

Thermal Annealing Effect on Recovery of Corrosion Properties of EP-450 Steel Irradiated in BN-600 Reactor to High Damage Doses

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Abstract. The paper gives the results of corrosion resistance investigation in a cooling pool for EP-450 steel (12Cr-13Mo-2Nb-B-V) irradiated in BN-600 reactor as a shroud tube material at temperature in the range between 360 and 520 °C to different damage doses. Corrosion behaviour of EP-450 steel after irradiation and isothermal annealing at temperature in the range between 650 and 750 °C during 1-10 hours is investigated. EP-450 corrosion behaviour dependence on irradiation parameters is established. It is found that shroud tube areas from the core bottom and centre are more susceptible to corrosion effect of water. In these areas uniform corrosion, as well as pitting one, is formed. It is shown that annealing at a temperature above 700 °C and for more than 3 hours ensures reduction of corrosion rate and EP-450 corrosion product release into cooling pool water by an order of magnitude, and prevents from development of local corrosion types in the form of pits and pittings.

Key Words: fast reactors, ferritic-martensitic steels, irradiation, corrosion.

1. Introduction

High radiation-resistant ferritic-martensitic steels are prospect materials for fast reactor cores [1-3]. Chromium ferritic-martensitic steel 12Cr-13Mo-2Nb-B-V (EP-450) was successfully used as a shroud tube material for BN-350 reactor fuel assemblies and is still used for BN-600 and BN-800 reactors [4-6]. It is expected to use ferritic-martensitic steel EP-450 for BN-1200 reactor shroud tubes and ferritic-martensitic oxide dispersion strengthened steel for claddings [7-9]. Wet storage of BN-1200 reactor spent fuel assemblies in a cooling pool is supposed.

However, during the storage of BN-600 spent fuel assemblies in the cooling pool high rates of corrosion and corrosion product (CP) release into the cooling pool water for spent fuel assembly structural elements, made of 12%-chromium ferritic-martensitic steels, were observed [4-6]. Along with higher corrosion and corrosion product release rates radionuclide concentration increases, thereby increasing radiation hazard level. Localized (pitting) corrosion may occur and lead to cladding depressurization with high active fission product (cesium, strontium, iodine) release into the environment [10]. Cladding depressurization risk diminishes environmental safety of spent fuel assembly storage in the cooling pool.

The paper gives research results of water corrosion resistance of EP-450 (12Cr-13Mo-2Nb-B-V) steel after irradiation in BN-600 reactor in the range of temperatures between 360 and 520 °C to different damage doses. Corrosion behaviour of EP-450 steel in water with pH=7.0 after irradiation and high-temperature isothermal annealing for 1-10 hours at 650, 700 and 750 °C is investigated. A new technique of storage of fast reactor spent fuel assemblies with structural elements made of 12%-chromium ferritic-martensitic steels in the cooling pool has been developed using the results obtained. A patent for the technique No. 2555856 (RU) dated 10.06.2015, IPC G21C19/06, was granted.

2. Materials and Test Procedure

2.1. Research subject

Specimens cut from EP-450 fuel assembly shroud are the research subject. The fuel assembly was operated in BN-600 reactor up to maximum damage dose $D_{\max} \approx 75$ dpa. Chemical composition of the EP-450 steel, examined according to TS 14-3-1511-87, is given in *Table I*.

TABLE I. EP-450 STEEL COMPOSITION (% WT).

C	S	P	Mn	Cr	V	Si	Ni	Nb	Mo	B	Fe
0.10-0.15	≤ 0.015	≤ 0.025	≤ 0.80	11.0-13.5	0.1-0.3	≤ 0.5	0.05-0.30	0.25-0.55	1.2-1.8	≤ 0.080	Residual

Test specimens are 30x15x2.5 mm plates cut out from different areas along the shroud (see *Table II*). Specimen cutting is carried out with the biggest specimen size along the shroud. Specimen material microstructure is a 1:1 duplex structure of tempered martensite (sorbite) and ferrite. Along ferrite-ferrite and ferrite-sorbite grain boundaries there are large spheroidal $M_{23}C_6$ carbides and smaller carbides in the form of precipitate chains inside martensite grains.

