CORROSION BEHAVIOR OF TUBE STEEL FOR BREST-OD-300 STEAM GENERATOR

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1. Introduction

An original design of vertical steam generator (SG) for BREST-OD-300 reactor was developed, featuring a steam superheating area in the upper riser part of helical heat-exchange tubes (HET). Under survice conditions, water environment inside of the heat-exchange tubes is expected in different states (water, water-steam mixture, superheated steam). This provides different corrosion effects on the metal of the HET secondary side [1-5]. Therefore, HET metal shall be corrosion resistant relative to the abovementioned working media in a wide range of operating temperatures of 340-540 ^{o}C at a pressure of 17 MPa. Liquid lead is used as a coolant in the primary circuit, thus the metal for the heat-exchange tubes shall be corrosion-resistant to the primary coolant as well. In view of the above, one of the important objectives when designing BREST-OD-300 innovative reactor facility is to develop a structural material capable of ensuring the required strength and specified durability of HET in the SG operating conditions.

For this purpose, a new nitrogen-containing austenitic silicon steel of EP302M grade was developed, as well as the technology for cold-rolled tube fabrication. This choice is based on the experience in application of EP302 steel, which is corrosion-resistant in lead coolants, and on obtained earlier at I.P. Bardin Central Research Institute for Ferrous Metallurgy positive test results in regards to high-strength nitrogen-containing cold-worked steels featuring high resistance to local types of corrosion in sea water and other chloride-containing media [6].

At NIKIET, I.P. Bardin Central Research Institute for Ferrous Metallurgy, CRISM "Prometey", a series of experiments and studies dedicated to experimental proof of satisfactory corrosion resistance of structural steels including EP302M steel for the fabrication of BREST-OD-300 SG HET is carried out, where the specimens made of 12Kh18N10T steel are tested for comparison.

The objectives of this study were as follows:

- evaluation of uniform corrosion rate, corrosion loss of the walls basing on the results of corrosion testing in liquid lead, water and superheated steam;

- evaluation of evironment effect on corrosion-mechanical properties of EP302M steel;

- evaluation of resistance to stress corrosion cracking (SCC), intergranular corrosion (IGC) and pitting corrosion (PC).

2. Corrosion resistance in liquid lead

At nonisothermal test benches of CRISM "Prometey", corrosion tests of EP302M steel in BREST-OD-300 coolant-simulating liquid lead flow with a dissolved oxygen (DO) content of ~ 10^{-6} mass % were carried out conditions with specimens ambient velocity of 0.5 m/s at a temperature of 500-550 °C. The specimens were tested under unstressed and prestressed conditions. Prestressed specimens tested @ stress level (0.4-0.8)·$\sigma_{0.2}$ up to 5000 h.

At the initial stage of oxidation with the exposure times up to 2000 h, a protective oxide film with an average thickness of ~ 3 μm forms on the surface. Later on, a discontinuity occurs in some areas, with the formation of the internal metal oxidation regions. As the test duration increases, formation of an oxide film with nonuniform thickness is observed. The average depth of the layer or the region with an increased internal oxidation was ~ 90 % higher than that of the stress-free specimens, which is typical for the stress levels that are significantly higher than the maximum allowed design values.

According to extrapolation to a 30-year-long life of the SG, the uniform corrosion allowance for the estimated thickness of the SG HET walls made of EP302M steel in contact with liquid lead at a temperature of 500-550 °C was no more than 0.1 mm based on the oxide film growth kinetics with no detachments before being exposed for 5000 h. The conservative values of allowance obtained on this basis for EP302M steel will be refined during the processing of the results of the bench tests with longer duration.

Studies on the effects of the lead coolant with DO of ~ 10^{-6} mass % on the short-term mechanical properties of EP302M steel have been carried out in test bench conditions based on the results of tensile tests at temperatures of 20 °C, 450 °C and 550 °C. Here, the effects of the lead coolant on the mechanical properties of EP302M steel proved to be insignificant, and from now on, they can be neglected. For this steel, changes in the mechanical properties from the contact with liquid lead remained within the range of experimental value variation. For the specified oxygen range, mechanical characteristics of this steel, which were obtained from tests in air, can be adopted as estimated characteristics.

The effects of lead coolant on stress-rupture strength and creep characteristics of EP302M steel were investigated based on the comparative tests lasting up to 20000 h at a temperature of 550 °C in air and in contact with liquid lead with DO of ~ 10^{-6} mass % for two specimen types: cylindrical ones from the industrial batch of tube billet and tube segments of the industrial heat. According to the test results for the constructions stressed while in service up to the values not exceeding 180 N/mm^2, the steel creep rate in the lead coolant is taken equal to the creep rate in air. Before completion of the stress-rupture tests in the lead coolant flow at CRISM "Prometey", the values of EP302M steel's stress-rupture strength in air with a safety margin should be taken as estimated values when considering coolant effects.

