), and the remaining is Fe. The test samples are disks with dimensions of \( \Phi 30 \times 10 \text{ mm} \). All samples are bulk heat-treated, i.e., precipitation-hardened (austenitization at \( T_{\text{aust}} = 1020 \text{ °C} \), for \( t = 20 \text{ min} \)) with a high-temperature non-conventional tempering \((T_{\text{temp}}=580 \text{ °C} \text{ and } t_{\text{temp}} = 2 \text{ h})\) resulting in, on the one hand, a stabilized microstructure before the nitriding process of the duplex treatment and, on the other hand, a higher toughness, accompanied by a lower substrate hardness of \( \text{HV}_s = 289 \text{ HV0.1} \). Such kind of heat treatment for this type of steel is used in equipment operating under cryogenic conditions. In such cases, toughness is a primary consideration, the provision of which is accompanied by lower strength and hardness characteristics.

The use of ceramic coatings can be useful in many ways in such steels, for example, for lubricant-free, i.e., dry machining to reduce the coefficient of friction, or in cryogenic applications such as food, chemical, pharmaceutical, or compressor applications where surface layer corrosion resistance and chemical neutrality are important aspects.

The duplex treatment applied in this study consisted of plasma nitriding followed by surface coating. The plasma nitriding process is accomplished at a temperature of 520 °C, with uniform holding time of 8 hours, a voltage of 600 V, and a pressure of 2 mbar. The nitrogen source was decomposed ammonia \((N_2:H_2 = 1:3)\). The thermochemical treatment resulted in a nitrided layer of 0.12 mm of average thickness possessing a \( \text{HV}_{\text{m}-\text{N}0.02} = 476 \text{ HV0.1} \) substrate hardness in the as-nitrided conditions, i.e., containing a “white layer” on the surface. The white layer is a 1-3-µm-thick compound layer forming on the top of the nitrided surface. Subsequently, these specimens were ground and polished before the deposition of...
the coating during which the white layer has partially been removed. The reason for it is that it can be porous, and the adherence of the ceramic coatings to this layer is generally poor.

Thus, the substrate underneath the ceramic coating has a somewhat lower than HV_{S,Nw} hardness, which is an average HV_{S,N} = 390 ± 49 HV0.05 hardness, measured on the cross section of the duplex-coated specimen, in a 0.2-mm-thick zone underneath the ceramic layer. These HV_{S,N} values are reported in Table 1.

The DLC coating is a multilayer system consisting of CrN + WC + a-C:HW + a-C:H layers moving from the direction of the substrate to the top layer. The deposition process was PVD for the underlayers, i.e., for CrN and WC, while it was a PECVD technique in the case of the DLC toplayer, i.e., a-C:H layer. The a-C:HW intermediate layer is developing during the deposition of the a-C:H toplayer. The layer thickness of the coatings was determined by the ball cratering method (Calotest), and the average of the measured values (four tests by sample) is shown in Table 1. Here, it should be noted that the simple and duplex-treated samples were coated in the same batch in the case of both types of coatings; thus, the measured difference in the coating thickness is explained by, on the one hand, the normal scattering of the coating due to technical reasons (thickness is somewhat varying by their location in the coating chamber) and, on the other hand, the scattering of the data originated from the general inaccuracy of the thickness measurement by optical microscopy. The hardness of the coatings was characterized by micro-Vickers indentation test accomplished on the top of the samples using F=0.1 N for the CrN coating and F=0.25 N for the DLC coatings. The hardness was 1372 HV0.01 for the monolayer CrN and 2802 HV0.025 for the multilayer DLC coating based on 10 measurements.

Analyzing the scratch resistance, the composite hardness (H_c) of the coated system must also be taken into consideration, which can be directly correlated with the critical load, since this feature varies with the coating characteristics like coating hardness and thickness (Ref. 37). In Table 1, the composite hardness values determined by 5 N loading force are indicated for the investigated systems.

