Protection of carbon steel against corrosion with a superhydrophobic coating

ABSTRACT

Under atmospheric conditions at 100% humidity, a surface phase film of moisture is formed on the surface of metals, in which air microimpurities NH₃, CO₂, H₂S, etc. are dissolved and almost completely hydrated with the formation of NH₄OH and acids H₂CO₃ and H₂S. The method of potentiodynamic polarization has been used to study the protective efficiency of a superhydrophobic coating on carbon steel in NaCl-based model media simulating saturation of the surface moisture film with carbon dioxide (IV) and/or ammonia under atmospheric conditions. Similar studies were carried out with uncoated electrodes. The superhydrophobic coating was obtained on the basis of laser texturing of the steel surface followed by hydrophobization with fluoroxy silane (wetting angle 165±2°, rolling angle 3±1°). The influence of the duration of exposure of electrodes in solution (0.25 - 168 h) on the kinetics of electrode processes, the rate of steel corrosion and the protective effectiveness of the superhydrophobic coating is considered. It has been shown that the presence of ammonium hydroxide or ammonia carbonate in solution increases the protective effectiveness of the coating compared to a purely chloride medium simulating harsh atmospheric conditions.

Keywords: carbon steel, corrosion, protection, superhydrophobic coating, contact angle, ammonia, carbon dioxide (IV), potentiodynamic polarization.

1. INTRODUCTION

Atmospheric corrosion of metals and alloys often occurs in the presence of aggressive components in the atmospheric air that are corrosion stimulants (in addition to oxygen), which can be, in particular, SO₂, H₂S, CO₂, NH₃, etc. They can be present in the atmosphere due to, for example, technological processes for the processing of metal sulfides (SO₂ and H₂S), the operation of livestock complexes (NH₃, CO₂ and H₂S), etc. This leads to high corrosive aggressiveness of the air environment, especially under conditions of relative air humidity close to 100%. At 100% humidity, a surface phase moisture film is formed on the surface of metals, in which air microimpurities NH₃, CO₂, H₂S dissolve and are almost completely hydrated with formation of NH₄OH and acids H₂CO₃ and H₂S.

A variety of coatings are used to protect metals against atmospheric corrosion: metal, polymer, paint and varnish, bituminous, oil-based, etc. Over the past two decades, intensive research has been carried out on the anticorrosion protective properties of hydrophobic and superhydrophobic coatings, characterized by a contact angle of wetting θ ≥ 150° [1-4]. Particular attention is paid to the application of protective films of superhydrophobizators, which make it possible to increase the contact angle to 165–171. One of the main mechanisms of the protective action of such coatings under conditions of electrochemical corrosion is related to prevention of supply of water molecules necessary for occurrence of partial electrode reactions to the metal surface. To form superhydrophobic coatings on metals, it is necessary to create a multimodal surface roughness followed by the deposition of hydrophobic materials with low surface energy [5,6]. Fluoroxy silanes, fluorocarbons, organic acids and amines with a long hydrocarbon chain, etc. are used as hydrophobic materials. Usually, the protective efficiency of such coatings is studied in a neutral chloride medium (3% NaCl solution [2,7,8]). The
rate of electrochemical corrosion is determined on the basis of polarization curves. The possibility of measuring the polarization curves on metals with a superhydrophobic coating indicates that the contact of a metal surface with the electrolyte solution is not completely ruled out. A number of studies states that the hydrophobic and superhydrophobic surface films are not continuous and the total fraction of the wetted area can reach 10% [4,7]. An electric double layer along the wetted area at the metal/solution interface invokes the electrochemical corrosion.

The aim of this work is to evaluate the protective effectiveness of a superhydrophobic coating based on fluoroxyisilane on carbon steel in a chloride medium containing ammonium hydroxide or ammonium carbonate, simulating the saturation of the surface moisture film with carbon dioxide (IV) and/or ammonia under atmospheric conditions.

2. EXPERIMENTAL

The studies were carried out on St3 carbon steel with a chemical composition, mass %: C – 0.20; Mn – 0.50; Si – 0.15; P – 0.04; S – 0.05; Cr 0.31; Ni – 0.23; Cu – 0.21; Fe – rest. A superhydrophobic coating was applied to the surface of steel electrodes in the Laboratory of Surface forces at the Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences. To obtain a coating, the St3 working surface was textured with a nanosecond IR laser [1].

