Study of the Glaze Layer Surface of Ceramic Tiles Before and After Ion-plasma Deposition of Protective-decorative Coating

Natalia Chumachenko¹, Vladimir Tyurnikov¹, Il’nur Khafizov¹

¹Samara, SamGTU, ASA, 194 Molodogvardeyskaya st., Samara, 443001, Russia
chumachenko@samgasu.ru

Abstract. The protective coating deposited by ion-plasma sputtering have a very vivid aesthetic and decorative properties that make them attractive for solving design problems, and also enhance the operating characteristics of the products (increases strength, hardness, durability). The main stages of obtaining protective and decorative coatings by electric arc method, namely condensation by ion bombardment (CIB), are considered. The properties of the cathode substance, and hence the compounds formed by these substances, depend on their position in the periodic table. The dependence of the coating properties and features of the electronic structure of the material from which the cathode is made is analyzed. The effect of ion-plasma treatment of the surface of glazed ceramic tiles on their properties is studied. The distinctive features of the structure of the glaze layer of domestic and foreign ceramic tiles are revealed.

1. Introduction

With the development of science, the use of nanotechnology has become the priority direction of development of new decoration technologies. Nanotechnology is the creation and use of materials, devices, and systems whose structure is regulated at the nanometre scale, i.e. within the size range of atoms and molecules [1].

Protective coatings applied by ion-plasma spraying have very bright aesthetic and decorative properties making them attractive for solving design problems, as well as increase the performance of products (increase strength, hardness, durability) [2].

Decorative properties of ceramic glazed tiles change after ion-plasma spraying. The aim of the work is to study the structure of the shard and the glaze layer of ceramic tiles of domestic and foreign production before and after ion-plasma spraying.

2. Methods and materials

Vacuum plasma spraying methods make it possible to obtain a wide range of monolayer, multilayer, and composite coatings based on nitride, carbide, carbonitride, oxide, boride compounds of refractory metals of IV-VI groups of the periodic table of elements.

The most promising is the electric arc method, called – ion bombardment condensation (CIB). The treatment is carried out in a vacuum chamber where the cathode is placed. An electric arc occurs between the chamber body and the cathode. From the cathode spot ions electrons and neutral particles fly out.
flying in a directed flow to the product located inside the chamber. Initially, the particles as it loosens the surface layer of the product, cleaning it and heating it to no more than 300-500 °C. Further deposition occurs on the surface of the material coating from which the cathode is made. If various gases (for example, nitrogen - or carbon-containing) are introduced into the chamber, nitride and carbide coatings are formed on the product surface.

Cathode substance properties and hence the compounds formed by these substances depend on their position in the periodic table. We have made an attempt to analyze the dependence of the coating properties obtained by vacuum plasma spraying, and the features of their electronic structure. The electronic structure is referred to the structure of the electronic shells of atoms. For vacuum plasma spraying elements of IV-VI groups: titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten are used. The main properties of these metals are presented in table 1.

There are mainly two electrons, only chromium and molybdenum one electron at the external energy level of the atoms of these elements. In addition, the transition metal elements are not fully filled d-sublevel of the second outside the level [3].

| №/n/n | Name. | Atom number | Tom weight, u. | Electrone gativity | Oxidation degree | The structure of the outer electronic shell | Crystal structure. |
|-------|-------|-------------|----------------|-------------------|----------------|-----------------------------------|-------------------|
| 1     | Titanium (Ti) | 22 | 47.9 | 1.54 | from + 1 to + 4 | 3d^2.4s^2 | hexagonal |
| 2     | Zirconium (Zr) | 40 | 91.22 | 1.3 | from + 1 to + 4 | 4d^2.4p^0.5s^2 | hexagonal |
| 3     | Hafnium (Hf) | 72 | 178.49 | 1.3 | from + 1 to + 4 | 5d^2.5p^0.6s^2 | hexagonal |
| 4     | Vanadium (V) | 23 | 50.942 | 1.63 | from +2 to +5 | 3d^3.4s^2 | volume-centered cube |
| 5     | Niobium (Nb) | 41 | 92.906 | 1.6 | from +2 to +5 | 4d^3.4p^0.5s^2 | volume-centered cube |
| 6     | Tantalum (Ta) | 73 | 180.948 | 1.5 | from +2 to +5 | 5d^3.5p^0.6s^2 | volume-centered cube |
| 7     | Chrome (Cr) | 24 | 51.996 | 1.66 | from +1 to +6 | 3d^3.4s^1 | volume-centered cube |
| 8     | Molybdenum (Mo) | 42 | 95.94 | 2.16 | from +1 to +6 | 4d^1.4f^0.5s^1 | volume-centered cube |
| 9     | Tungsten (W) | 74 | 183.85 | 2.36 | from +1 to +6 | 5d^1.5f^0.6s^2 | volume-centered cube |

Therefore, in the formation of chemical bonds, the elements of transition metals involve not only the electrons of the external level. But also the electrons of the d-sublevel of the second outside level.