### 2.2 Instrumented Scratch Test

The progressive loading scratch tests were carried out on a Universal Scratch Tester (UST-2) as shown in Fig. 1. This 3D scratch tester combines the benefit of the next-generation scratch tester’s head and a high-resolution, integrated 3D profilometer, allowing the unique in-line analysis of failures while scratching. During the test, the depth of the indenter, penetrating the specimen, is gradually increased and scratch grooves are forming on the coated surface. A scratch diagram containing the friction coefficient, the normal load, the frictional force, the depth of the instrument, or the acoustic emission signals vs. scratch length is automatically recorded. At the end of the scratching, UST-2 automatically moves the sample under the optical profilometer to create a full 3D panorama picture of the scratch and scratch groove profile with roughness data at a chosen scratch length. The measured data and the 3D images are combined automatically allowing to correlate adhesion with surface roughness and topography, as well as to analyze the morphology of the scratch track showing the locations of characteristic damage and failure points.

Due to the limited visibility of the automatically recorded high information content scratch diagrams, their reprocessed, simplified versions are shown in the current paper. The scratch behavior is characterized, on the one hand, by the friction coefficient and the normal loading force vs. scratch length diagrams and, on the other hand, by the optical microscopic panorama photographs of the scratch grooves showing the characteristic regions of the different damage mechanisms in higher-magnification images. The resistance of the coatings is evaluated based on the critical and subcritical forces which initiate different damage mechanisms of the coated system.

Based on the morphological features of the scratch grooves and the magnitude of the related normal loads, the ductility, the cohesion, and the bonding strength of the coating are analyzed. During predicting the failure mode and damage mechanisms, the guidance of the ASTM C1624 was followed, which clearly states that the adhesive and cohesive failures depend on the coating thickness and relative brittleness or ductility of the coating and the substrate.

The scratch test parameters, applied in the current research, are given in Table 2. The effect of the different loading rates, used for technical reasons, will be taken into account during the evaluation of the test results.

### 3. Results and Evaluation

#### 3.1 Scratch Test on the Simply Coated DLC Test Piece: Sample 1

Figure 2 shows the friction coefficient (μ) and the normal load (L) curves vs. scratch length (l) diagrams. The panorama

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**Table 1** Characteristics of the substrates, the coatings and the substrate + coating composite systems

| Element           | Feature | Sample 1 | Sample 2 | Sample 3 | Sample 3 |
|-------------------|---------|----------|----------|----------|----------|
| Substrate         | Nitriding | No | Yes | No | Yes |
| HV_{S,N} (F=1 N)  | 289 ± 4.9 | 476± 16.7 | 390 ±49 | 390 ±49 |
| HV_{SN}w (F=1 N) | ... | ... | ... | ... |
| HV_{SN} (F=5 N)  | ... | ... | ... | ... |

| Coating Type      | DLC multilayer | CrN monolayer |
|-------------------|----------------|---------------|
| Substrate + coating| Single | duplex | Single | duplex |
| Thickness, μm     | 3.5 ± 0.7 | 3.6 ± 0.8 | 3.8 ± 0.4 | 4.0 ± 0.4 |
| Hardness, HV_{coat} | 2802 ± 368 (F=0.1 N) | 1372 ± 114 (F=0.1 N) | 628± 67 | 1237± 216 |
| Composite hardness, HV_{c} (F=5 N) | 1332± 88 | 2100± 236 |
photograph of the scratch groove taken by optical microscopy and the regions belonging to the subcritical and critical forces—defined from the friction force and morphological analyses—are shown in Fig. 3. At the subcritical force, $L_{C1} = 13.6$ N microcracks are initiated at the two sides of the crack, which propagate as the indenter moves forward. It is shown by the lateral cracks in Fig. 3(a). At $L_{C2} = 19.8$ N, the crack formation and propagation continues and buckling spallation takes place. This is identified by the regions in which detached coating along both sides of the groove appears.
as shown in Fig. 3(b). The reason behind the spallation is the buckling taking place first ahead of the stylus, which is followed by the cohesive cracking in the coating behind the stylus. At the critical force, \( L_{C3} = 40.4 \) N, the coating starts to be delaminated from the substrate. Toward the end of the scratch, ultimately gross spallation takes place which shows sections of detached coating within and extending beyond the groove. This failure mode is characteristic for coatings that have low adhesion strength and possess high compressive residual stresses. The value of the coefficient of friction (\( \mu \)) also shows a sharp increase from 0.12 at \( L_{C1} \) up to 0.33 at \( L_{C3} \). The reason for this is that after the initial cracking, as the indenter proceeds further on, small, detached particles of the DLC coating move along the scratch hampering the movement of the indenter and increasing the friction coefficient.

