

HIGH-TEMPERATURE CORROSION RESISTANCE OF THE AUSTENITIC STEELS IN THE PRESENCE OF CHLORINE-CONTAINING ON-TUBE DEPOSITS^{*1}

I. KLEVTSOV^{*2}, H. TALLERMO^{*3},
T. BOJARINOVA^{*4}, T. LAUSMAA^{*5}

Tallinn Technical University,
Thermal Engineering Department
116 Kopli St., 11712 Tallinn, Estonia

High-temperature corrosion resistance of a number of boiler steels was tested experimentally in laboratory and industrial conditions in the presence of chlorine-containing external deposits. Empirical kinetic equations for calculation of corrosion depth depending on operational time and temperature were established, and the dependence of corrosion resistance of the austenitic steels on the alloying elements ratio Ni/Cr was analyzed.

Introduction

Estonian oil shale is the most important local low-grade fuel of calorific value $Q_i^r \approx 8.4$ MJ/kg, content of ash $A^d \approx 51.3\%$ and moisture $W_i^r \approx 11.7\%$. Almost all national electricity (92%) is produced at the two big power plants, *Balti* (Baltic) and *Eesti* (Estonia), by pulverized firing (PF) of oil shale. The amount of pulverized-fired oil shale is about $10 \cdot 10^6$ tons per year that produces 8 TWh electricity.

As for PF process, Estonian oil shale is one of the most complicated fossil fuels. Its inorganic matter produces in the PF process a lot of chemically active compounds that accelerate both fouling and high-temperature corrosion of superheaters and reheater tubes mainly due to the presence of KCl. Periodical cleaning of high-temperature heating surfaces from external ash deposits additionally accelerates the corrosion process [1]. Considering intensive corrosion of tubes the live steam and reheater steam temperatures in oil shale boilers were reduced to 515/525 °C.

Laboratory and industrial examinations of corrosion resistance of various alloys carried out at Thermal Engineering Department of Tallinn Technical

^{*1} Presented at Symposium on Oil Shale in Tallinn, Estonia, November 18–21, 2002.

^{*2} Corresponding author: e-mail klevtsov@sti.ttu.ee

^{*3} E-mail harrit@sti.ttu.ee, ^{*4} e-mail bojarin@sti.ttu.ee, ^{*5} e-mail tlausmaa@sti.ttu.ee

University revealed the most significant factors governing corrosion process. For austenitic alloys one of such factors is the Ni/Cr ratio discussed in this paper in detail.

Corrosion Tests

Both laboratory and industrial experiments were carried out according to the method presented earlier [2]. Metal temperature was 500, 540, 580 and 620 °C during laboratory experiments and 505–520°C during industrial experiments. Electrical precipitator ash was used in laboratory experiments; its Cl content was around 0.5%. Seven austenitic steels with various Ni and Cr content were tested. Duration of laboratory tests for some steel grades was around $3 \cdot 10^3$ hours, and duration of industrial tests up to $25 \cdot 10^3$ hours. Corrosion resistance of protective coating with large Ni content, settled on pearlitic steel tube specimen, was also tested in laboratory and in PF oil shale boilers. In both cases the gas flame method was applied for making the coating.

Discussion of Results

Tests data were treated separately for each particular temperature range as regression on test duration. The decrease in tube wall thickness due to high-temperature corrosion was defined by the following empirical equation:

$$\ln \Delta S = a + b \ln \tau, \quad (1)$$

where ΔS is corrosion depth, mm;

b exponent of the corrosion process,

τ test duration, h;

and a coefficient depending on many factors including metal temperature.

In Figure 1 the regressions are presented for the metal temperature of 580 °C. Exponent b defines the dependence of high-temperature steel corrosion process on time. The greater b , the more intensive the corrosion process, or the deeper the corrosion of the tubes' outer surface. The exponent often depends on the fossil fuel burning temperature, but laboratory tests did not distinctly show such dependence for austenitic steels.

The results of laboratory and industrial corrosion tests of various boiler steels and pearlitic steel *12X1MΦ* with coating containing 73% Ni and 16% Cr have shown that the resistance of superheater tubes to chlorine corrosion depends on the content of alloying elements as well as on the particular element content ratio. It was also found that the exponent of corrosion process b has the most unequivocal dependence on the ratio.

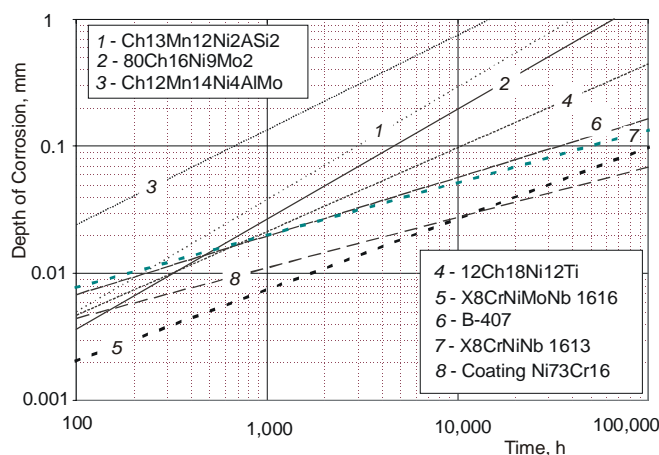


Fig. 1. Corrosion of boiler steels in the presence of chlorine in stable on-tube deposits

In this work an attempt was made to interpret the dependence of exponent, calculated for the corrosion process of various steels, on the content of particular alloying element in the metal.

