Efficiency of using Nitride and Oxy-Nitride Coatings for Protection Against High-Temperature Oxidation and Embrittlement of the Surface Layer of Steel Structures

G.Zh.Moldabayeva1*, A.L.Kozlovskiy1,2, E.I. Kuldeyev1, A.Kh. Syzdykov1, N.S. Buktukov3

1 Department Petroleum Engineering, Satbayev University, Almaty, 050013, Kazakhstan (G.Zh.M.), (A.L.K. kozlovskiy.a@inp.kz), (E.I.K., e.kuldeyev@satbayev.university), (A.Kh.S. a.syzdykov@satbayev.university).
2 Laboratory of Solid State Physics, The Institute of Nuclear Physics, Ibragimov st., 050032 Almaty, Kazakhstan
3 Mining Institute Named after D.A. Kunaev, Almaty 050013, Kazakhstan (N.S.B. n.buktukov@mail.ru)
* Corresponding author e-mail: g.moldabayeva@satbayev.university

Abstracts

The problem of gas swelling and high-temperature degradation of steels and alloys is one of the limiting factors during long-term operation of materials operating at high temperatures (about 400 - 700°C), as well as when interacting with various gaseous media. To solve this problem, the paper proposes the use of thin-film Al - O - N and AlN coatings obtained by magnetron sputtering (which is one of the most common and well scalable methods in modern materials science) to protect against high-temperature degradation, as well as associated gas swelling (in case of hydrogenation) and to maintain stability to wear. The main purpose of using AlN and Al – O – N coatings as protective materials is to increase the resistance of steel structures to the processes of hydrogenation and high-temperature oxidation, operating under conditions of aggressive exposure to high temperatures and hydrogen. Moreover, the use of these coatings is aimed at reducing the rate of degradation and oxidation by reducing diffusion processes associated with the migration of implanted hydrogen into the surface layer. During the studies aimed at determining the effectiveness of increasing the wear resistance and strength of steel structures due to applied coatings, it was found that the use of Al – O – N and AlN coatings makes it possible to increase resistance to high-temperature degradation by more than 5 times compared to the results of changes in the strength characteristics of 316 L steel. Moreover, in the case of determining the coefficient of dry friction, it was found that the processes of hydrogenation and high-temperature heating without their combination (i.e., first hydrogenation of the samples and then thermal heating) lead to almost equivalent changes in the strength parameters for the coatings under study. At the same time, a comparison of the obtained results of changes in strength parameters and wear resistance of coatings showed that Al – O – N coatings are more resistant to high-temperature degradation, for which the decrease in strength parameters is less pronounced than for AlN coatings.

Key words: oxy-nitride coatings; gas swelling; high-temperature corrosion; friction; tribological tests; wear resistance

Introduction

The heat resistance of steels and alloys is one of the important indicators that determine not only the ability of materials to resist oxidation at high temperatures due to increased diffusion of elements, but is also a key criterion for determining the scope of application in industry. So, for example, steels and alloys capable of withstanding temperatures from 400 to 700°C cannot be used for the development of thermocouple covers, pipelines operating at high temperatures, as well as muffles, etc. [1-3]. With prolonged thermal exposure during operation, steels and alloys, especially iron-containing ones, undergo destructive oxidation due to the formation of oxide phases in the surface layer, which in turn leads to a decrease in their strength, as well as the formation of oxide films in the form of build-ups, which have a fairly low resistance to mechanical stress, as well as lower thermal conductivity. As a result, the formation of oxide films on the surface of steels and alloys can lead to destructive embrittlement during long-term operation. To solve this problem, it is proposed to use protective coatings that have high corrosion resistance to external influences. This limitation is due to the fact that as the operating temperature increases, the amplitude of thermal vibrations increases, the change of which leads to an acceleration of the processes of diffusion of elements in the steel, which in turn can lead to destructive embrittlement due to the occurrence of uneven distribution of elements in the composition [4,5]. The combination of high temperatures (during operation) and gas media can lead to an acceleration of the corrosion processes of near-surface layers not only due to the formation of oxide films on the surface of...
steel structures, but also the introduction of gas ions into the structure of the near-surface layer, thereby increasing the thickness of oxides due to diffusion processes. At the same time, the most dangerous type of corrosion can be distinguished among gas corrosion - hydrogenation, which occurs when materials interact with various media, including not only gas media, but also aqueous media [6,7]. The process of hydrogenation itself consists of the penetration of hydrogen into the surface layer of the material and, due to its mobility and low solubility, as well as its high ability to agglomerate in voids and microcracks, is capable of forming gas-filled bubbles, an increase in the density and size of which leads to destructive embrittlement of the near-surface layer due to deformation opening of these bubbles (explosive mechanism at high gas concentrations) [8-10]. Moreover, in the case of combining the processes of hydrogenation (during operation) and thermal heating, the gas swelling processes will intensify due to the fact that with growth in temperature, the effects of thermal expansion occurring in the structure can lead to accelerated diffusion of hydrogen in the structure and its more pronounced agglomeration in cavities and voids, which will accelerate the process of destruction and embrittlement [11,12]. In view of this, the search for solutions to curb the processes of gas swelling under high-temperature exposure is one of the most important areas of research in materials science and metallurgy. The most optimal solution to problems associated with protection against corrosion and degradation of steel and alloys, in addition to the use of technological solutions associated with strain-induced dislocation hardening of near-surface layers, is magnetron sputtering of thin films and coatings on the surface of steel structures, in particular, nitride or oxide coatings, the application of which makes it possible not only to increase the resistance to corrosion and degradation, but also to increase the wear resistance and strength characteristics [13-15].