TABLE II. BRIEF CHARACTERISTIC OF OPERATING PARAMETERS OF EXAMINED SPECIMEN AREAS.

Examined area	Coordinate from core centre, mm	Damage dose, dpa	Temperature, °C
Core bottom	-630– -570	18–22	366–372
Core centre	20–80	73–74	441–453
Core top	460–520	26–35	510–520
Out of core	740–800	~ 0	~ 535

2.2. Corrosion test procedure

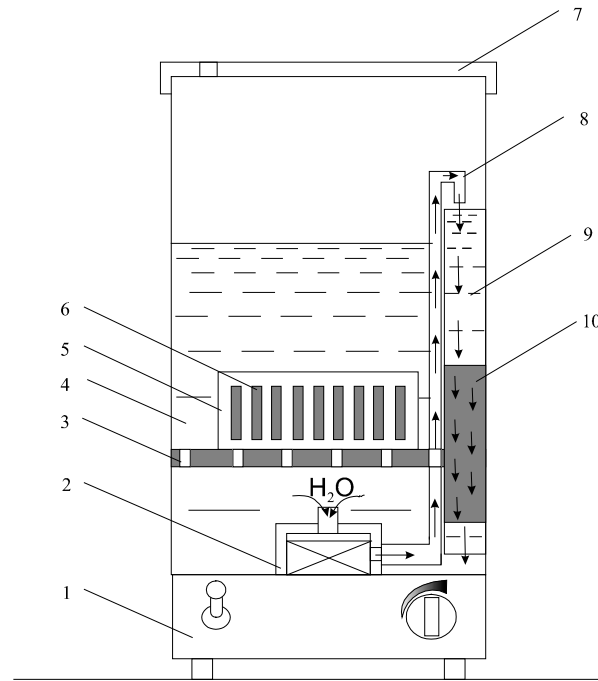
Corrosion tests are carried out in a facility with autonomous pH maintenance (see *Fig. 1*). The facility consists of a 10 l organic glass vessel 4, a rotary vane pump 2 with a magnetic drive 1 in the lower part of the vessel.

The pump drains the water out of bottom space and delivers it through a silicone pipe 8 to a filtration column 9. The filtration column is filled with inorganic GTD-M sorbent 10 treated in an ammonia mold.

The water goes through the filtration column under the action of gravity, then it is enriched with hydroxyl ions, and goes back to the vessel for corrosion tests. pH is maintained by loading a certain amount of sorbent and changing water flow through the filtration column. With depletion of hydroxyl ions a sorbent vessel is additionally loaded with a new sorbent batch.

In the bottom part of the vessel a false bottom 3 is fixed, and organic glass magazine racks 5 with specimens 6 are installed. The vessel 4 has a cover 7 with a hole for contacting with atmospheric air.

Corrosion tests are carried out in compliance with GOST 9.502-82 requirements [11]. Tests are carried out at room temperature during 500, 1000 and 2000 hours. There are three specimens per one time point. The ratio of a medium to a specimen surface is $10 \text{ cm}^3/\text{cm}^2$ and above. Water medium pH is measured with a 673M pH meter on a daily basis.



1 – magnetic drive, 2 – rotary vane pump, 3 – false bottom, 4 – vessel for corrosion tests, 5 – magazine rack, 6 – specimens, 7 – cover, 8 – pipeline, 9 – filtration column, 10 – inorganic sorbent

FIG. 1. Facility for corrosion tests with autonomous pH maintenance.

2.3. Corrosion properties estimation procedure

Corrosion resistance of test specimens is estimated by their appearance and weight changes, and by local damage density and depth [12].

Visual check of specimen surface state is carried out in a hot cell through shielded glass with a binocular of a 12-fold magnification. General specimen state, distribution and colour change of oxide films on the specimen surface, local damage occurrence and distribution, as well as their amount on a specimen are visually inspected.