To impart superhydrophobic properties to the surface, the surface energy of the formed texture was lowered by chemisorption of the 

\[
(CF_3)(CF_2)\_d(CH_2)\_dO(CH_2)\_dC(OCH_3)\_d
\]

hydrophobizing agent from the vapor phase, followed by drying of the resulting coating at 130°C for 1 hour. The wetting angle on the obtained superhydrophobic samples was 165±2°, and the rolling angle for droplets with a volume of 15 μL was 3±1°. The samples under study (due to design features: the samples were pressed into a fluoroplastic frame with a visible area of the working surface close to 0.5 cm²) were not treated with ultraviolet irradiation in the presence of ozone plasma. Such treatment leads to an increase in the number of chemisorption-active centers in the form of hydroxyl or carboxyl surface groups and promotes the chemisorption of a hydrophobic agent on them [9].

NaCl solution (50 g/L) was used as a background electrolyte. The chloride environment corresponds to the most severe conditions of atmospheric corrosion. The effect of the presence of NH₄OH in the air was simulated by adding 400 mg/L NH₄OH to the background solution. The effect of the combined presence of metal corrosion promoters NH₄OH and CO₂ in the air was modeled by adding (NH₄)₂CO₃ salt (analytical grade) to the background solution at a concentration of 400 mg/L. Such a salt is formed by the interaction of NH₄OH and H₂CO₃, formed by the dissolution of NH₃ and CO₂ in a moisture film. Polarization potentiodynamic (potential scan rate of 0.66 mV/s) curves were measured on electrodes without and with a protective coating using an IPC-Pro MF potentiostat (produced at the Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences). The potentials were measured relative to a saturated silver-silver chloride reference electrode and were recalculated to the standard hydrogen scale. The counter electrode is smooth platinum. The studies were carried out at room temperature in a three-electrode cell with separated anode and cathode spaces. The polarization curves were measured 15 minutes after the electrodes had been immersed in the solution and every 24 hours for 168 hours without removing the electrodes out of the solution. Corrosion currents (iₜₐᵣ₉) were calculated by extrapolating the Tafel sections of the polarization curves to the corrosion potential. The protective effect of the hydrophobic coating was calculated by the formula:

\[
Z, \% = \frac{(i_{Cor} - i_{Cor0})}{i_{Cor0}}
\]

where \(i_{Cor,0}\) and \(i_{Cor}\) are the electrochemical corrosion rates in the absence and in the presence of the superhydrophobic coating respectively.

The contact angles (θ) were measured using a tensiometer (EASYDROP, KRUSS, Germany).

3. RESULTS AND DISCUSSION

Medium with NH₄OH

Steel with a superhydrophobic coating, both in an environment with NH₄OH and in its absence, is characterized by a significantly higher value of the corrosion potential \(E_{Cor}\) after 0.25 h of exposure than in the absence of a coating (Figure 1). In both cases, the anodic process is inhibited for the coated electrode compared to the unprotected electrode.

The corrosion current on a hydrophobic electrode in the presence of NH₄OH is 50 times, and in its absence, 67 times less than that on an uncoated electrode. In time, the corrosion potentials of the electrodes shift in the negative direction and converge for electrodes with and without coating. In a purely chloride medium, after 72 h of exposure, the \(i_{Cor}\) values for coated and uncoated electrodes became almost the same (Figure 2a, Table 1), and in the presence of NH₄OH, \(i_{Cor}\) for the electrode with superhydrophobic coating was 7 times less (Table 2). With a further increase
in the exposure time, \( i_{\text{cor}} \) for a hydrophobic electrode in a chloride solution becomes even higher than that for an unprotected one (Table 1), and in the presence of ammonia, even after 168 hours, the corrosion rate of a hydrophobic electrode is 5 times lower (Table 2).

![Polarization curves](image)

**Figure 1.** Polarization curves measured on a steel electrode without (1) and with a superhydrophobic coating (2) after exposure for 0.25 h to NaCl (a) and NaCl + NH\(_4\)OH (b) solutions

**Slika 1.** Polarizacione krive merene na čeličnoj elektrodi bez (1) i sa superhidrofobnom prevlakom (2) posle izlaganja rastvorima NaCl (a) i NaCl + NH\(_4\)OH (b) u trajanju od 0.25 h

![Polarization curves](image)

**Figure 2.** Polarization curves measured on a steel electrode without (1) and with a superhydrophobic coating (2) after exposure to NaCl solution for 72 h (a) and NaCl + NH\(_4\)OH medium for 168 h (b)

**Slika 2.** Polarizacione krive merene na čeličnoj elektrodi bez (1) i sa superhidrofobnom prevlakom (2) posle izlaganja rastvoru NaCl tokom 72 h (a) i medijumu NaCl + NH\(_4\)OH 168 h (b)

