Features of silicon-containing coatings deposition from ablation plasma formed by a powerful ion beam

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Abstract. This paper presents the research of features of silicon-containing coatings deposition from ablation plasma, which is formed by a powerful ion beam at the influence on a microsized pressed powder of SiO$_2$. Experimental research have been conducted with a laboratory setup based on a TEMP-4M pulsed ion accelerator in a double-pulse forming mode; the first is negative (300-500 ns, 100-150 kV), and the second is positive (150 ns, 250-300 kV). A beam composition: C$^+$ ions (60-70 %) and protons, the ion current density on the target is $25\pm5$ A/cm$^2$. An electron self-magnetically insulated diode has been used to generate the ion beam in the TEMP-4M accelerator. The properties of obtained silicon-containing films have been analyzed with the help of IR spectroscopy. A surface structure has been studied by the method of scanning electron microscopy.

1. Introduction
The durability of traditional materials used in the industrial power engineering in high-temperature corrosive environments is low. The resources on the increase of durable high-temperature stability and resistance to chemical and abrasive wear among various steels based on iron with alloy additives used in heat-power engineering have practically been depleted. It leads to the necessity to study the possibilities of new high-temperature corrosion-resistant materials application and high technologies of products manufacturing on their basis. Nowadays, the most prospective material is silicon-containing coatings, allowing to obtain desired combinations of properties, such as a high strength-to-weight and stiffness-to-weight ratio, heat resistance, wearability, high thermal conductivity and thermal properties, radiation durability, etc [1]. It is known that antireflection coatings (ARCs) became one of the basic components for mass-production manufacturing of solar batteries in 2006. The given coatings are obtained with the help of various methods (thermal evaporation, plasma-chemical deposition from a vapour phase, etc.). The first works on surfacing the silicon-containing coatings on a GaAs substrate were investigated and published in 1976 in the paper [2]. In this work the compounds of SiO$_2$ and Si$_3$N$_4$ were used as silicon-containing coatings. As a result, the authors obtained complex silicon-containing coatings, which had a high heat resistance. The paper [3] presents the method of obtaining SiO$_2$ films on semi-spherical kovar arbors of various sizes. SiO$_2$ was deposited on a kovar substrate by a method of magnetron sputtering. The thickness of a silicon-containing coating was 13 micrometers in the depth of 0.3 micrometers.

In the paper [4] monocrystalline titanium and silicone coatings (one-layer TiO$_2$, double-layer SiO$_2$/TiO$_2$, tri-layer SiO$_2$/SiO$_2$ – TiO$_2$/TiO$_2$) were obtained by a sol-gel method. The measured average optical reflection power (400-1000 nm) is about 9.3, 6.2, 3.2 % for one-layer, double-layer, and tri-layer coatings, respectively. In the work [5] the authors show that with the use of silicon-containing
SiO$_2$ coatings it is possible to decrease the disturbances in photoresistors without using additional antireflection coatings. The authors of the paper [6] added hydrophobic SiO$_2$ nano-particles in polyurethane lacquer coatings by means of mechanical mixing and ultrasonic dispersion. As a result, they obtained nanocomposite coatings, the corrosion resistance of which was improved (the corrosion rate of a nanocomposite coating was, approximately, 20-70% lower than the rate of the original polyurethane lacquer). Silicon-containing coatings are often combined with the coatings based on titanium dioxide [7-9]. Complex coatings TiO$_x$SiO$_2$ (X – mole %) were obtained by the sol-gel method. In the paper [9] nano-crystalline films TiO$_x$SiO$_2$ with a high photocatalytic activity were prepared on a glass substrate. The films were heat treated at 500°F for TiO$_2$ crystal growing. Obtained TiO$_x$SiO$_2$ films were put into a methyl orange (MO) water solution (10 mgL$^{-1}$) and irradiated by ultraviolet (UV). As a result, it was shown that the TiO$_x$SiO$_2$ films possessed a high photocatalytic activity. The authors used the UV-spectrophotometric method to control by the methyl orange decrease the reconstruction of the main absorption peak at 464 nm.

The results showed that the complete corrosion was reached after 1.5 hours. Despite the fact that at present silicon-containing coatings are obtained, mostly, by the sol-gel method, it is necessary to point to the main disadvantages of this method. Firstly, this is a complex and multistage chemical process, and, secondly, it is necessary to use costly catalysts that must be extracted from the final product on completion the process. Therefore, the given paper presents the results of the investigations of silicon-containing coatings deposition from ablation plasma formed by a powerful ion beam.