Interest in nitride and oxy-nitride coatings and ceramics is primarily due to the combination of their thermophysical and strength parameters, which makes them one of the most promising materials for protection against gas swelling due to high resistance to the formation of gas-filled areas in the structure [16,17], high-temperature corrosion due to low values of thermal expansion coefficients [], as well as high strength characteristics, that can significantly increase the wear resistance of materials and reduce surface wear under mechanical stress. So, for example, the application of oxy-nitride coatings based on Cr-O-N compounds made it possible to increase wear resistance due to intergranular boundary effects, as well as high levels of resistance to external influences [18-20]. The application of oxy-nitride coatings based on Ti-Al-ON compounds [21] made it possible to increase not only thermal stability, but also increase oxidation resistance. The use of (CrₓAl₁₋ₓ)(OᵧN₁₋ᵧ) coatings in work [22] made it possible to increase resistance to oxidation and structural degradation associated with corrosion processes. The authors of this work also showed that the use of oxy-nitride coatings makes it possible to increase the resistance of materials to processes associated with electrochemical corrosion due to higher corrosion currents. This property opens up broad prospects for the use of oxy-nitride coatings as protective materials against corrosion.

Based on the above, the main aim of this work is to determine the effectiveness of using AlN and Al – O – N coatings as a basis for creating protective materials against high-temperature degradation and hydrogenation, processes that are the most dangerous when operating steel structures under conditions of exposure to aggressive environments and elevated temperatures. Particular attention in the works was paid to studying the dependencies of changes in the strength characteristics and wear resistance of samples before and after hydrogenation and thermal heating for a long time.

Materials and methods
Two types of coatings AlN and Al – O – N, obtained by magnetron sputtering on the surface of steel 316 L, were chosen as the samples under study, the choice of which as a substrate is due to its high strength parameters, as well as high resistance to pitting or crevice corrosion when interacting with aggressive environments (chlorine environment or sea water), which is due to the presence of molybdenum in the composition of these steels. Sputtering of the coatings was carried out using the high-frequency magnetron sputtering method, implemented on an Auto 500 installation (Edwards). An aluminum target (K. Lesker, USA) was chosen for sputtering AlN and Al – O – N coatings. Sputtering of AlN coatings was carried out at a discharge power of 250 W, with a working gas supplied in the form of a mixture of argon (40 %) and nitrogen (60 %), supplied at a pressure of 5·10⁻³ mbar. Sputtering of Al – O – N coatings was carried out by supplying a gas mixture (N₂ + O₂) in a ratio of 50%: 50%, the operating pressure was 5·10⁻³ mbar, the discharge power was 250 W. The thickness of the coatings was monitored by ellipsometry, according to which the thickness of the applied coatings was about 600 ± 10 nm. The thickness control of the applied coatings was determined by ellipsometry and by evaluation of the lateral.
cleavages of the coated steel surface using scanning electron microscopy. According to the data obtained from the study of structural features, the studied coatings are X-ray amorphous, which is due to the features of the application of such coatings by magnetron sputtering.