**Table 1.** Kinetic parameters of the St3 electrode with and without a superhydrophobic coating and the protective effect of the coating (Z,\%) in a 50 g/L NaCl medium

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Without coating</th>
<th>With coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duration, h</td>
<td>( b_a, V )</td>
<td>( b_c, V )</td>
</tr>
<tr>
<td>0.25</td>
<td>0.038</td>
<td>0.075</td>
</tr>
<tr>
<td>24</td>
<td>0.044</td>
<td>0.031</td>
</tr>
<tr>
<td>48</td>
<td>0.058</td>
<td>0.034</td>
</tr>
<tr>
<td>72</td>
<td>0.042</td>
<td>0.039</td>
</tr>
<tr>
<td>96</td>
<td>0.036</td>
<td>0.027</td>
</tr>
</tbody>
</table>

*S- Stimulation
Corrosion of steel is limited by the anodic process. The protective effect of the coating (Z,%) in a 50 g/L NaCl + 400 mg/L NH₄OH medium is durable than in the presence of ozone plasma before hydrophobization, the superhydrophobic coating studied in a chloride medium turned out to be less effective than in the presence of such a treatment [9]. The bond of the hydrophobic layer with the substrate when the electrode was immersed in the chloride medium was weakening over time, and after 72 hours rather large areas with a damaged coating and a contact angle reduced to 80° were formed, where corrosion products were clearly fixed.

Accordingly, the protective effect (Z,%) of the hydrophobic coating in a chloride medium disappears after 72 hours, and in an environment with NH₄OH, the value of Z is equal to 80% even after 168 hours(Table 2). Figure 3 shows the photographs of water droplets on the surface of a hydrophobic electrode after 72 hours of exposure to a NaCl solution, from which it can be seen that the contact angle remains greater than 90° on some parts of the surface, and on others it is less than 90°. The latter indicates metal corrosion on certain areas.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Without coating</th>
<th>With coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duration, h</td>
<td>( b_o, V )</td>
<td>( b_o, V )</td>
</tr>
<tr>
<td>0.25</td>
<td>0.032</td>
<td>0.100</td>
</tr>
<tr>
<td>24</td>
<td>0.030</td>
<td>0.020</td>
</tr>
<tr>
<td>48</td>
<td>0.035</td>
<td>0.020</td>
</tr>
<tr>
<td>72</td>
<td>0.030</td>
<td>0.035</td>
</tr>
<tr>
<td>96</td>
<td>0.029</td>
<td>0.024</td>
</tr>
<tr>
<td>168</td>
<td>0.034</td>
<td>0.024</td>
</tr>
</tbody>
</table>

In the absence of NH₄OH already after 48 hours and, moreover, with a longer exposure, the anodic process is facilitated on a hydrophobic electrode compared to an uncoated electrode. In the presence of NH₄OH, an electrode with a superhydrophobic coating is characterized by inhibition of the anodic process compared to an unprotected electrode during the entire exposure time (Figure 2b). Apparently, in a chloride environment, the aggressive chloride ions contribute to an increase in the number of wetted areas, the development of a corrosion process, and the rapid degradation of the protective properties of the superhydrophobic coating. In the latter case, corrosion products are visualized on the surface. Obviously, due to the absence of electrode treatment by ultraviolet radiation, the presence of ozone plasma before hydrophobization, the superhydrophobic coating studied in a chloride medium turned out to be less effective than in the presence of such a treatment [9]. The bond of the hydrophobic layer with the substrate when the electrode was immersed in the chloride medium was weakening over time, and after 72 hours rather large areas with a damaged coating and a contact angle reduced to 80° were formed, where corrosion products were clearly fixed.

The presence of ammonium hydroxide in the chloride solution reduces its aggressiveness towards an electrode with a superhydrophobic coating. It can be assumed that in the absence of sodium chloride in the solution and in the presence of only ammonium hydroxide in the moisture film on the surface, the superhydrophobic coating on steel will be characterized by a sufficiently high protective efficiency for a long time.

It follows from the Figures and tables that the Tafel coefficients of the slope of the anodic polarization curves \( b_o \) change little with increasing exposure time of the electrodes in the solution and are close for electrodes with and without coatings. For the cathode curves, however, the values of \( b_c \) decrease sharply after a daily exposure and remain low throughout the subsequent period for both types of electrodes.

