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Article

Application of the Hollow Cathode Spaces (HCS) Surface Cleaning and Thermal Activation Method in the Deposition of Wear-Resistant Nitride Coatings on a Stainless Steel Substrate

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Abstract

The article compares the properties of coatings deposited on a stainless steel substrate with surface preparation using the Hollow Cathode Spaces (HCS) and Ion Bombardment (IB) methods. After coating deposition, the wear resistance of the samples increases by 40–50% compared to uncoated samples, while the use of the HCS method ensures wear resistance that is 15% higher than the IB method. Samples with coatings deposited using the HCS and IB methods demonstrate very similar friction coefficient values, with an insignificant (10%) decrease in this indicator for the HCS samples. The best wear resistance is observed for the HCS sample, the surface of which was prepared at a bias voltage of –1200 V. This bias voltage value ensures the best parameters for the coated sample compared to samples whose surface preparation was carried out at a higher (–1500 V) or lower (–900 V) bias voltage. A substrate bias voltage of –1200 V provides not only improved wear resistance in the pin-on-disc test but also improved resistance to damage in the scratch test. Analysis of the interface between the coating and the stainless steel substrate revealed that the HCS method produces a transition layer 15–25 nm thick. This transition layer includes zirconium, nickel, and iron, with a small amount of chromium. The IB method also produces a similar transition layer in the interface area, but with a thicker thickness of 100–150 nm.

Keywords: hollow cathode spaces; ion bombardment; stainless steel; wear; friction; pin-on-disc test

1. Introduction

AISI 321 stainless steel is widely used in many industries [1–4]. Products made from this steel can withstand high temperatures for long periods without losing their properties. These properties are due to the alloy's 0.5% titanium content. This composition results in a strong, hermetic weld that is resistant to corrosion.

Among the advantages of this steel are [1,5,6]:

- high corrosion resistance, due in part to the presence of chromium;
- high heat and thermal shock resistance, allowing it to be used at temperatures up to +600 °C. At this temperature, the steel's structure remains unchanged for a considerable period;
- good weldability, ensured by its low carbon content;
- good ductility, which improves the machinability of products made from this steel.

In addition, this steel is classified as hygienic and is widely used in the food and medical industries. Although AISI 321 steel has a number of useful properties and is widely used in various industries, increasingly stringent requirements for modern materials necessitate the search for ways to further improve its performance. In particular, increased wear resistance of AISI 321 steel products is required. To further enhance the wear resistance of AISI 321 steel products, special modifying coatings of various compositions and deposition methods are effectively used [1,6–10]. Coatings deposited on an AISI 321 steel substrate using Physical Vapor Deposition (PVD) have demonstrated high effectiveness in terms of corrosion resistance and wear resistance [9,10].

The performance of coatings in general, and PVD coatings in particular, is associated not only with their mechanical and chemical properties, but to a significant extent with the strength of adhesion between the coating and the substrate. In turn, adhesion is ensured by effective preparation of the substrate surface – cleaning from microcontamination and thermal activation [11–18]. Cleaning and heating (thermal activation) of the substrate surface can be accomplished using infrared heating or laser beam exposure [12,14,19–22]. These methods have certain advantages, but require additional equipment and complicate the technological process. Preliminary treatment of the substrate surface with an accelerated ion stream is used in most cases due to its relative simplicity and the use of equipment already available in the vacuum plasma unit [13,14,16,18,22–28]. This method is implemented by bombarding the substrate surface with ions (metals, gases, or a mixture of these [28,29]), whereby the energy of the accelerated ions is transferred to the substrate atoms, producing a dual effect. On the one hand, weakly bound atoms (primarily contaminants) are knocked out from the substrate surface (cleaning), and on the other hand, the surface layers of the substrate are heated (thermal activation) [11,30–32]. At high energy, the impacting ions can be embedded in the outer layers of the substrate, making it possible, for example, to achieve surface nitriding or implant atoms of the sputtered metal into the substrate [20,32–35]. Another effect of ion bombardment can be a decrease in the roughness of the substrate surface and a reduction in its defects [15,19–21]. The ion bombardment process is influenced by a number of factors, including the ion energy and ion flux density (depending on the substrate bias voltage, cathode arc current, substrate and cathode materials, and working gas composition), the angle of ion incidence relative to the substrate surface (depending on the substrate and tooling geometry, substrate movement kinetics, and its surface microgeometry), and treatment duration [20,31,36–40]. Substrate bias voltage is one of the key process control parameters and typically ranges from 200 to 1500 V [32,41]. Despite its relative simplicity and high efficiency, the ion bombardment method also has some significant disadvantages. These include uneven distribution of ion current density across the plasma flow cross-section, which results in uneven heating of the workpieces [15,39,42]. The power of the ion flux also determines the possibility of re-deposition of contaminants (including the material of the equipment and chamber walls) onto the substrate [43–46]. Furthermore, this method requires a fairly long period of operation of the cathode systems, which is associated with high energy consumption.

Another method for efficient substrate surface preparation is ion cleaning in a self-sustaining stationary glow discharge plasma [11,13,27,43–45]. This method is based on the acceleration of gas plasma ions onto the substrate surface, with the substrate itself acting as the glow discharge cathode or as an additional negative electrode relative to the plasma. This treatment allows for efficient cleaning and thermal activation of the substrate surface, ensuring good coating adhesion [47–50]. At the same time, irregular distribution of the electric field strength over the surface of the substrate being treated can lead to uneven heating [51,52]. This problem is solved using various glow discharge schemes, among which the use of a “hollow” cathode is very effective. This implies the presence of a closed or quasi-closed equipotential cavity in such a cathode, within which the discharge is localized

due to the fact that the emitted electrons oscillate, repeatedly reflecting from its walls. During the process of such oscillation, a significant increase in the degree of gas ionization and the density of the glow discharge plasma occurs [53].

In this study, we used a method for heating and cleaning the surface of workpieces using a glow discharge, using Hollow Cathode Spaces (HCS) [54]. The hollow cathode effect was achieved through the specific arrangement of the workpieces, which are positioned in a vacuum chamber on a rotary table. Their surfaces form a partially enclosed internal region—the quasi-cavity of the hollow cathode.

To eliminate the influence of additional factors on the results of the study, a coating of a simple two-component composition (ZrN) was deposited.

2. Materials and Methods

The studied coatings were deposited on a VIT-2 PVD system (IDTI RAS – MSUT «STANKIN», Moscow, Russia) [55–60]. A distinctive feature of this system is the use of filtered cathodic vacuum arc deposition (FCVAD) systems [61,62], which ensure efficient separation of the microdroplet phase in combination with a Controlled Accelerated Arc (CAA-PVD) system [29,63–65], which ensures high energy efficiency.

