Protection of steel with a superhydrophobic coating against atmospheric corrosion in conditions of livestock buildings

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Abstract

Superhydrophobic coatings were obtained by texturing the steel surface with a nanosecond IR laser followed by treatment with ultraviolet radiation in the presence of ozone plasma. Further, hydrophobization was carried out using the methoxy{3-[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)oxy]propyl}silane hydrophobizing agent. The contact angle on the obtained samples was $172.6 \pm 1.2^\circ$. Corrosion tests of St3 steel samples without and with a superhydrophobic coating were carried out in an atmosphere with 100% humidity and the presence of corrosion stimulants CO₂, H₂S and NH₃ in pairs and simultaneously all three in the maximum permissible concentrations for livestock buildings. After 100 days of exposure of the samples in the atmospheres under study the contact angle decreased to 167–162°. Such a slight decrease in the contact angle indicates the high protective properties of the superhydrophobic coating. There were no corrosion losses in samples with a superhydrophobic coating; on the contrary, an insignificant weight gain was observed. Under conditions of 100% humidity, a moisture film forms on the surface of the samples, in which gases present in the atmosphere dissolve and hydrolyze. In this case, solutions of H₂S, H₂CO₃, NH₄OH are formed. The presence of these substances on the surface contributes to the formation of insoluble corrosion products in the pores of the coating, which leads to an insignificant weight gain of the samples. At the same time, steel samples without a protective coating underwent intense corrosion.

Keywords: *atmospheric corrosion, steel, protection, superhydrophobic coating, corrosion stimulants, contact angle.*

Received: November 12, 2021. Published: November 24, 2021

doi: [10.17675/2305-6894-2021-10-4-16](https://doi.org/10.17675/2305-6894-2021-10-4-16)

Introduction

Atmospheric corrosion of metals and alloys often occurs in the presence of aggressive components in the atmospheric air that are corrosion stimulators (CS) (in addition to

oxygen), which can be, in particular, SO₂, H₂S, CO₂ and NH₃. They are 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). Moreover, according to the standards for livestock buildings, the permissible concentrations of hydrogen sulfide and ammonia can reach 10 mg/m³ and 20 mg/m³, respectively (the concentration of CO₂ is not standardized). This leads to a highly corrosive air environment, especially if the relative humidity (H) is close to 100%.

Over the past two decades, abroad and in Russia, an intensive study of hydrophobization and superhydrophobization of surfaces has been carried out to protect metals against corrosion in corrosive environments. The effect of coatings increasing the contact angle of wetting with water to $\geq 150^\circ$ is considered. Much attention is paid to the application of protective films of superhydrophobizing agents, which make it possible to increase the contact angle to 165–171°. The research results are summarized in a number of reviews [1–4]. To form superhydrophobic coatings on metals, it is necessary to create a multimodal surface roughness followed by the application of hydrophobic materials with low surface energy. Various methods are used to create surface roughness, such as chemical etching [5], chemical vapor deposition [6], nanosecond laser surface treatment [7], *etc.* Fluoroxysilanes, fluorocarbons, organic acids and amines with a long hydrocarbon chain, *etc.* are used as hydrophobic materials.

Usually, the protective effectiveness of such coatings is studied in a neutral chloride solution, a salt fog chamber, or under conditions of 100% humidity [8, 9].

Earlier, we carried out gravimetric corrosion tests of St3 carbon steel samples with a superhydrophobic coating based on methoxy{3-[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)oxy]propyl}silane for 112 days under conditions of 100% humidity [10]. Corrosion losses were absent, the contact wetting angle after the experiment had the same value as before the start of the experiment (172°).

The aim of this work is to evaluate the protective effectiveness of superhydrophobic coatings on carbon steel in the presence of high concentrations of aggressive components NH₃, CO₂ and H₂S in the air under conditions of 100% humidity.

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.

Superhydrophobic coatings based on the methoxy-{3-[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)oxy]propyl}silane hydrophobizator were 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 according to the method described in [10]. The wetting angle on the obtained superhydrophobic samples was $172.6 \pm 1.2^\circ$, the roll-off angle was $2.5 \pm 1^\circ$.

Gravimetric corrosion tests of steel samples with and without a superhydrophobic coating were carried out in sealed desiccators, in which the specified concentrations of the corrosion stimulants under study were created at 100% humidity according to [11].