The adhesion of coatings to the steel surface was studied by determining the critical load when the coating is peeled off (method for determining adhesive strength). Experiments to determine the critical load were performed on a Unistest framework SKU UT-750 (Unistest, USA). An indenter with a Rockwell-type diamond tip (curvature radius of about 200 μm) was used as an indenter. The tests were carried out by moving the indenter along the surface of the coatings at a constant speed of 10 mm/min with a load changing from 0 to 100 N. Determination of strength parameters (hardness) was carried out using the indentation method, implemented using a Duroline M1 microhardness tester (Metkon, Bursa, Turkey).

For indentation, an indenter in the form of a Vickers diamond pyramid was used (the load was chosen to be 10 N). Hardness measurements were carried out using the indentation method, where a Vickers pyramid (136°) was used as an indenter. The selection of indentation modes was carried out taking into account the thickness of the applied coatings, so that the magnitude of the applied load on the indenter did not lead to penetration of the indenter deeper than the thickness of the applied coating. Moreover, after each measurement, a visual inspection of the indenter print was carried out in order to establish its geometry, as well as its depth.

Tribological tests of the studied AlN and Al – O – N coatings were carried out according to the “ball on disk” scheme with an applied load on the ball (friction body) of 50 N, the sliding speed was chosen to be 0.2 m/s, the number of cycles was 20,000. During the tests, the dry friction coefficient was recorded, the change in which reflects the tribological characteristics of the coatings (wear resistance), and their change as a result of external influences characterizes the effects of hardening and resistance to degradation processes.

Experiments to determine the resistance of coating materials to high-temperature degradation processes and gas swelling processes were carried out according to the following scheme: initially, the studied coatings applied to the surface of 316 L steel were subjected to hydrogenation, then the samples were thermally annealed for a long time. Hydrogenation was carried out by electrochemical charging (current density 20 mA/cm²) in an aqueous solution of 3% sodium hydroxide and 3 g/l CH₃N₂S at a temperature of 80°C for 24 hours. Simulation of hydrogenation processes can be carried out both by hydrogenation and by high-dose proton irradiation, taking into account the thickness or depth of the damaged layer during hydrogenation. In the case of proton irradiation, thicknesses can reach the order of several tens of microns, which in the case of thin-film coatings is not always effective for the hydrogenation degree assessment. After that, the samples under study were subjected to thermal heating at a temperature of 700 °C for 500 hours in order to initiate the processes of gas swelling associated with the migration processes of hydrogen in the samples and the formation of gas-filled inclusions. The samples were annealed for 500 hours in one cycle without stops or breaks. Control over maintaining the temperature in the furnace chamber was carried out using thermocouples. After thermal annealing of the samples at a given temperature, the samples cooled along with the furnace for 20-24 hours until they reached room temperature. The test time is determined by the possibility of simulation of degradation processes initiated by the diffusion effect of oxygen when heating samples to a given temperature for a long time. The choice of this time period is determined by the cyclic processes of operation of such coatings.

The morphological features of the coatings under study, as well as 316 L steel after hydrogenation and thermal annealing, were studied by constructing 3D reconstructions of the surface profile obtained using the atomic force microscopy method. Surface images were taken in semi-contact mode on a Smart SPM atomic force microscope (AIST-NT, Zelenograd, Russia). All images of morphological features, presented in the form of 3D reconstructions of the surface of steel and coatings, depending on the type of external influences, were performed using the same shooting mode in semi-contact mode. The size of the scanning area was 10 by 10 μm.

Results and discussion

Determination of the influence of high-temperature corrosion processes, alongside hydrogenation processes (gas corrosion) of the surface layers of steels is one of the important criteria that make it possible to establish not only the influence of degradation factors on the stability of materials, but also to determine the degradation mechanisms that affect the strength parameters and wear resistance.

Figure 1 presents the results of 3D reconstruction of the morphological features of the studied samples (steel 316 L, AlN and Al – O – N coatings applied to the surface of the steel), reflecting changes in morphology as a result of thermal effects (long-term high-temperature heating) and hydrogenation. The
results obtained reflect changes in the morphology of the surface of the samples as a result of the processes of high-temperature oxidation (during thermal heating) and gas swelling (during hydrogenation and subsequent thermal heating), characterizing surface degradation associated with the formation of oxide inclusions (growths, films), as well as deformation distortion caused by the processes of hydrogen agglomeration and the subsequent formation of deformation inclusions in the form of spherical hillocks.