A planetary rotation fixture is located within the vacuum chamber, comprising 12 racks (rods) with sample mounting devices. A negative voltage ranging from 0 to -1500 V is applied to the fixture, with a permissible current of 30 A. The vacuum chamber walls serve as the anode. A Zr cathode (99.8%) was used.

The gas (nitrogen) pressure ranged from 130 to 1300 Pa, and the sample surface temperature was monitored using an Ircon Modline Plus Infrared Thermometer (Fluke Process Instruments, Everett, WA, USA) and remained in the range of 500–600 °C.

Two alternative processes for surface preparation of products before coating deposition were compared: Hollow Cathode Spaces (HCS) and Ion Bombardment (IB).

Hollow cathode spaces (HCS) Cleaning and heating are performed in a glow discharge plasma at a pressure of 5.0 Pa. Parts in a vacuum chamber form hollow cathode spaces. Argon (Ar) uses as the working gas. Initially, for the HCS cleaning and heating processes, a minimum voltage is applied to the turntable, at which the glow discharge begins (approximately -100 V). As the microarcs disappear, the voltage increases until the sample temperature reaches 650 °C. Ion cleaning and heating occur by bombarding the surface (glow discharge cathode) with positively charged gas ions accelerated in the cathode layer of the discharge. A detailed description of the processes of cleaning and thermal activation of the surface using the HCS method is contained in [54].

Ion bombardment (IB) Arc evaporators are switched on to generate metal plasma, and the arc-burning current on all evaporators is 90 A. The pressure in the working chamber is not higher than 0.005 Pa. A negative voltage of -100 V from a high-voltage power source is applied to the rotary table with the parts fixed on it. As the heating proceeds and the probability of microarcs decreases, the voltage gradually increases until the surface temperature of the parts reaches 650 °C.

The structure of the deposited coatings included a thin adhesion layer of metallic zirconium (30–50 nm thick) and a wear-resistant ZrN layer approximately 3 μm thick.

To study the effect of HCS process parameters (bias voltage) on the wear resistance of the coated samples, three deposition processes were conducted. Table 1 shows the sample designations depending on the substrate bias voltage used in the HCS process. The remaining parameters were held constant for all three deposition processes. Samples with different HCS process parameters, as well as a sample prepared using the IB method, were compared.

Table 1. Designation of samples depending on the magnitude of the bias voltage on the substrate.

Designation of samples	HCS 1	HCS 2	HCS 3
Substrate bias voltage, V	–900 V	–1200 V	–1500 V

Scratch testing was performed using a Nanovea scratch tester (Nanovea, Irvine, CA, USA) in accordance with ASTM C 1624 [66] over a load range of 0–40 N using a conical diamond indenter with an angle of 120° and a radius of $100\ \mu\text{m}$. Three measurements were taken for each type of coating, after which the average value and the range of values were determined.

An automated mechanical tester, the SV-500 (Nanovea, Irvine, CA, USA), was used to study the hardness. The measurement method was performed using instrumental indentation with a Berkovich pyramidal indenter. The measurement modes were at the maximum load at 20 mN.

A DUCOM POD-4.0 (Ducom Instruments Pvt. Ltd., Bangalore, India) universal tribometer was used to conduct friction and wear tests using a pin-on-disk/ball-on-disk system. The loading scheme used in this device ensured that the working fluid (ball) load was set independently of the friction console, which reduced vibrations in the system and increased the accuracy of the tests. The load was 10 N, and the rotation speed was 100 rpm. Furrow radius 10–12 mm. The tests were conducted over 30,000 s (about $8\frac{1}{2}$ h), using an indenter (ball) made of ASTM 52100 bearing steel, the properties of which are similar to those of the sample material. The wear resistance was determined according to ASTM G99 [67]. The testing was conducted at room temperature and without any lubricant. The wear results are presented as the volume loss in cubic millimeters for the test sample (coated disk) and as the mass loss for the ball. Three measurements were taken for each type of coating, after which the average value and the range of values were determined.

3. Results

3.1. Comparison of the Effectiveness of Using HCS and IB Methods

The hardness of all deposited coatings, measured using a nanoindenter, was 27.3 ± 1.2 GPa. No significant difference in hardness was observed between coatings deposited using the HCS and IB methods.

The results of the pin-on-disk wear resistance study for substrates of various compositions with coatings deposited using the IB and HCS methods, as well as without coating, are shown in Figure 1a. After coating deposition, the wear resistance of the samples increased by 40–50% compared to uncoated samples, with the HCS method providing 15 % higher wear resistance than the IB method.

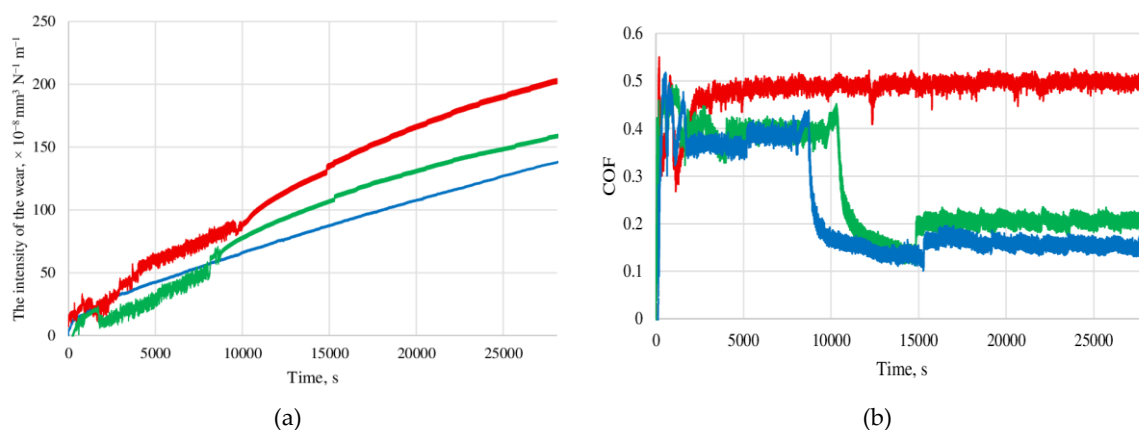


Figure 1. Pin-on-disc test results for substrates of different compositions with coatings deposited using ion bombardment (IB, green line) and glow discharge (HCS, blue line) methods, and without coating (red line) wear value (a) and friction coefficient as a function of time (b).

