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Corrosion Resistance of Fe-Cr-Al-Si Alloys with Low Chromium Content

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Abstract

Within the framework of this work, alloys with a chromium content of 5 to14 wt%, aluminum from 0 to 4 wt% and silicon from 0 to 4 wt%. The samples were tested for resistance to oxidation with calm dry air (800 °C, 0.1 MPa) for 60 hours; in high-parameter water (350 °C, 16 MPa), for 300 hours; in steam (400 °C, 10 MPa), for 72 hours and superheated steam (1100 °C, 0.1 MPa) for 1 hour.

The compositions most resistant to corrosion under the specified conditions were determined, and the existence of a synergistic effect of silicon and aluminum as alloying elements of iron alloys was confirmed.

Keywords: fuel cladding; PWR; tolerant fuel, ferrite steel; corrosive resistance steel.

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1. INTRODUCTION

At the moment, alloys of the Fe-Cr-Al system are being studied in the world for their application as fuel rod cladding for nuclear reactors [1-3]. The chromium content in these steels ranges from 10 to 20 wt.%, the aluminum content is from 3 to 5 wt.% [3]. The use of these alloys will avoid the steam-zirconium reaction in the case of beyond-design PWR accidents [2]. However, these formulations are prone to decomposition of the solid solution, especially when irradiated, which leads to their embrittlement [4].

The purpose of this work is to study the corrosion resistance of Fe-Cr-Al, Fe-Cr-Si and Fe-Cr-Al-Si alloys in high-temperature water, steam and superheated steam.

2. EXPERIMENTAL

It were melted 31 samples with different concentration of components in a laboratory arc furnace. The ingots were melted in an atmosphere of argon purified by pre-melting the zirconium getter. The raw material for the samples was a coarse-grained powder of

extremely pure iron, granules of aluminum A00 and iodide chromium. The percentage content of the components in each of the samples is shown in table 1.

Table 1: Content of components in the samples (by weight).

№	Cr, %	Al, %	№	Cr, %	Al, %	№	Cr, %	Si, %	№	Cr, %	Si, %	Al, %
1	8	1	9	12	1	17	8	1	25	12	3	-
2	8	2	10	12	2	18	8	2	26	14	1	-
3	8	3	11	12	3	19	8	3	27	14	2	-
4	8	4	12	12	4	20	10	1	28	14	3	-
5	10	1	13	14	1	21	10	2	29	5	2	2
6	10	2	14	14	2	22	10	3	30	5	1	3
7	10	3	15	14	3	23	12	1	31	5	1	4
8	10	4	16	14	4	24	12	2				

For the conduct of corrosion tests, plates of each composition were prepared. The plate size is on the average 15 x 20 x 0.8 mm. It was drilled a hole of 3 mm in diameter for a suspension in every sample. The surface of the plates was treated with 300 mesh abrasive paper. After machining, the samples were cleaned of organic contaminants by sequential washing in soapy water, acetone and ethyl alcohol.

Measurement of the masses of the samples was carried out by electronic scales with an accuracy of 0.00001 g.

Measurement of the surface areas of the samples was carried out with an electronic caliper with an accuracy of 0.01 mm.

The tests were carried out in a laboratory oven controlled by a digital thermal interface, which allowed reducing the temperature error to 1 °C.

It was used a scanning electron microscope JEOL to make the micrographs.

After surface treatment, the samples were hung on a nichrome holder and placed in the oven 6 times for 10 hours. The test temperature was 800 °C. After every 10 hours, the mass of the plates was measured. During the tests, alloys, further testing of which seemed problematic due to the shedding of the oxide film, were eliminated.

After the air tests, a number of corrosion experiments were conducted in a steam-water environment at a temperature of 350 °C and a pressure of 16 MPa. The time of each test was 100 hours. The total time gained was 300 hours. Samples were placed on special holders in thick-walled steel autoclaves; 12.5 ml of steam-water mixture was required for each plate during the experiment, which makes it possible to speak

of independence of the sample states with respect to each other. These conditions mimic the standard operating mode of the PWR.

