Nanobarrier coating for elements of gas chromatograph

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Abstract. In this paper, we consider a method of protecting the surface of the components of a gas analytical system from corrosion and adsorption of sulfur-containing compounds. To solve this problem in the oil and gas industry, in particular in industrial analytical equipment, silicon coatings are used that are inert with respect to the measured substances. Based on the analysis, the regularity of the formation of films of silicon films obtained by plasma-chemical deposition (PECVD) on stainless steel products was investigated.

1. Introduction

It is known that high concentrations of corrosive substances lead to corrosion with tangible economic consequences, such as the failure of the contacting elements - filters, regulators, sampling containers, analyzer tubes. Despite its properties, stainless steel corrodes. When analyzing the composition of natural gas according to State Standard 31371-2008 [1], a gas chromatograph is used, the analytical path of which consists of stainless steel elements (stop and control valves, fittings, sample introduction device, capillaries).

The corrosive environment causes the degradation of both the column material and the stationary phase. When gas contains water, oxygen, acid oxides, hydrogen sulfide, mercury or mercaptans, a number of serious problems arise related to the nature of steel. The considered compounds actively react with steel both by themselves and in various combinations, depending on concentrations, cause various problems. When analyzing low concentrations of moisture - in units of ppm, or dew points (below -60 °C), adsorption becomes a serious problem. Steel is a hydrophilic material capable of accumulating firmly held water films on its surface. This leads to the fact that the in-line analysis of gas humidity becomes inertial - stabilization of readings can take hours. The mercury content in the gas is the cause of the amalgamation, as a result of which the analyzes become unsuitable. In the case of accumulation of mercury in the nodes of analytical equipment or installations for the liquefaction of natural gas, amalgamation can lead to man-made disasters [2].

Quite important is the fact that the elements of silicon are resistant to many acids, as it is stable in air when heated to 900 °C [3]. Plasma-chemical technology makes it possible to vary the properties of the films obtained by changing the composition of the gas mixture, the substrate temperature and the conditions of ion bombardment on a relatively cold substrate [4].
2. Experimental details
The work was carried out on a designed installation for plasma-chemical deposition in the Engineering Institute of Kazan Federal University. The deposition of coatings was carried out from the reagent (tetrabromosilane SiBr4) with a purity of at least 95.5%. Carrier gas is argon with a purity of at least 99.999% according to Russian technical specifications 2114-003-37924839-2016. The deposition process was carried out by initiating a glow discharge from a high-voltage power source and dissociating tetrabromosilane in a vacuum.

The work included the deposition of thin silicon films on samples of two types: type 1 - 10 × 10 mm flat plate 1 mm thick from 45X steel, type 2 - tubular sample no longer than 100 mm long, internal diameter 22 mm, external 25 mm (tolerance at a diameter of 1.5 mm) of AISI 316L steel. The samples were polished, cleaned with petroleum ether, then dried and placed in a special holder in the reaction zone of the chamber.

3. Results and Discussion
The thickness of the coating deposited on the samples was measured through the profilometer TR200 in different lines of the surface. On sample M4, the thickness from the right side was 521 and from the left side was 400 nm (Figure 1).

![Figure 1. Step of the coating from the initial surface of the sample on M4, (a) right and (b) left side.](image1)

On sample M5 (Figure 2), the measurement was performed in the center and the thickness was 400 nm.

![Figure 2. Step of the coating from the initial surface of the sample on M5 in the middle.](image2)
The corrosion test was carried out according to State Standard [5]. For the test, a coated sample and a witness plate were used. Samples that were tested for resistance were preliminarily prepared in the following way: for evaluation and comparison of surfaces, before deposition, the plates were half closed with vacuum tape and film growth was carried out respectively on the other half. After the experiment on the deposition of silicon, the side on which the adhesive tape was removed and the surface was cleaned with petroleum ether. Both plates were weighed on the scales and were dipping in a solution of the ferric chloride (FeCl₃·6H₂O) for five hours, taking into account the fact that every half hour the samples were unloaded and fixed on frames (Figure 3).

![Figure 3. State of samples with an interval dipping of 30 minutes.](image)

As can be seen in the figures, exfoliation in the area where the coating was not observed, while the surface without coating was wetted and corroded with a solution. Further, the test of samples kept in the solution for microhardness was carried out. The microhardness of the coated sample was 11.6 GPa, which is close to the true value - (11.5 GPa) and the microhardness of the corroded uncoated surface is 46 GPa, which should have 179 GPa. These measurements give a statement about the presence of the fact that silicon kept on the sample surface and, regardless of the test in the solution, retained its properties, in contrast to the corroded initial surface.

To study the structure of the coating on the elemental composition, the scanning electron microscope “EVO 50 XVP” (Carl Zeiss) with the probe microanalysis system “INCA Energy - 350” (Oxford Instruments) was used. In figure 4 that the coating, which is adhesive and dense, in some places has submicron voids, which affects its porosity. However, the film is distributed fairly uniformly over the entire surface of the substrate. Figure 4 shows the size of grains measured in different places.

![Figure 4. Silicon grain size.](image)
The detected elements in the EDX spectra with a coating (Figure 5) confirm the presence of silicon on the surface. Other elements are associated with elements of stainless steel underlayer. Since at low vacuum the free path of atoms can reach 80 cm, we should expect the presence of impurities in the growing film mainly due to water vapor [4]. In order to avoid oxygen atoms that could be formed in the film, was achieved with a prolonged annealing of the chamber before the inlet of the working gas.

![Figure 5. Elemental composition on the coated area.](image)

4. Conclusions
As a result of the work, it was studied that the surface of the components of the gas analytical system needs a coating that creates a barrier when measuring the concentration of impurities of sulfur-containing compounds. In the course of work, a test for resistance to pitting corrosion was carried out, the elemental composition of the coating was determined, which showed the presence of a significant silicon content (8.33%) and, as a result, good protective properties of the coating.

References
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