

LABORATORY TESTS OF HIGH-TEMPERATURE CORROSION OF STEELS B-407, X8CrNiNb1613 AND X8CrNiMoNb1616 UNDER IMPACT OF ASH FORMED AT PULVERIZED FIRING OF OIL SHALE

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High-temperature corrosion of three austenitic boiler steels, B-407, X8CrNiNb1613 and X8CrNiMoNb1616, was tested experimentally in laboratory in conditions of superheater of oil shale boiler in the presence of chlorine-containing external deposits. The empirical kinetic equations for calculation of corrosion depth depending on operational time and temperature were established. The best corrosion resistance was shown by steel X8CrNiMoNb1616.

Introduction

Estonian oil shale, an important local low-grade fuel, is utilized at Balti and Eesti Power Plants in pulverized firing (PF) and in recently erected circulating fluidized bed (CFB) boilers. About $10 \cdot 10^6$ tonnes oil shale are consumed per year producing $8 \cdot 10^6$ MW·h electricity. Estonian oil shale is one of the more complicated fossil fuels. Combustion of inorganic matter produces several chemically active compounds leading to both fouling and accelerated high-temperature corrosion of superheater and reheater tubes. This is mainly due to the presence of potassium chloride [1].

Acceleration of high-temperature corrosion in the presence of chlorine has been a serious problem drawing much attention over the years. First the problem was encountered in coal-firing boilers [2, 3], later in waste incinerators [4], and recently in boilers for firing biomass as an alternative energy source [5–7]. Unfortunately, because of different nature of combustion and fouling processes, deposit formation and impact to tube metal when oil shale is combusted, it is almost impossible to predict

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corrosion of tubes in oil shale boilers on the basis of these researches. For precise prediction, one has to examine material of tubes in conditions very close to actual operation conditions in oil shale boilers.

A detailed investigation on high-temperature corrosion of Russian boiler steels under the influence of oil shale ash was carried out at Thermal Engineering Department of Tallinn University of Technology (TED TUT) during the last four decades [1]. Up to the present the laboratory and industrial tests on corrosion did not reveal the “ideal” grades of boiler steels that could be operated at elevated temperatures in the presence of oil shale deposits for a long time. To continue the above-mentioned investigations austenitic steels B-407 (ASTM), X8CrNiNb1613 and X8CrNiMoNb1616 (DIN 17459) were examined.

Corrosion Tests

Laboratory corrosion tests of boiler steels were carried out in accordance with standard techniques [8, 9]. These tests were performed in electrically heated vertical tube-type furnaces with an inner diameter of 40 mm (Fig. 1).

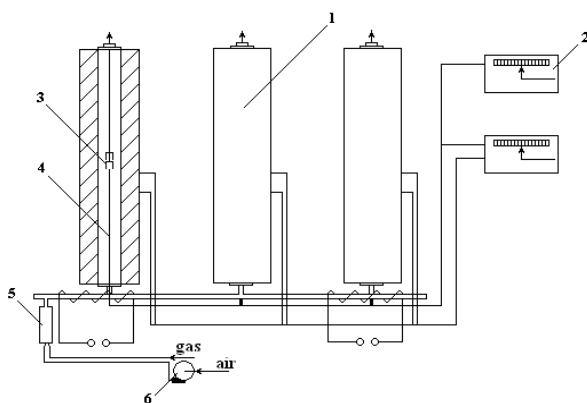


Fig. 1. The laboratory unit for investigation of high-temperature corrosion of metals:

- 1 – electrical furnaces;
- 2 – tools for temperature measurement and control;
- 3 – test specimens;
- 4 – thermocouples;
- 5 – combustion chamber;
- 6 – fan

Combustion products of natural gas were directed into the furnaces by a pipe header. To avoid condensation of water vapor, the pipe header was heated by electrical heating coils. Natural gas is burnt in a special combustion chamber where excess air factor was maintained in the range of 1.25–1.30. The combustion gas velocity in the furnaces was about 0.15–0.18 m/s. According to gas analysis, the content of O₂ and CO₂ in combustion products of natural gas was ~4 and ~10%, respectively.

Every furnace had an isothermal zone not less than 100 mm in length. The maintenance of constant temperature in the isothermal zones of the furnaces as well as temperature measurements was realized automatically by the use of analog control units and thermocouples as a sensors. During experiments the temperature of the furnaces was maintained at 540, 580 and 620 °C with accuracy ± 2 °C.