After testing in water, some promising samples were subjected to a stress-test applied to the claddings of fuel elements from zirconium: 72 hours in a vapor at a temperature of 400 °C and a pressure of 10 MPa. The compositions were tested under the numbers (see table 1.1): 8, 11, 15, 26, 29, 30, 31. Sample number 9, was tested as a non-corrosive standard.

For further research, it was created an installation simulating a PWR failure with loss of a coolant. The installation scheme is shown in Figure 1.1.

The heating element is a pipe with silicon carbide strips arranged parallel to the axis of the tube. The channel for steam, as well as the capacitor for evaporating water, is a quartz tube with a closed rubber stopper end. Deionized water comes from a vessel that provides the ability to control the amount of incoming liquid.

It was made a pen-ceramic plug to increase the vapor pressure in the working volume of the installation. This material is resistant to high temperatures and does not degrade when exposed to water vapor.

In the installation, the incoming water is heated, followed by evaporation, then the steam continues to overheat and at the stage of passing near the sample has a temperature of 1100 °C. Then, the vapor is partly retained by the plug, which leads to the impossibility of sucking air into the reaction space.

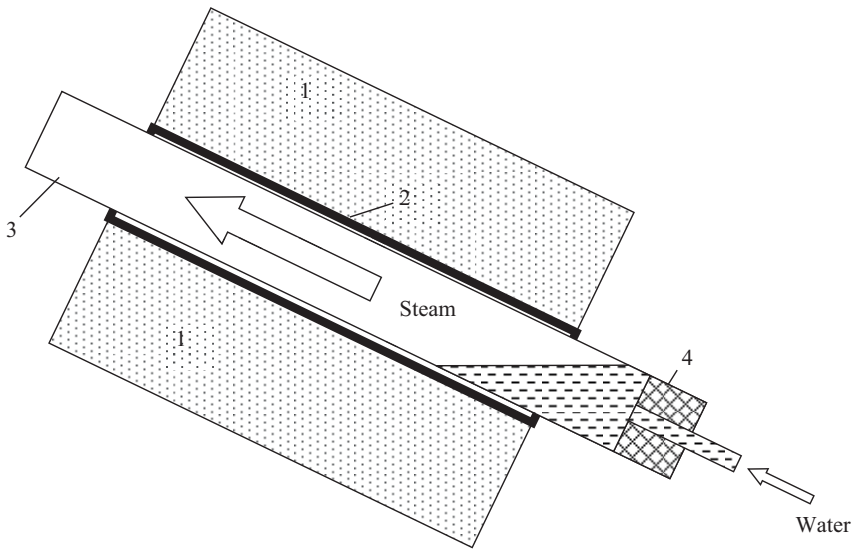

Figure 1: Schematic diagram of the installation "Dewdrop". 1 – Furnace body, 2 – Heater, 3 – Quartz tube, 4 – Rubber stopper.

To remove air from the reaction space and to obtain a steady stream of vapor, prior to carrying out the oxidation experiments, the installation was maintained at

an operating temperature with an increased steam flow rate for an hour. After this preparatory operation, the steam consumption was reduced to the required level and a sample was introduced into the plant volume.

For the tests, flat samples were prepared, similar to the procedure specified in the first paragraph of this chapter. The composition of the samples was selected during the corrosion test in water and steam and are given in table 2. The samples were called the "second generation".

Table 2: Compositions of "second generation" samples.

№	Cr, wt.%	Si, wt.%	Al, wt.%	S+P+C+Mn, wt.%
1	5	2	3	0,1
2	5	1	4	0,1
3	5	1	5	0,1
4	8	0	5	0,1

3. RESULTS AND DISCUSSION

3.1. Discussion of air test results

Figure 2.1 shows a graph illustrating the dependence of the oxide weight gain on time for different compositions of alloys. The graph shows that the alloys were divided into 2 groups: corrosion-resistant and non-corrosive. This makes it possible to construct the dependence of corrosion resistance on the content of alloying elements. Thus, it can be noted that samples doped with 1% aluminum are not resistant to corrosion. It is also evident that the chromium content of less than 10%, in the absence of silicon, does not allow achieving corrosion resistance. It can be concluded that small (up to 4% by weight) simultaneous additions of silicon and aluminum, even with a chromium content of less than 8% by weight, lead to significant corrosion resistance.