Coatings deposited on a steel substrate significantly affect the tribological properties of the samples, reducing the friction coefficient from 0.5 to 0.2, i.e., by a factor of 2.5 (Figure 1b). From a tribological standpoint, samples with coatings deposited using the HCS and IB methods demonstrate very similar friction coefficient values, with an insignificant (10%) decrease in this indicator for the HCS samples. This result is due to the fact that the use of the HCS or IB methods primarily affects the

interface area of the coating and the substrate and, accordingly, the adhesion strength between them. The influence of the substrate surface preparation method on the properties of the coating surface layer is not as significant, but there is a relationship between the condition of the substrate surface and the structure (in particular, the grain size) of the deposited coating [68–71]. For example, it was found that (Cr,Al)N coatings vary in their texture and mechanical properties, particularly hardness and residual stresses, depending on the surface condition of the 316L steel substrate. The substrate surface condition influences the direction of coating texture growth, which in turn influences the magnitude of residual stresses that promote spinodal decomposition of the metastable cubic phase of the coating [68].

3.2. Determining the Optimal Value of Substrate Bias Voltage Using the HCS Method

Such a key parameter of the HCS process as bias voltage has a significant impact on the quality of substrate surface preparation and, accordingly, the quality of the coating as a whole [72–75]. The results of the study of the effect of bias voltage on wear resistance in the pin-on-disc test are presented in Figure 2. At a bias voltage of –900 V, the wear resistance of the HCS samples is lower than that of the IB sample, and at a bias voltage of –1500 V, the wear resistance of the HCS sample is almost identical to that of the IB sample. The best wear resistance is observed for the HCS 2 sample, the surface of which was prepared at a bias voltage of –1200 V. Thus, the initially determined bias voltage of –1200 V ensures the best parameters of the coated sample compared to the samples whose surface preparation was carried out at a higher (–1500 V) or lower (–900 V) bias voltage.

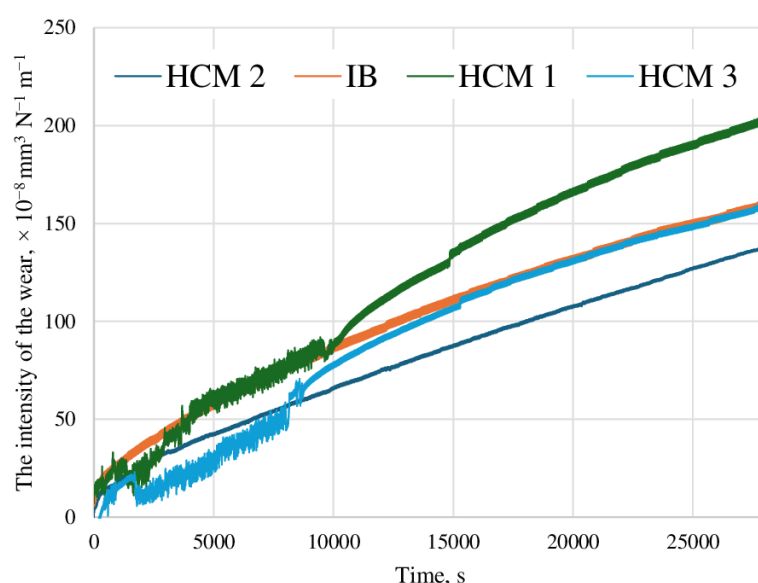


Figure 2. Comparison results of wear resistance of samples with different HCS process parameters, as well as a sample prepared using the IB method in the pin-on-disc test.

Since the studies were conducted at only three bias voltage values, it is possible that the optimal bias voltage value differs from –1200 V and may be biased upward or downward.

To find the optimal bias voltage value, we will construct an approximating curve for the wear rate versus bias voltage (Figure 3). As is known, an approximating curve (empirical formula) is an approximate functional relationship obtained based on experimental data [76,77]. Thus, the approximation task consists of constructing a function that most accurately reflects the overall trend. To assess the adequacy of the approximating curve to the available experimental data, the approximation reliability value (determination coefficient) R^2 is used, which determines the proportion of the variance of the dependent variable determined by the independent variables. In this case, the second-degree polynomial (quadratic function) most accurately (with the best value of

$R^2 = 1$) describes the general relationship between wear and bias stress. The corresponding relationships are presented on the graph and as a formula (see Figure 3).

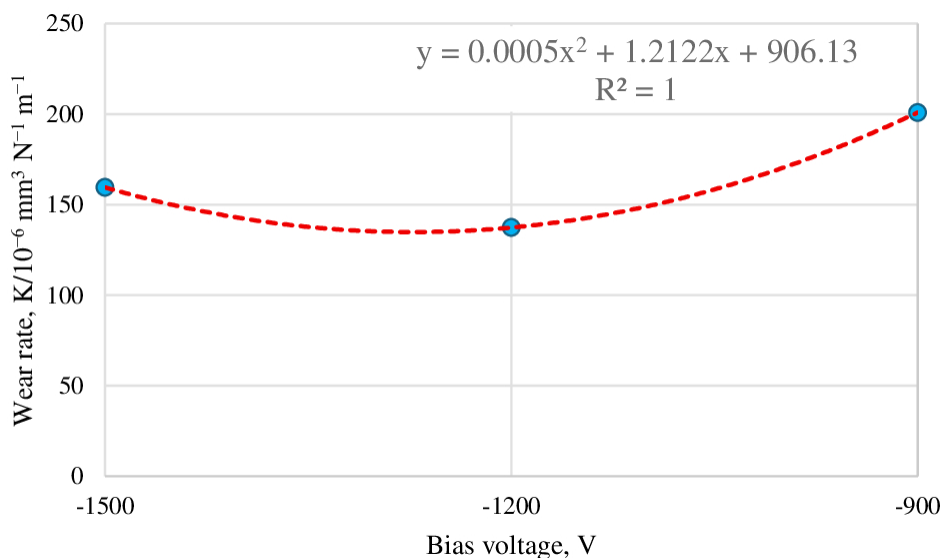


Figure 3. Wear intensity versus bias voltage. Finding the approximating function.

Having obtained the approximating function, we determine the optimal value of the bias voltage. To do this, we determine the extremum of the function. In our case, this is the point in the function's domain where the function value is minimal (the wear is minimal). Finding the extremum of a function involves finding the derivative of the function, determining the point at which the derivative is zero (or nonexistent if the function has a discontinuity), and checking whether the derivative changes sign at this point. A change in the derivative's sign indicates the presence of a minimum.

Let's determine the optimal value of the bias voltage.

The approximating dependence is determined by the quadratic formula

$$y = 0.0005 \cdot x^2 + 1.2122 \cdot x + 906.13,$$

where x is the substrate bias voltage, V; y is the wear value after completion of the experiment ($10^{-6} \text{ mm}^3/\text{N} \cdot \text{m}$).

We find the first derivative of the function:

$$y' = 0.001 \cdot x + 1.2122.$$

We equate it to zero:

$$0.001 \cdot x + 1.2122 = 0, \text{ thereby } x_1 = -1212.2.$$

We calculate the values of the function

$$f(-1212.2) = 171.416.$$

Let's check. We'll use the sufficient condition for an extremum of a function of one variable. We'll find the second derivative:

$$y'' = 0.001.$$

We calculate:

$$f''(-1212.2) = 0.001 > 0.$$

Thus, the minimum value of the function corresponding to the optimal substrate bias voltage, ensuring minimal wear, was obtained. This value is -1212.2 V , which is practically identical to the value of -1200.0 V used in the experiments.

