Plasma nitriding in complex post-processing of stainless steel parts obtained by additive laser technology

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Abstract. Considered are the prospects of applying complex post-processing for an additive manufactured product with the deposition of a multilayer composite coating [Ti0.2C0.8/a-C40] at the final stage. It is shown that heat treatment, finish milling, ion-plasma nitriding and burnishing with a sliding diamond indenter of a PH1 steel part obtained by selective laser melting (SLM) before deposition of a thin-film coating provides the coating with a minimum surface roughness $R_a = 82-86$ nm and a maximum hardness of $25.2 \pm 1.4$ GPa with an increase in the microhardness of the entire “coating-substrate” system.

1. Introduction

Additive manufacturing (AM) is one of the most advanced and promising technologies, since a complex part is formed by direct growing, rather than subtracting material from the workpiece as in traditional production. One of the most common types of AM is selective laser melting (SLM). Like any new technology, it is not free from shortcomings, among which the most serious are considered: non-melting of the powder [1] and the presence of residual stresses [2] arising due to uneven thermal effect during part growing. The simultaneous development of these disadvantages leads to high porosity inside the product [3] and high values of roughness on its surface.

One of the common materials used to make SLM parts is PH1 high chromium stainless steel powder. The steel obtained by this method is chemically similar to steels 15-5 PH, DIN 1.4540 and UNS S15500. These steels are often used in the medical, aerospace, and mechanical engineering industries. Recently, more and more studies are found dedicated to microstructures and magnetic properties [4], fatigue life [5] mechanical and corrosion properties [6] of these steels obtained by the SLM method. The use of a post-processing complex can improve the performance of a product made of such steels. Effects of machining, electro-polishing and laser surface re-melting improve fatigue life [7]. Good prospects for the use of the SLM technology have been demonstrated to obtain the part of shut-off valves, wedge of the high pressure wedge gate valves from the PH1 steel powder [8].

A promising method of post-processing is the deposition of diamond-like carbon films [9] and nanocomposite multilayer coatings [10] with high hardness. Multilayer coatings are more resistant to
erosion wear than single-layer ones; in particular, there is an increased erosion resistance of the [Ti<sub>3</sub>C<sub>0.8</sub>/a-C]<sub>40</sub> coating, which consists of 40 pairs of alternating layers of titanium carbide and amorphous diamond-like carbon [10]. However, such coatings have high internal compressive stresses, which leads to poor adhesion of the films to the substrate material [9]. The soft surface of the steel substrate to be coated is one of the main causes of cracking and sometimes complete destruction of such a coating. Therefore, the search for ways to maximize the hardening of the steel substrate surface is extremely important, especially for products obtained by additive laser technology.

Treatments with sliding indenter, specifically frictional treatment [11, 12] and industrial technology of nanostructuring burnishing [13, 14] can become promising technologies for strain hardening of the surface of parts obtained by the SLM method.

Plasma nitriding in combination with deformation treatment with a sliding indenter is an effective method for hardening surface modification of stainless steels [12, 15].

The aim of this work is to study the possibility and efficiency of using ion-plasma nitriding and burnishing with a sliding diamond indenter in the integrated technology of post-processing of a product formed by the SLM method from PH1 stainless steel powder, with deposition of a multilayer composite coating [Ti<sub>3</sub>C<sub>0.8</sub>/a-C] of ~2 microns thick on the modified surface.

2. Materials and methods

The part of shut-off valves, wedge of the high pressure wedge gate valves [8], was made of EOS PH1 martensitic stainless steel powder containing C 0.05%, Cr 14.72%, Ni 4.69%, Cu 4.08%, Mn 0.83%, Si 0.41%, Mo 0.13%, Nb 0.22%, Fe rest. by SLM method. SLM was done on an EOSINT M280 unit, the parts were made by layer-by-layer horizontal adding, the thickness of the layer being 30 μm.

After SLM, the part was subjected to various post-processing, including various combinations of the following procedures: heat treatment, finish milling, ion-plasma nitriding, burnishing and thin film deposition.