A technique based on specimen weight loss is taken as a corrosion resistance criterion [12]. Specimen initial weight m_0 is measured first. After storage in the medium the weight m_1 is measured. Then oxide films are removed from the specimens in a solvent which does not affect metal, and the weight m_2 is measured. Oxide films are removed from specimen surface in compliance with GOST 9.907-83 [13] in an aqueous solvent containing 20% HCl ($\rho=1.17 \text{ g/cm}^3$) and with 0.5% hexamethylenetetramine as an inhibitor. The following corrosion properties are estimated using these three values:

- weight loss (corrosion losses)

$$q_1 = (m_0 - m_2)/S; \quad (1)$$

- specific weight of corrosion products (CP) left on the specimen surface,

$$q_2 = (m_1 - m_2)/S; \quad (2)$$

- CP release into water (on metal basis)

$$q_3 = q_1 - \gamma \cdot q_2 = q_1 - A \cdot n \cdot q_2 / M = [m_0 - m_2 - A \cdot n \cdot (m_1 - m_2) / M] / S, \quad (3)$$

where S is a specimen surface area; $\gamma=A \cdot n/M$ is a constant depending on corrosion product content and equal to metal fraction in oxide film (for γ -FeOOH $\gamma=0,693$); A is metal atomic weight; n is amount of metal atoms in an oxide molecule; M is oxide molecular weight.

Pit depth is measured with a dial indicator needle probe.

Average rates of corrosion and release of test specimen corrosion products into water are determined in compliance with GOST 21910-76 [14] by the following equations

$$\overline{v_{q1}} = \frac{m_0 - m_2}{S \cdot t}, \quad (4)$$

$$\overline{W_{q3}} = \frac{m_0 - m_2 - \gamma(m_1 - m_2)}{S \cdot t}, \quad (5)$$

where $\overline{v_{q1}}$ is an average corrosion rate during tests, $\text{g}/(\text{m}^2 \cdot \text{h})$; S is a specimen surface area, m^2 ; t is test time; $\overline{W_{q3}}$ is an average CP release rate during tests, $\text{g}/(\text{m}^2 \cdot \text{h})$; γ is a stoichiometric coefficient considering metal content in corrosion products.

Level of protection from specimen corrosion Z (%) after annealing as compared with specimen initial state is measured by the equation [14]

$$Z_{q1} = 100 \cdot (\overline{v_{q1,0}} - \overline{v_{q1,TA}}) / \overline{v_{q1,0}}, \quad (6)$$

where $\overline{v_{q1,0}}$ and $\overline{v_{q1,TA}}$ are average corrosion product release rates before and after thermal annealing, $\text{g}/(\text{m}^2 \cdot \text{h})$.

Level of water protection from EP-450 corrosion product release Z (%) after annealing as compared with specimen initial state is measured by the equation similar to that of (6)

$$Z_W = 100 \cdot (\overline{W_{q3,0}} - \overline{W_{q3,TA}}) / \overline{W_{q3,0}}, \quad (7)$$

where $\overline{W_{q3,0}}$ and $\overline{W_{q3,TA}}$ are average corrosion product release rates before and after specimen thermal annealing, $\text{g}/(\text{m}^2 \cdot \text{h})$, respectively.

3. Results and Discussion

3.1. Effect of operating parameters on corrosion of EP-540 steel in water with pH=7.0

The results of corrosion tests of shroud tube specimens carried out for 500, 1000 and 2000 hours in water with pH=7.0 are given in *Fig. 2* in the form of weight loss and pitting corrosion depth dependence on location along the core.

According to the data obtained, corrosion characteristics of irradiated EP-450 steel are mostly determined by location of specimens along the core (*see Fig. 2*). It is found that core centre and bottom areas are susceptible to the largest corrosion effect. There are uniform and pitting corrosion features in these areas. Internal sodium-facing surface of shroud tubes is predominantly exposed to both corrosion types, while there are only separate pitting corrosion sites on the external surface. Rather thick, loose light-brown or puce corrosion products are formed on both surfaces of specimens from core centre and bottom areas, while on core top and out of core areas thin, dense dark-gray oxide films are formed. With test time increase weight loss values for EP-450 specimens from core centre and bottom areas increase linearly from 4-12 g/m^2 at 500 h to 35-44 g/m^2 at 2000 h (*see Fig. 2.a*).

