Hot-salt corrosion of alloys PT-7M, 42XHM, Inconel 690, Incoloy 800

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Abstract. The Article contains the results of the study performed for the samples made from alloys PT-7M, 42XHM, Inconel 690, Incoloy 800 for resistance against hot salt corrosion in the mixture of crystallized NaCl and KBr salts, in ratio 300:1 by weight, and in the temperature range from 150 °C to 300 °C, both in contact with the air and in a leak-tight autoclave in the atmosphere of saturated water steam. Regularities of hot salt corrosion behavior in the alloys under the study were detected under testing conditions. The atmosphere of saturated water steam inhibits development of halt salt corrosion of alloy ITT-7M in the entire temperature range of the testing.

1 Introduction

This study was carried out to evaluate hot-salt corrosion resistance of the tube samples made of PT-7M, 42XHM, Inconel 690, and Incoloy 800 alloys upon contact with crystalline chlorides and alkali metal bromides in the temperature range from 150 °C to 300 °C, which is typical for heat-exchange equipment operation. Titanium alloys used in heat-exchange equipment are exposed to hot-salt corrosion in the aforementioned salts provided that the appropriate conditions take place [1].

2 Mechanism of hot salt corrosion of titanium alloys

The researchers [2 – 4] tie the hot-salt corrosion with a set of consecutive reactions:

Titanium and titanium alloy oxide film reacts with crystalline salts and water forming sodium titanate (Na_2TiO_3) and hydrogen chloride (HCl) which further reacts with titanium in (2) as follows:

During its release hydrogen is absorbed by the metal which consequently leads to its hydrogenation. Titanium tetrachloride will be hydrolyzed under the influence of water vapors forming hydrogen chloride and, finally, through a set of intermediate hydrolysis products, titanium oxide (TiO_2):

Hydrogen chloride can further react with titanium in (2) forming titanium tetrachloride (TiCl_4), and so on. The suggested mechanism conditions the intensification of hot-salt corrosion.

3 Materials and procedure of the studies

The following samples were tested: a 13x1.5 mm PT-7M alloy tube fragment of 40 mm length; a 13x1.5 mm 42XHM alloy tube fragment of 20 mm length; a 25.5x3.5 mm Inconel 690 alloy tube fragment of 20 mm length; a 12.5x1.5 mm Incoloy 800 alloy tube fragment of 20 mm length. Chemical composition of the samples is available in Tables 1 and 2.

Table 1. Chemical composition of PT-7M and 42XHM samples (% mass).

Material	Ni	Cr	Fe	Ti	Al	Zr	Si	O	H	N	Mn	Σ_{red}
PT-7M	-	-	0.25	basis	1.9	2.3	0.12	0.07	0.006	0.03	-	0.30
42XHM	basis	42.1	0.6	0.25	0.4	-	0.25	-	-	-	0.2	-

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Table 2. Chemical composition of Inconel 690 and Incoloy 800 samples (% mass).

Material	C	Ni	Cr	Fe	Mn	Cu	Al	Ti	Si, not more than	S, not more than	P, not more than
Inconel 690	0.019	basis	30.1	9.2	0.35	0.2	-	0.5	0.35	0.003	0.0012
Incoloy 800	0.09	32	21.3	other	1.45	0.73	0.47	0.24	0.81	0.007	-

Relative corrosion tests of the samples were conducted in a corrosion test facility (Fig. 1) in a mixture of NaCl and KBr crystalline salts taken in a ratio of 300:1 by mass, which corresponds to the ratio in sea water; the size of salt crystals did not exceed 0.3 mm. Test duration was 500 h. The test temperatures (150, 180, 200, 240, 290 °C) fully cover the temperature range of heat-exchange equipment operation. To exclude any interference, the samples of different materials were tested separately in different digesters; the tests for each

temperature were conducted on three samples. During the tests the following conditions were simulated:

- air atmosphere contact behavior;
- water vapor contact behavior.

Before testing, the samples were degreased, washed in distilled water, and dried in the oven at 100°C. After that they were put in a mixture of salts poured into a ceramic cup which was placed into the digester. When testing under air atmosphere contact the digester cover was not sealed; no water was poured into the digester.

Fig. 1. Corrosion test facility digester.

4 Results of comparative corrosion testing of samples

Below are the pictures of PT-7M, 42XHM, Inconel 690, and Incoloy 800 alloy samples after the tests in a mixture of crystalline salts under atmospheric and water vapor

pressure in the temperature range of 150-290 °C (Figs. 2 – 9). The pictures of the sample surfaces were taken at 20^x zoom.

Fig. 2. PT-7M alloy samples after the tests in a mixture of crystalline salts under contact with air atmosphere.

Fig. 3. PT-7M alloy samples after the tests in a mixture of crystalline salts under saturated water vapor pressure.

Fig. 4. 42XHM alloy samples after the tests in a mixture of crystalline salts under contact with air atmosphere.

Fig. 5. 42XHM alloy samples after the tests in a mixture of crystalline salts under saturated water vapor pressure.

Fig. 6. Inconel 690 alloy samples after the tests in a mixture of crystalline salts under contact with air atmosphere.

Fig. 7. Inconel 690 alloy samples after the tests in a mixture of crystalline salts under saturated water vapor pressure.

Fig. 8. Incoloy 800 alloy samples after the tests in a mixture of crystalline salts under contact with air atmosphere.