Heat treatment (HT): quenching from 1040°C (tempering for 30 min) with cooling in oil and further heating up to 480°C for 4 hours with air cooling. Heat treatment was followed by surface finish milling (FM) involving a MIKRON VCE600 unit by face mill.

Ion-plasma nitriding (IPN) was carried out in a shaft vacuum furnace and included preliminary cleaning for 30 minutes at a temperature of 430...450°C, with further saturation of the surface with nitrogen in a vacuum chamber at pressure of ~10<sup>-1</sup> Pa, current of ~60 A, voltage of 60 V and bias voltage of 300 V. During the ion-plasma nitriding, a constant temperature was maintained in the range from 500 to 540°C.

Burnishing of nitrided surfaces with a sliding spherical indenter made of a natural diamond with a radius of 2 mm was carried out on an OKUMA MA-600HII machining center at a burnishing speed \( v_b = 15 \text{ m/min} \) and 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 \( n = 3 \).

Nanocomposite thin films were obtained by co-deposition of arc sputtered titanium and carbon cathodes [10]. Multilayer coatings consisted of forty pairs of TiC and pure carbon layers of 20-25 nm individual thick and had a total thickness of about 2 μm. The coating was deposited by arc sputtered cathodes: Ti (constant current) and graphite C (current pulse frequency 10 Hz).

The studies were conducted on two series of samples, cut by the electric spark method from SLM-part (wedge), subjected to two post-processing combinations:

1) heat treatment (HT) + finish milling (FM) + coating deposition;
2) HT + FM + IPN + burnishing + coating deposition.

The surface roughness was studied using a Wyko NT-1100 optical profilometer. Sample surface was studied with a Tescan VEGA II XMU scanning electron microscope (SEM). Shimadzu XRD-7000 X-ray diffractometer with CrKα radiation was utilized for X-ray diffraction phase analysis. A Shimadzu HMV-G21DT unit together with the reconstructed imprint method, featuring the load on the Vickers indenter of 0.098 N, 0.25 N, 0.49 N, 0.98 N, 1.96 N, was used for determining the microhardness of the “coating-substrate” system. The nanomechanical characteristics of thin-film
coatings were determined by the instrumental indentation method using a NanoTest600 mechanical testing system. The indentation hardness was determined on the loading/unloading curve at a given maximum indentation depth of the Berkovich indenter of 200 nm, which is nearly 10 times less than the coatings thickness. This made it possible to determine the hardness of the coatings without a noticeable effect of the strength of the metal substrate.

3. Experimental results and discussion
Surface of an SLM-part subjected to the considered combined post-processing with a thin-film [Ti$_{0.2}$C$_{0.8}$/a-C]$_{40}$ coating deposition as a finishing method (figure 1) was studied by scanning electron microscopy and optical profilometry.

![Figure 1. SEM images (a), (c) and 3-d profilometry (b), (d) of surface [Ti$_{0.2}$C$_{0.8}$/a-C]$_{40}$ coating deposited on substrate, formed by SLM method and subjected to heat-treatment followed by finish milling (a), (b), and additional nitriding and subsequent burnishing (c), (d).](image)

The SEM image and 3-d profilometry shown in figure 1 (a) and (b), indicate that the multilayer coating deposited on the part after heat treatment and finish milling is characterized by significant unevenness and heterogeneity. The average parameters of the surface roughness $R_a$ of the specified coating are 310 and 180 nm when measured, respectively, on surface areas with dimensions of
211.2×277.5 μm and 42.5×55.8 μm (table 1). A thin-film coating deposited on a part subjected to additional post-processing of ion-plasma nitriding and burnishing is marked by significantly higher uniformity and homogeneity (figure 1 (c) and (d)) and significantly lower average values of the roughness parameter $Ra = 82-86$ nm (table 1).