3.3. Research of Wear Patterns of Samples and Structure of the Interface Between the Coating and the Substrate

The wear patterns of the samples after the pin-on-disc test show obvious differences (Figure 4). Only the HCS 2 coating is fragmentarily preserved in the central portion of the wear striation. Along

the edges of the wear striation, this sample exhibits smooth coating wear without the formation of distinct boundaries. On the remaining samples, the coating in the wear striation area is completely lost, and the striation itself has clearly defined boundaries. The widest wear striation (and, consequently, the greatest volume of material removed, as confirmed by the previously presented data) is observed on sample IB, which correlates with the previously obtained data (see Figure 1).

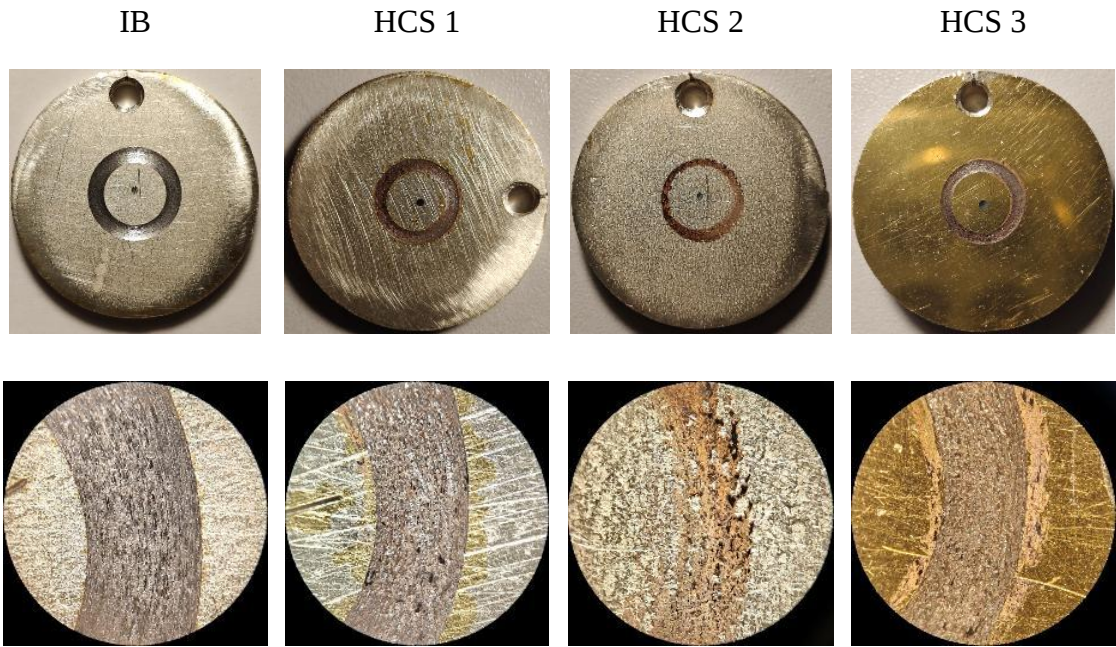


Figure 4. General view of the worn surface of coated samples after pin-on-disc testing (optical microscope).

Figures 5 and 6 show a more detailed view of the surface wear striations during the pin-on-disc test on a stainless steel specimen with HCS 2 and IB coatings, respectively. The failure of the HCS 2 coating is characterized by fragmentary breakouts, but no clearly defined striation edge is formed; significant areas of intact coating remain within the striation (Figure 5). Conversely, the wear of the IB coating (Figure 6) is characterized by the formation of clearly defined striation edges; within the striation itself, the coating is completely lost.

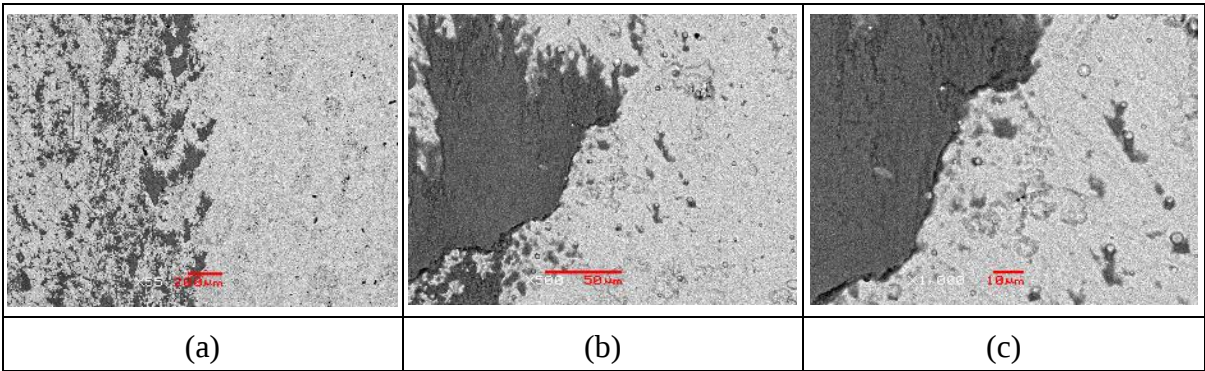


Figure 5. Surface wear behavior of a stainless steel specimen with HCS 2 coatings in a pin-on-disc test, at magnifications of ×55 (a), ×500 (b), and ×1,000 (c).

