

Multilayer corrosion-resistant ceramic-metal coatings on stainless steel obtained by magnetron sputtering

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Abstract. In this work, multilayer ceramic-metal coatings (Metal/nitride ceramics/ Metal/oxide ceramics) with increased corrosion resistance were obtained. The structure of each layer of the obtained coatings was researched using the transmission electron microscope JEOL JEM-2100. The metal layers had a columnar crystal structure, the layers of nitride ceramics predominantly had a nanocrystalline structure (grain size was about 15 nm), the layers of oxide ceramics were amorphous. Corrosion resistance was evaluated on a potentiostat P-45X in a 0.5 M NaCl solution using a three-electrode cell. The created coating reduced the corrosion rate of the stainless steel substrate by an order of magnitude.

Keywords: multilayer ceramic-metal coatings, magnetron sputtering, corrosion resistance.

1. Introduction

Stainless steel is actively used in all industries due to its hardness, corrosion resistance, etc. During long-term operation in aggressive conditions (sea water and mechanical stress) stainless steel products require additional protection. The formation of protective coatings on stainless steel products will increase the service life and expand the application options of stainless steel. A corrosion-resistant coating with enhanced physical and mechanical characteristics provides such protection. The coating may have a different composition, and the methods of formation may be different [1–10]. Magnetron sputtering makes it possible to form layers of various thicknesses, compositions, and characteristics, including metal and ceramics layers on various substrates [11–13]. By changing the composition of the target and the composition of the gas atmosphere in the vacuum chamber, multicomponent layered coatings can be sprayed, modeled, and combined for the tasks.

The metal layer is presented in the form of the nickel layer, which makes it possible to minimize the arising stresses at the substrate-coating interface. Nickel is easily passivated in air and under the action of strong oxidizing agents, which can lead to corrosion resistance, but only if the coating is absolutely continuous. Nitride ceramics layer is presented in the form of silicon aluminum nitride, which is characterized by high hardness and wear resistance. It does not interact with most inorganic acids, but penetration of solvent ions along the grain boundaries to the substrate is possible if the coating structure is inhomogeneous. The outer layer of oxide ceramics is silicon alumina, consisting of silicon oxides and aluminum oxides, which are characterized by high hardness and corrosion resistance. This layer seals all previous layers, preventing the penetration of solvent ions, in particular, oxygen ions and, especially, chlorine ions, through the intercrystalline space.

The purpose of this work is to form multilayer ceramic-metal coatings (Metal/nitride ceramics/ Metal/oxide ceramics) and to study the composition, structure, and corrosion properties of the obtained coatings.

2. Materials and methods

Stainless steel AISI 301 was used as a substrate. Samples with a diameter of 40 mm were made from it. The specimens pre-mechanically polished with diamond paste to a roughness of $R_a = 0.08 \pm 0.008 \mu\text{m}$ and flushed with deionized water and ultrasonically washed in ethanol at room temperature.

The coatings were formed using the magnetron sputtering method under a changing gas atmosphere (argon, nitrogen, oxygen) in the UVN-05MD KVANT. Vacuum unit was equipped with two magnetrons and an ion source. As a target, the monolithic metal target and the composite target consisting of aluminum, silicon, and some metals was used. Before sputtering the metal layer, the samples was exposed to ion-beam treatment in order to activate the surface and remove possible contaminants ($I_{beam} = 15$ mA; $U_{ac} = 10$ kV; $t = 10$ min; $P_{Ar} = 0.05$ Pa) by ion source. The coating sputtering was carried out in stages. First, the metal layer was formed by magnetron sputtering the corresponding metal target onto the substrate in the argon atmosphere ($I = 1.92$ A; $U = 616$ V; $t = 150$ s; $P_{Ar} = 0.3$ Pa, $\tau = 4$ μ s, $f = 50$ kHz). Next, the sample was turned to the next composite target using the rotary table mechanism. The nitride-ceramic layer was sputtered in a nitrogen-argon atmosphere ($I = 3.01$ A; $U = 393$ V; $t = 2000$ s; $P_N = 0.09$ Pa, $\tau = 5$ μ s, $f = 50$ kHz). Then, the sample was rotated to the first metal magnetron, and the metal layer is sprayed. The final oxide-ceramic coating was sprayed using a composite target in the argon-oxygen atmosphere ($I = 1.95$ A; $U = 516$ V; $t = 3600$ s; $P_O = 0.03$ Pa, $\tau = 4$ μ s, $f = 50$ kHz).