2. Experimental

Experimental investigations were conducted at the TEMP-4M pulsed ion accelerator with a self-magnetically insulated diode with the following parameters: accelerating voltage – 200-250 kV, current on the target 150-200 A/cm$^2$, ion beam pulse duration (C$^+$ +H$^+$) 80 ns, the ion beam energy density on the target reached 4 J/cm$^2$. The pulsed ion accelerator consists of the following basic units: a pulse voltage generator, a double forming line, main and pre-TR gas dischargers, a vacuum strip diode, consisting of polarizing and grounded electrodes. The polarizing graphite electrode of the diode is connected through the pre-TR gas discharger with the internal electrode of the double forming line. The middle DBF electrode is connected with the pulse voltage generator [10].

The method of silicon-containing coatings deposition from ablation plasma formed by a powerful ion beam is as follows: the pulsed ion beam generated by the TEMP-4M accelerator falls on the target and dissipates it, making the ablation plasma. From this ablation plasma the deposition of the dissipated material on the substrate occurs. Figure 1(a) demonstrates the experimental scheme of the target, substrate and ion beam layout as well as the photo of the experiment (Figure 1(b)).

![Figure 1. Scheme of the experiment on silicon-containing coatings deposition from ablation plasma formed by a powerful ion beam.](image)

The target is installed inclined to the ion beam at the distance R from the anode of the diode. The dissipated surface of the target is inclined at an angle $\alpha$=30–60° (the indication from the surface)
towards the ion beam propagation. Normally to the target surface at the distance d from the target the substrate is installed parallel or at a small angle to the target surface ($\theta < 30^\circ$). In the research as a target the commercial samples of SiO$_2$ micron-sized particles are used. The SiO$_2$ powder was pressed in a tablet with a diameter of 2 cm and a thickness of 0.2 cm. To compare the coatings obtained from the powdery SiO$_2$, the authors suggested using common window glass as a target (GOST 111-65) with the size of 7*10 cm. A titanium foil with a thickness of 50 micrometers was chosen as a substrate (GOST 14958-69).

3. Results and Discussion

The properties of obtained silicon-containing films were analyzed with the help of IR-spectroscopy and scanning electron microscopy. Figure 2 shows photos of the original substrate as well as the target and substrates after the powerful ion beam irradiation.

![Figure 2](image)

*№1, №2 – cutout of the target part for analytical research of the obtained coating.*

Figure 2 shows the recorder of the powerful ion beam on the target, proving the glass dissipation under the influence of a concentrated energy flux (4 J/cm$^2$). The target material is deposited on the titanium substrate (it is possible to judge about it according to the change of the substrate colour after the ion beam impact – a bright blurred spot is observed). The same situation is observed in the case when the SiO$_2$ tablet is used as a target. But in this case the spot is more focused, and it has brighter colour. To conduct IR-spectroscopy 8 samples were prepared (Table 1).

| №   | Comment                                                                 |
|-----|-------------------------------------------------------------------------|
| 1   | Common window glass (GOST111–65)                                        |
| 2   | Titanium foil (GOST 14958–69)                                           |
| 3   | Commercial sample of SiO$_2$ micron-sized particles                      |
| 4   | Pressed tablet from SiO$_2$ micron-sized particles                       |
| 5   | Part of the substrate having the maximum colour after glass irradiation (part №1, Figure 3a) |
| 6   | Peripheral area of a beam imprint on the substrate № 2, marked in Figure 3(a) |
| 7   | Part of the substrate having the maximum colour after the SiO$_2$ tablet irradiation (part №1, Figure 3b) |
| 8   | Peripheral area of a beam imprint on the substrate № 2, marked in Figure 3(b) |

Figure 3 presents the results of the IR-spectroscopy. The IR-spectroscopy is conducted with the IR-Fourier Nicolet 5700 spectrometer (a spectral dimension is 0.09 cm$^{-1}$). The spectrometer is equipped with attachments of the diffuse reflection and single-shot ATR for the analysis of liquid, solid and powdery materials. Figure 3 demonstrates typical absorption spectra of infrared irradiation of studied...
samples. Analyzing spectra (samples 2-7) according to water presence in its various conditions, it is possible to denote the following fact. An absorption band is 1500-1700 cm$^{-1}$, corresponding to deformation oscillations of OH-groups (sample 3). Frequencies in the area of 3200-3750 cm$^{-1}$ correspond to OH-groups stretching vibrations. The appearance of this band is caused by the presence of adsorbed water in the samples.

![Figure 3. R- investigated samples spectra.](image)