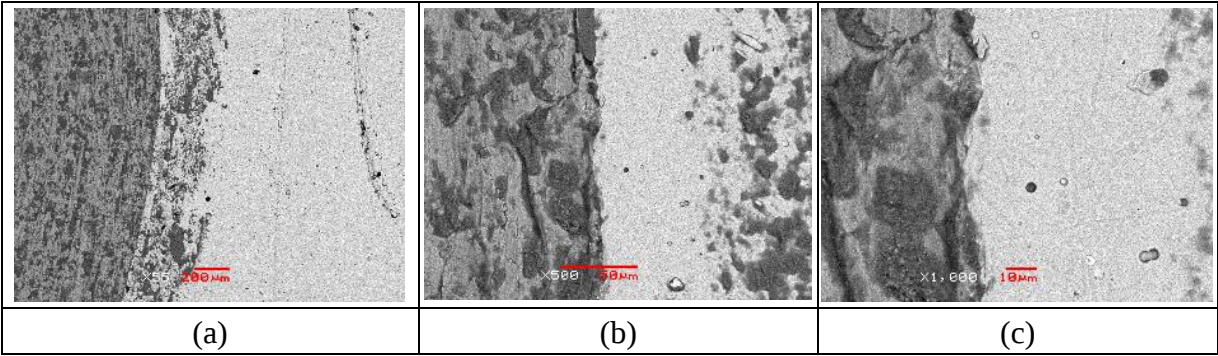
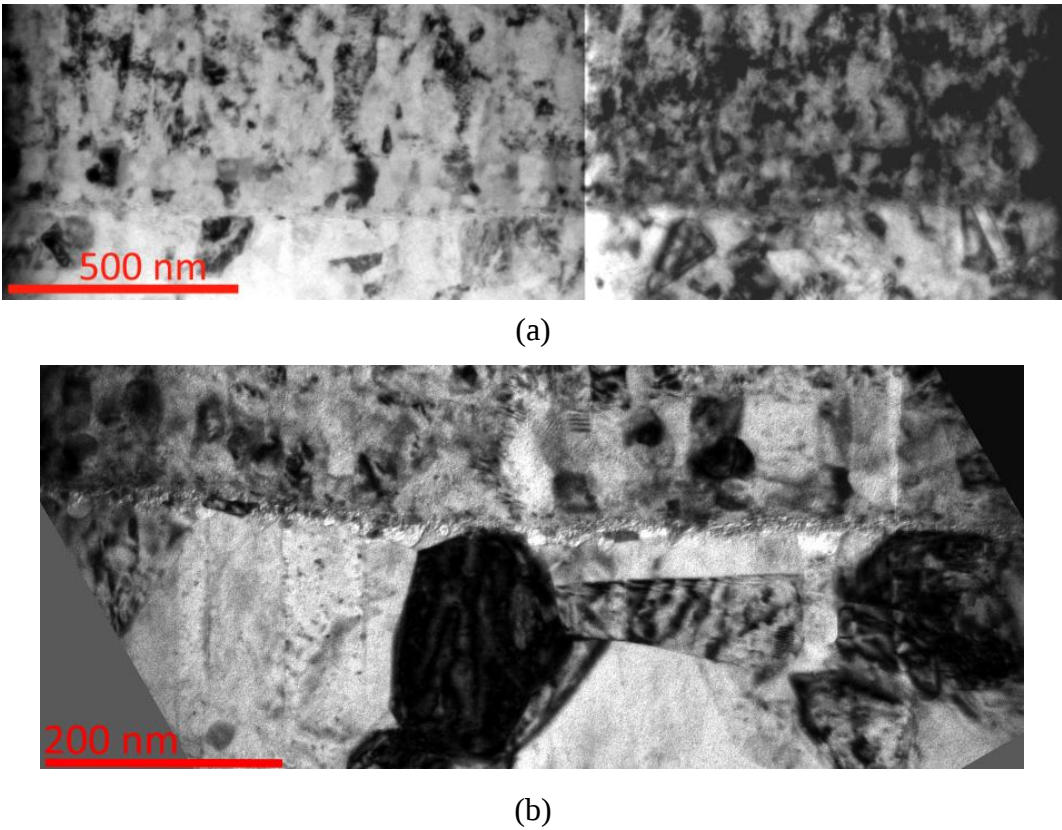


Figure 6. Surface wear behavior of a stainless steel specimen with IB coatings in a pin-on-disc test, at magnifications of ×55 (a), ×500 (b), and ×1,000 (c).

An analysis of the interface between the coating and the stainless steel substrate using the HCS method (Figure 7) shows that there are no noticeable discontinuities or adhesion issues in this area. A transition layer 15–25 nm thick is observed between the coating and the substrate (Figure 7b–7d). This layer is formed by a mixture of iron (approximately 43 at.%), zirconium (approximately 38 at.%), chromium (approximately 18 at.%), and nickel (approximately 1–2 at.%). It is worth noting the significant decrease in the nickel content in this layer compared to the substrate (approximately 20 at.%). Structurally, this layer is characterized by a nanoscale granular structure with grain sizes of 10–30 nm.