The surface morphology was studied using the LEO EVO-50XVP scanning electron microscope JEOL. The phase composition of the coating specimens was determined by a DRON-7 X-ray diffractometer. To study the resulting coating layers, the cross-section foils prepared by an Ion Slicer EM-09100IS device were used. Diffraction patterns were analyzed using a JEM-2100 transmission electron microscope. The elemental composition of the coating was analyzed by an energy dispersive X-ray microanalysis (EDXMA) attachment for an INCA-Energy electron microscope.

Corrosion resistance was studied by conducting accelerated electrochemical tests on the P-45X potentiostat in a 0.5 M NaCl solution using a three-electrode cell. The auxiliary electrode was a graphite electrode, the reference electrode was an Ag/AgCl silver chloride electrode, and the working electrode was a sample with the obtained coating. After placing the working electrode into the solution, exposure was carried out for 1 hour to stabilize the conditions. By changing the voltage, the current value was fixed, while the potential sweep rate was 0.5 mV/s.

3. Results and discussion

As a result of the work, the coatings shown in the Fig.1 were obtained. These coatings consist of two metal layers (thickness of about 0.5 μ m), an intermediate layer of nitride ceramics (thickness ~ 1.2 μ m) and an outer layer of oxide ceramics (thickness ~ 2 μ m).

The metal layers (the first and third from the substrate) had a columnar crystal structure with a crystal size of about 500 nm. The second layer (nitride ceramics) had a nanocrystalline structure (grain sizes about 15 nm) and contains the AlN phase. This was also confirmed by microdiffraction images having ring diffraction, as in [14–15]. The outer layer (oxide ceramics) was amorphous. In microdiffraction images, it was displayed as a halo.

Sputtering of a metal layer onto a stainless steel surface was able to prevent the appearance of an intermediate amorphous layer at the substrate-coating interface (Fig.2). In the case of magnetron sputtering of nitride ceramics directly onto a stainless steel substrate, the formation of a nanocrystalline coating occurred through the formation of an amorphous layer, which could reach from 25 to 200 nm (Fig.2b). This intermediate layer negatively affected the physical and mechanical characteristics of the coating. Namely, in this case, a significant difference in thermal expansion coefficients occurred between the substrate and the coating, which manifested itself in poor adhesion and peeling of the coating during storage in air.

The destruction of coatings with an intermediate amorphous oxide layer in a humid atmosphere occurred within half a year after sputtering coating, as evidenced by the results of field tests. Over

time, the coating peeled off. The study of corrosion resistance in electrochemical experiments was not carried out, since the coating is not durable even under atmospheric conditions.

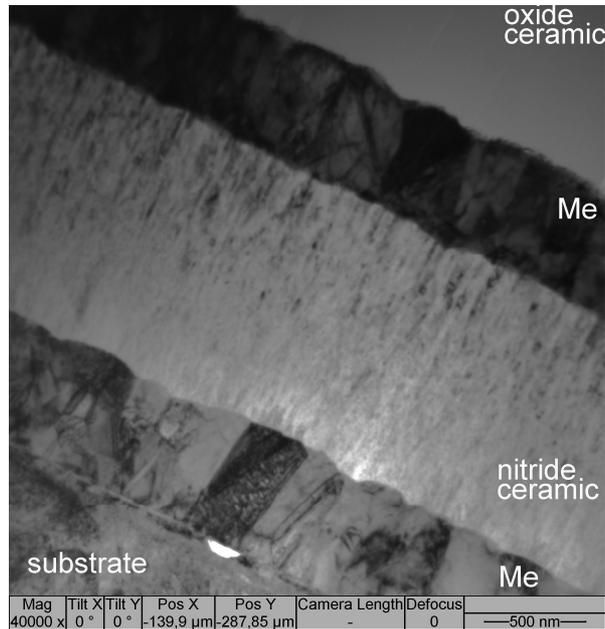


Fig.1. The profile of coating.

During the study of the elemental composition of each of the layers (Fig.3) of four-layer coatings (Metal/nitride ceramics/ Metal/oxide ceramics), it was revealed that the element content in the target and in the coating composition is directly related. The composition of the gas affected the sputtering of either aluminum silicon oxides (in an oxygen atmosphere), or aluminum silicon nitrides (in a nitrogen atmosphere).