Weight loss of specimens q_1 from core top and out of core areas is 1-2 g/m^2 after testing for 500-2000 h, and has a slight tendency to increase along with test time increase.

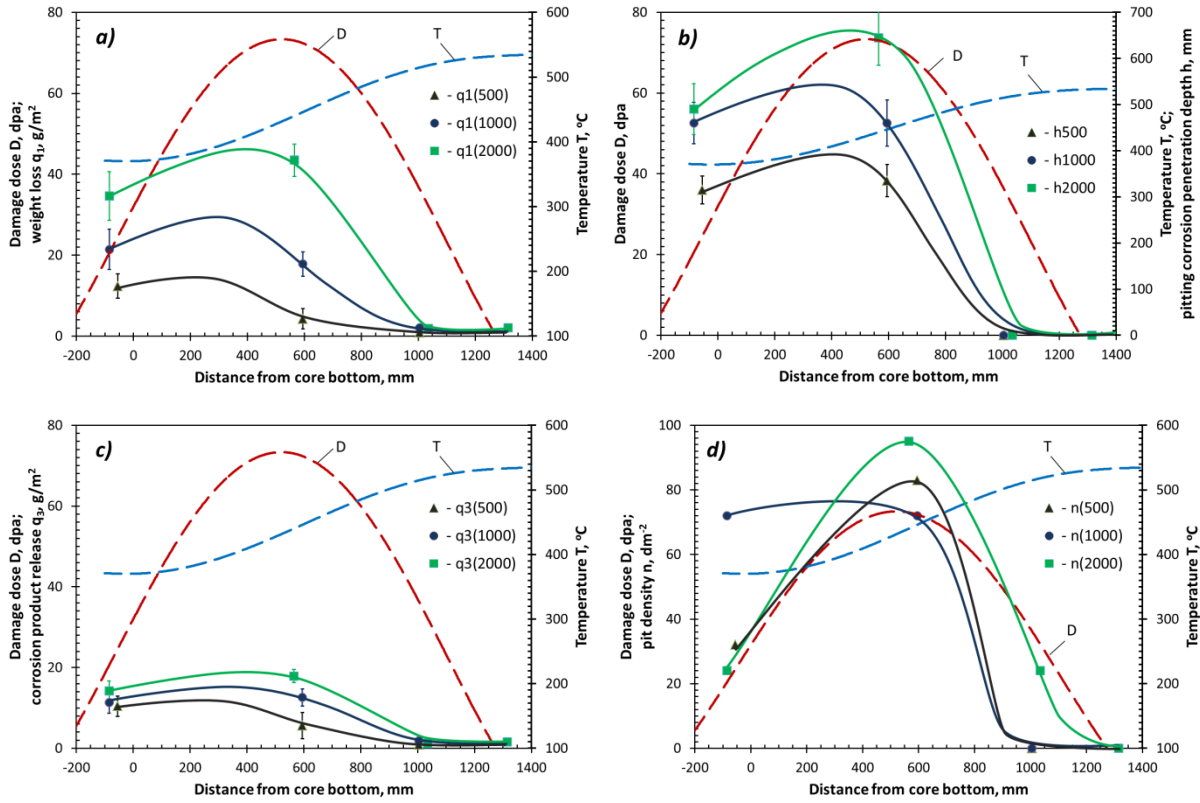


FIG. 2. Relation of damage dose D , operating temperature T , weight loss (a) and pitting corrosion penetration depth (b), corrosion product release (c) and pit density (d) variations along the shroud tube during EP-450 steel corrosion tests in water with $\text{pH}=7.0$ for 500, 1000 and 2000 h.

Pitting corrosion depth h and density of pits on specimen surface n have similar relation to location along the core (see Fig. 3). Maximum values for pit depth are registered on core centre and bottom specimens, while specimens from core top and out of core areas are slightly exposed to this corrosion type. As opposed to uniform corrosion pitting one tends to retard, and its development kinetics is almost parabolic.

In terms of total weight loss and pitting corrosion depth specimens from several elevations on the core are in the following sequence:

Core centre > Core bottom > Core top = Water-fuel emulsion area = Top welding joint.