### 3.2 Scratch Test on the Duplex-Treated DLC Sample: Sample 2

The scratch test diagram obtained for the DLC duplex coating is shown in Fig. 4, while Fig. 5 displays the related panorama image of the scratch groove along with the magnified...
The magnified details of the scratch track reveal the main damage mechanisms being arc tensile cracking at $L_{C1}$ (Fig. 8a) and conformal cracking between $L_{C1}$ and $L_{C2} = 39.7$ N (Fig. 8b), where both damage mechanisms are characteristics of cohesive failure. The irregularly shaped arcs, as shown in Fig. 8(a) and (b), are opening toward and away from the normal load) appears inside the scratch groove, as shown in Fig. 5(a), alluding to better adhesion between the coating and the substrate material.

Here, it should be noted that in the case of Sample 2 the loading rate was 1.7 times higher, compared to that of Sample 1; therefore, the mentioned critical damages appear earlier along the length of the scratch track, which at the same time are caused by higher loads.

The average values of the critical and the subcritical forces, derived from 3 to 3 measurements, for the DLC simply coated and the DLC duplex-treated samples, are shown in Fig. 6. The higher the critical load, the better is the fracture resistance and adhesion of the coating to the substrate.

### 3.3 Scratch Test on the Simply Coated CrN Test Piece: Sample 3

The simply coated monolayer CrN showed higher value of critical loads as compared to the simply coated multilayer DLC coating (Fig. 7), i.e., the initial microcracking occurred at $L_{C1} = 33$ N and the delamination of the coating started at $L_{C3} = 53.9$ N. Since the composite hardness, affected by the entire coating+substrate system, is less than half for this coating of that of the DLC coating, better adhesion can be assumed for the monolayer CrN coating than for the multilayer DLC coating.

The magnified details of the scratch track reveal the main damage mechanisms being arc tensile cracking at $L_{C1}$ (Fig. 8a) and conformal cracking between $L_{C1}$ and $L_{C2} = 39.7$ N (Fig. 8b), where both damage mechanisms are characteristics of cohesive failure. The irregularly shaped arcs, as shown in Fig. 8(a) and (b), are opening toward and away from the

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**Fig. 5** Panorama photograph of the scratch track in the duplex-treated DLC layer revealing the connection between the different critical loads and the related damage mechanisms

**Fig. 6** Comparison of subcritical/critical forces obtained for Sample 1 and Sample 2

Images of the regions representing the characteristic failure modes at the subcritical/critical forces. The damage mechanisms and the way the DLC coating delaminates from the substrate are very similar to those of Sample 1, but the main point of distinction is represented by the significantly higher, namely more than twice, critical loads—$L_{C1} = 25.1$ N, $L_{C2} = 45.18$ N, and $L_{C3} = 92.38$ N—at each characteristic damage mechanism.

Some differences in relation to the mechanism of the first microcracking events appearing at the $L_{C1}$ loads can also be mentioned. While in the case of the simply coated DLC sample angular cracking extending laterally beyond the edges of the scratch can be observed in Fig. 3(a), in the case of the duplex-treated DLC coating the initial cracking (caused by higher $L_{C1}$
direction of scratching, respectively. These occur in brittle coatings on a ductile substrate. The first indicates the initiation of the brittle failure of the coating in the form of a series of nested microcracks, while the second one occurs when the coating attempts to conform to the shape of the scratch groove, as the load increases. This type of damage is followed by mild buckling between \( \text{LC}_2 \) and \( \text{LC}_3 \) (Fig. 8b, right side), and toward the end of the scratch (Fig. 8c) wedging spallation takes place at \( \text{LC}_3 \) and beyond. These latter two damage mechanisms are characteristic of adhesive failure.