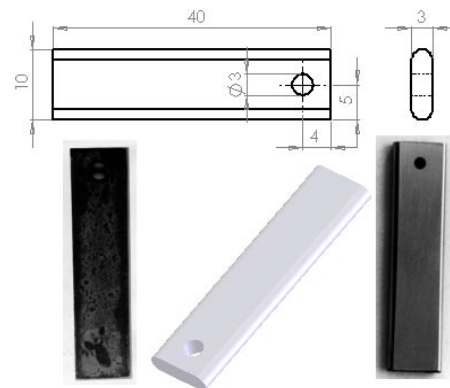


Fig. 2. Test specimens, new (right) and corroded (left)

Corrosion tests were performed on flat electrically polished specimens (Fig. 2) with dimensions $3 \times 10 \times 40$ mm, which were cut from original boiler tubes. Chemical composition of examined steels is presented in Table 1.

Table 1. Chemical Composition of Examined Steels

	Steel grade			
	12Ch18N12T*	X8CrNiNb1613	X8CrNiMoNb1616	B-407
Content, %				
C	0.12	0.04	0.04–0.10	0.05–0.10
Si	0.80	0.30–0.60	0.30–0.60	1.0
Mn	1.00–2.00	1.50	1.50	1.50
Cr	17.9–19.0	15.0–17.0	15.50–17.50	21.0
Ni	11.0–13.0	12.0–14.0	15.50–17.50	31.40
Mo	–	–	1.60–2.00	–
P	0.035	0.035	0.035	–
S	0.020	0.015	0.015	0.150
Nb	–	1.2	1.2	–
Ti	0.70	–	–	0.50
Cu	0.30	–	–	–

* Designation of Russian steel accords with specification given in [11].

Sets of three specimens were tested at each temperature and for every time interval (totally 12 sets or 36 specimens for a particular steel). Prior to the tests all specimens were degreased, precisely measured and weighed. Then they were coated with a mixture of oil shale ash and ethyl alcohol for imitation of oil shale on-tube deposits. Electrical precipitator ash, with chlorine content of about 0.5%, was used in the laboratory experiments. The coated specimens were dried at the ambient temperature (20–25 °C) and placed with special hanger rods into the furnaces previously heated up to the particular temperatures.

To compensate the consumption of chlorine in the imitated deposits, recoating of the specimens at regular intervals was realized. The specimens

were taken out, cooled at ambient temperature and recoated with fresh ash-alcohol mixture every 10 hours of exposure. The full chemical composition of the Estonian oil shale fly ash used in corrosion tests is as follows, %: SiO₂ 28.4; Fe₂O₃ 3.66; Al₂O₃ 14.46; CaO 32.02; MgO 3.78; SO₃ 9.91; K₂O 6.71; Na₂O 0.56; Cl 0.50.

Oxide scale on the tested specimens was removed in the environment of liquid sodium by blowing ammonia [10]. The quantity of corroded material was determined as the difference in the mass of clean specimens before and after testing. The accuracy of weighing was ± 0.1 mg. On the basis of mass difference the corrosion depth (ΔS , mm) was calculated.

Discussion of Results

The results of laboratory tests are presented as kinetic diagrams of corrosion depth of examined steels in coordinates $\ln \Delta S - \ln \tau$ (Fig. 3, *a-c*).

The results of earlier laboratory tests of Russian steel 12Ch18N12T (TY 14-3-460-75) are shown in Fig. 3, *d* for comparison. In logarithmic coordinates the kinetic curves of high-temperature corrosion are straight lines and usually expressed by the following empirical correlation:

$$\ln \Delta S = \alpha - \beta T^{-1} + (\gamma + \varepsilon T) \ln \tau \quad (1)$$

where ΔS – corrosion depth, mm;

T – metal temperature, K;

τ – time, h;

α , β , ε , γ – coefficients depending on ash characteristics of the particular fuel, grade and temperature of the metal. Coefficient $(\gamma + \varepsilon \cdot T)$ is defined as exponent of the corrosion process. All these coefficients are determined experimentally.

As it could be seen from Eq. (1), an exponent of the corrosion process is generally proportional to operating temperature of the metal. Regression lines of the steel 12Ch18N12T (see Fig. 3, *d*) demonstrate just this classical case, giving the following empirical equation:

$$\ln(\Delta S) = -8.12 - 297/T + (-0.84 + 0.00178 \cdot T) \ln \tau \quad (\text{St Err } 0.34) \quad (2)$$

A similar dependence was established by fitting the data of corrosion tests of the steel B-407 (solid lines in Fig. 3, *a*). The regression equation in this case is

$$\ln(\Delta S) = -3.5 - 3077/T + (-1.11 + 0.00184 \cdot T) \ln \tau \quad (\text{St Err } 0.3) \quad (3)$$

This equation is used for prediction of the corrosion depth of the steel B-407. By comparison of Equations (2) and (3) it could be mentioned that the relation between the exponent of the corrosion process and metal temperature is practically the same (the same slope of the lines) for both

cases. The absolute value of the corrosion depth of the steel B-407 is about the same as that of steel 12Ch18N12T in the range of investigated temperatures and test duration 1,000 h (Fig. 4).