Microphotographs of the surface of oxide films of the most representative samples were made in a scanning electron microscope with an increase in x2000. These micrographs are presented in figures 2.2-2.5.

Figure 3 shows that an increase of the amount of chromium changes the structure of the oxide film: loose formations have been replaced by globules of the order of 2 μm.

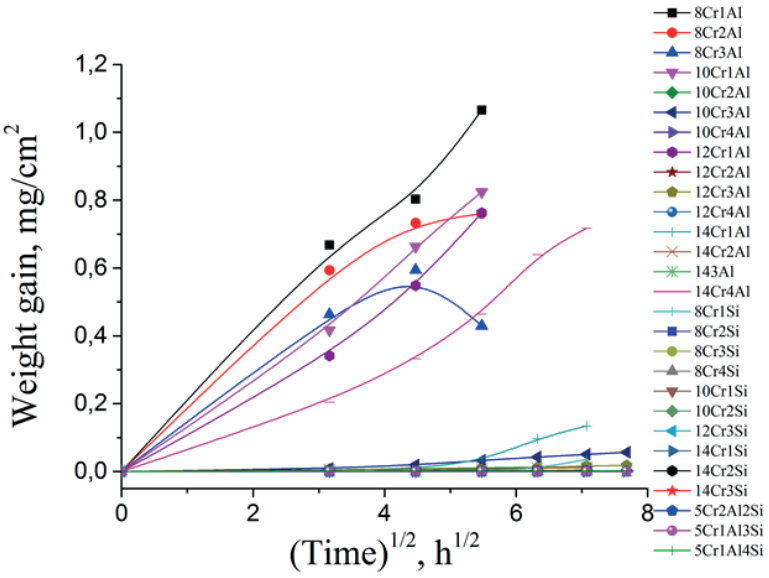

Figure 2: Oxide weight gain versus time graph for different compositions.

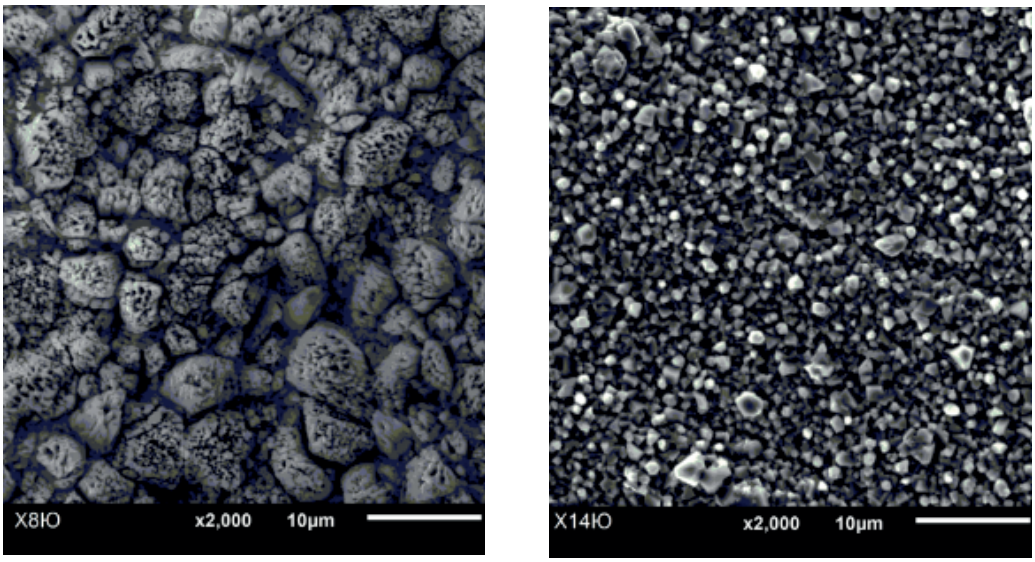

Figure 3: Microphotographs of 8Cr-1Al and 14Cr-1Al alloys after 60 hours of corrosion.

