Adhesion strength of Ti$_{1-x}$C$_x$ – DLC multilayer nanocomposite thin films coated by ion-plasma deposition on martensitic stainless steel produced by selective laser melting followed by plasma-nitriding and burnishing

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Abstract. [Ti$_{0.2}$C$_{0.8}$/a-C]$_{40}$ multilayer thin films composed of forty pairs of TiC and pure carbon layers were formed on a selective laser melted (SLM) martensitic stainless steel by means of ion-plasma deposition process. SLM steel was pre-treated by one of the two following schemes: (1) oil quenching from 1040°C followed by heating to 480°C for 4 hours and air cooling (HT), finish milling (FM); (2) HT, FM, ion-plasma nitriding followed by burnishing. Mechanical failure mode and critical load $L_C$ for damaging the coatings were determined using linear scratch tests performed at linearly-increased normal force. Indentation by conical diamond tip were carried out in order to assess an elastic recovery and energy dissipation coefficient defined as the ratio of plastic to total deformation energy. The scratch test results showed that the post-processing of the substrate strongly influenced the failure mode of the coating and increased the critical load from 320 mN to 920 mN. Indentation revealed that nitriding and burnishing before coating deposition increase the elastic recovery of the [Ti$_{0.2}$C$_{0.8}$/a-C]$_{40}$ coating-substrate system from 24% to 68%. The energy dissipation coefficient drops from 79% to 45%.

1. Introduction
Additive manufacturing (AM) is the most modern and rapidly developing technology to produce complex parts in medicine, aerospace, automotive, and other industries. A number of AM technologies are widely used, for example, direct laser sintering (DMLS) [1] and selective laser fusion/melting (SLM) consisting in a layer-by-layer formation of a product by laser beam scanning of a powder layer deposited on a substrate [2]. The common problems of such technologies are a high-temperature gradient between layers [3] and rapid cooling leading to cracking and delamination of parts due to significant residual stresses. In this regard, heat treatment is the conventional post-processing technology, which reduces the level of residual stresses and the porosity of products synthesized by the AM methods [4].
A high-quality product with minimum defects is a difficult task due to the combination of many technological parameters. Powder size distribution and laser scanning speed strongly affect the most important parameters of the product, such as porosity and surface roughness. Thus, low scanning speed provides lower porosity, but increases the synthesis time [5]. Another source of defects during the SLM process is the retention of non-melted areas of the powder. [6]. Nevertheless, in [7] it is noted that the SLM parts demonstrate mechanical and operational properties comparable to prototypes after conventional machining.

Mechanical performance of a structural steel could be improved by deposition of diamond-like carbon films (DLC) or DLC-based multilayer thin-film coatings [8], which increase wear resistance and reduce the friction coefficient of machine parts and mechanisms. The nanocomposite coating also provides an increase in the corrosion resistance of the steel base [9]. However, very high hardness and large internal compressive stresses limit DLC application due to poor film adhesion to the substrate material [10]. High hardness difference between DLC multilayer wear-resistant thin-film coatings and relatively low-strength structural steels substrate lead to destruction of the "base-to-coating" bonding under external loading. The poor resistance of thin high-strength coatings to lateral bending leads to mechanical failure and fatigue wear. In this regard, surface hardening of a base before applying the coating is advisable to preserve the "base-coating" bonding during operation.

Along with other surface techniques, plasma nitriding produces a surface layer with a hardness of up to 1600HV and tens of microns thick. However, the saturation of steel with nitrogen increases surface roughness [11], which negatively affects the adhesion of the applied thin coatings and the product performance.

It is possible to improve the roughness and achieve additional hardening of the surface using modern technologies of surface plastic deformation. Such technologies include surface mechanical attrition treatment (SMAT) [12], shot peening [13], ultrasonic impact treatment [14] and ultrasonic impact-frictional treatment [15], frictional treatment by sliding indenter [16], industrial technology of nanostructuring burnishing [17, 18], etc. Among the mentioned techniques, frictional treatment with a sliding indenter provides high-quality surface of high-chromium stainless steel with a roughness parameter Ra around 100 nm [19] as well as additional surface hardening and favorable compressive stresses [20] improving the adhesion of thin coatings.

The work aims to assess the effect of post-processed (plasma nitriding followed by sliding indenter burnishing) substrate of SLM martensitic stainless steel on the resistance of TiC-DLC multilayer thin films to contact loads.