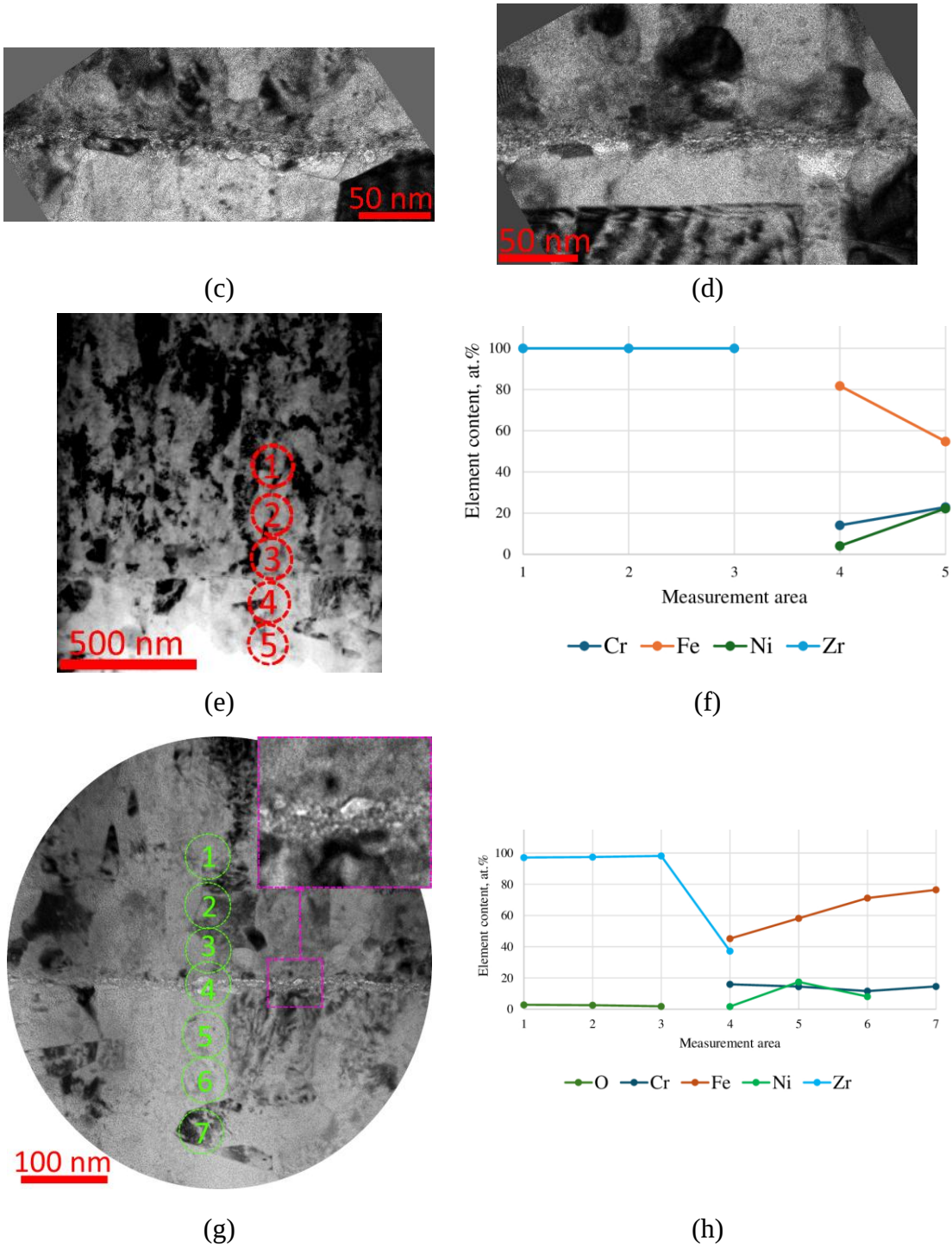


Figure 7. Internal structure and composition of the interface layer of the HCS-coated stainless steel sample: (a-d) – interface layer structure; (e-h) – element content analysis of the interface layer.

Further studies of the elemental composition in the interface area reveal weak interdiffusion of coating elements (zirconium) and the substrate (iron, nickel, chromium) (Figure 8). This adhesion is no longer observed at a distance of 30 nm from the interface layer.

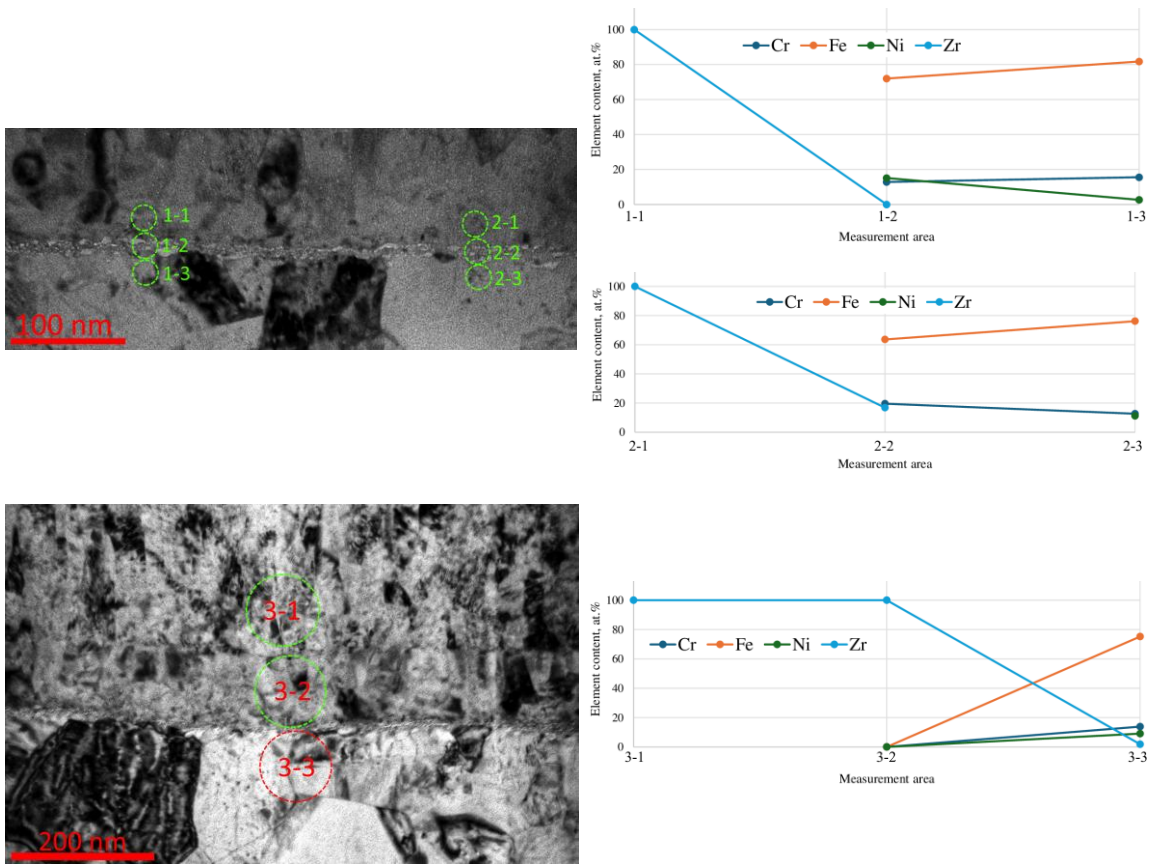
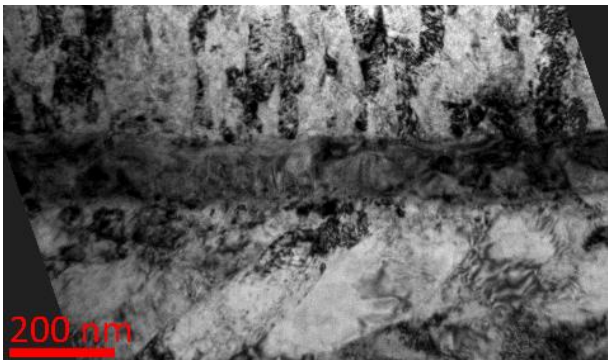


Figure 8. Composition of the interface layer of a stainless steel sample with an HCS coating.

When using the IB method, the interface has some differences. A layer with a thickness of 100–150 nm is formed in the interface region (Figure 9a). In this layer, an increased nickel content (up to 20–28 at.%) and a decreased chromium content (from 15–18 to 2–4 at.%) are observed (Figure 9). At the same time, directly in the surface layer of the substrate, at a depth of about 150 nm, a decrease in the nickel content is observed from 11–12 at.% to values close to 0. Thus, in terms of elemental composition, the studied transition layer includes zirconium (60–63 at.%), nickel (20–28 at.%), iron (6–18 at.%) with an insignificant chromium content (2–4 at.%). Interdiffusion of the coating and substrate elements is minimal, as in the case of the HCS coating. Only in one case is a slight diffusion of iron into the coating observed (Figure 9c).