Figure 4 shows that an increase of the amount of aluminum in the alloy leads to an increase in the protective properties of the film on the surface of the sample.

Figure 5 shows that an increase of the amount of chromium changes the structure of the oxide film: the globular formations become much smaller, on the sample there are sites with a thin oxide film, free from globules.

Figure 6 shows that an increase of the amount of silicon in the alloy leads to a reduction in the globular formation of the oxide and, correspondingly, to an increase in the protective properties of the film on the surface of the sample.

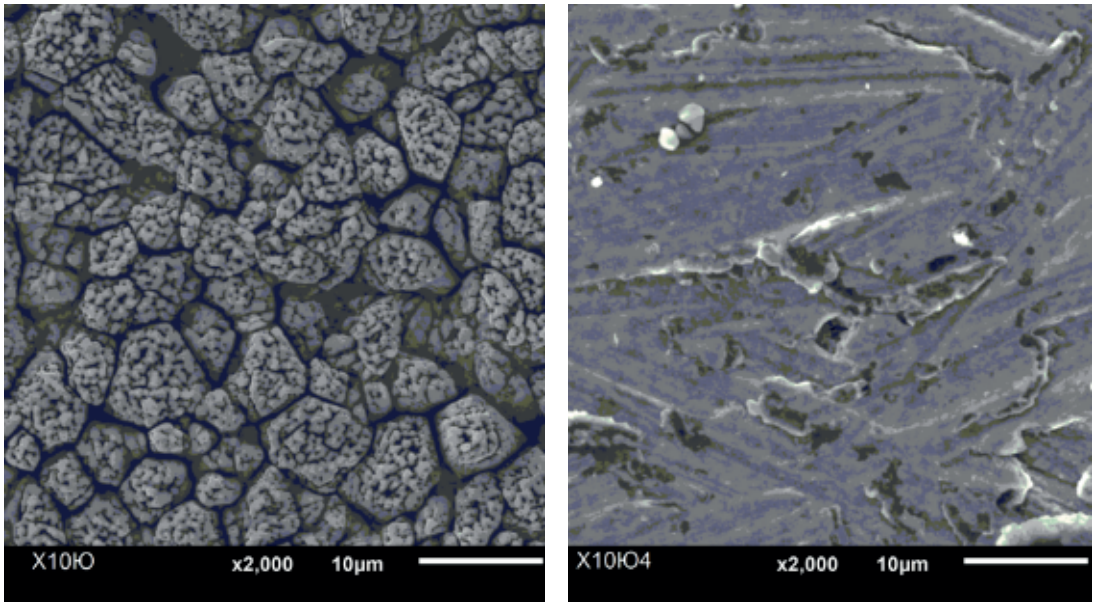

Figure 4: Microphotographs of 10Cr-1Al and 10Cr-4Al alloys after 60 hours of corrosion.