Medium with \((\text{NH}_4)_2\text{CO}_3\)

Steel with a superhydrophobic coating after 0.25 h immersion in the solution has a corrosion potential 400 mV more positive than that of an uncoated electrode (Figure 4). The anodic process on the electrode with coating is inhibited compared to the unprotected electrode, as it is observed in the NaCl solutions in the absence and presence of NH₄OH (Figs. 1 and 2). And the cathodic process of oxygen depolarization, on the contrary, is facilitated in comparison with unprotected steel (Figure 4). Corrosion current of steel with the superhydrophobic coating is reduced by 36 times. Corrosion of steel is limited by the anodic process.
Figure 4. Polarization curves measured on a steel electrode without (1) and with superhydrophobic coating (2) after exposure for 0.25 h to 50 g/L NaCl + 400 mg/L (NH₄)₂CO₃ solution

Slika 4. Polarizacione krive merene na čeličnoj elektrodi bez (1) i sa superhidrofobnom prevlakom (2) posle izlaganja 0,25 h u 50 g/L NaCl + 400 mg/L (NH₄)₂CO₃ rastvora

Figure 5. Polarization curves measured on a steel electrode without (1) and with superhydrophobic coating (2) after exposure for 24 h to 50 g/L NaCl + 400 mg/L (NH₄)₂CO₃ solution

Slika 5. Polarizacione krive merene na čeličnoj elektrodi bez (1) i sa superhidrofobnom prevlakom (2) posle izlaganja tokom 24 h u 50 g/L NaCl + 400 mg/L (NH₄)₂CO₃ rastvora
Table 3. Kinetic parameters of the St3 electrode with and without a superhydrophobic coating and the protective effect of the coating (Z, %) in a 50 g/L NaCl + 400 mg/L (NH₄)₂CO₃ medium

<table>
<thead>
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<th>Parameter</th>
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<tr>
<td>Duration, h</td>
<td>bₐ, V</td>
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</tr>
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<td>0.25</td>
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<tr>
<td>168</td>
<td>0.035</td>
<td>0.041</td>
</tr>
</tbody>
</table>

After a 24-hour exposure of the electrode with a protective coating to the same corrosive environment, the corrosion potential is drastically reduced, taking on the value -0.436 V. $E_{cor}$ of unprotected steel is reduced less significantly (-0.567 V) (Figure 5, Table 3). The corrosion rate of an uncoated electrode nearly halves, whereasthat of protected electrode, being an order of magnitude lower, becomes twice as much. On the next day, the corrosion potential of both electrodes continues to decrease slightly (Table 3), but for the superhydrophobized electrode it keeps at 120 mV on both the second and third days, and on the fourth and seventh days becomes 47-54 mV i.e. less negative.

The corrosion rate of the protected electrode on the second and third days is approximately an order of magnitude, and on the fourth and seventh days it is more than an order of magnitude lower than that of the unprotected one. During the entire time of exposure of the electrodes to the solution, the anodic process on the superhydrophobic electrode is inhibited in comparison with the unprotected electrode. The cathodic process is facilitated during 3 days, on the fourth and seventh days it is inhibited in comparison with the cathodic process on an uncoated electrode (Figure 6).

Figure 6. Polarization curves measured on a steel electrode without (1) and with superhydrophobic coating (2) after exposure for 96 h to 50 g/L NaCl + 400 mg/L (NH₄)₂CO₃ solution

Slika 6. Polarizacije krive merene na čeličnoj elektrodi bez (1) i sa superhidrofibnom prevlakom (2) nakon 96 h izlaganja u 50 g/L NaCl + 400 mg/L (NH₄)₂CO₃ rastvora
Apparently, the inhibition of the anodic and cathodic processes simultaneously on the 4th–7th days determines the decrease in \( I_{\text{cor}} \) compared to the previous day. Obviously, the areas of the surface of the hydrophobic electrode activated on the second and third days turned out to be partially healed with sparingly soluble corrosion products (most likely, iron carbonate) over time, which led to a decrease in the corrosion rate.

As noted above, in a chloride environment without additives, after 15 minutes of exposure, the coated electrode has a 67 times lower corrosion rate than the unprotected electrode (Table 1). Approximately half (36 times) the difference in corrosion rates is observed at the initial moment in the presence of \((\text{NH}_4)_2\text{CO}_3\) (Table 3). However, over time, this difference in the chloride environment rapidly decreases. So, after 24 hours, \( I_{\text{cor}} \) of the hydrophobic electrode is 13 times lower, after 48 hours, 2 times, after 72 hours their rates are the same, and after 96 hours, the corrosion rate of the coated electrode is 3 times higher (Table 1).