Extensive gross spallation was not discovered in the applied loading range, also suggesting that the adhesion between the coating and the substrate is better than in the case of the simply coated DLC layer, where this severe form of failure appeared.

3.4 Scratch Test on the Duplex-Treated CrN Specimen: Sample 4

The critical force resulting in the delamination of the coating of the CrN duplex-treated sample is \( \text{LC}_3 = 82.7 \) N (Fig. 9), which is significantly higher than that of the simply coated CrN layer. This proves better adhesion and higher fracture resistance of the duplex-treated CrN coating, compared to its simply coated version.

The first type of cracking, caused by loading higher than \( \text{LC}_1 \), can be identified as arc tensile cracking, open toward the direction of the scratching, and form behind the indenter that is combined with lateral cracks extending beyond the edge of the crack (Fig. 10a). At loads between \( \text{LC}_2 \) and \( \text{LC}_3 \), a slight indication of buckling spallation can be observed, combined
with chipping starting from the tensile cracks (Fig. 10b). The chipping is different from the adhesive and cohesive failures, as it can be characterized by the rounded region of coating being removed spreading in a lateral direction from the edges of the scratch groove. These damage mechanisms are starting to be more intensive with the increasing loading force, but the measure of this type of damage and the delamination is unambiguously less severe than it was observed in the case of Sample 3, i.e., the simply coated CrN specimen.

As shown in Fig. 11, the effect of the duplex treatment on the scratching behavior of the CrN-coated samples can be evaluated, as follows:

- The nitriding process, increasing the substrate hardness, did not improve the resistance of the coating to the sub-critical damage mechanisms connected to the cohesive failure resistance of the brittle coating material.
- At the same time, the critical force, characterizing the adhesion strength of the coating, at which the spallation, i.e., delamination of the coating is started, has been improved significantly, namely by 53%.
- The duplex treatment is favorable from the point of view of delaying the critical failure, i.e., increasing the reliable operation capability of the coating.
4. Discussion

The effect of the duplex coating technology and the behavior of the studied two coating materials (DLC and CrN) can be more efficiently compared with a purposefully constructed, summarizing illustrations, providing possibility to analyze the effect of the applied surface treatment in a more comprehensive way. In addition, this analysis needs to be supplemented by an assessment of the effect of other factors, too, such as the loading rate, the thickness, the hardness of the coating, or the hardness of the substrate under the coating, which also influence the scratch resistance of the coated material system.

4.1 Comparison of the Adhesion Resistance Based on Scratch Diagrams

Due to the very different scratch resistance of the tested coatings, the maximum normal load during the progressive loading scratch tests was different. Therefore, the usual scratch diagrams, i.e., friction coefficient vs. scratch length curves, illustrated in Fig. 2, 4, 7, and 9 are difficult to be compared directly, while their consolidated diagram (Fig. 12) in the function of the normal load already indicates the beneficial effect of the duplex treatment on the reduction in the friction coefficient and the possible improvement in the adhesion resistance of the coatings.

Nitriding treatment resulted in an increased hardness of the substrate (see HVs value for Sample 2 and Sample 4 in Table 1). For both types of top coatings, i.e., for the CrN and the DLC, the friction coefficient values are significantly reduced in the case of duplex-treated samples. That is, the realization of the contact with a low coefficient of friction provided by the ceramic layers is greatly influenced by the condition and hardness of the substrate under the hard top layer, i.e., its ability to support the coating. The improvement in the adhesion resistance can be characterized by the difference of the $L_{C3}$ forces obtained for the simply coated and duplex-treated samples, that is $\Delta L_{C3} = 28$ N, representing a 53% improvement, in the case of the CrN coating, while it is $\Delta L_{C3} = 54.2$ N, which corresponds to an improvement of 138% in the case of the given DLC coating. From Fig. 12, it can also

![Diagram](image-url)
be established that DLC coating provides lower coefficient of friction having both types of substrates, i.e., that of with or without nitriding.