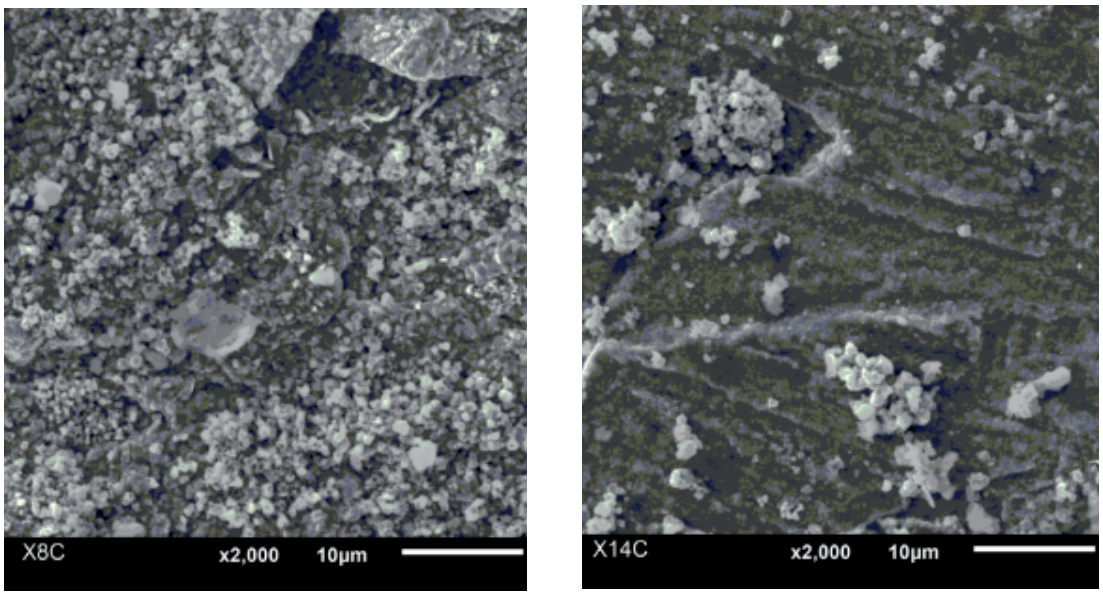

Figure 5: Microphotographs of 8Cr-1Si and 14Cr-1Si alloys after 60 hours of corrosion.

3.2. Discussion of water test results

Figure 7 presents a comparative graph of the dependence of the oxide weight gain on time for the studied alloys and zirconium alloys currently used in the nuclear industry. It is seen that in the case of parabolic corrosion the value of the weight gain of Fe-Cr-Al-Si alloys at 1000 hours of corrosion is an order of magnitude lower than that of zirconium alloys, which indicates excellent corrosion resistance.

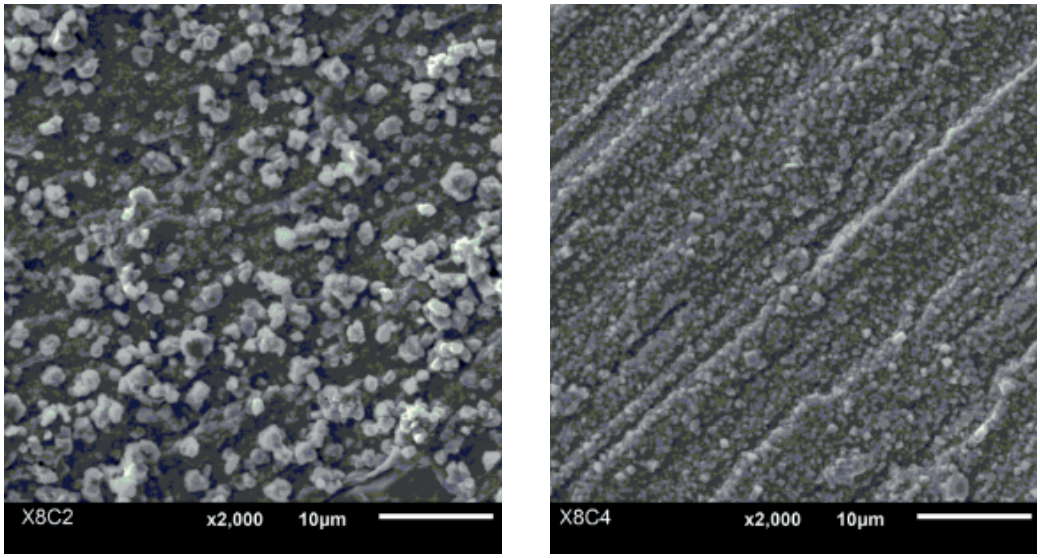

Figure 6: Microphotographs of 8Cr-2Si and 8Cr-4Si alloys after 60 hours of corrosion.