Before and after exposure of the coated samples under the specified conditions, the wetting angles were measured at 3–5 different points on the surface for the distilled water droplets with volume 2–3 μL using a tensiometer (Easy Drop, KRUSS, Germany). Moreover, the samples were preliminarily washed with bidistillate, blotted with filter paper and kept in air for an hour before weighing and measuring the contact angle. A scanning electron microscope (JSM 6390, JEOL, Japan) was used to assess the condition of the coating surface.

Results and Discussion

The structure of the initial superhydrophobic surface of the steel sample is shown in Figure 1. Multilevel roughness is clearly visible.

Figure 1. SEM images of the initial surface of steel with superhydrophobic coating.

Corrosion tests of steel samples with and without a protective coating were carried out in an atmosphere with 100% humidity in the presence of two stimulants (CO_2 and H_2S ; NH_3 and H_2S and CO_2 and NH_3) and simultaneously all three in maximum permissible concentrations for livestock buildings. Table 1 shows the corrosion rates of unprotected steel samples under the specified conditions, and in Figure 2 the appearance of the samples after testing is shown.

Table 1. Corrosion rates of St3 steel without coating in the presence of CSs NH_3 , H_2S and CO_2 in concentrations equal to 20 mg/m^3 , 10 mg/m^3 and 0.2 vol.%, respectively, at 100% relative humidity.

Conditions	$\text{CO}_2 + \text{H}_2\text{S}$ $\tau = 106$ days	$\text{CO}_2 + \text{NH}_3$ $\tau = 106$ days	$\text{NH}_3 + \text{H}_2\text{S}$ $\tau = 97$ days	$\text{CO}_2 + \text{H}_2\text{S} + \text{NH}_3$ $\tau = 97$ days
K , $\text{g}/(\text{m}^2\text{h})$	0.0233	0.0396	0.0049	0.0081

As can be seen from Figure 2, steel samples in the presence of corrosion stimulants under conditions of 100% humidity undergo significant corrosion.

The degradation of the superhydrophobic coating during exposure to an aggressive environment can be judged by the change in the wetting angle value, since it is determined by the structure and state of the surface layer [8]. Figure 3 shows the changes in time of the values of the wetting angles under different conditions of the experiment.

Figure 2. Appearance of St3 steel samples after exposure to 100% humidity in the presence of $\text{CO}_2 + \text{H}_2\text{S}$ (1), $\text{CO}_2 + \text{NH}_3$ (2), $\text{NH}_3 + \text{H}_2\text{S}$ (3), $\text{CO}_2 + \text{H}_2\text{S} + \text{NH}_3$ (4). Duration of tests, days: 1 and 2 – 106; 3 and 4 – 97.

Figure 3. Change in time of the contact angle of wetting of a superhydrophobic coating on a steel electrode after holding it under conditions of 100% humidity in the presence of $\text{CO}_2 + \text{H}_2\text{S}$ (1), $\text{CO}_2 + \text{NH}_3$ (2), $\text{NH}_3 + \text{H}_2\text{S}$ (3), $\text{CO}_2 + \text{H}_2\text{S} + \text{NH}_3$ (4). Test duration, days: 1 and 2 – 106; 3 and 4 – 97.

In the first 10–30 days, a decrease in the contact angle value is observed in atmospheres containing hydrogen sulfide. The smallest decrease is typical for the atmosphere with $\text{CO}_2 + \text{H}_2\text{S}$ – about 3° , the largest – about 10° – in atmospheres with $\text{NH}_3 + \text{H}_2\text{S}$ and

$\text{CO}_2 + \text{H}_2\text{S} + \text{NH}_3$. But by 50 days, the contact angle increases to 169° in the first case and 167° in the last two, reaching within 100 days the values of 162° in the atmosphere with $\text{CO}_2 + \text{H}_2\text{S}$ and $165\text{--}166^\circ$ in atmospheres with $\text{NH}_3 + \text{H}_2\text{S}$ and $\text{CO}_2 + \text{H}_2\text{S} + \text{NH}_3$. Images of water droplets on the surface of the samples at different time intervals are shown in Figure 4–7.

Figure 4. Images of water droplets on the surface of a superhydrophobic coating at different times of exposure of the samples in an atmosphere with CO_2 and H_2S under 100% humidity conditions.