2. Materials and methods

2.1. Materials and treatments

Specimens of martensitic stainless steel were manufactured using selective laser melting in an EOSINT M280 unit and consist of horizontal layers 30 μm thick. The EOS PH1 powder with particles size ranged from 10 to 50 μm and the 48% fraction of 30-40 μm. The chemical composition of EOS PH1 steel is given in table 1.

| Chemical element | C  | Cr  | Ni  | Cu  | Mn  | Si  | Mo  | Nb  | Fe  |
|------------------|----|-----|-----|-----|-----|-----|-----|-----|-----|
| Content (wt.%)   | 0.05 | 14.72 | 4.69 | 4.08 | 0.83 | 0.41 | 0.13 | 0.22 | bal. |

Before TiC-DLC composite thin-film deposition, selective laser melted specimens were treated by one of the post-processing schemes below:

- oil quenching from 1040°C followed by heating to 480°C for 4 hours and air cooling (HT), finish milling in CNC machining center MIKRON VCE600 by face mill (FM);
- HT, FM, ion-plasma nitriding at a temperature of 500-540°C, burnishing.
Ion-plasma nitriding was carried out in a shaft vacuum furnace HSV-9.18/6-V2 and included preliminary cleaning for 30 minutes at a temperature of 430...450°C, followed by saturation of the surface with nitrogen in a vacuum chamber at a pressure of ~ 10⁻⁰⁷ Pa, current ~ 60 A, voltage 60 V and a bias voltage of the sample ~ 300 V. During ion-plasma nitriding, a constant temperature in the range from 500 to 540°C was maintained.

Burnishing of the specimen's surface was carried out in OKUMAMA-600HII machining center by a spherical indenter made of a natural diamond with a radius of 2 mm using a liquid lubricant-coant fluid. Burnishing technological mode was as follows: burnishing speed \( v_b = 15 \text{ m/min} \), feed \( f_b = 0.025 \text{ mm/pass} \), normal load (burnishing force) \( F_b = 250 \text{ N} \), number of working scanning passes of the indenter \( n = 3 \).

2.2. Thin films deposition

Nanocomposite films were obtained by co-deposition of arc sputtered titanium and carbon cathodes [8]. Multilayer coatings consisted of forty pairs of TiC and pure carbon layers of 20-25 nm individual thick and a total thickness of about 2 μm. Titanium cathode was sputtered at an arc source constant current, and a graphite cathode was sputtered at a pulse transmission frequency (\( f = 10 \) Hz). Sputtering of carbon at such a pulse frequency made it possible to obtain TiC layers with titanium and carbon content of about 20 and 80 at.%, respectively ([Ti0.2C0.8/a-C]40).

2.3. Thin films characterisation

Both indentation and scratch tests were conducted using a conical indenter with a diamond tip radius of 25 μm in a NanoTest600 system. The scratch tests were performed at a constant traveling speed of 1 μm/s and a linearly-increased normal load up to 1000 mN. Critical load \( (L_c) \) was determined as the normal load corresponding to the scratch distance at which the first coating failure appeared. The failure identification and distance measurements were carried out using scanning electron microscopy. The mechanical failure modes were identified according to the ASTM C1624 standard [21]. Indentation tests were carried out at a loading/unloading rate was of 25 mN/s and a maximal load of 2500 mN. Maximum indentation depth \( (h_{\text{max}}) \) and residual depth \( (h_p) \) after unloading were determined to calculate the elastic recovery \( (R_e) \) according to equation (1) [22, 23]:

\[
R_e (\%) = \left(1 - \frac{h_p}{h_{\text{max}}} \right) \times 100, \tag{1}
\]

An energy dissipation coefficient \( (K_d) \) defined as the ratio of the plastic deformation energy to the total deformation energy was calculated as suggested by Recco et al. [24]. The plastic deformation energy \( (W_p) \) can be obtained by the difference between total deformation energy \( (W_t) \) and elastic deformation energy \( (W_e) \). \( W_t \) and \( W_e \) correspond to the areas under the loading and unloading curves, respectively.

3. Result and discussion

Scratch tests of the coating applied to the heat-treated substrate (non-hardened) showed that the first signs of failure were observed at the load 320 mN (figure 1 (a) and figure 2, curve 1). When the scratch depth reached 400-500 nm, typical for a hard coating on a ductile substrate, conformal cracking occurred as the coating was bent into the scratch track (figure 1 (a)).