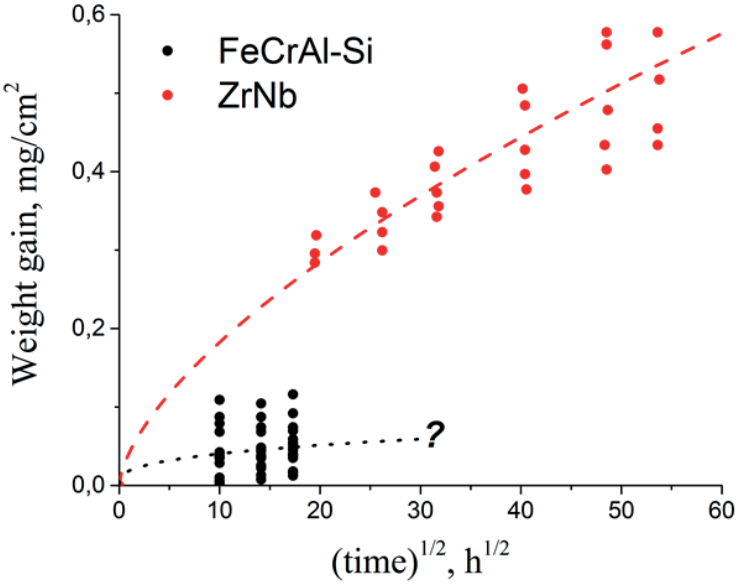

Figure 7: Comparative graph of corrosion dependence of zirconium alloys and alloys under study.

3.3. Discussion of steam test results

Figure 8 shows the histogram of the weight gain of the sample oxide after the so-called stress test, the standard procedure for verifying fuel batches from zirconium.

It can be seen from the figure that the 12Cr-1Al sample has the smallest weight gain, however, this is the result of the detachment of the oxide film particles (brown water color indicates this), which indicates the least durable protective film. Accordingly, the greatest corrosion resistance of the samples presented is alloy 14Cr-1Si. However, there is reason to believe that this alloy is prone to embrittlement.

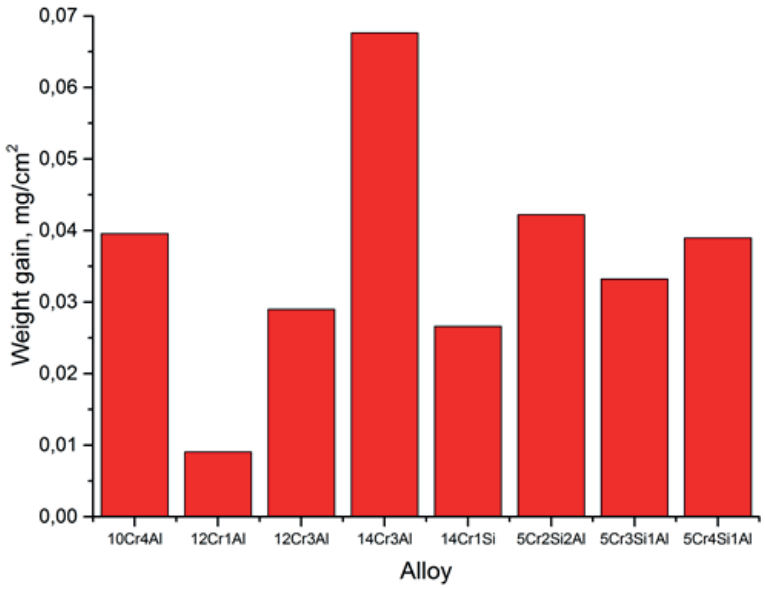

Figure 8: Histogram of weight gain after a stress test.

3.4. Discussion of overheated steam test results

Figure 9 shows the histogram of sample weight gain after corrosion in an overheated steam for 1 hour. The compositions are given in table 2.2. Also in the figure are given the data of the weight gain of EP-823 after corrosion under the same conditions.