Mathematical treatment of experimental data gives the following equations for weight loss q_1 and maximum pitting corrosion penetration depth $h_{\max}$ depending on damage dose D , operating temperature T and cooling time t in water with $\text{pH}=7.0$:

$$\ln q_1 (\text{g/m}^2) = -17,55 + 1,03 \cdot \ln t + 0,59 \cdot \ln D + 7510/T; R^2 = 0,87; n = 21, \quad (4)$$

$$\ln h_{\max} (\mu\text{m}) = -21,91 + 0,54 \cdot \ln t + 2,05 \cdot \ln D + 14700/T; R^2 = 0,99; n = 14. \quad (5)$$

According to these equations penetration depth of both corrosion types is in direct proportion to damage dose D and decreases with irradiation temperature T , though their kinetics differ: uniform corrosion linearly depends on time t , while pitting corrosion depth $h_{\max}$ is in parabolic relation with it. High determination level $R^2 > 0.87$ shows satisfactory convergence of experimental and estimated data.

There is strong (almost quadratic) dependence of EP-450 pitting corrosion depth on damage dose (Equation (5)).

3.2. Effect of thermal annealing on corrosion of irradiated EP-540 steel

The investigation results of the effect of annealing at 650, 700 and 750 °C on corrosion of irradiated EP-450 steel are given in *Table III*. The examined specimens are cut out from the shroud located in the core top with operating parameters $D_{avg}=25-45$ dpa, $T_{avg}=500-520$ °C. Corrosion tests are carried out in water with pH=7.0 for 2000 h. *Fig. 3* shows dependence curves of weight loss, oxide film thickness and corrosion product release (on metal basis) variations on annealing time at temperatures of 650, 700 and 750 °C.

According to the data obtained, annealing at temperature of 650 °C for 1-10 hours has a negative effect on all corrosion properties of irradiated EP-450 steel. Corrosion losses increase by ~3-4 times (*see Fig. 3.a, Table III*). Oxide thickness increases by ~2-3 times as opposed to raw steel (*see Fig. 3.b*). Corrosion product release into water increases by ~4-5 times (*see Fig. 3.c, Table III*) up to ~50-60 % of total corrosion losses during all the range of annealing time (*see Fig. 3.d*).

TABLE III. EFFECT OF THERMAL ANNEALING ON CORROSION OF IRRADIATED EP-540 STEEL.

Specimen state		Corrosion type ¹	$q_1, \text{g/m}^2$	$q_1/t, 10^{-3} \text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$	$Z_{q1}, \%$	$q_3, \text{g/m}^2$	$q_3/t, 10^{-3} \text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$	$Z_{q3}, \%$
Initial state (after unloading from the reactor)		U + P	2.38	1.19	0	1.32	0.66	0
After thermal annealing:								
T, °C	t, h							
650	1.0	U + P	8.15	4.08	<0	4.74	2.37	<0
650	3.0	U + P	6.23	3.12	<0	3.39	1.70	<0
650	10.0	U + P	5.53	2.77	<0	3.07	1.54	<0
700	0.5	U + P	6.51	3.26	<0	3.83	1.92	<0
700	1.0	U + P	4.13	2.06	<0	2.65	1.33	<0
700	3.0	U + P	2.63	1.32	<0	1.14	0.57	13.6
700	10.0	U	0.98	0.49	58.8	0.82	0.41	37.9
750	0.5	U + P	2.66	1.33	<0	1.55	0.78	<0
750	1.0	U	0.48	0.24	79.8	0.17	0.09	87.1
750	3.0	U	0.56	0.28	76.5	0.28	0.14	78.8
750	10.0	U	0.54	0.27	77.3	0.35	0.18	73.5
¹ – corrosion type: U – uniform, P – pitting.								

Corrosion properties of annealed specimens correlate with their appearance. During annealing for 1 and 3 hours loose puce corrosion products are generated on both specimen surfaces (internal and external sides of the shroud tube).

Increasing annealing time to 10 hours decreases its negative effect. In this particular case puce corrosion products are generated only inside the shroud tube. However, spotted specimen surface after oxide film being removed indicates that irrespective of annealing time it mostly affects internal side of the shroud tube. After all annealing times steel specimens are exposed to pitting corrosion as well as to uniform one (*Table III*).