In the case of the original samples not subjected to hydrogenation, it is clear that the structure of AlN and Al – O – N coatings has a similar morphological nature, the difference being the presence of small inclusions on the surface of AlN coatings associated with magnetron sputtering processes. In the case of Al – O – N coatings, the number of such inclusions is much smaller. It should also be noted that the resulting coatings repeat the morphological features (irregularities, stripes from polishing) of the original samples, and the results of tests to determine the critical load showed that, regardless of the thickness of the coatings (in the range from 100 to 600 nm), the adhesive strength is maintained, which indicates good adhesion of the coatings to the steel surface.

According to the obtained data on changes in the morphological features of the studied samples after thermal annealing (see data in Figure 1b), it was found that the most pronounced changes are observed for samples of 316 L steel, the surface of which, as a result of thermal heating, is covered with growths, the formation of which is due to oxidation effects. Diffusion processes associated with the possible introduction of oxygen into the surface layer of a material when it comes into contact with the atmosphere play a very important role in the degradation and oxidation processes of materials (especially steels or alloys that contain iron). Introduced oxygen under the influence of high temperature, which is characterized by an increase in thermal vibrations of the crystal lattice, and as a result of greater mobility, is able to occupy empty positions (vacancies) or fill in the interstitial space, thereby leading to deformation distortion of the crystal structure. Moreover, in the case of iron-containing steels and alloys, the introduction of oxygen can lead to the initiation of processes of formation of iron oxides, which, as a result of thermal effects, can undergo phase transformations, thereby exacerbating corrosion processes. In this case, the use of protective coatings prevents the direct exposure of oxygen to the steel surface, thereby reducing the rate of degradation of the steel surface due to the presence of the protective coating. Moreover, in the case of AlN and Al – O – N coatings, changes in morphological features are insignificant, which indicates high resistance to high-temperature oxidation of these coatings, and the mechanisms of resistance to degradation can be explained by the structural features of these coatings due to the presence of Al – N chemical bonds in the composition of both types of coatings. In contrast to coatings, after high-temperature heating processes for 500 hours, the formation of build-ups in the form of oxide inclusions is observed on the surface of 316 L steel, the presence of which indicates degradation of the near-surface layer due to the processes of oxygen diffusion into the near-surface layer with the subsequent formation of build-ups, which leads to surface degradation. Moreover, in the case of hydrogenation and subsequent thermal heating, the degradation processes of the surface layer of 316 L steel are caused not only by the accumulation of oxide inclusions, but also by gas-filled bubbles, the formation of which occurs due to the agglomeration of hydrogen in places of structural damage.

In the case of modeling hydrogenation processes (without subsequent thermal annealing), the surface layer of 316 L steel is a deformed surface with formations in the form of hillock-like bubbles (see data in Figure 1c), characteristic of the formation of gas-filled cavities (as a result of the accumulation of hydrogen in the surface layer). At the same time, it is clearly visible that the largest accumulation of these inclusions on the surface is observed near the grooves, which are the so-called defect sinks, near which hydrogen accumulation and agglomeration occurs. The introduction of oxygen as a result of diffusion processes into the surface layer, as well as the agglomeration of implanted hydrogen, occurs near the structural defects that have arisen in the structure of the coatings as a result of their production. At the same time, the presence of any deformation distortions associated with layer-by-layer magnetron sputtering (i.e., a rise in thickness by layer-by-layer sputtering) can lead to the appearance of longitudinal structures as a result of the layering of one layer on another, which manifest themselves under the influence of temperature and corrosion processes, due to a greater predisposition to deformation displacement to the surface due to existing deformation distortions. As a result, in addition to hillocks, structural distortions in the form of longitudinal stripes or grooves may form on the surface. In the case of AlN and Al – O – N coatings, the formation of similar hillocks (bubbles) is also observed, but their size and quantity (concentration in the selected area for measurement) is much less than for steel 316 L, which indicates a higher resistance of these coatings to deformation-induced processes of extrusion of a deformed volume onto the surface during the formation of gas-filled cavities in the near-surface layer. The appearance of such hillocks in the form of spherical inclusions on the surface can be described quite
well by the Evans model [23,24], according to which the formation of gas-filled bubbles in the near-surface layer is accompanied by the accumulation of tensile-type deformation distortions, as well as an increase in pressure in the cavity filled with gas (in this case, hydrogen), which leads to increased pressure on the walls and an increase in its volume. The spherical inclusions observed on the surface after hydrogenation and as a result of thermal heating are in good agreement with the Evans model [23,24], which describes the processes of gas swelling in steels and alloys, as well as subsequently in ceramic materials, associated with the accumulation of implanted helium in the surface layer. In this case, hydrogen, like helium, by its nature has high mobility during implantation, as well as low solubility, which allows it to agglomerate quite well in voids, forming gas-filled bubbles that can exert deformation pressure on the structure, thereby squeezing part of the volume onto the surface in the form of a hillock or spherical inclusion.