Table 1. The PH1 SLM part post-processing effect on the average overall surface roughness $Ra$ of [Ti$_{0.2}$C$_{0.8}$/a-C]$_{40}$ coating.

| Post-processing                               | $Ra$ (nm) (area size 211.2×277.5 (μm)) | $Ra$ (nm) (area size 42.5×55.8 (μm)) |
|----------------------------------------------|--------------------------------------|--------------------------------------|
| HT + FM + coating deposition                 | 312                                  | 182                                  |
| HT + FM + IPN + burnishing + coating deposition | 86                                   | 82                                   |

According to X-ray diffraction analysis data, the steel synthesized from PH1 powder by the SLM method after heat treatment contains α-martensite in the structure [6] and a small amount of carbides.

X-ray diffraction pattern, presented in figure 2, shows that the surface layer of a part with a multilayer coating [Ti$_{0.2}$C$_{0.8}$/a-C]$_{40}$ deposited on a nitrided and subsequently burnished surface has the following phase composition: α-phase, γ'-phase (Fe$_4$N iron nitride), CrN nitride chromium and TiC titanium carbide. During an X-ray study with CrKα radiation, a layer 5-7 µm thick is analyzed. The thickness of the multilayer coating is about 2 μm. Therefore, along with the α, γ' phases and CrN belonging to the nitrided layer, the X-ray method also detects the TiC carbide in the surface layer, which is a part of the multilayer coating along with amorphous diamond-like carbon (a-C) [10].

![Figure 2](image_url)  
**Figure 2.** X-ray diffraction pattern of part surface produced by SLM using PH1 stainless steel powder after deposition of multilayer coating [Ti$_{0.2}$C$_{0.8}$/a-C]$_{40}$ on surface after heat treatment, finish milling, ion-plasma nitriding and burning.

The availability of iron and chromium nitrides of the revealed compositions (γ'-Fe$_4$N and CrN) in the high-chromium steel surface layer after ion-plasma nitriding at temperatures of 500-540°C is typical for nitriding at temperatures of 500°C [15-18]. Until recently, it was believed that the lower temperature threshold for the nitride phases detection is 425°C [19]. However, in [20], using X-ray
photoelectron spectroscopy, the formation of Cr-N and Fe-N bond formation was detected even at a nitriding temperature of 350°C.

Figure 3 shows the dependences between the ‘coating-substrate’ system microhardness for a part grown by the SLM method from PH1 steel powder and the penetration depth of the Vickers indenter. The microhardness of the surface layer with a multilayer coating applied to a heat-treated and milled substrate reaches 1200 HV at the penetration depth of the Vickers indenter $h = 0.55 \ \mu m$ (figure 3, point 1 on the solid line, the load on the indenter is $P = 0.098 \ \text{N}$). As the load on the indenter increases, the microhardness of the coated surface layer decreases. Thus, with an increase in the penetration depth of the indenter to $h = 1.60 \ \mu m$, the microhardness decreases to 725 HV (point 3, $P = 0.49 \ \text{N}$). With a further increase in the load on the indenter to 0.98 and 1.96 N, the penetration depth of the indenter increases to $h = 2.48$ and $3.51 \ \mu m$, and the microhardness decreases to 620 and 610 HV, respectively.

The microhardness of the surface with a coating applied to a part that was subjected to heat treatment, milling, nitriding, and subsequent burnishing reaches 2500 HV at an indenter penetration depth $h = 0.37 \ \mu m$ (figure 3, point 1 on the dashed line, $P = 0.098 \ \text{N}$). With an increase in the load on the indenter to 0.25 N and the penetration depth of the indenter to $h = 0.72 \ \mu m$ (point 2), there is a sharp decrease in the microhardness of the part surface with a multilayer coating to 1820 HV. The subsequent increase in the load on the indenter leads to a further decrease in the microhardness of the coated surface layer up to 1390 HV at $h = 2.33 \ \mu m$ and $P = 1.96 \ \text{N}$ (figure 3, point 5 on the dashed line).