The observed improvement in the scratch resistance, characterized by the $L_{\text{crit}}$ values, can be explained by the increased $H_c$ composite hardness of the tested coated systems, which has modified this case by the increased substrate hardness due to nitriding, as shown in Fig. 13. It is also seen in this figure that the same increase in the substrate hardness ($\Delta H_S = 101$ HV0.1) caused a higher increase in the composite hardness in the case of the DLC-coated system ($\Delta H_{c,DLC} = 768$ HV0.1) than that of the CrN-coated system ($\Delta H_{c,CrN} = 609$ HV0.1). Thus, the efficiency of the applied surface treatment was greater for this type of coating. Altogether, the better support of the coating provided by the nitrided layer acting as a sub-layer beneath the coating improved the composite hardness, consequently the scratch behavior of the substrate/coating composite system as compared to that of the precipitation-hardened sample.

The composite hardness of a coated system is influenced by the hardness and the thickness of the coating (Ref. 37); therefore, the effect of these factors on the scratching behavior is not discussed separately, since it is considered by the composite hardness.

At the same time, we need to address here the potential effect of the different loading rates on the critical load (Ref. 36). It is known from the literature that the value of the critical load, $L_{\text{crit}}$, is constant if the load gradient $dL/dx$ is constant (Ref. 38, 39) regardless of the absolute value of the load rate and scratching speed. The measure of the possible changes of the critical load, resulting from the different loading rates, is evaluated as a function of this $dL/dx$ characteristic, comparing our current results with those reported in the work (Ref. 39). It is seen from Table 3 that the critical load, obtained from the scratch tests performed on a 3.5-µm-thick TiC coating in similar test circumstances (Ref. 39), increased slightly, namely by 16% when the load gradient increased by 100% in the range of 20-40 N/mm. In our case, where the $dL/dx$ was increased similarly by 100% in the same $dL/dx$ range of 20-40 N/mm, the increase in the critical load measured on the duplex-coated CrN sample was 53%, compared to the simply coated one, which is more than three times higher than that reported in the reference work. Besides, the increase in the $L_{\text{crit}}$ measured on the DLC duplex coatings, was 138%, almost 10 times higher reported in Ref. 39, while the increase in the $dL/dx$ ratio, this case, was only 65% in the range of 20-33 N/mm.

Based on these results, it seems reasonable to conclude that the observed increase in $L_{\text{crit}}$ cannot be attributed exclusively to the change in loading rate, but also to the beneficial effect of the duplex technology on scratch resistance. These findings are supported by the results of our ongoing round robin scratch tests, as well, accomplished on the same coating systems, with a constant ($dL/dx = 10$ N/mm) load gradient in the laboratory of the University of Miskolc. These results will be reported soon to strengthen our conclusions on the better scratch resistance of the duplex-coated samples investigated in the current study.

4.2 Comparison of Damage Mechanisms Based on Subcritical Forces

Based on Fig. 14, summarizing the critical and subcritical forces determined during the scratch test, the following establishments can be made:

- In the case of DLC top coating
  - The duplex treatment effectively (by 2.4 ± 2.8 times) increased both the resistance of the coating to cracking and its adhesion to the substrate;
  - The duplex treatment influences neither the subcritical damage mechanisms—i.e., tensile cracking at LC1 followed by buckling spallation at LC2—nor the main failure mechanism, i.e., delamination and gross spallation at the LC3 critical force.