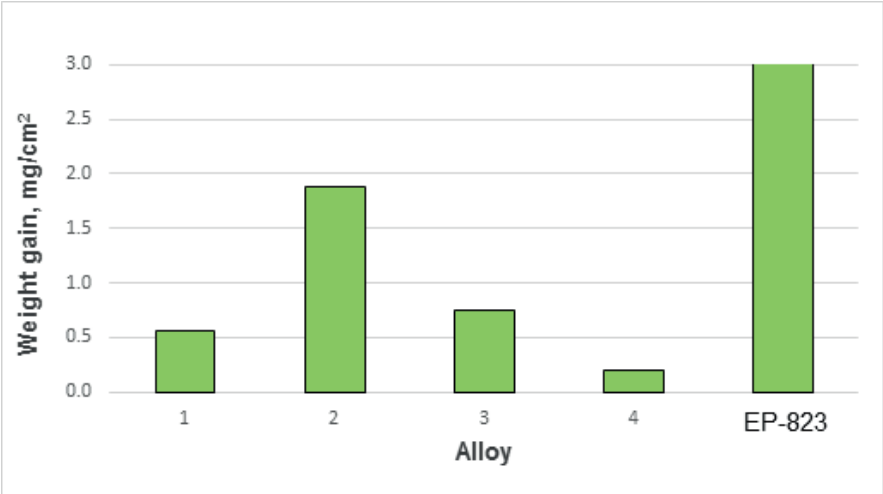

Figure 9: Histogram of sample weight gain after corrosion in superheated steam.

Figures 10-13 show micrographs of samples after corrosion.

These micrographs show that the corrosion film has needle formations grew on the surface of samples 1, 3 and 4. Corrosion film on sample 2 has structure inherited from alloy's structure. Histogram shows that film with needle formations are better

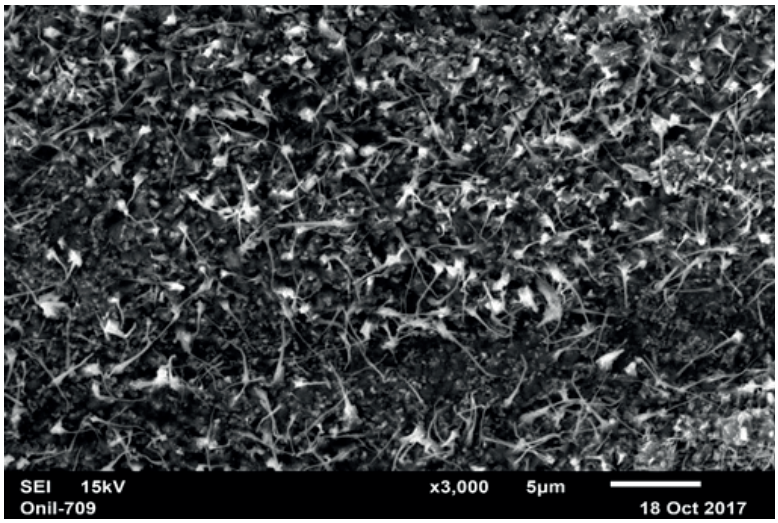

Figure 10: Micrograph of sample №1 after 1 hour of corrosion.

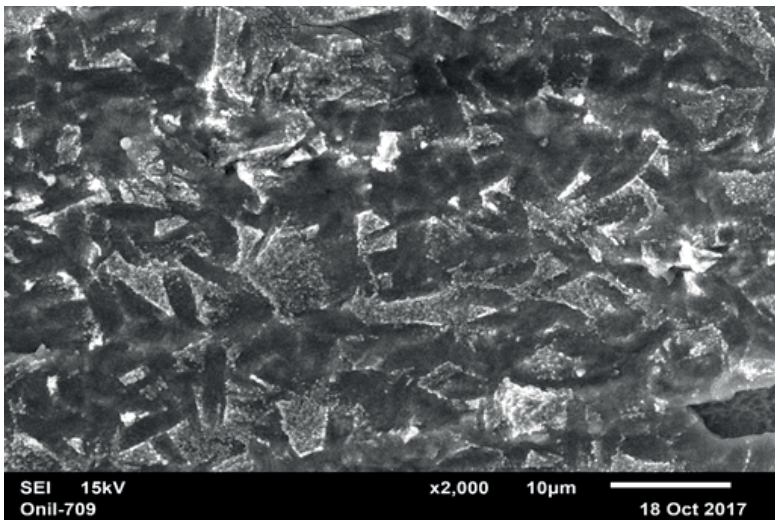

Figure 11: Micrograph of sample №2 after 1 hour of corrosion.

corrosion stopper, unlike grain surface. Best properties have small-needled formations. Causes of that phenomena are under research.