Figure 5. Images of water droplets on the surface of a superhydrophobic coating at different times of exposure of the samples in an atmosphere with NH_3 and CO_2 under 100% humidity conditions.

Figure 6. Images of water droplets on the surface of a superhydrophobic coating at different times of exposure of the samples in an atmosphere with NH_3 and H_2S under 100% humidity conditions.

Figure 7. Images of water droplets on the surface of a superhydrophobic coating at different times of exposure of the samples in an atmosphere with $\text{CO}_2 + \text{NH}_3 + \text{H}_2\text{S}$ under 100% humidity conditions.

Under conditions of 100% humidity, a moisture film forms on the surface of the samples, in which the gases present in the atmosphere dissolve and hydrolyze. In this case, a solution of H_2S and H_2CO_3 is formed in an atmosphere with $\text{CO}_2 + \text{H}_2\text{S}$. In an atmosphere with $\text{NH}_3 + \text{H}_2\text{S}$, the resulting solutions of NH_4OH and H_2S upon interaction should form the salt $(\text{NH}_4)_2\text{S}$, which is almost completely hydrolyzed due to the fact that it is formed by a weak base and a weak acid, with the appearance of the starting compounds. Similarly, in an atmosphere with $\text{NH}_3 + \text{CO}_2$, NH_4OH and H_2CO_3 are present in the moisture film. In an atmosphere with $\text{CO}_2 + \text{H}_2\text{S} + \text{NH}_3$, $(\text{NH}_4)_2\text{S}$ and $(\text{NH}_4)_2\text{CO}_3$ are formed, which are also completely hydrolyzed to form two weak acids and a weak base.

The initial decrease in the contact angle in media containing H_2S is apparently associated with the activating effect of hydrogen sulfide in the pores of the coating (wetted areas on the superhydrophobic surface, the proportion of which can reach 10% [8]), but later the formation of poorly soluble iron sulfide occurs, partially healing defects. The contact angles that persist after 100 days of exposure, exceeding 160° , indicate a good protective

effectiveness of the investigated superhydrophobic coatings in the presence of corrosion stimulants in maximum permissible concentrations. This is consistent with the data obtained on the basis of polarization measurements on the electrodes with a superhydrophobic coating in NaCl solutions with $(\text{NH}_4)_2\text{S}$ or $(\text{NH}_4)_2\text{CO}_3$ additives [12].

In an atmosphere with $\text{CO}_2 + \text{NH}_3$, the smallest decrease in the contact angle value over time is observed, and it is monotonous. By day 100, it has a value of about 167° (Figure 4). This is apparently due to the minimal activating effect of NH_4OH and H_2CO_3 with respect to the coating.

Weighing the electrodes with a superhydrophobic coating before and after exposure under appropriate conditions showed that there are no corrosion losses, on the contrary, an insignificant weight gain is observed. In the atmosphere with $\text{CO}_2 + \text{H}_2\text{S}$, in the first 14 days, the weight gain of the coated samples is observed by 0.0005–0.0006 g, after 106 days – by 0.0053–0.0054 g due to the formation of insoluble sulfide products. After washing and drying the surface, the contact angle was at least 160° . In an environment with $\text{CO}_2 + \text{NH}_3$, the picture with the weight gain is similar. In the presence of $\text{NH}_3 + \text{H}_2\text{S}$, the weight gain of the samples is practically absent during the entire test period; in the presence of all three stimulants, the weight gain of the samples is not more than 0.0001 g during the entire period.

Conclusion

A superhydrophobic coating formed on the surface of St3 steel samples based on a fluorooxysilane and characterized by a contact angle of about $172.6 \pm 1.2^\circ$ fully protects the metal against corrosion for 100 days in an atmosphere with 100% humidity and the presence of CO_2 , H_2S and NH_3 corrosion stimulants in pairs and simultaneously all three in maximum permissible concentrations.

At the same time, the contact angle of wetting with water remains in the range of 167 – 162° , depending on the type of stimulants present.

Steel samples unprotected by the coating underwent intense corrosion under the investigated conditions.

Acknowledgments

This work was supported by the Ministry of Science and Higher Education of the Russian Federation in the framework of agreement No. 075-15-2021-709 (unique project identifier RF-2296.61321X0037).

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