In the presence of \((\text{NH}_4)_2\text{CO}_3\) in a chloride solution, the corrosion current of an unprotected electrode is approximately the same order as in the absence of an additive. The corrosion current of the coated electrode after 15 min of exposure is 1.5 times higher, after 24 hours it is about the same order, after 48–72 hours it is 5 times, and after 96 hours it is almost 100 times lower than that in the solution without the additive of carbonate (Table 1). As noted above, the reason for this is related to the protective properties of carbonate corrosion products that heal the wetted areas on the hydrophobic electrode. Thus, the presence of ammonium carbonate reduces the aggressiveness of the chloride solution towards the superhydrophobic coated electrode. It can be assumed that in the absence of sodium chloride in the solution, the superhydrophobic film on the steel surface will be characterized by a sufficiently high protective efficiency.

Comparison of the protective properties of a superhydrophobic coating in media with \(\text{NH}_4\text{OH}\) or \((\text{NH}_4)_2\text{CO}_3\) shows that after 15 minutes of exposure to a solution, the corrosion current in a carbonate medium is about 2 times higher, and over time, on the contrary, it becomes much lower and, for example, after 168 hour it is 7 times lower. Comparison of the values of the protective effectiveness of the superhydrophobic coating shows that it is noticeably higher in a carbonate environment (Tables 2 and 3). Obviously, the healing of wetted areas in the superhydrophobic coating with iron carbonate contributes to its higher protective efficiency than in the presence of \(\text{NH}_4\text{OH}\). This is also evidenced by the fact that the corrosion current in solutions with \(\text{NH}_4\text{OH}\) increases over time, while in a carbonate medium, on the contrary, it decreases (Tables 2 and 3).

4. CONCLUSION

1. The protective effectiveness of a superhydrophobic coating on carbon steel was studied under conditions simulating an atmosphere with 100% humidity and the presence of impurities of corrosive gases \(\text{CO}_2\) and/or \(\text{NH}_3\), using a sodium chloride solution (50 g/L) containing ammonium carbonate or ammonium hydroxide. The chloride environment corresponds to the most severe conditions of atmospheric corrosion.

2. The presence of ammonium hydroxide in the chloride solution contributes to a higher protective efficiency of the superhydrophobic coating on the steel electrode, which reaches 80% after 168 hours of exposure, compared with a pure chloride environment, where the protective effect of the coating disappears after 72 hours.

3. Saturation of the chloride solution with aggressive air components \(\text{NH}_3\) and \(\text{CO}_2\) contributes to a higher protective efficiency of the superhydrophobic coating on the steel electrode compared to the environment without additives.

4. The protective properties of the superhydrophobic coating in a medium with ammonium carbonate turned out to be higher than in a medium with ammonium hydroxide, which is associated with the possibility of healing wetted areas in the coating with iron carbonate formed during iron ionization in these places.

Acknowledgments

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5. REFERENCES

IZVOD

ZAŠTITA UGLJENIČNOG ĆELIKA OD KOROZIJE SUPERHIDROFOBNIM PREMAZOM

U atmosferskim uslovima pri 100% vlaznosti na površini metala se formira površinski fazni film vlage u kome se rastvore iskoro potpuno hidriraju vazdušne mikro nečistoće NH₃, CO₂, H₂S itd. U atmosferskim uslovima pri 100% vlaznosti, na površini metala se formira površinski fazni film vlage u kome se nalaze mikro nečistoće vazduha NH₃, CO₂, H₂S itd., koje se rastvore i skoro potpuno hidratiraju sa stvaranjem NH₄OH i kiselina H₂CO₃ i H₂S. Metoda potenciodinamičke polarizacije je korisnaca za proučavanje zaštitne efikasnosti superhidrofobne prevlake na ugljeničnom čeliku u modelnom mediju na bazi NaCl koji simulira zasićenje filma površinske vlage ugljen-dioksidom (IV) i/ili amonijakom u atmosferskim uslovima. Superhidrofobni premaz je dobijen na osnovu laserskog tekstuiranja čelične površine praćene hidrofobizacijom fluoroalkiliranom (ugao vlaženja 165±2°, ugao kotriljanja 3±1°). Razmatran je uticaj trajanja izlaganja elektroda u rastvoru (0,25 - 168 h) na kinetiku elektrodnih procesa, brzinu korozije čelika i zaštitnu efikasnost superhidrofobnog premaza. Pokazalo se da prisustvo amonijum hidroksida ili amonijumkarbonata u rastvoru povećava zaštitnu efikasnost premaza u poređenju sa čisto hloridnim međumom koji simulira oštare atmosferske uslove.

Ključnici: ugljenični čelik, korozija, zaštita, superhidrofobni premaz, kontaktni ugao, amonijak, ugljen-dioksid (IV), potenciodinamička polarizacija.

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