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Effect of the composition and processing methods of structural stainless steels on the final corrosion resistance

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Abstract. In this paper, the effect of treatment by vacuum ion plasma methods, such as ion implantation and magnetron coating, on the structural-phase state and corrosion resistance of stainless steels is investigated. Corrosion resistance is compared between various stainless steels with the surface modified by several methods. The corrosion rate of the studied steels was determined using electrochemical corrosion studies under potentiostatic conditions. It is found that specimens with multilayer ceramic coatings have the maximum corrosion resistance (0.8×10^{-9} A/cm^2), while the corrosion resistance of untreated VNS-5 steel specimens is minimum (1.2×10^{-6} A/cm^2).
Keywords: stainless steel, magnetron sputtering, ion implantation, corrosion resistance.

1. Introduction

Stainless steel is a steel alloy containing mainly iron, chromium (16÷28%), and nickel (3÷32%). There are several grades varying in chemical composition [1], which are used in many industries, including chemical, oil and gas, aerospace, food, medicine, mechanical engineering and shipbuilding ones. The widespread use of these steels is explained by their high quality, durability, heat resistance, strength, and corrosion resistance. Despite the high corrosion resistance due to passivation, chromium is prone to local corrosion in chloride media [2].

The action of aggressive media can be reduced by various methods, including the use of corrosion inhibitors [3], addition of alloying elements, or deposition of coatings of various compositions. There exist various methods of protective coating application, such as electrochemical, sol-gel and plasma methods, magnetron sputtering, laser cladding [4], etc., as well as a combination of these and other methods [5] resulting in multilayer multicomponent coatings. Potential methods of applying such layers are ion deposition, electroplating, sputtering, and atomic layer deposition [6–7]. Magnetron sputtering is one of the effective methods of physical deposition, which, as a rule, forms coatings with a high adhesion resistance [8]. High-energy ion implantation also allows the formation of thin layers without an interface and significantly improves the corrosion resistance of the processed material.'

Aluminum implanted into the material forms aluminum oxide, Al_2O_3, on the surface, which not only promotes corrosion resistance in aggressive media [9] but also increases thermal stability. Aluminum films were doped with boron to increase their hardness [10]. It was shown [11] that the Al–B-based coatings have increased hardness and wear resistance. In addition, it was established [12] that carbon implantation increases the microhardness of the surface layers by 1.8 times.

In the present paper, we estimate the corrosion resistance of different stainless steels without treatment as well as subjected to ion implantation and magnetron sputtering of various targets to form multilayer multicomponent coatings.

2. Materials and Methods

Specimens to be analyzed were made of stainless steel of various grades (VNS-5, AISI 304, and 30HGSNA) processed by various methods (two-stage quenching followed by tempering, ion implantation, and magnetron sputtering to form multilayer coatings).

Producing of the multilayer Zr-Y-O/Si-Al-N coating was carried out in several stages by the magnetron method using a universal setup UVN-05MD («Elektronvak», Russia) having two vacuum chambers. The first vacuum chamber is developed for a deposition of metallic and nitride coatings, while the second chamber is used for fabrication of oxide coatings [13]. Ion implantation is performed using a UVN-05MD KVANT vacuum unit (Elektronvak, Russia) equipped with the Dionis implanters. Dionis is used for implantation of gas ions. Ions used for implantation are C^+ [9].

All prepared specimens were put to accelerated corrosion tests in an R-40X potentiostat/galvanostat (Electrochemical Instruments, Russia) in the sea salt solution (3.5% NaCl) in the potentiostatic mode at the potential sweep rate 1 mV/s in the range from –2 V to 2 V.

The studies were carried out by means of the equipment of the «Nanotech» center for Collective Use (Tomsk, Russia). The surface morphology after electrochemical tests was studied under scanning electron microscopes: LEO EVO-50XVP (Zeiss, Germany) and Apreo S LoVac (Thermo Fisher Scientific, USA).

3. Results and Discussion

Several sets of specimens were prepared to compare their corrosion resistance: untreated stainless steel, quenched steel, these two implanted with aluminum, boron, oxygen, or carbon ions, as well as steels with two types of multilayer coatings, namely, with a metal sublayer or multicomponent ceramic coatings.

By secondary ion mass spectroscopy, it was found that the thickness of the implanted layer was no more than 200 nm for all treatment types. Four-layer coatings were deposited to a thickness of no more than 6 μm and consisted of two intermediate metal sublayers (of a fine-grained structure) with an outer amorphous ceramic sublayer and a nanocrystalline Si-Al-N layer. The thickness of the ceramic coating was about 10 μm. Its layers based on oxynitride did not exceed 0.5 μm and were in an amorphous state, while the Zr-Y-O layers were nanocrystalline.

The prepared specimens were tested in the potentiostat/galvanostat, and the derived results are presented in Figure 1 in the form of Tafel curves.