In the case of AlN and Al – O – N coatings, the structural features of which determine the inhibition of hydrogen agglomeration into large gas-filled cavities, the formation of hillocks is less pronounced, and the formed hillocks themselves are much smaller in size than in the surface layer of 316 L steel. The observed changes in the surface of the studied samples of 316 L steel without a coating after high-temperature corrosion tests (modeling of gas corrosion) are associated primarily with the destruction of gas-filled inclusions formed as a result of hydrogenation, which, during prolonged thermal heating, are destroyed due to the achievement of critical values of internal pressure in the cavities, the increase in which is due to diffusion and migration processes of hydrogen, as well as oxygen (the appearance of which is associated with thermal oxidation of the surface).

The result of these processes is destructive swelling (formation of growths and their partial opening), which is also accompanied by the appearance of grooves on the surface of the samples associated with the corrosive processes of exfoliation of the resulting oxide growths and the destruction of gas-filled cavities in the near-surface layer.

In the case of high-temperature heating for a long time (500 hours), the formation of hillock-like spherical inclusions is observed on the surface of the coatings, the occurrence of which is due to deformation processes associated with the formation of oxide inclusions in the coating, the accumulation of which leads to partial displacement of the volume to the surface. At the same time, changing the type of coating from AlN to Al-O-N leads to less pronounced changes in morphology, and the concentration of formed hillocks on the surface is much lower. This effect is primarily due to the higher resistance to external influences of Al-O-N coatings, which are determined by the structural features of chemical and crystalline bonds. In the case of hydrogenation, alterations in surface morphology are caused primarily by the formation of agglomerates in the form of gas-filled hydrogen bubbles in the surface layer of coatings, the presence of which results in deformation-induced extrusion of volume onto the surface in the form of hillocks or spherical inclusions. Moreover, this process of deformation extrusion is more pronounced for samples subjected to hydrogenation and subsequent thermal exposure, due to the fact that with prolonged thermal exposure, slightly soluble hydrogen becomes more mobile, which leads to an increase in the volume of areas in which it agglomerates due to the merging of smaller inclusions. In this case, a rise in the mobility of implanted hydrogen due to thermal effects and increased thermal vibrations of coating atoms results in acceleration of degradation processes due to agglomeration processes, resulting in a rise in deformation stress in the damaged layer, also caused by a growth in the volume of gas-filled inclusions on the surface.

For deposited AlN coatings, surface degradation processes are less pronounced and consist of an increase in the number of small inclusions, which were also observed (to a much smaller size) on the surface of the coatings after hydrogenation. An increase in the size of these inclusions, as well as their concentration, indicates the migration of hydrogen in the near-surface layer, which is accompanied by the enlargement of gas-filled cavities and an increase in their volume. Also, for AlN coatings, as in the case of 316 L steel samples, an increase in surface roughness is observed, which is much less pronounced than for steel. In the case of Al-O-N coatings, high-temperature degradation processes lead to an increase in the density of hillock-like inclusions on the surface, characteristic of the formation of defective inclusions associated with a change in volume, but their number is significantly less than similar inclusions on the surface of steel 316 L and AlN coatings. This difference in the change in the morphological features of the surface of the studied samples indicates a higher resistance of Al-O-N coatings to degradation processes, causing surface deterioration due to the formation of oxide films, as well as gas swelling, which indicates a decrease in the rate of degradation due to the structural and strength characteristics of these coatings. In the case of prolonged high-temperature heating, the main mechanism of degradation of coatings is the interaction of oxygen from the atmosphere, which can penetrate into the coatings with the subsequent

© Engineered Science Publisher LLC 2024 | 5
formation of oxide inclusions by filling vacancies or penetrating into the interstitial space, thereby destroying chemical and crystalline bonds. In the case of Al – O – N coatings, oxide inclusions can form due to the breaking of chemical bonds and the subsequent formation of aluminum oxide in the form of individual grains. In turn, the formation of oxide inclusions in the structure of coatings creates additional deformation distortions and stresses, and prolonged temperature exposure results in a rise in the mobility of these inclusions, which promotes their agglomeration with each other, and as a result, a growth in the concentration of which negatively affects the strength properties. In this case, the presence of deformation inclusions can contribute to the rapid propagation of microcracks under external mechanical influences, which leads to cracking or a decrease in adhesive strength with lower mechanical loads on the samples.