4. CONCLUSION

1. It were considered alloys with a chromium content from 5 to 14 wt%, aluminum from 0 to 4 wt%, and silicon from 0 to 4 wt%. Samples were tested for resistance to oxidation in calm air at 800 °C for 60 hours; in water of high parameters (350 °C, 16 MPa), for 300 hours; in steam (400 °C, 10 MPa) for 72 hours and in superheated steam (1100 °C, 0.1 MPa) for 1 hour.

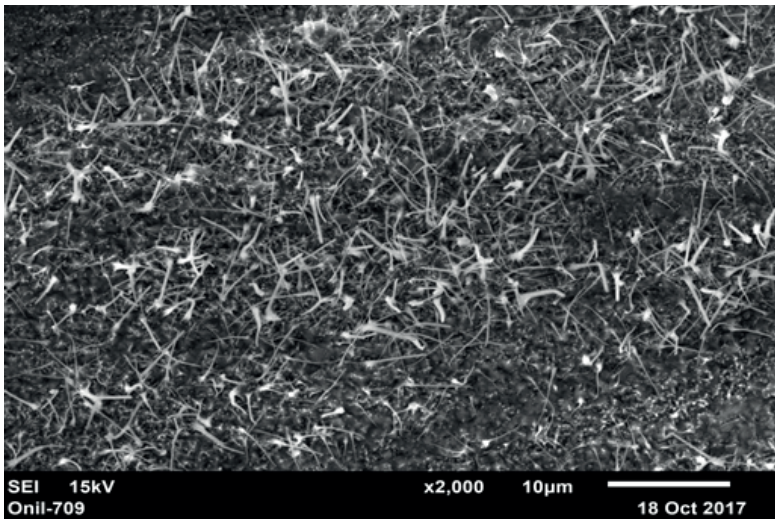

Figure 12: Micrograph of sample №3 after 1 hour of corrosion.

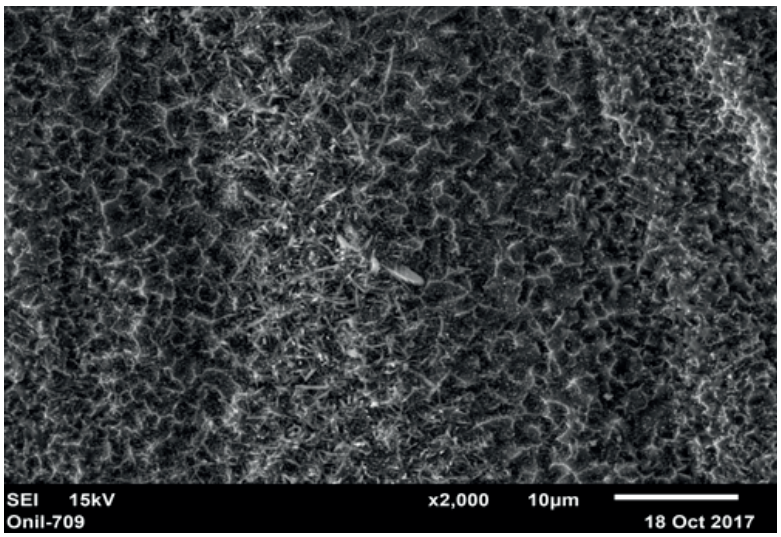

Figure 13: Micrograph of sample №4 after 1 hour of corrosion.

2. Dependences of the rate of oxidation of alloys on composition were obtained and the lower limit of Cr+Al+Si content in alloys possessing sufficient corrosion resistance was determined.

3. The existence of a synergistic effect of the influence of silicon and aluminum on the corrosion resistance of iron alloys has been confirmed.

4. It has been shown that Fe-Cr-Al-Si alloys are promising samples from the viewpoint of corrosion resistance.

ACKNOWLEDGMENT

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