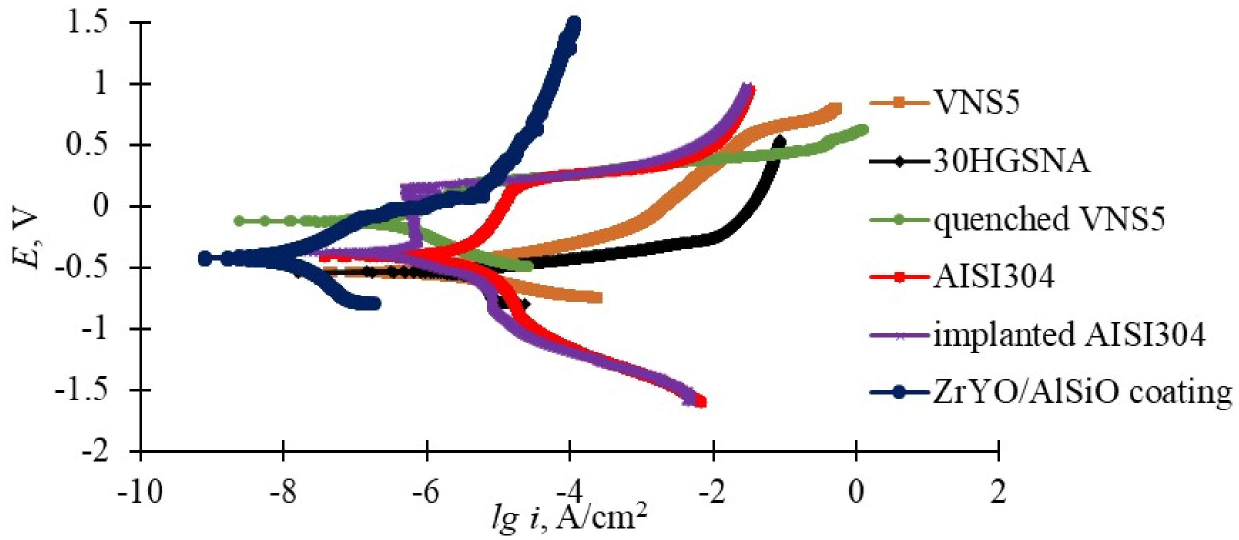
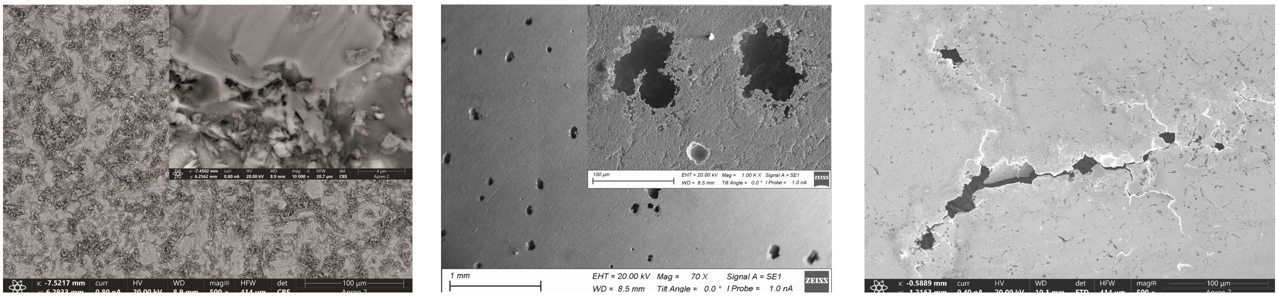


Fig. 1. Polarization curves obtained with the potentiostat/galvanostat for stainless steel specimens after surface modification by various methods.

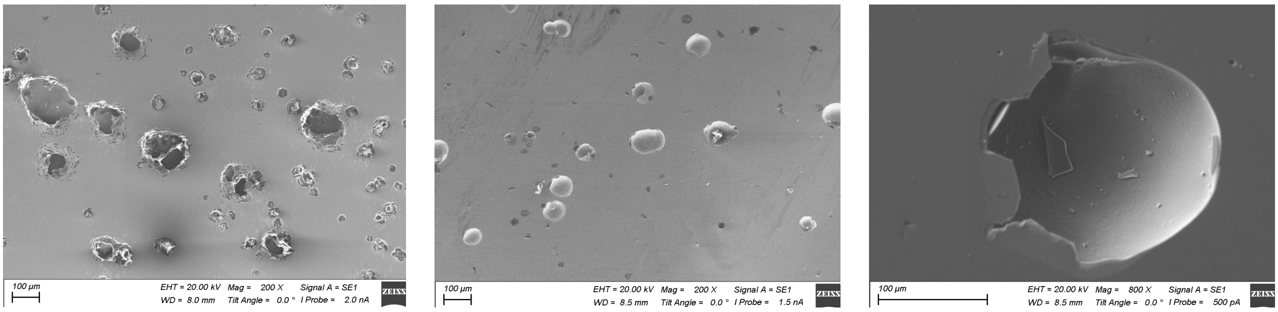
Since the corrosion rate is directly proportional to the current density, specimens with the multilayer ceramic coating (0.8×10^{-9} A/cm^2) have the maximum corrosion resistance, and untreated VNS-5 steel specimens (1.2×10^{-6} A/cm^2) have the minimum corrosion resistance, which differs by three orders of magnitude. These data agree with the results of electrochemical tests. The surface morphology after corrosion tests is shown in Figures 2–3.