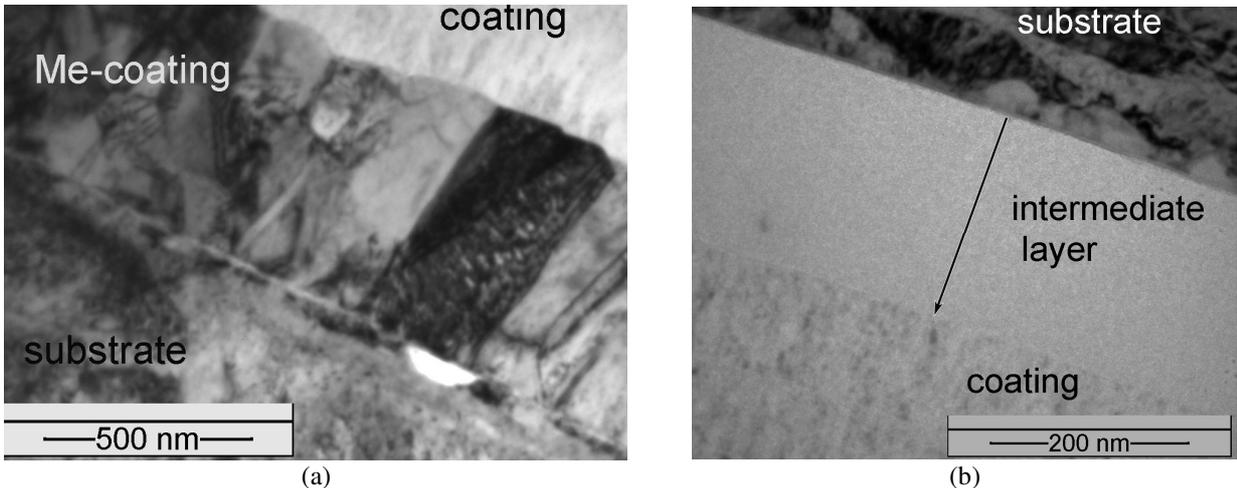


Fig.2. The profile of coating: interface of substrate / Me (a) and interface of substrate / nitride ceramic coating (b).

Tafel curves (Fig.4) were plotted during accelerated electrochemical testing of Metal/nitride ceramics/ Metal/oxide ceramics coatings that remain resistant in a humid atmosphere. For coated samples, the curves were shifted to the region of higher voltage values and lower current values, i.e. the rate of corrosion decreases. Although the stainless steel substrate also was an area of passivation of the material before dissolution, the presence of a breakdown in this area indicated pitting.

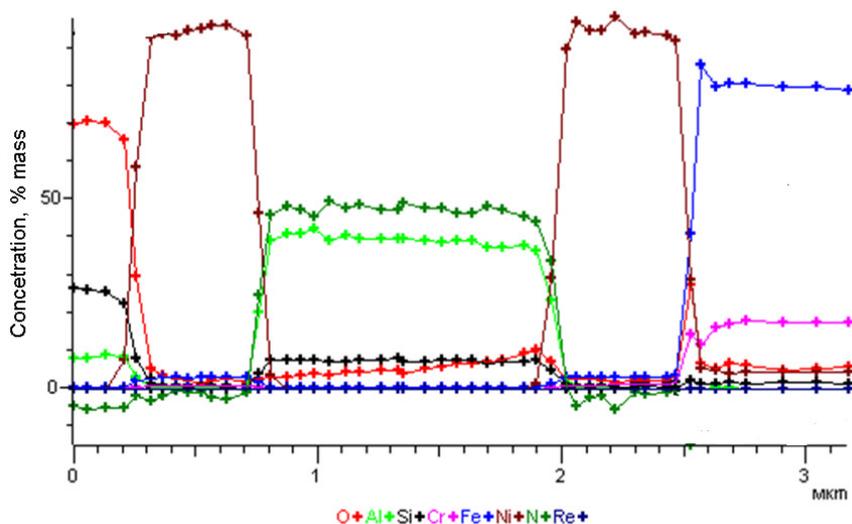


Fig.3. The distribution of elements along the depth of coating.

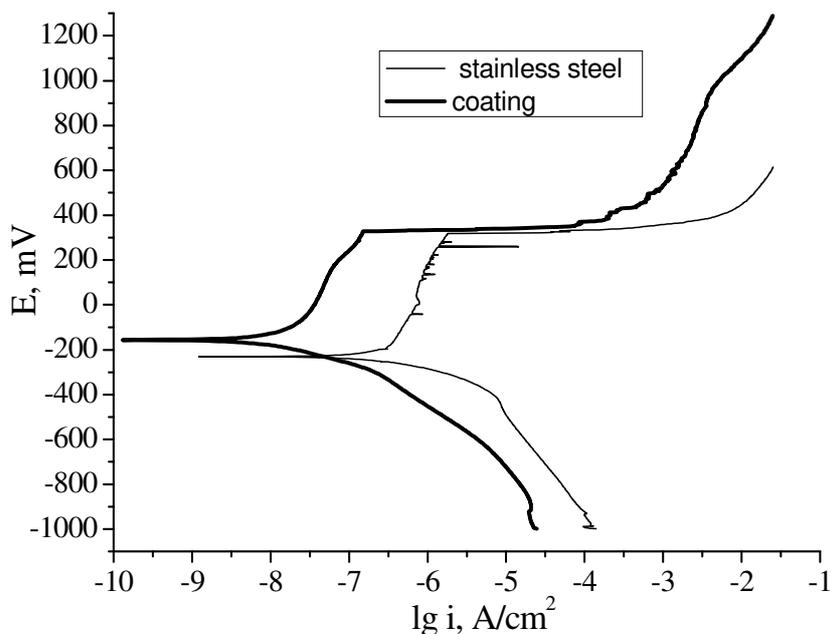


Fig.4. Current-voltage dependences for samples with the obtained coating and stainless steel samples.