Fig. 9. Incoloy 800 alloy samples after the tests in a mixture of crystalline salts under saturated water vapor pressure.

The rate of the hot-salt corrosion in PT-7M alloy under contact with air atmosphere increases with the temperature rise. The traces of hot-salt corrosion are found at 180 – 190 °C; with the temperature rise the depth of localized damages, i.e. pits, grows. The surfaces of PT-7M alloy samples, tested at 290 – 300 °C, show the deepest localized corrosion damages. According to the results of metallographic research we can state that the average pit depth ranges from 0.2 mm to 0.3 mm, the

maximum depth is 0.75 mm. It should be noted that the hot-salt corrosion is of intergranular nature (Fig. 10). Hydrogen content in the metal of the samples, tested at 290 – 300 °C, was measured in the corrosion damages area, after an appropriate preparation of the sample surface, with the help of a spectral method, and ranged from 0.010 % mass. to 0.014 % mass., which exceeds the initial hydrogen content of 0.006 % mass. in the sample.

Fig. 10. a) localized corrosion damages on the surface of PT-7M alloy samples after the tests under air atmosphere contact at 290 – 300 °C (6,5^x). b) surface layers condition in the localized damages area at 50^x zoom (intergranular fracture).

As shown in Fig. 3, when research under saturated water vapor atmosphere, the surface of PT-7M alloy samples lost its metallic luster with the temperature and pressure rise. In these conditions no traces of hot-salt corrosion were observed, the sample surfaces passive state was preserved at all test temperatures. Localized surface corrosion to a depth not exceeding the machining marks is observed.

Surfaces of 42XHM alloy samples (Fig. 4), tested in crystalline salts under air atmosphere contact at a temperature from 150 °C to 250 °C, lost their metallic

luster. Surfaces of 42XHM alloy samples, tested at 290 – 300°C, showed localized corrosion damages in the form of pits with corrosion product scurf of green color, i.e. mixtures of oxides, chromium chlorides and nickel (Fig. 11). When tested in the saturated water vapor medium, surfaces of 42XHM alloy samples (Fig. 5) showed pitting corrosion damages. According to the results of metallographic examination the depth of damages after the tests both in the air and water vapor atmospheres did not exceed 0.15 mm. No intergranular fracture was observed.

Fig. 11. Localized corrosion damages on 42XHM alloy sample after the tests under air atmosphere contact at 290 – 300 °C (12.5^x).

After the research under air atmosphere contact at a temperature from 150°C to 250°C, surfaces of Inconel 690 alloy samples (Fig. 6) lost their metallic luster. Surfaces of Inconel 690 alloy samples, tested at 240 – 250 °C, 290 – 300 °C, are fully covered in general corrosion product deposits. The sample surfaces showed

no localized corrosion damages. After the test in the saturated water vapor medium (Fig. 7), the sample surfaces showed localized corrosion damages in the form of elongated pits, the depth of which did not exceed 0.15 mm.

After the research under air atmosphere contact, surfaces of Incoloy 800 alloy samples (Fig. 8) lost their metallic luster. After the tests at 240 – 250 °C, 290 – 300 °C the sample surfaces showed a dense layer of general corrosion products. After the research in the saturated water vapor medium (Fig. 9) at 150 – 160 °C, 180 – 190 °C, 200 – 210 °C, the surfaces of all Incoloy 800 alloy samples showed corrosion spots the areas of which grow with the temperature rise. The sample surfaces, researched at 240 – 250 °C, 290 – 300 °C, are covered in a layer of corrosion products. According to the results of metallographic examination, after the research in the air atmosphere and water vapor media, the sample surfaces showed no traces of localized corrosion (pittings, pits, cracks).

The hot-salt corrosion of PT-7M alloy samples under contact with air atmosphere was observed at test temperatures of 180 – 190 °C and higher. It appears that the most dangerous behavior for the heat-exchange equipment made of PT-7M alloy is the contact with crystalline chlorides and alkali metal bromides in the air atmosphere at 290 – 300 °C. Saturated water vapor provides for a stable surface passivation and impedes hot-salt corrosion in the whole analyzed range of temperatures. Basically, this can be explained by an assumption that at high water vapor pressure the formation of titanium tetrachloride is suppressed, as well as are reactions 2 and 3, but it needs to be experimentally validated.

We should note that it is possible to increase the hot-salt corrosion resistance of titanium alloys by decreasing the impurity concentration at grain boundary. Thus, the hot-salt corrosion resistance increase was observed in submicrocrystalline modifications of titanium alloys with grain sizes ranging from 0.2 µm to 1 µm obtained by equal channel angular extrusion [5, 6].

We can state that 42XHM, Inconel 690, and Incoloy 800 alloy samples demonstrated a higher corrosion resistance during the tests as compared to PT-7M alloy samples.

5 Conclusion

1. According to the test results, the temperature threshold for the hot-salt corrosion onset in PT-7M titanium alloy under contact with air atmosphere is 180 °C.
2. As for the hot-salt corrosion development the most dangerous behavior for PT-7M alloy is the contact with crystalline salts like chlorides and alkali metal bromides in the air atmosphere at 300 °C (from the analyzed range of temperatures).
3. Contact with saturated water vapor impedes PT-7M hot-salt corrosion in the whole range of test temperatures.
4. 42XHM, Inconel 690, and Incoloy 800 alloy samples demonstrated a higher corrosion resistance during the tests as compared to PT-7M alloy samples.

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