(a) (b) (c)

Fig. 2. SEM images of the uncoated steel substrate after corrosion in the 3.5 wt % NaCl solution: 30HGSNA (a), AISI304 (b), VNS-5 (c).

Untreated steels are characterized by uniform surface corrosion with the formation of iron oxides (Figure 2a), or intergranular corrosion accompanied by grain boundary cracking and grain breakout (Figure 2c), or deep pitting with pits about 500 μm in depth and 100 μm in diameter (Figure 2b). The study of corrosion resistance of the quenched steel shows that pits do not change in size (diameter 100 μm), but their number is significantly reduced, and the depth is about 200 μm (Figure 3a). Pits formed after corrosion tests on the surface of the carbon implanted specimens are significantly reduced in number, and their depth does not exceed 50 μm (Figure 3b). When depositing a three-layer coating, the defect density does not exceed 2 per 1cm^2 (Figure 3c). This is due to the fact that the corrosion resistance of coatings depends on the presence of defects in the surface sublayer, by which the electrolyte penetrates into the sublayer and causes mechanical delamination of the surface sublayer.



(a) (b) (c)

Fig. 3. SEM images after corrosion in the 3.5 wt % NaCl solution: VNS-5 (a), quenched and C ion implanted VNS-5 (b), AISI 304 with the 3-layer coating (c),

The corrosion resistance of the product, whether treated or not, significantly depends on the fracture mechanism of its material. Thus, untreated metals have a native film, consisting mainly of chromium oxides (for stainless steel). In this case, fracture occurs along grain boundaries or structural defects, which is accompanied by the breakout of both individual grains and groups of grains, causing the so-called pitting corrosion. The compacted layer formed on the steel surface during heat treatment is characterized not only by refined grains but also by the reduced intergranular space, which hinders the corrosion process. Such treatment is much less effective than surface modification by implantation of Al, B and O ions. Despite the fact that the ions penetrate no deeper than 200 nm, they are embedded in the intergranular space (boron ions), blocking the electrolyte penetration. While on the surface, they form corrosion-resistant oxides Al_2O_3 or carbides with chrome, iron, and nickel, which reduces the corrosion rate by 3–5 times. Deposition of a chemically inert coating almost blocks the penetration of electrolyte ions into the substrate material and increases the corrosion resistance by an order of magnitude. In this case, the limiting stage of corrosion is the delivery of electrolyte ions to the steel surface, as well as the removal of the resulting reaction products, which can also block the electrolyte penetration. Multilayer ceramic coatings, along with chemical stability, are characterized by high hardness, heat resistance, as well as increased plasticity due to the presence of many thin layers no thicker than 0.5 μm.

The corrosion rate of the initial material is an order of magnitude higher than that of a similar but coated material according to the calculated values of the linear corrosion rate P (Table 1).

Table 1. Corrosion resistance parameters.

Specimen	Current density I_{corr}, μA/cm^2	Linear corrosion rate P, mm/year	Corrosion stability class
Annealed VNS-5	0.669	0.0052	Highly stable (class 3)
implanted VNS-5	0.222	0.0017	Highly stable (class 2)
VNS-5	1.528	0.0119	Stable (class 4)
Ceramic coatings	0.044	0.0003	Absolutely stable (class 1)

4. Conclusions

All methods of surface modification given in this article have a positive effect on the physical, mechanical and corrosion properties of the material. It was found that different grades of stainless steel had different corrosion resistance. Vacuum ion plasma methods improved the corrosion resistance by several orders of magnitude. For some grades of stainless steels, ion implantation alone could reduce the corrosion rate on retention of their main properties. For others, both quenching and implantation were ineffective. They require an outer insulating layer, such as a ceramic coating ensuring the sufficient corrosion protection.

Thus, steel specimens with the magnetron sputtered multilayer ceramic coating were characterized by the maximum corrosion resistance 0.8×10^{-9} A/cm^2, and untreated VNS-5 specimens had the minimum values 1.2×10^{-6} A/cm^2.

The article provides an insight into the advantages of different processing methods on different materials, especially when used in aggressive environments.

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5. References

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