Using instrumental indentation at a given maximum penetration depth of the Berkovich indenter 200 nm, it was found that the nanoindentation hardness is $12.2 \pm 0.8 \ \text{GPa}$ for a thin-film coating deposited on the surface of an SLM part after heat treatment and finish milling, and $25.2 \pm 1.4 \ \text{GPa}$ for a multilayer coating applied on the part surface, additionally subjected to ion-plasma nitriding and burnishing. These strength characteristics of the coatings closely correspond to the microhardness values at points 1 in figure 3 for relevant coatings and substrates.
Thus, when measuring the microhardness of the “coating-substrate” system using the reconstructed imprint method with a load on the Vickers indenter of 0.098 N and an indenter penetration depth of 0.37-0.55 μm (points 1 in curves in figure 3), the role of substrate hardness is insignificant. With a further increase in the penetration depth of the indenter, as the loads increase, the strength of the metal base of the part has an increasing effect. This is mainly due to observed in figure 3 reduction of the “coating-substrate” system microhardness. The surface of an SLM part after heat treatment and milling has a microhardness of 500 HV when measured with a load on the indenter \( P = 0.098 \) N. With an increase in the load on the indenter to \( P = 1.96 \) N, a decrease in the surface microhardness to 420 HV is observed due to a decrease in the depth of the surface layer of steel in the amount of strain hardening from finish milling. The microhardness of the surface after plasma nitriding and burnishing is 1570 HV when measured with a load of \( P = 0.098 \) N (~3 times higher than the microhardness of a heat-treated and milled part) and decreases to 1290 HV at \( P = 1.96 \) N.

Consequently, carrying out the post-processing of a part grown by the SLM method according to the two considered schemes, before the [Ti0.2C0.8]/a-C coating deposition to the part, not only forms various metal substrates, the level of hardness of which differs by a factor of 3. Multilayer coatings obtained on different substrates in one technological cycle of application differ in the degree of uniformity and homogeneity, surface roughness and hardness. Comparative analysis of the results of SEM, profilometry, nanoindentation, and microhardness measurements (figure 3) shows that on the surface of the part after a full complex of post-treatments, including nitriding and burnishing, a higher-quality homogeneous coating with a lower surface roughness is formed (figure 1 (c) and (d), table 1), which is twice as hard as the coating on steel after its heat treatment and surface milling, and also provides a 2.1-2.3 times increase in the microhardness of the entire “coating-substrate” system when measured with loads on the Vickers indenter in the range of 0.25-1.96 N.

The multilayer coating [Ti0.2C0.8]/a-C formed on a hard (1570 HV) nitrided and burnished surface is inferior in hardness (25.2 ± 1.4 GPa) to a single-layer diamond-like coating (33.4 ± 4.4 GPa) [10]. This may be due to the fact that the Ti0.2C0.8 titanium carbide interlayers have a lower hardness than the a-C interlayers (for example, the hardness of TiC in a composite laser coating is 2500-2900 HV [21]), as well as partial graphitization of a-C layers when bombarded with Ti’ ions during the deposition of titanium-containing layers [10].

4. Conclusion

The complex application of post-treatments (heat treatment, finish milling, nitriding, burnishing and thin-film coating) for a part formed by the SLM method from PH1 high-chromium stainless steel powder contributes to the effective formation of high-strength multilayer titanium carbide-diamond-like carbon coatings on surface-hardened steel as on a “solid basis”. Carrying out only heat treatment and finish milling of the part before [Ti0.2C0.8]/a-C coating deposition provides the nanoindentation hardness of the coating of 12.2 ± 0.8 GPa and its surface roughness \( Ra = 180-312 \) nm. Coating the steel surface, which was additionally subjected to ion-plasma nitriding and burnishing with a sliding diamond indenter, provides a more uniform and homogeneous [Ti0.2C0.8]/a-C coating with a surface roughness \( Ra = 82-86 \) nm and a nanoindentation hardness of 25.2 ± 1.4 GPa, as well as a 2.1-2.3-fold increase in the microhardness of the entire “coating-substrate” system when measured with loads up to 1.96 N.

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