(a)

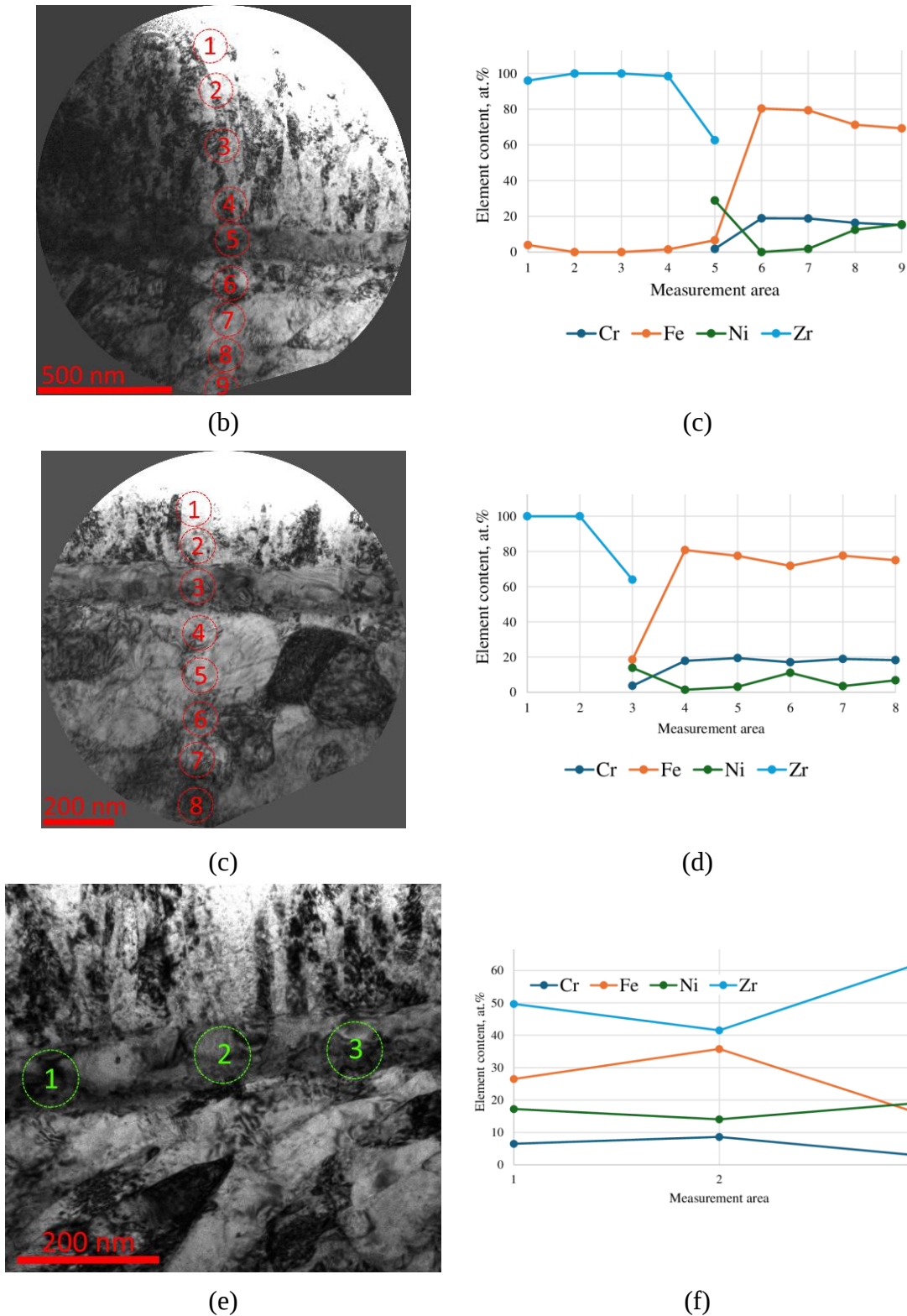


Figure 9. Internal structure and composition of the surface layer of a stainless steel specimen with an IB coating in the pin-on-disc test: **(a)** – interface layer structure; **(b-d)** – study of the change in the element content in the direction perpendicular to the interface; **(e,f)** – change in the element content along the interface layer.

It is possible to assume the formation of nickel-zirconium in the layer under consideration, which is a binary inorganic compound of nickel and zirconium with the formula $ZrNi$, Ni_5Zr , or Zr_2Ni . Nickel-zirconium is known to form during the sintering of stoichiometric quantities of pure substances (nickel and zirconium) [78–80]. At concentrations above 1 wt.% zirconium in the alloys, corrosion resistance decreases, ductility, and machinability deteriorate. This occurs due to the

precipitation of a significant amount of the second phase (the metallic compound Ni_5Zr) along the grain boundaries of the solid solution.

3.4. Resistance of Samples with the Studied Coatings to Destruction During Scratch Testing

The scratch test is a generally accepted method for determining coating-to-substrate adhesion. Research has shown that the best scratch test failure resistance was achieved with the HCS-2 surface preparation method (Figure 10). While the initial failure force (L_{C1}) was fairly similar for all samples (around 4 N), with a slight advantage for the HCS-2 sample (4.5 N), the HCS-2 sample demonstrated a significant advantage in the total coating failure load (L_{C2}) 8–9 N (compared to 6–7 N for the other samples). Thus, the HCS-2 surface preparation conditions not only ensured better wear resistance in the pin-on-disc test but also better scratch test failure resistance.

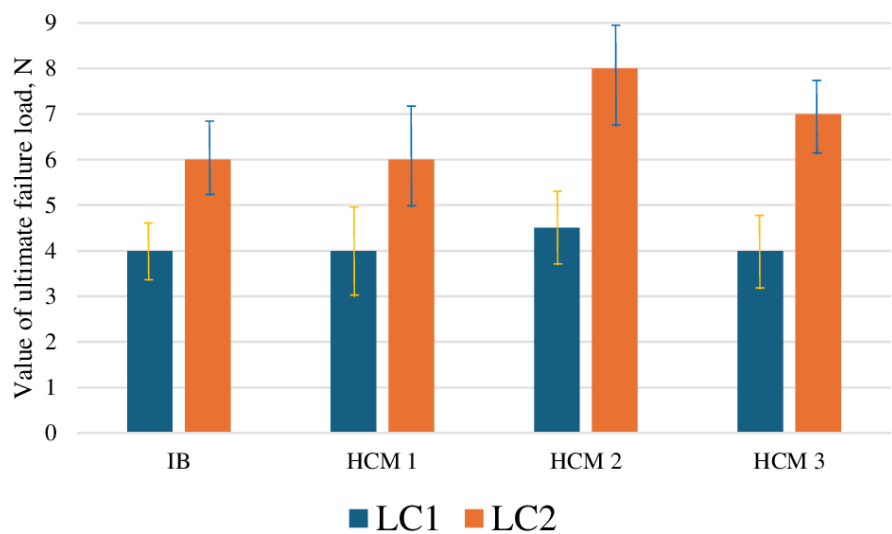
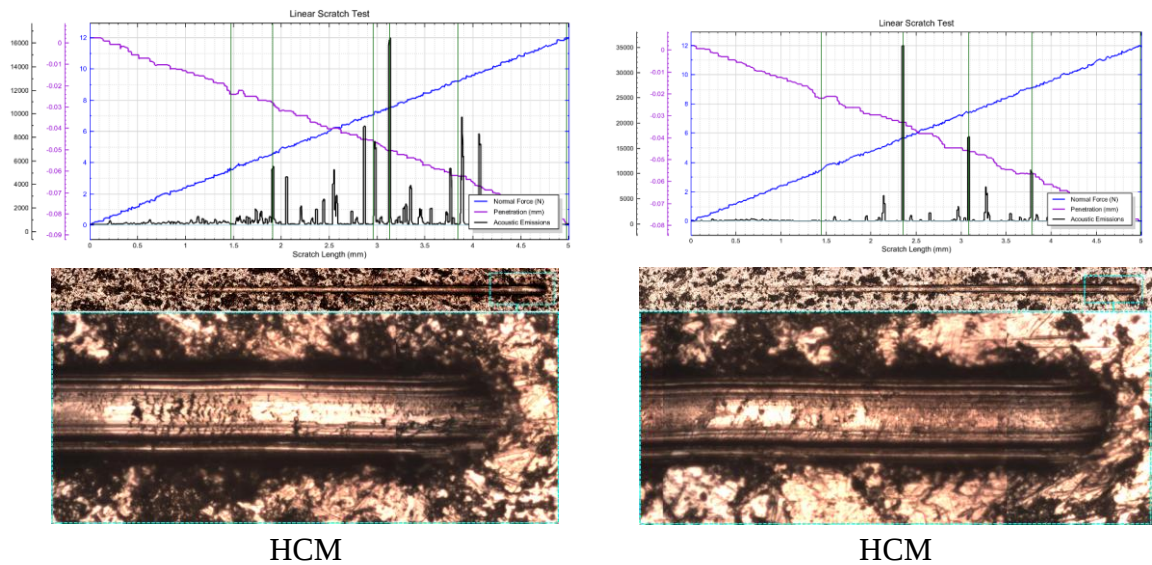