However, the attempt to use the same type of Correlation (1) to fit the corrosion tests data of the steels X8CrNiNb1613 and X8CrNiMoNb1616 led to the following paradoxical results.

First: The increase in metal temperature decreases the exponent of the corrosion process of steel X8CrNiNb1613 giving the following equation:

$$\ln(\Delta S) = 12.4 - 16,368/T + (2.02 - 0.00188 \cdot T) \ln \tau \quad (\text{St Err } 0.16) \quad (4)$$

The regression lines (dotted lines in Fig. 3,b) intersect in this case at point $\tau \approx 100,000$ hours (not shown). It means that the corrosion of the steel exposed longer than 100 thousands hours is more intensive at lower temperatures that is in contradiction with Arrhenius rate equation.

Second: The exponent of corrosion process of steel X8CrNiMoNb1616 shows the temperature coefficient $\varepsilon = 0.0049$ that is 2.5 times higher than for steels 12Ch18N12T or B-407 (dotted lines in Fig. 3,c). The corrosion process is defined as follows:

$$\ln(\Delta S) = 28.2 + 16,530/T + (-3.6 + 0.0049 \cdot T) \ln \tau \quad (\text{St Err } 0.182) \quad (5)$$

The regression lines intersect at the range of $\tau = 100\text{--}200$ hours. It means that in this case corrosion intensity of the steel exposed less than 100 hours is higher at lower temperatures that is also in contradiction with Arrhenius rate equation.

Both cases could be explained only by scattering of the experimental data (characterised by standard error, St Err), which are always more perceptible when it is necessary, on the basis of short-term tests, to predict the corrosion process for a period of time that is 20–200 times longer than duration of experimental tests. To improve the reliability of the prediction of corrosion depth for these two steels the tests data were approximated by the regression equations that have the same dependence of exponent of corrosion process on metal temperature as two previous austenitic steels.

Thus, the following empirical equations for prediction of corrosion depth of the steels X8CrNiNb1613 and X8CrNiMoNb1616, depending on operational time and metal temperature, were established:

for X8CrNiNb1613:

$$\ln(\Delta S) = 6.0 - 620/T + (-1.12 + 1.8 \cdot 10^{-3} \cdot T) \ln \tau \quad (\text{St Err } 0.188) \quad (6)$$

for X8CrNiMoNb1616:

$$\ln(\Delta S) = -13.5 + 4027/T + (-0.97 + 1.8 \cdot 10^{-3} \cdot T) \ln \tau \quad (\text{St Err } 0.194) \quad (7)$$