Annealing at temperature of 700 °C for 0.5 and 1 hour has a negative effect on corrosion resistance of irradiated steel as well (*see Fig. 3, Table III*): corrosion rate and corrosion product release increase by ~2-2.5 times as compared with the initial state, and corrosion is of both uniform and pitting types.

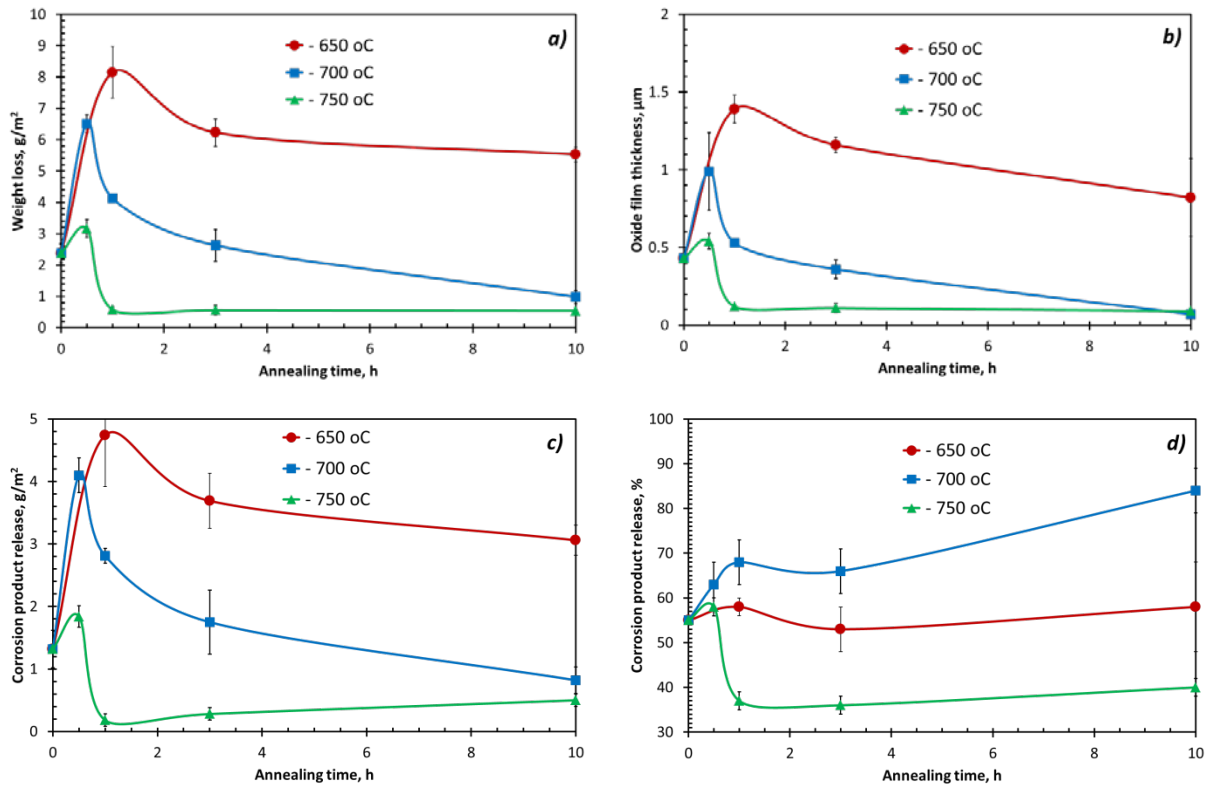


FIG. 3. Annealing parameters effect on changes in weight loss (a), oxide film thickness (b) and release of irradiated EP-450 steel corrosion products into water (c, d).

Annealing for 3 hours almost does not affect steel corrosion behaviour: corrosion rate, corrosion product release rate, and corrosion type remain almost the same. Only increasing annealing time to 10 hours has a positive effect: weight loss, oxide thickness and corrosion product release decrease by ~1.5 times as compared with the initial state (supply condition), and there is only uniform corrosion detected. However in this particular case at almost all annealing times corrosion product release into water is up to 70-85 % from total steel corrosion losses (see Fig. 3.d).