Figure 10. Study of resistance of coated samples to destruction during scratch testing.

Although the coating on the stainless steel substrate is destroyed under relatively high loads (L_{C2} = 6–9 N), no large areas of coating peeling off from the substrate are observed, i.e., the destruction occurs mainly due to processes in the coating itself, and not due to peeling of the coating from the substrate (Figure 11).



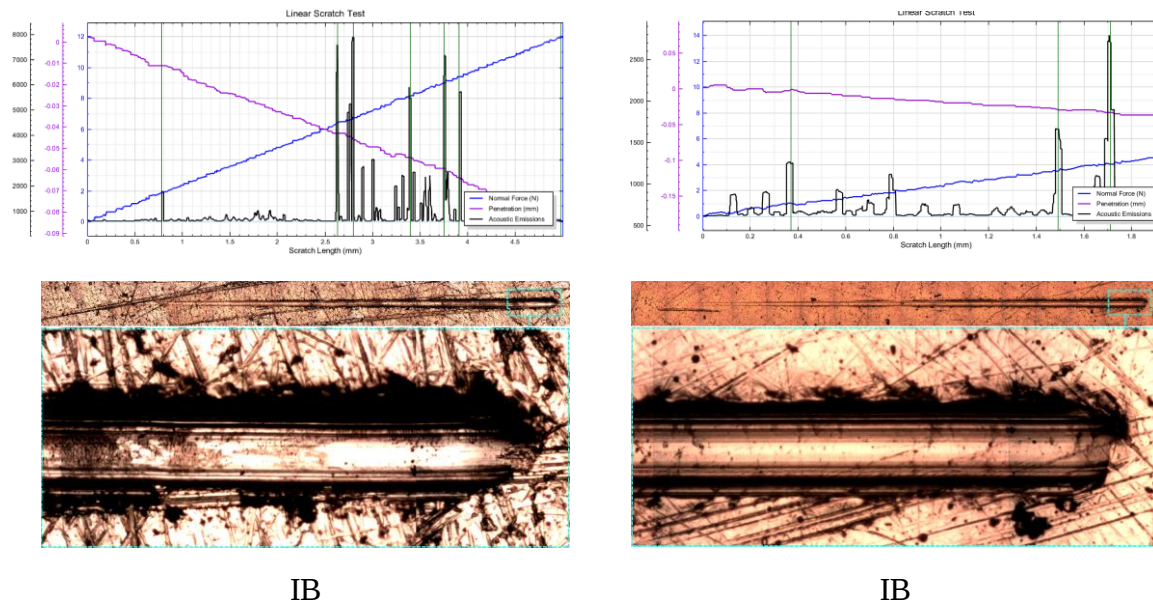


Figure 11. Nature of destruction of HCS and IB coatings on AISI 321 steel substrate.

4. Conclusions

- After coating deposition, the wear resistance of the samples increases by 40–50% compared to uncoated samples, with the HCS method providing 15% higher wear resistance than the IB method.
- Coated samples deposited using the HCS and IB methods demonstrate very similar friction coefficient values, with a slight (10%) decrease in this indicator for the HCS samples.
- The best wear resistance is observed for the HCS 2 sample, the surface of which was prepared at a bias voltage of -1200 V. Thus, the initially determined bias voltage of -1200 V ensures the best parameters for the coated sample compared to samples whose surface preparation was carried out at a higher (-1500 V) or lower (-900 V) bias voltage.
- The minimum value of the function corresponding to the optimal substrate bias voltage, ensuring minimal wear, was calculated. This value is -1212.2 V, which is practically identical to the -1200.0 V value used in the experiments. Accordingly, a bias voltage of -1200 V can be recommended for preparing the surface of a stainless steel substrate using the HCS method.
- Analysis of the nature of the interface between the coating and the stainless steel substrate using the HCS method revealed that a transition layer 15–25 nm thick is formed. This layer is formed by a mixture of iron (approximately 43 at.%), zirconium (approximately 38 at.%), chromium (approximately 18 at.%), and nickel (approximately 1–2 at.%).
- When using the IB method, a layer 100–150 nm thick is formed in the interface area, which includes zirconium (60–63 at.%), nickel (20–28 at.%), iron (6–18 at.%) with an insignificant content of chromium (2–4 at.%).
- The HCS-2 sample demonstrated a significant advantage in terms of the coating failure load (L_{C2}) 8–9 N (compared to 6–7 N for the other samples).

Thus, the HCS-2 surface preparation conditions provide not only better wear resistance in the pin-on-disc test but also better resistance to damage in the scratch test.

Author Contributions: Conceptualization, Y.B., A.V.; Methodology, Y.B., C.S., F.M. and A.S.; Resources, A.V.; Data curation, C.S., T.B. and Y.P.; investigation, C.S., F.M., A.S., I.S., E.E., T.B., and Y.P.; Supervision, Y.B. and A.V.; Writing—original draft preparation, A.V.; Writing—review and editing, A.V., T.B. and C.S.; Project administration, A.V. and C.S. All authors have read and agreed to the published version of the manuscript.

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