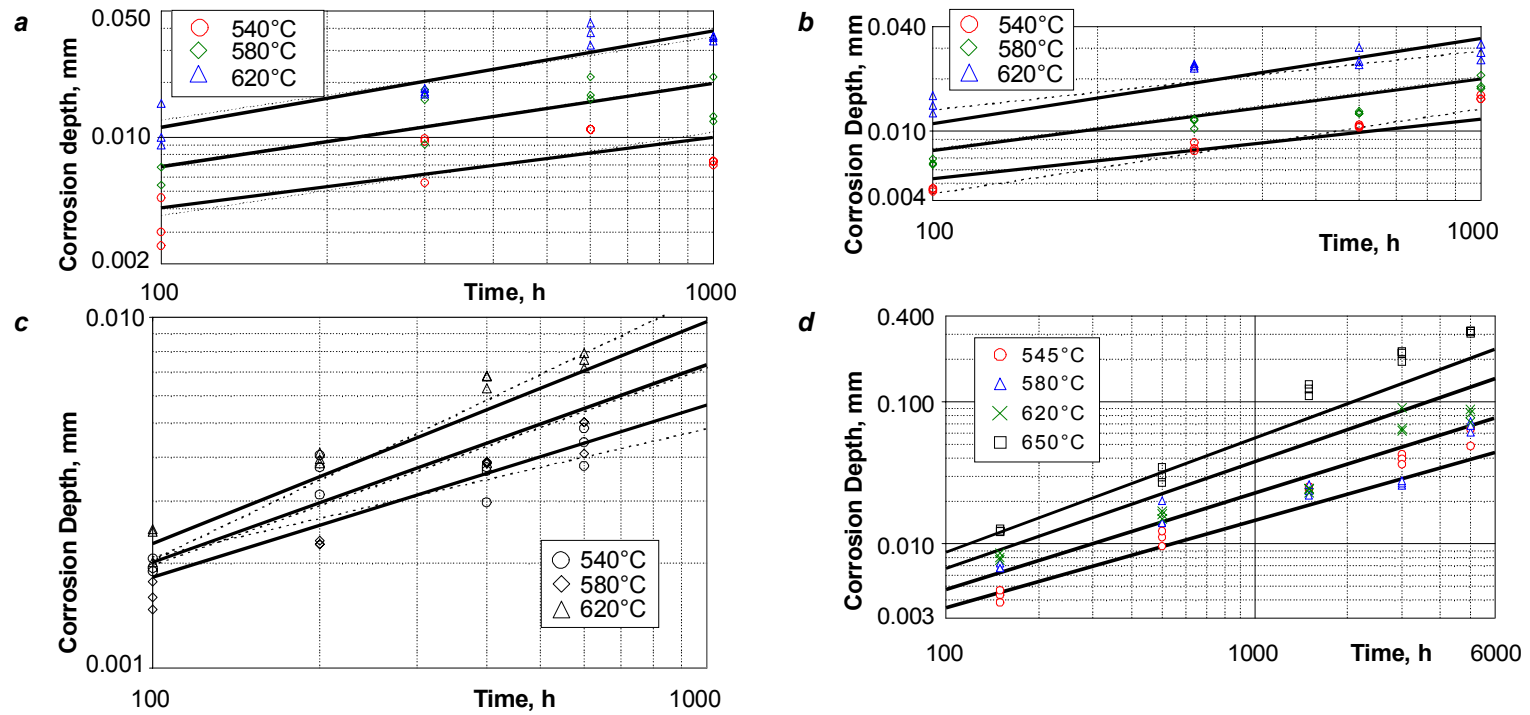


Fig. 3. Corrosion depth of steels: (a) B-407; (b) X8CrNiNb1613; (c) X8CrNiMoNb1616; (d) 12Ch18N12T: laboratory tests and regression lines

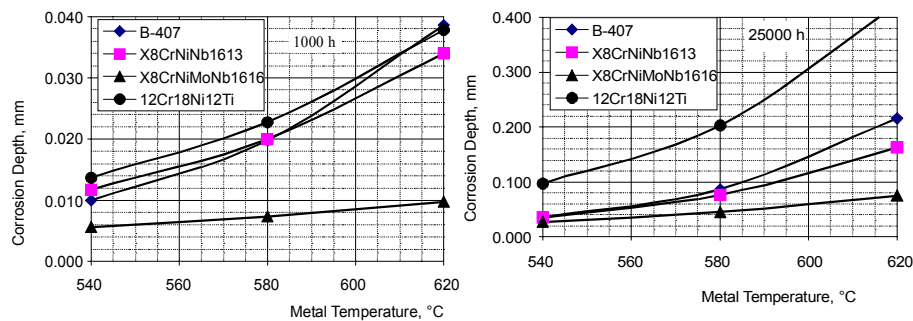


Fig. 4. Corrosion depth after 1,000 and 25,000 h of exposure

On the basis of established regression equations some predictions of corrosion depth of examined steels are presented in Table 2 and Fig. 4. Time period 25,000 h corresponds to general major overhauls interval.

Table 2. Corrosion Depth of Austenitic Steels under Impact of Fly Ash of Oil Shale PF, ΔS , mm

Steel	$\tau = 1,000$ h			$\tau = 25,000$ h		
	540 °C	580 °C	620 °C	540 °C	580 °C	620 °C
B-407 (3)*	0.010	0.020	0.039	0.035	0.087	0.215
X8CrNiNb1613 (6)	0.012	0.020	0.034	0.035	0.076	0.163
X8CrNiMoNb1616 (7)	0.006	0.007	0.010	0.027	0.045	0.075
12Ch18N12T (2)	0.014	0.023	0.038	0.097	0.202	0.422

* In brackets the number of the corresponding equation in text.

Corrosion resistance of steels 12Ch18N12T, B-407, X8CrNiNb1613 after 1,000 h is about the same. Corrosion depth of steel X8CrNiMoNb1616 is much less.

After 25,000 h all of the steels except for steel 12Ch18N12T have practically the same corrosion resistance at 540 °C. There are essential differences in properties of the steels at higher temperatures. The best corrosion-resistant steel is X8CrNiMoNb1616, the worst one – B-407. At the same time corrosion depth of the steel B-407 at 620 °C is two times less than that of the steel 12Ch18N12T. These results were obtained by the corrosion tests under stable layer of the oil shale ash deposits, however, periodic destruction of the oxide scale that occurs in the real conditions in a boiler sharply accelerates corrosion. Thus the final form of equation for prediction of the high-temperature corrosion in the presence of oil shale ash could be established only after industrial tests in the real boiler conditions.

Conclusions

1. The empirical equations for prediction of corrosion depth of examined steels under a stable layer of oil shale ash deposit were established.
2. According to the laboratory corrosion tests, the best corrosion-resistant steel is X8CrNiMoNb1616.

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