3. Corrosion resistance in water and superheated steam

The corrosion tests of EP302M steel specimens cut from long-length HET, and 12Kh18N10T steel specimens as well, are carried out in the autoclave testing complexes at NIKIET. Corrosion resistance measurements are made in accordance with GOST 9.908-85.

During the high-precision corrosion tests, thermal engineering parameters at SG inlet and outlet (temperatures of 350 ^{o}C and 525 ^{o}C, pressure of 17 MPa) are consistently maintained, and chemical indices of quality of simulated water and steam media are continuously measured, including the electrical conductivity of 0.10±0.05 μS/cm and the DO concentration of 30 μg/dm^3 (in water) and 10 μg/dm^3 (in superheated steam). DO measured at 25 ^{o}C [7].

Fig. 1 shows a fragment of oxide film on surface of the metallographic section of the EP302M steel specimen after tests in water at 350 ˚C.

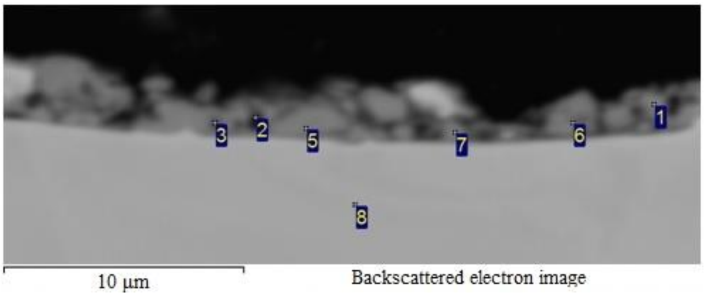

FIG. 1. Oxide film on the EP302M steel surface (backscattered electron image). Tested in water at 350 ^oC for 1000 hrs

Basing on the element analysis results, the oxide film (defining points 1 through 7, Fig. 1) consists predominantly of the iron oxides with small amounts of chromium and nickel oxides with the average mass fractions of iron, chromium and nickel in the film of ~ 50%, ~ 15 % and ~ 10 %, respectively) and the oxide film thickness after 1000 h of testing not exceeding 4 µm. Defining point 8 in the base metal of EP302M steel was used for comparison. The uniform corrosion rate of the new austenitic EP302M steel calculated basing on the results of testing in water at 350 ^oC, was 1.5 times lower than that of the austenitic corrosion-resistant 12Kh18N10T steel that is commonly used in the nuclear industry [8].

Fig. 2 shows the structure of the oxide film formed on specimen with the electrochemically polished surface after testing in superheated steam.

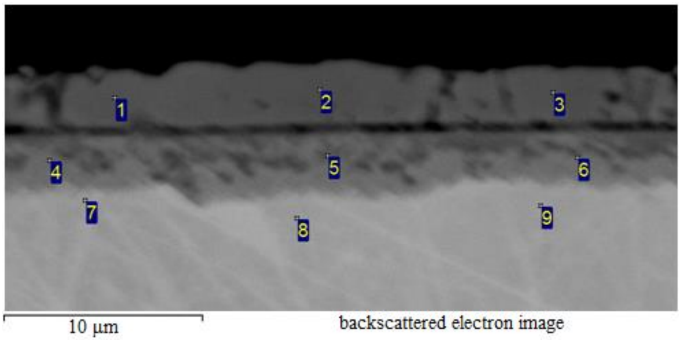

FIG. 2. Oxide film on the EP302M steel surface (backscattered electron image). Tested in superheated steam at 525 ^oC for 1000 hrs

As can be seen from the above Fig. 2, a double-layer oxide film forms on the metal surface. Its outer layer is represented by iron oxide, which stoichiometrically corresponds to Fe_3O_4 magnetite (points 1-3). The inner layer is represented by a mixed spinel with complex composition (points 4-6), in which the average mass fractions of chromium (Cr), iron (Fe) and nickel (Ni) are 27 %, 22 % and 19 %, respectively, and the thickness of this oxide film after 1000 h of testing is 5 - 7 µm.

The uniform corrosion rate of EP302M steel calculated based on the results of the autoclave tests in superheated steam at 525 ^oC was 2 times lower than that of 12Kh18N10T steel [8].

The analysis of the effects of metal ageing factor on the corrosion behavior of EP302M steel in superheated steam showed that the additional heat treatment of HET metal at 550 ºC for 1500 h which simulated ageing at SG operating temperatures, has a significant effect on the corrosion behavior in superheated steam (Fig. 3).