4. Conclusion

As a result of the work, the multilayer cermet coatings (Metal/nitride ceramics/ Metal/oxide ceramics) obtained by magnetron sputtering on stainless steel. These coatings have good adhesion, in contrast to coatings with an intermediate amorphous layer at the substrate-coating interface (Nitride ceramics/ Metal/oxide ceramics), and increase the corrosion resistance of stainless steel tenfold.

Thus, multilayer cermet coatings (Metal/nitride ceramics/ Metal/oxide ceramics) acquired the properties of each of the layers, and a synergistic effect appeared. In addition, the layering created several barriers to the diffusion of chloride ions from the environment [13, 16]. The thinness of these layers increased the elasticity of the final coated material.

Acknowledgements

The work was performed as per to the State research task for ISPMS SB RAS, project No. FWRW-2021-0003.

5. References

- [1] Ichijo K., Hasegawa H., Suzuki T., *Surf. Coat. Technol.*, **201**(9–11), 5477, 2007; doi: 10.1016/j.surfcoat.2006.07.016
- [2] Abd El-Hafeez G.M., El-Rabeie M.M., Gaber A.F., et al., *J. Coat. Technol. Res.*, **18**, 581, 2021; doi: 10.1007/s11998-020-00426-0
- [3] Dorofeeva M.S., Dorofeeva T.I., Gritsenko B.P., Sergeev V.P., *IOP Conf. Ser.: J. Phys.*, **1115**, 032067, 2018; doi: 10.1088/1742-6596/1115/3/032067
- [4] Shang Q., Zhou Y., Xia, G., *J. Coat. Technol. Res.*, **11**, 509, 2014; doi: 10.1007/s11998-014-9573-z
- [5] Fotovvati B., Namdari N., Dehghanhadikolaei A., *J. Manuf. Mater. Process.*, **3**, 28, 2019; doi: 10.3390/jmmp3010028
- [6] Zand R.Z., Verbeken K., Adriaens A., *Prog. Org. Coat.*, **72**, 709, 2011; doi: 10.1016/j.porgcoat.2011.08.001
- [7] Li S., Song J., Zhou C., Gong S., Han Y., *Intermetallics*, **13**(3–4), 309, 2005; doi: 10.1016/j.intermet.2004.07.020
- [8] Chang C.-L., Huang C.-S., *Thin Solid Films*, **519**(15), 4923, 2011; doi: 10.1016/j.tsf.2011.01.054
- [9] Rivera L.P., Camps E., Muhl S., Basurto R., Zeinert A., *Mater. Res. Bul.*, **99**, 306, 2018; doi: 10.1016/j.materresbull.2017.10.044
- [10] Kiryukhantsev-Korneev P.V., Pierson J.F., Bauer J.P., et al., *Glass Phys. Chem.*, **37**, 411, 2011; doi: 10.1134/S1087659611040109
- [11] Musil J., Baroch P., *Vacuum*, **87**, 96, 2013; doi: 10.1016/j.vacuum.2012.02.023
- [12] Strnad G., Jakab-Farkas L., Papp S., Fekete A. Z., Biro D., Vida-Simiti I., *Appl. Mech. Mater.*, **657**, 246, 2014; doi: 10.4028/www.scientific.net/amm.657.246
- [13] Dorofeeva T.I., Gubaidulina T.A., Sergeev V.P., Fedorischeva M., *Metals*. **12**(2), 254, 2022; doi: 10.3390/met12020254
- [14] Fischer M., Trant M., Thorwarth K., Crockett R., Patscheider J., Hug H.J., *Sci. Technol. Adv. Mater.*, **20**(1), 1031, 2019; doi: 10.1080/14686996.2019.1666425
- [15] Gubaidulina T.A., Dorofeeva T.I., Sergeev V.P., Kalashnikov M.P., Voronov A.V., *AIP Conf. Proc.*, **2509**, 020084, 2022; doi: 10.1063/5.0084705
- [16] Whitney D.L., *Am. Miner.*, **87**, 405, 2002; doi: 10.2138/am-2002-0404