Based on the observed changes in the morphological features of 316 L steel and the studied AlN and Al – O – N coatings as a result of thermal effects and hydrogenation, it can be concluded that the use of AlN and Al – O – N coatings applied to the surface of the steel leads to a significant reduction in surface degradation associated with swelling processes (formation of hillocks and deformation inclusions), which helps to increase the resistance of materials to external influences. The resistance of AlN and Al – O – N coatings to corrosion processes initiated by high-temperature influences can be explained by low thermal expansion rates (3.5 × 10⁻⁶ K⁻¹) compared to steels (0.011 – 0.015 K⁻¹), which causes lower mobility of atoms in the crystal structure, and as a result, reduces the rate of degradation of the surface layer under prolonged thermal exposure. In the case of the structural features of AlN and Al – O – N coatings, one can note the amorphous nature of the resulting coatings, which does not allow rapid degradation of the coating due to the structural features.

© Engineered Science Publisher LLC 2024 | 6
Figure 1. 3D reconstruction of the morphological features of the studied samples in the initial state (a), after thermal annealing for 500 hours (b), after hydrogenation without thermal annealing (c), after hydrogenation and subsequent thermal annealing (d).

Figure 2 presents the results of a comparative analysis of changes in the dry friction coefficient of the studied samples after external influences (thermal annealing for 500 hours, hydrogenation and the combination of two processes simulating the processes of high-temperature gas corrosion). In the case of the initial values of the dry friction coefficient in comparison of the values for steel 316 L and applied coatings, the established differences are of the order of 6 – 8 % (compared to the value of the dry friction coefficient for steel 316 L) due to an increase in the surface roughness of the coatings in comparison with the steel surface, which in turn results in a slight friction resistance growth.

For 316 L steel in the initial state, the main changes in the dry friction coefficient are observed after 14000 - 15000 consecutive cycles, which are expressed in an increase in the dry friction coefficient, and as a consequence, a deterioration in the wear resistance of the surface under mechanical influence. In the case of thermal heating and hydrogenation, the effects of reduced wear resistance caused by an increase in the dry friction coefficient occur much earlier after 11000 – 12000 cycles (in the case of thermal heating) and after 10,000 cycles (in the case of hydrogenation and thermal heating). At the same time, the maximum values of the dry friction coefficient achieved as a result of cyclic tests indicate degradation acceleration and reduction in the wear resistance of the 316 L surface exposed to thermal effects and hydrogenation. Moreover, the observed increase in the coefficient of friction in this case indicates not only a decrease in wear resistance, but also a decrease in the strength parameters of steel as a result of prolonged exposure. In the case of thermal annealing and hydrogenation of 316 L steel samples, a slight increase in the dry friction coefficient is observed (about 10–15% compared to the initial value), which is due to changes in the morphological features presented in Figure 1. At the same time, the beginning of a decrease in wear resistance during thermal annealing and hydrogenation for samples of steel 316 L is slightly shifted (the beginning of a pronounced change in the dry friction coefficient is observed after 10,000 cycles), which indicates more pronounced processes of destructive changes in strength properties caused by oxidation processes (formation of oxides in the surface layer during thermal annealing) and gas-filled bubbles (during hydrogenation). It should also be noted that during simulation of the processes of high-temperature degradation (long-term thermal heating) and hydrogenation, the change in the dry friction coefficient, and as a consequence, the specific volumetric wear of the surface, is significantly
higher than in the initial state (by 20 – 25 % during thermal heating and 45 – 50 % during hydrogenation). This increase in the values of specific volumetric wear (see data in Figure 3) is due to the accumulation of structural distortions in the surface layer associated with the formation of oxides (during thermal heating), which have a destructive effect on the stability and strength properties of steel. As a result of modeling hydrogenation processes, the observed agglomerates in the form of gas-filled bubbles (see data in Figure 1) exert deformation distortion on the crystal structure near the formed bubbles, which, under mechanical influence, leads to their destruction due to an increase in deformation distortion under external influence, which results in embrittlement and peeling of the damaged area near the gas-filled bubble destroyed by deformation distortion. In the case of simulation of high-temperature gas corrosion processes (hydrogenation of samples followed by thermal annealing), deterioration of the dry friction coefficient for steel 316 L is observed both at the beginning of testing (growth from 0.33 to 0.47 – 0.48), and the destruction process during testing begins after 5,000 – 6,000 cycles, and after 20,000 cycles, the value of the coefficient is more than two times higher than the initial value and three times higher than the initial value before testing. This behavior of changes in the value of the dry friction coefficient indicates a strong influence of thermally induced processes of gas swelling on a decrease in strength parameters (wear resistance), expressed in the destruction of the near-surface layer and its destruction under external mechanical influences (in this case, friction).