It should be noted that annealing at temperature of 700 °C leads to significant changes in corrosion product formation on annealed specimen surface. Loose puce corrosion products are generated on both sides of specimens only during short-term annealing (up to 0.5 h).

There are differences in corrosion behaviour between internal and external shroud surfaces with annealing time increased to 1 hour or more. Black corrosion products with small areas in the form of puce stripes and stains are predominantly generated on the external surface of specimens annealed for 1 hour. With annealing time increase to 3 and 10 hours only black corrosion products are generated on the external side of the shroud tube. On the internal surface of specimens annealed for 1 and 3 hours there are both black and puce oxide films, though with increased annealing time puce oxide area reduces. Further annealing time increased to 10 hours at temperature of 700 °C generates only black oxide films on both surfaces. Spotted specimen surface with removed oxide film appears only after annealing for 0.5-3 hours. While after annealing for 10 hours specimen surface with removed oxide film has a metallic luster.

According to *Fig. 3* and *Table III*, annealing at temperature of 750 °C (except for initial holding for 0.5 h) slightly improves corrosion behaviour of irradiated EP-450 steel. Corrosion losses and corrosion product release are by ~4-5 times less after annealing for 1-10 hours than without it. Fraction of corrosion products released into water under annealing at temperature of 750 °C does not exceed 30 % of total steel corrosion losses.

According to *Table III*, thermal annealing for 1-10 hours has a protective effect both against steel corrosion and corrosion product release into water, which is ~75-80 %.

In this particular case loose puce corrosion products occur only at holding for 0.5 hour and then only on the internal surface. Annealing for more than 1 hour generates uniform thin black corrosion products on both specimen sides (*see Fig. 3.b*). And after their removal there is a metallic luster surface.

According to the data obtained, a new technique of spent nuclear fuel storage is introduced (RF patent No. 2555856 dated 10.06.2015) with the following patent claim. Storage of spent nuclear fuel from fast neutron reactors with sodium coolant includes unloading of a spent fuel assembly from the reactor, its cleaning from residual sodium, putting into unpressurized shrouds at the bottom of a cooling pool filled with deionized water. The technique differs from conventional ones by thermal annealing of a spent fuel assembly before putting it into the shroud. Annealing is carried out in inert atmosphere at temperature of 700-750 °C for 1-10 hours under atmosphere pressure equal to that inside fuel pin at annealing temperature.

According to the patent claim, annealing time is from 1 to 10 hours. However, for the technical result lower temperature corresponds to longer annealing time.

4. Conclusions

The effect of operating parameters of irradiation in temperature range between 360 and 520 °C, at damage doses from 20 to 75 dpa and high-temperature annealing at 650, 700 and 750 °C during 0.5...10 h on corrosion behaviour of EP-450 ferritic-martensitic steel in water with pH=7.0 has been investigated.

It is found that irradiated EP-450 steel is susceptible to advanced general and pitting corrosion with corrosion product release up to 60-75 % of total corrosion losses.

Empirical expressions for calculation of corrosion losses and pitting corrosion penetration depth depending on time, damage dose and temperature of steel storage in cooling pool water with pH=7.0 have been obtained.

It is found that annealing for 0.5 h at all test temperatures, and at 650 °C during any test time (up to 10 h) declines corrosion resistance of irradiated EP-450 steel.

EP-450 steel corrosion resistance increases under annealing for specified time at specified temperature: T=700 °C, $t > 3$ h and T=750 °C, $t > 1$ h. Annealing at T=750 °C has the strongest effect; in this case corrosion rate decreases by ~4-5 times. Annealing for more than 1 h at T=750 °C almost does not affect steel corrosion resistance.

Optimal annealing parameters for irradiated EP-450 steel in terms of corrosion are: T=750 °C during $t=1-3$ h.

According to the data obtained, a new storage technique for spent nuclear fuel of fast reactors with structural materials made of 12%-chromium ferritic-martensitic steels has been developed (RF patent No. 2555856 dated 10.06.2015).

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