For common window glass (sample 1) we observe the collision of peaks, corresponding to the oscillations of bonds Si–O–Si and Si–O–H. For Sample 2 (a titanium substrate) are typical the peaks, corresponding to the oscillations of bonds Ti–O–Ti. On the absorption spectrum of infrared irradiation for the SiO$_2$ micron-sized powder (sample 3) are present the absorption bands of 480, 800, 1100 cm$^{-1}$. 
These bands can be interpreted as asymmetric oscillations of external Si–O-bonds. The bond at 970 cm\(^{-1}\) can be associated with Si–O–H oscillations. The pulsed ion beam impact on the SiO\(_2\) powder leads to the fact that on the IR-spectrum (sample 1) there is no frequency in the area of 3200-3750 cm\(^{-1}\) (OH-groups oscillations). However, in this case the absorption bands from 1100 to 1150 cm\(^{-1}\) are observed, and they can be interpreted as asymmetric oscillations of external Si–O-bonds [11-12]. The band in the area of 790 cm\(^{-1}\) can be interpreted by Si–O–Si bonds. IR-spectra for Samples 5, 6, 8 are identical to the IR-spectrum of the original titanium substrate. For sample 7 on the IR-spectrum two peaks are observed that deal with the oscillations of Si–O–Si (1020 cm\(^{-1}\)) and Ti–O–Ti (1400 cm\(^{-1}\)) bonds. Also, here we may observe absorption bands within the range of 1500-1700 cm\(^{-1}\) and the frequency in the area of 2000-2500 cm\(^{-1}\), corresponding to the oscillations of OH-groups. Let us compare the IR-spectra of Samples 3 and 4. After the pulsed ion beam impact on the SiO\(_2\) powder the number of peaks on the IR-spectrum has decreased (there is no frequency in the area of 3200-3750 cm\(^{-1}\), corresponding to the oscillations of OH-groups), and the deformation of peaks, corresponding to the oscillations of Si–O–Si and Si–O–H bonds, has occurred (the peaks have become narrow). At the exposure of the pulsed ion beam on the tablet made from the SiO\(_2\) powder the surface heating occurs, which, probably, facilitates the deformation of the mentioned peaks due to the changes in the phase composition of the surface layer. It is necessary to note the occurrence of the peak responsible for the oscillation of the Ti–O–Ti bond in Sample № 7. It can be explained by the chemical reaction of titanium oxidation either in plasma, or by interreacting of the sample with air oxygen at the further contact. Then, investigations were conducted with the help of the JEOL JSM-7500FA scanning electron microscope (Figure 4).

Figure 4. Microphoto of substrates’ surface: a) sample № 5, b) sample № 6, c) sample № 7, d) sample № 8.

Figure 4 demonstrates the absence of a homogeneous coating on all the samples. However, on samples 6-8 SiO\(_2\) is presented as circular particles with a diameter of 100-150 nm. When the SiO\(_2\) powder is used as a target, the appearing coating in the centre of a plasma imprint is presented as an
assembly of the particles with a regular shape. The coating is homogeneous, any other clusters of coarse or soldered particles are not met on it. It is difficult to say the same about the periphery of the plasma imprint, where the agglomerates, presenting a soldered joint of several particles, can be seen. Particles morphology for the given sample is presented by spheres with a rough surface (Figure 5). The size of these particles reaches several micrometers, while the size of the particles forming the coating in the centre of the plasma imprint reaches hundred of nanometers.

The elemental analysis of samples was conducted with the help of the energy dispersive X-ray spectroscopy method. Let us cite the results only for the titanium substrate and Sample № 7 as for the most informative example. The results of EDX-analysis are shown in Table 2.

![Figure 4. Microphoto of the substrate surface (sample № 8).](image)

**Table 2.** Content ratio of basic elements and additives in the obtained silicon-containing coating (sample 7) and in the original substrate (sample 2) according to the data of EDX-spectra.

| Element | Wt.% | Element | Wt.% |
|---------|------|---------|------|
| Ti      | 22.07| Ti      | 84.34|
| Si      | 7.91 | Si      | 0.02 |
| O       | 64.04| O       | -    |
| N       | -    | N       | 15.48|
| Ni      | 0.06 | Ni      | 0.16 |
| Na, Mg, Al, K, Ca, Fe | 5.98 | -       | -    |

It can be seen from the results of EDX spectroscopy that the coating obtained from ablation plasma formed by a powerful ion beam consists of 3 main elements: titanium, silicon and oxygen. The presence of such elements as sodium, potassium and calcium is explained by the presence of these elements in the SiO₂ powder. Magnesium, aluminum and ferrum were, hypothetically, inserted as a result of scattering of target holder structural components. In the original titanium substrate (sample 2) oxygen is lacking. After irradiation in Sample № 7 its weight content exceeds 50 % from the total weight content of the elements. Oxygen in the surface layer can occur in 5 the most probable states: SiOₓ, TiOₓ, adsorbed O₂, OH-groups and adsorbed H₂O. The IR-spectrometry of Sample № 7 proves the statement that the significant part of oxygen is contained in SiOₓ and TiOₓ oxides.

**4. Conclusion**

Therefore, in this work the silicon-containing coating from ablation plasma formed by a powerful ion beam was obtained. These coatings are not a solid solution, but they contain the deposited SiO₂ and TiO₂, having formed as a result of substrate surface oxidation. The coating morphology presents the surface, being covered intensively by the agglomerate of circular particles with a size of 100-150 nm. Obtained silicon-containing coatings may find their application in different fields of science and technology.

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