![Graphs showing dry friction coefficient](image)

Figure 2. Results of the tribological tests of the studied samples, presented in the form of a dependence of the change in the dry friction coefficient on the type of external influences on the samples (all graphs of the changes in the dry friction coefficient are shown on the same scale for a more clear comparison of the established changes): a) 316 L; b) AlN coating; c) Al-O-N coating

Figures 2b and 2c present the results of changes in the values of the dry friction coefficient for samples of AlN and Al – O – N coatings before and after experiments simulating corrosion and degradation processes. Comparing the results of changes in the dry friction coefficient values for coating samples after long-term thermal heating and hydrogenation, we can conclude that minor changes associated with an increase in the dry friction coefficient compared to the initial values are due to changes in the morphological characteristics of coatings resulting from external influences. These changes are caused primarily by the formation of hillock-like inclusions resulting from thermal effects and hydrogenation, which leads to the creation of additional obstacles and, as a consequence, an increase in the dry friction coefficient. It should be noted that the general trend of changes in the dry friction coefficient depending on the number of cycles, indicating the wear resistance of coatings for samples after thermal heating and hydrogenation, does not differ from the trend of changes in this value obtained for the original samples. Such an observation indicates the preservation of the stability of the strength properties (in this case, wear resistance) of the coatings, both to the effect of thermal heating and to hydrogenation processes. In the case of modeling the processes of high-temperature gas corrosion, the change in the values of the dry friction coefficient for AlN and Al – O – N coatings is less pronounced (at the beginning of tests) than for steel 316 L, and the stage of wear resistance deterioration for AlN coatings appears after 10,000 cycles (in the initial state, the manifestation was observed after 150,000 cycles), and for Al – O – N coatings, wear resistance deteriorates after 13,000 – 14,000 cycles (in the initial state, a decrease was observed after 16,000 cycles). The maximum decrease in wear resistance (i.e., an increase in the dry friction coefficient) after 20,000 cycles was about 60% for AlN coatings and 48 % for Al – O – N coatings, while for steel
316 L the change in the dry friction coefficient was more than 103 % compared to the initial value. Figure 3 shows the results of a comparative analysis of the change in volumetric wear after tribological tests of the samples under study. The results were assessed by comparative analysis of changes in dry friction coefficients at the beginning and end of the tests, considering the distance traveled (the number of test cycles).

![Figure 3](image_url)

Figure 3. Results of changes in specific volumetric wear of the surface of steel samples and coatings depending on the type of external influences

Analyzing the obtained data on changes in the coefficient of dry friction and specific volumetric wear of the surface during high-temperature gas corrosion tests, we can conclude that the use of AlN and Al – O – N coatings makes it possible to reduce the wear resistance of the surface by more than 2 times in comparison with samples of 316 L steel (without coatings), and in the case of high-temperature heating (for at least 500 hours), due to their thermophysical parameters (low coefficient of thermal expansion) AlN and Al – O – N coatings and structural features make it possible to increase the wear resistance of the surface to mechanical stress by more than 3 – 4 times. Such high stability indicators are due to the low influence of thermal expansion on the crystalline structure of AlN and Al – O – N coatings, which leads to a decrease in the rate of surface corrosion. At the same time, the main degradation mechanism for AlN and Al – O – N coatings during high-temperature corrosion, according to the data of [21,22], is due to the possibility of the formation of oxide inclusions in the form of Al2O3 in the composition of the coatings, the formation of which is limited by the structural features of the coatings, and these inclusions exhibit the most significant destructive effect on the strength properties at much higher temperatures (more than 1200°C).