Further load increasing led to a layer-by-layer detachment of the coating until total spallation at the normal force 440 mN and the scratch depth 1300 nm. (figure 1 (a) and figure 2, curve 1). Typical for ductile material, pile-ups formed on both sides and at the end of the track. Nevertheless, no large area interfacial spallation occurred even at the maximal scratch depth of about 2500 nm (figure 1 (a)).

Scratch tests of the coating applied to a hardened (nitriding + burnishing) steel substrate indicated significant changes in the deformation and fracture mechanism (figure 1 (b) and figure 2, curve 2). The maximal scratch depth decreased to 1100 nm (figure 2, curve 2), no pile-ups and conformal cracking were observed (figure 1 (b)). The film failure began in a buckling spallation mode. Though
this mode corresponds to interfacial failure, a critical load $L_C$ was 3 times higher comparing the coating on a heat-treated substrate, reaching about 920 mN.

Indentation curves of coating specimens are presented in figure 3. One can see in figure 3 curve 1, that the coating on a soft substrate exhibited greater deformation during indentation achieving a maximal depth of 4120 nm while the residual depth was 3100 nm, which significantly exceeds the thickness of the deposited coating. The initial section of the loading curve (marked by arrows in figure 3) contains a sequence of small plateaus, indicating the coating cracks [8] in the load and indentation depth range up to 750 mN and 1.2 µm, respectively.

![Figure 1](image1.png)

**Figure 1.** Scratch tracks of the [Ti$_{0.8}$C$_{0.2}$/a-C]$_{40}$ coatings deposited on SLM steel after heat treatment (a) and after plasma nitriding followed by burnishing (b).

![Figure 2](image2.png)

**Figure 2.** Normal force and scratch depth during the test of [Ti$_{0.8}$C$_{0.2}$/a-C]$_{40}$ coatings deposited on SLM steel after heat treatment (curve 1) and after plasma nitriding followed by burnishing (curve 2).

The coating deposited on hardened (nitriding + burnishing) substrate showed a maximal indentation depth of 1880 nm, and the residual depth of 600 nm, which is 3 times less than the coating thickness. Up to the indentation load of 2500 mN, there were no signs of failure on the indentation curves, indicating significant resistance to contact loads of the coating-substrate system.
The calculated elastic recovery of the specimens was 68% and 24% for the coatings on hardened (nitriding + burnishing) and soft (after heat treatment) substrates, respectively. It also can be seen that the area between the loading and unloading curves is greater for the case of the heat-treated substrate. The energy dissipation coefficient $K_d$ of the coating deposited on the hardened substrate was 45% and 79% for the coating on the heat-treated steel, evidencing that the post-processed specimen dissipates less plastic deformation energy. From the results, it can be concluded that nitriding followed by burning post-processing increased the elastic response of the coating-hardened substrate system as plastic deformation predominates during indentation of the coating applied to the soft heat-treated specimen.

![Load vs depth indentation curves of [Ti$_{0.2}$C$_{0.8}$/a-C]$_{40}$ coatings deposited on SLM steel after heat treatment (curve 1) and after plasma nitriding followed by burnishing (curve 2).](image)

4. Conclusions
Scratch tests showed that comparing the conventional heat-treatment (quenching + heating to 480°C) of SLM steel, additional post-processing by plasma-nitriding and burning improves the resistance of ion-plasma deposited [Ti$_{0.2}$C$_{0.8}$/a-C]$_{40}$ multilayer composite thin-films to contact loads. The critical load $L_C$ during linear scratch tests increases from 320 mN to 920 mN, and the coating failure mechanism changes from conformal cracking to buckling spallation.

Indentation using the conical indenter with the diamond tip radius of 25 μm showed that supplementary nitriding followed by burnishing of the SLM steel substrate before deposition of [Ti$_{0.2}$C$_{0.8}$/a-C]$_{40}$ coating increase the elastic recovery of the coating-substrate system up to 68% from 24% after conventional heat-treatment. The energy dissipation coefficient $K_d$ drops from 79% to 45%, indicating the coating on hardened (nitriding + burnishing) SLM steel experiences much lower plastic deformation than the coating on heat-treated one.

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