- In the case of the CrN monolayer
  - The improvement was observed mainly in terms of the coating adhesion, while the magnitude of loading forces causing the subcritical events was basically not changed;
  - Nevertheless, the duplex treatment slightly modified the

### Table 3 Comparison of the load gradient and the critical force values based on the current research and literature data (Ref. 39)

| Test parameter                              | Simple DLC | Duplex DLC | Simple CrN | Duplex CrN | TiC | TiC |
|---------------------------------------------|------------|------------|------------|------------|-----|-----|
| Coating thickness, µm                       | 3.5        | 3.6        | 3.8        | 4.0        | 3.5 | 3.5 |
| Loading range, $L_{\text{min}} - L_{\text{max}}$, N | 1-60       | 1-100      | 1-60       | 1-120      | no data | no data |
| Loading rate, $dL/dt$, N/min                | 120        | 200        | 120        | 240        | 100 | 120 |
| Scratching speed, $dx/dt$, mm/min           | 6          | 6          | 6          | 6          | 5   | 3   |
| Load gradient, $dL/dx$, N/mm                | 20         | 33         | 20         | 40         | 20  | 40  |
| Critical load, $L_{\text{crit}}$, N         | 39         | 93         | 53         | 81         | 25  | 29  |
| Increase in the load gradient               | 65%        | 100%       | 100%       |            |     |     |
| Increase in the critical load               | 138%       | 53%        | 16%        |            |     |     |
| Total scratch length, mm                    | 3          | no data    |            |            |     |     |
| Scratching instrument                       | Standard Rockwell C diamond (tip radius: 0.2 mm) | Standard Rockwell C diamond (tip radius: 0.2 mm) |
| Source of data                              | Current research, Test lab: Rtec Instruments Switzerland | Ref. 39 |

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characteristic damage mechanisms of the coating at the subcritical loadings. At LC1 force, the coating failure started with arc tensile crack formation in both cases, but in the case of the duplex-treated samples this was accompanied by lateral cracking, as well. At LC2 force, mild buckling has started in the simply coated CrN layer, while the damage mechanism was identified as buckling spallation combined with chipping in the duplex-treated coating:

- The main failure mechanism started at LC3 loading was similar, in the case of both types of substrates, i.e., the coating was delaminated by wedging spallation, appearing in a milder form in the case of the duplex-coated CrN system.

5. Summary and Conclusions

The current study presents the experiences of the instrumented scratch tests carried out on two different types of hard ceramic coatings, namely monolayer CrN and multilayer DLC coatings, which were deposited on X42Cr13/W tool steel having the condition of, on the one hand, precipitation-hardened and over-tempered and, on the other hand, identically bulk heat-treated completed with a nitriding operation.

Based on the experimental results derived from the instrumented scratch tests supplemented by optical microscopic analyses of the scratch morphology, and comparative analysis of the differently treated and coated substrate material, the following conclusions can be made.

Duplex treatment resulted in systematically better scratch resistance for both types of investigated coatings, i.e., for both the monolayer CrN and the multilayer DLC coatings. This manifested itself in higher critical and subcritical forces, as well as less damage as compared to those of the simply coated specimens.

The DLC multilayer coating on the nitrided substrate material, i.e., the duplex-treated DLC samples, showed the best scratch resistance with $L_{cr} = 93.4$ N. In other words, the duplex-treated samples showed significantly better adhesion and higher fracture resistance (against cohesive failure), as compared to the simply coated specimens. The improvement in the critical force was 138% for the DLC coating and 53% for the CrN coating which can be attributed predominantly to the duplex treatment besides a slight effect of the applied different loading rates during the scratch testing.

The applied duplex treatment did not influence the characteristic damage mechanisms at the subcritical and critical loadings, in the case of the DLC coating, while it slightly modified the failure modes observed at the certain critical forces, in the case of the CrN-coated material systems.

Altogether, the same surface treatment applied resulted in a higher improvement in the composite hardness for the multilayer DLC coating system, i.e., plasma nitriding was more efficiently used for this type of hard coating.

The improved scratch resistance of the duplex-treated samples can be explained by the beneficial effect of nitriding operation, which is manifested itself in the increased substrate hardness, providing this way stronger support for the hard ceramic coating, and in a higher effective surface hardness of the coatings as a result of the increased composite hardness of the material system.

Based on the executed research work, it can be clearly stated that the scratch resistance of the tested X42Cr13/W tool steel can efficiently be increased by applying the so-called duplex treatment, i.e., nitriding the substrate steel material preceding the coating procedure.

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