The corrosion resistance and neutron-absorbing properties of coatings based on amorphous alloys

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Abstract. The object of the present study was the corrosion-resistant amorphizing alloys with an increased content of boron for cladding the surface of metals, rapidly quenched alloys without boron for protective coatings on a high-boron cladding layer, as well as steel samples with a protective coating with a high content of boron and without boron. The aim of the work is to investigate the corrosion resistance of a coating in water at the temperature of 40 °C in conditions of an open access of oxygen for 1000 h, as well as the features of the microstructure of clad samples before and after the corrosion tests. New data on the corrosion resistance of Cr18Ni10Ti steel samples with a protective layer from a rapidly quenched alloy Ni-19Cr-10Si (in wt.%) on a high-boron coating have been obtained.

1. Introduction
Studies on the development of high-boron neutron-absorbing coatings [1] confirmed the correctness of the chosen direction. However, the leaching of boron [2] in an aqueous medium at elevated temperatures and an open access of oxygen and, respectively, increasing the boron concentration in water are observed. Therefore, this work was carried out to estimate the corrosion resistance of coatings clad by a protective layer before and after the tests in an aqueous medium.

2. Production of samples with a high-boron coating with and without a non-boron protective layer
The methodology of coating the steel was the principle of "a high-boron layer - a layer without boron" in one technological cycle. The "high-boron component - nickel boron alloy Ni-7wt.%Cr-4wt.% Fe-4.5wt.% Si-4.5wt.%B" mixture in the ratio of 1:1 was used as the initial material for cladding. The homogenization of the powder was performed for 30 min in a planetary ball mill with addition of ethanol to prevent its oxidation. The resulting mixture was discharged from the container, slightly dried and applied in the form of a pasty mass to the surface of plates from the steel Cr18Ni10Ti with a diameter of 25 mm and a thickness of 3 mm. The plates had a side board of 1.5 mm in height and 2 mm in width. Two or four layers of a ribbon of the protective microcrystalline alloy Ni-Cr-Si was applied on the surface of a part of the plates that was welded to the plate by a spot electrocontact welding. Then the plates were placed in a vacuum furnace SShV-1.25/25I-1000 and exposed to cladding in a vacuum of 5x10⁻⁵ mm Hg at the temperature of 1100±25 °C. The temperature was controlled by a chromel-alumel thermocouple and visually by the time of a full spreading of the melt over the surface of a clad sample. The heating rate was about 20 °C/min, then the sample was held at the temperature of full spreading for 15 min. After that, the temperature was lowered to 600-700 °C.
and the sample was held for 1 h, then the heating was turned off and the sample was cooled with the furnace[3]. A part of the samples with and without a cladding protective layer was exposed to corrosion tests; a part of the samples was prepared for a microstructural and X-ray microspectral analysis.

3. Corrosion tests of samples with a protective cladding layer

To determine the corrosion resistance of the cladding layer, two samples from each part were placed in glass flasks with a capacity of 0.5 l that were filled with distilled water and loaded into a thermostatic drying oven PE-4610. The temperature in the working space of the thermostat was maintained at 40 ± 0.5 °C. The duration of tests was 1450 h. The boron concentration in the solution was measured by a mass-spectrometer. These data are presented in table 1.

**Table 1.** Results of the corrosion tests of clad samples.

| Batch number | Characteristics of the clad coating | The weight of samples before the tests (g) | The weight of samples after the tests (g) | The concentration of boron (µg/l) |
|--------------|------------------------------------|------------------------------------------|------------------------------------------|----------------------------------|
| 1            | High-boron coating                 | 13.2543                                  | 13.2546                                  | 33.78                            |
|              |                                    | 13.6903                                  | 13.6894                                  |                                  |
| 2            | High-boron coating + two layers of a ribbon | 13.1251                                  | 13.1252                                  | 28.60                            |
|              |                                    | 13.1144                                  | 13.1155                                  |                                  |
| 3            | High-boron coating + four layers of a ribbon | 13.8037                                  | 13.6552                                  | 22.02                            |
|              |                                    |                                           |                                           |                                  |

4. Study of the microstructure of samples before and after the corrosion tests

Investigation of the distribution of elements in the "coating-substrate" contact area was carried out using a scanning electron microscope "CamScan - 4DV" equipped with a wave-crystal diffraction spectrometer WDX-3PC. To study the contact zone structure, the reflected electron imaging mode was used at an accelerating voltage of 15 kV. Since the electron reflection coefficient increases with the atomic number of the element, a lighter contract of images in reflected electrons corresponds to areas with a larger average atomic number. The results of metallographic studies are presented in figures 1 - 3.

**Figure 1.** Microstructures of samples with a two-layer protective layer: a) before the corrosion tests; b) after the corrosion tests (the marker size in the lower right corner of the images is 100 µm).
A protective layer with a thickness of about from 200 to 300 μm is clearly visible at the sample transverse section before the corrosion tests (figures 1a, 2a). This layer is absent at the sample after the tests (figure 1b). Assuming that there was dissolution of the protective layer, the weight loss of the sample with a diameter of 25 mm should be about 0.3-0.5 g, whereas in reality it is 0.0011 g. The transverse section of the sample before the tests was done along its diameter, the section of the sample after the tests was done approximately in a distance of 1/3 of the diameter. Since the high-boron plating powder fills the space inside the cylindrical sample with less than 100% of density and the melt wets well the steel, the formation of a concave meniscus in melting takes place due to capillary forces.

Figure 2. Photomicrographs of the sample cross section with a protective layer before the tests: a, b) in reflected electrons; c) in backward electrons; d, e, f) in a characteristic X-ray radiation of the corresponding element.
As the protective layer melts a little bit earlier than the layer containing boron and the temperature gradient is directed from the edges of the sample to its center, it is quite probable that the central parts of the sample are enriched by a non-boron melt and its content at the peripheral parts of the sample can be little up to its complete absence. This is indirectly confirmed by the fact that the change in the weight of all the samples during the corrosion tests is insignificant and no sharp difference in the boron concentration in water after the tests (see table 1) is observed. It seems appropriate in further works to divide the processes of application of a high-boron coating and a protective layer into two separate stages.

Figures 2 and 3 show data on the distribution of the basic and alloying elements at the "protective layer - cladding layer" border of the sample before the tests and near its surface after the tests.

**Figure 3.** Micrographs of the sample cross section with a protective layer after the tests: a, b) in reflected electrons; c) in backward electrons; d, e, f) in a characteristic X-ray radiation of the corresponding element.
As follows from these data (figure 2a-c), no discontinuities, pores, or foreign inclusions are observed at the "protective layer - cladding layer" border. The distribution of elements (figure 2d-f) shows an active chemical interaction of the melts of the protective and cladding layers without allocation of foreign phases. During the corrosion tests, the microstructure (figure 3a-c) and the distribution of elements (figure 3d-f) did not undergo significant changes, which indicate the stability of the cladding layer even in the absence of a protective coating.

5. Conclusion
- A laboratory technique for the joint application of a protective layer and a high-boron coating onto the surface of corrosion-resistant steel samples has been developed.
- Samples have been made and investigation has been performed of the corrosion resistance of the coating in an aqueous medium at an open access of oxygen and at the temperature of 40 °C for 1450 h. It has been found that the two-layer coating in the form of a 50 µm thick ribbon applied on the surface of a high-boron layer decreases the concentration of boron in water by 1.2 times, and the four-layer coating by 1.5 times.

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References
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