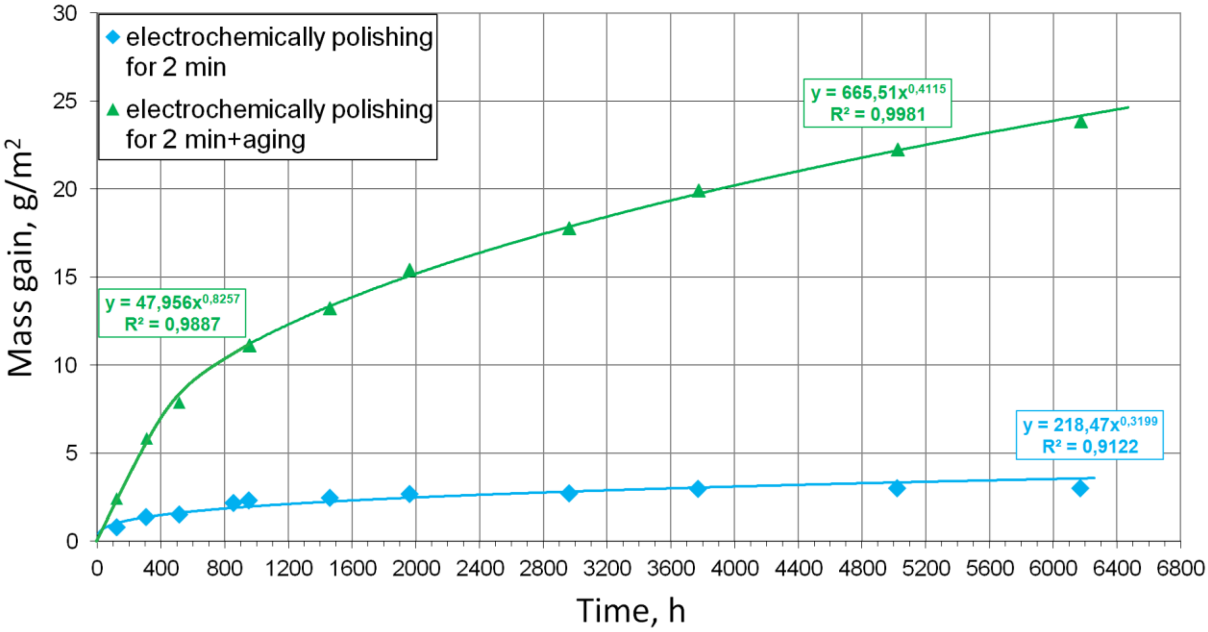

FIG. 3. Mass gain of EP302M steel with different modes of surface in superheated steam at 525 ^oC

Basing on extrapolation of the autoclave corrosion test data, the estimated uniform corrosion add to thickness for EP302M steel HET walls for 30-years-long service life of the SG in contact with water at a temperature of 350 °C based on the tests for 1000 h was established 0.05 mm, and in contact with superheated steam at 525 °C – 0.1 mm based on the tests for 6000 h [8-11].

The stress-corrosion tests of the specimens in the form of tube segments (Fig. 4) were carried out for the first time in the simulated water and steam SG environments at temperatures of 350 ^{o}C and 505 ºC and a pressure of 17 MPa in accordance with GOST 19040-81 [12]. The representative stress-strain curve for the EP302M steel specimen in the form of a tube segment at low strain rate ($3 \cdot 10^{-6} s^{-1}$) in superheated steam is shown in Fig. 5.

FIG. 4. A segment-type specimen machined from SG tubing after SSRT-testing in superheated steam at 505 ^oC