Figure 4a presents the results of a comparative analysis of changes in the hardness of 316 L steel samples and the studied AlN and Al – O – N coatings in the initial state, as well as after high-temperature heating and hydrogenation processes leading to a destructive change in strength parameters. The results are presented in the form of a comparative diagram, which also shows the values of softening (∆H), which characterizes the destructive change in hardness associated with degradation processes of the surface layer as a result of hydrogenation or thermal heating, which initiates oxidation (for steel, the formation of oxides in the form of build-ups or films). According to the obtained data on changes in hardness for the studied samples of 316 L steel, the most pronounced changes associated with softening processes are observed after exposure to high temperatures on samples subjected to hydrogenation. In this case, the softening is about 24 %, while thermal annealing and hydrogenation affect the decrease in hardness by no more than 3 – 3.5 %. For AlN and Al – O – N coatings, the maximum decrease in hardness is observed only in the case of simulation of high-temperature gas corrosion processes for which the decrease in ∆H is 7.3 % and 4.5 %, respectively. In the case of samples subjected to thermal heating and hydrogenation (separately), the maximum decrease in ∆H was no more than 1 %, which is within the permissible error.
Figure 4. Results of the strength characteristics of the studied samples: a) change in hardness; b) change in the adhesive strength of the coatings under study.

Figure 4b reveals the assessment results of the value of critical load leading to separation of the coating from the surface of the steel, which characterizes the adhesive strength of the coatings and adhesion to the surface of the substrate (in this case, steel). As can be seen from the data presented, the most pronounced changes in the reduction in adhesive strength are observed for samples of AlN and Al – O – N coatings subjected to high-temperature gas corrosion tests, after which the reduction is about 8.6 % and 5.8 %, respectively. In the case of other types of external influences (thermal heating and hydrogenation), the decrease in adhesive strength is less than 1 %, which indicates a fairly high resistance of AlN and Al – O – N coatings to external influences that can result in destruction and peeling them from the substrate surface. Analyzing the data obtained, we can conclude that the use of AlN and Al – O – N coatings as protective anti-corrosion coatings opens up the possibility of using them not only for protection against high-temperature oxidation (under prolonged thermal exposure), but also against processes associated with gas corrosion (hydrogenation), as well as high-temperature gas corrosion, which is the most dangerous for steel structures, due to the fact that the destruction processes in this case are associated with both hydrogen agglomeration and oxidation processes (oxide formation) as a result of thermal heating.

Conclusion

During the studies, the dependences of changes in the strength and tribological parameters of the studied AlN and Al – O – N coatings used to protect steel from corrosion were established. The experiments were carried out considering the maximum approximation to the actual operating conditions of steel in the case of exposure to gaseous media and high temperatures. Analysis of the morphological features of the studied steel and coating samples depending on the type of external influences (temperature heating, hydrogenation) reflects changes associated with the formation of hillock-like inclusions in the form of gas-filled cavities, the presence of which results in deformation embrittlement and partial peeling of the surface (for steel after simulation of superhydrogenation processes), and in the case of coatings with an increased density of gas-filled inclusions, associated with diffusion and migration processes leading to hydrogen agglomeration in gas-filled cavities.

During experiments carried out related to the determination of degradation processes and their influence on changes in strength properties and wear resistance, it was found that long-term thermal annealing of samples after hydrogenation leads to an acceleration of destruction processes (embrittlement, a decrease in strength and wear resistance), which indicates that the presence of hydrogen in the composition of the near-surface layer due to thermal expansion of the crystalline structure of the damaged layer leads to accelerated agglomeration of hydrogen into gas-filled bubbles, which leads to an increase in deformation distortions and destabilization of the strength properties of the material.

The observed hardening effect for Al – O – N coatings, which also results in a growth in resistance to high-temperature gas corrosion, is due to the effect of filling the interstitial space with oxygen, which leads to a strengthening of the structure of the coatings, as well as an increase in the number of structural distortions of the crystal lattice, which in turn prevents the processes of oxidation (during high-temperature heating) and hydrogenation with the subsequent formation of gas-filled bubbles.
In conclusion, it should be noted that further research of these coatings will focus on the potential application of AlN and Al – O – N coatings as anti-corrosion coatings to protect against the negative impact of aggressive media, in particular, NaCl, HCl with different concentrations. The aim of such research will be to increase the possibilities of using these coatings for protection against external influences.


**Conflicts of Interest:** The authors declare no conflicts of interest.

**Funding:** This research was carried out with the financial support of the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan (BR21881822 Development of technological solutions for optimizing geological and technical operations when drilling wells and oil production at the late stage of field exploitation, 2023-2025).

**References**