Atomic d-states are similar to the electronic states of ion skeletons, but there are a number of differences [4]. The localized wave functions of the d-states extend much further from the nucleus than the typical wave functions of the skeleton electrons. Therefore, when an extra electron is added to the d-state, the nucleus charge is compensated and the potential well near the atom becomes deeper. In a deeper potential well. s-electron levels decrease. This leads to a decrease in the radius of the s-state. which reduces the distance between the nearest neighbors compared to the corresponding distances in the compounds of non-transition metals. It follows that transition metals and their compounds are more compact. have greater binding energy and greater elasticity than elements of non-transition metals.

Another distinctive feature which is due to the electronic structure of the atoms of the elements of refractory metals of group IV-VI is their high resistance to various chemical influences under normal
conditions. At high temperatures their chemical activity increases, and they form compounds not only with halogens, oxygen, and sulphur, but also with carbon and nitrogen.

The influence of ion-plasma treatment of the glazed ceramic tiles surface on their properties was studied.

Experiments were carried out on ceramic glazed white tiles of domestic and imported production (Italy, Spain and Germany). The influence of the type of coating on the strength characteristics, chemical and thermal strength, and change in surface hardness were studied.

The optimal parameters for the application of titanium and titanium nitride coatings on glazed ceramic tiles of silver and gold shades, respectively, were experimentally selected, mainly by varying the pressure of the reaction gas.

Ceramic tiles after plasma treatment were tested according to the standard GOST [5, 6].

Experiments have shown that the coating improves or does not change the physical and mechanical properties of the tiles. Another task was to study the effect of the type and the glaze composition on the coating properties. To solve this problem, a microscopic study of the surface and the glaze layer of ceramic tiles before and after the ion-plasma application of protective and decorative coating was carried out.

Microscopic examination was performed using an Intel Play microscope combined with a personal computer at 60x magnification.

3. Results and discussions

Vertical sections of ceramic tiles were investigated before and after the application of ion-plasma method of protective and decorative coating of titanium or titanium nitride (Figure 1). The study showed that changes in the structure of the glaze after applying a protective and decorative coating at this resolution are not observed. All sections clearly show two layers of different structure and color: 1 – ceramic shard; 2 – glazed layer.

The layer thickness deposited by ion-plasma deposition is so small that it is indistinguishable on the cut at this increase. Therefore, the tiles surfaces with a matte and glossy structure before and after the application of ion-plasma coating were studied. Titanium and titanium nitride film is coated with a continuous layer of glaze with a bumpy surface of dark color. On the "vertex bumps" there are particles reflecting light which brightens the surface. Thus, the light reflects not all the coating, but only some of its particles.

![Figure 1](image-url)

Figure 1. Vertical cut of ceramic tiles produced in different countries: a) Russia; b) Italy; c) Spain; d) Germany.

The size of the particles and their location on the surface is different for tiles with glossy or matte surface. On the surface of glossy tiles particle sizes are up to 0.03 mm. On the surface of matte their size increases and in some cases reaches 0.08 mm (Figure 2).
The distance between reflective particles also differs depending on the surface structure. For glossy surface, it ranges from 0.03 to 0.58 mm. and for matte one it is less than 0.02 - 0.17 mm.

The glossy surface coating has a less pronounced bumpy relief while the matte coating has large depressions and bumps.

4. Conclusions
In the microscopic study of plasma-treated surface of ceramic glazed tiles the following results were obtained:

1. The structure of shard and glaze layer of ceramic tiles of domestic and foreign production is studied.
2. There were no significant differences between the structure of the shard tiles of domestic and foreign production.
3. Some distinctive features in the structure of the glaze layer between ceramic tiles of domestic and foreign production are revealed.
4. The study of the surface of ceramic glazed tiles after ion-plasma treatment revealed the distinctive features of coatings with matte and glossy structures.
5. The ion-plasma treatment does not change the following properties: tiles size, thermal resistance, water absorption. After the processing the bending strength and hardness increases according to the Mohs scale.

References
[1] M. C. Roco. R. S. Williams and P. Alivisatos. Nanotechnology in the next decade. Forecast areas of research: from English. Moscow: ed World. p 292. 2002
[2] V. I. Zin. N. G. Chumachenko. A. K. Ushamirsky. The Possibilities of nanotechnology in the production of facing ceramics: current status and prospects of building materials development: the 8-th academic readings of building sciences department RAASN. Samara. pp. 185-186. 2004
[3] V. Schreter. K-H. Lautenslager. H. Babrak. Chemistry: Ref. book from German M.: Chemistry. 1989. from English ed: GDR. p 648. 1986.
[4] A. F. Shchurov. Introduction to the physics of ceramics: Textbook for students studying Physics. N. Novgorod: ed Nizhny Novgorod University press. p 166. 1994
[5] GOST 27180-86 (ST SEV 4870-84) Ceramic tiles. Test method.
[6] GOST 6141-91 (ST SEV 2047-88) Glazed ceramic tiles for internal wall cladding. Technical conditions.