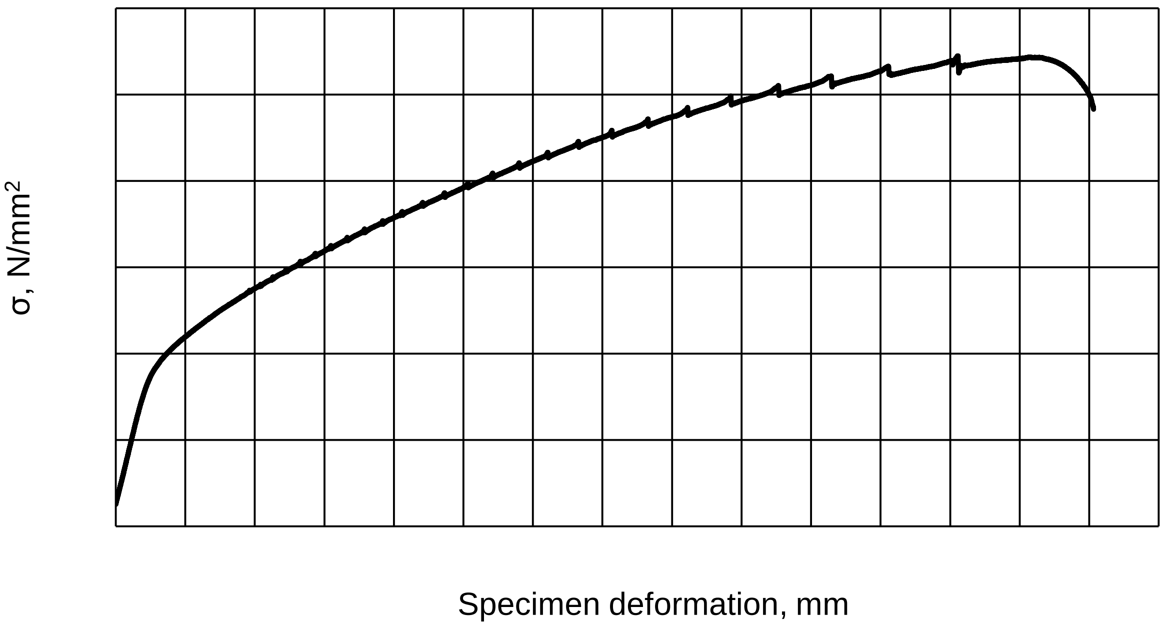

FIG. 5. SSRT diagram of EP302M steel in superheated steam at 505 ^{o}C

According to the results of the tests at the low strain rate of $3\cdot10^{-6}$ s^{-1} in water and steam at a pressure of 17 MPa and temperatures of 350 and 505 ^{o}C, the tensile strength of EP302M steel is within the ranges of 545-595 and 520-550 MPa, respectively, the yield strength, with an allowance for a strain of 0.2%, is in a range of 170-210 MPa, the maximum total post-fracture elongation is in a range of 50-60 %. The same plasticity index for the referent austenitic steel is in a range of 20-40%. The fractographic investigation of fractures of the ruptured EP302M-Sh steel specimens showed a ductile intergranular fracture pattern [13].

Experimentally shown that electrochemical polishing of the surface makes the metal less sensitive to slow-strain corrosion cracking in water environment at 350 ^{o}C [13].

The comparative tests at a strain rate of $6\cdot10^{-5}$ s^{-1} in superheated steam and air at a temperature of 505 ^{o}C showed that the HET metal in its initial state has the same strength and ductility indices as the metal tested in air.

Comparison of the creep data for EP302M steel in air and superheated steam indicates no effects of superheated steam on the metal's creep resistance at a stress level of 235 MPa and test duration of 1000 h. The relatively high stress level used in the tests allows to apply this conclusion to the design stress levels. Visual examination of the specimens after the completion of the tests showed no surface cracks and signs of corrosion cracking. A continuous oxide film had formed on the specimen surfaces, protecting the metal against corrosion cracking. HET metal also showed high resistance to corrosion cracking in the simulated SG steam environment during the tests under static loading conditions.

4. Resistance to intergranular and pitting corrosion

Resistanse to intergranular and pitting corrosion of the EP302M steel specimens cut from commercial tube batch is studied at I.P. Bardin Central Research Institute for Ferrous Metallurgy. The IGC resistance tests were carried out using an electrochemical potentiodynamic reactivation method as per GOST 9.914-91 and a chemical "AMU" method as per GOST 6032-2003 [14]. Rate of specimen pitting corrosion was determined by a chemical method and an electrochemical method as per GOST 9.912-89 [15].

The effects of ageing duration on the resistance of the HET specimens to IGC and pitting corrosion were studied at a temperature of 650 °C and exposure periods 1-50 h, as well as at a temperature of 550 °C for 2000 h. It was determined that EP302M steel had no tendency to IGC after sensitizing annealing at 650 °C for 50 h. After thermal ageing for 2000 h at 550 °C tube specimens made from EP302M steel showed no susceptibility to IGC and pitting corrosion [6].

Conclusions

The following experimental results obtained:

- based on the data obtained from corrosion testing of the non-stressed EP302M steel specimens, estimated uniform corrosion allowances to the thickness of the HET walls for 30-years design life of the SG were: 0.1 mm in superheated steam at a temperature of 525 °C, 0.05 mm in water at 350 °C, and 0.1 mm in liquid lead coolant at 550 ºC (with regulated oxygen values of ~ 10^{-6} mass. %);
- it was experimentally verified by the results of the tensile strength tests at temperatures of 20 °C, 450 °C and 550 °C that the effects of lead coolant with a dissolved oxygen level of ~ 10^{-6} mass. % on the short-term mechanical properties of EP302M steel are insignificant, and they may be neglected;
- comparative stress-corrosion tests in superheated steam and in air at 505 ^{o}C showed absence of negative superheated steam effects on strength and plastic characteristics of EP302M steel;
- HET metal demonstrated high resistance to corrosion cracking, intergranular and pitting corrosions.

According to the analysis of the experimental investigation results, it can be concluded that EP302M steel proposed as the structural material for HET is able to ensure reliable operation of BREST-OD-300 steam generators for 30-year design life both in terms of uniform corrosion rate. Stress-corrosion properties under complience with requirements to the quality of lead coolant and secondary side environment.

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