The corrosion process exponents b of all steels tested in the presence of oil shale ash are presented in Table 1 and Fig. 2. For reference the b values for two austenitic steels determined in air and steam (water vapor) environment are presented as well.

Table 1. Corrosion Exponent b for Various Steels in Different Environment

Steel grade	Content and ratio of alloying elements			Corrosion exponent b in environment of		
	Cr, %	Ni, %	Ni/Cr	Flue gas + Cl	Air	Steam
12Ch18Ni12Ti	18	11.8	0.66	0.66	0.37	0.40
X8CrNiNb1613	16.03	12.16	0.76	0.42		
X8CrNiMoNb1616	16.65	16.75	1.01	0.56		
B-407	21	31.4	1.50	0.46		
80Ch16Ni9Mo2	16.4	8.8	0.54	0.87	0.45	0.77
Ch13Mn12-Ni2ASi2	12.7	2.04	0.16	0.89		
Ch12Mn14Ni4AlMo	12	4.3	0.36	0.75		
Coating	16	73	4.56	0.4		

In Figure 2 the values of exponent b of tested austenitic steels are presented depending on the ratio Ni/Cr accompanied by the power correlation curve. The correlation is actually in very good agreement with experimental data and could be used for preliminary prediction of corrosion exponent of particular steel in the presence of Cl from oil shale ash or some other source.

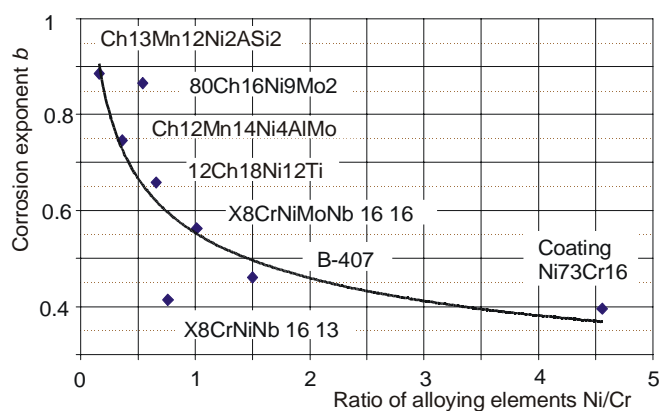


Fig. 2. Corrosion of austenitic steels in the presence of Cl

The exponents of corrosion process of perlitic-ferritic steels were analyzed with respect to the Cr content and the dependence is presented in Fig. 3. The difference between the exponent values determined in the presence of oil shale ash and in air environment is very small, and tends to increase in air. As seen from Fig. 3, the exponent decreases with increasing Cr content. The minimum value $b = 0.47$ belongs to the steel 10CrMo 9 10 containing 2.0–2.5% Cr. In general, the exponents b for perlitic-ferritic steels with Cr content of 0.7–2.5% are in the range $b = 0.53$ –0.47.

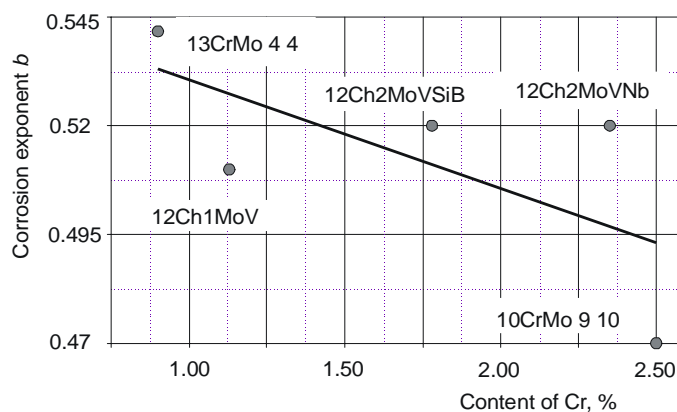


Fig. 3. Corrosion of perlitic-ferritic steels in the presence of Cl

Laboratory tests have shown that two German austenitic steels, X8CrNiMoNb16 16 and X8CrNiNb16 13, and perlitic steel with protective coating have the best resistance to high-temperature corrosion. Tubes from the majority of steel grades tested in laboratory conditions were then subjected to long-term testing in oil shale PF boilers. Some results are presented in Figs 4–8.

Steel X8CrNiNb16 13 was tested in boiler TP-101 No. 3A of Estonian Power Plant. Test duration was 24,700 hours, average temperature 511 °C. Total amount of tube test sections was 26; measured corrosion depth varied from 0.3 up to 1.3 mm. These values were much higher than those predicted by Formula (1) on the basis of laboratory tests. The explanation of the phenomenon may be as follows below.

The above-presented Formula (1) is valid if during the operation boiler tubes do not experience partial or total destruction (removal) of oxide layer from the outer surface due to such reasons as boiler cleaning forces, weight of deposits, or thermal shock caused by sharp change in boiler operating conditions. If the entire destruction of the oxide layer occurs, then the corrosion process resumes from the clean surface with maximum available intensity ($b = 1$). In the case of continuously repeating cycles of oxide layer partial or entire destruction after certain time intervals, the total corrosion depth may be assessed by the following empirical equation [1]:

$$\Delta S' = \Delta S \cdot \{1 + \xi \cdot [B(\tau / \tau_0)^{1-b} - 1]\} \quad (2)$$

where $\Delta S'$ is corrosion under stable oxide layer (1);

factor ξ designates the portion of oxide layer removed in each cycle,

$\xi = 1$ means periodical removal of entire oxide layer;

factor B takes into account the influence of initial stage on the entire corrosion process;

τ_0 is the period between cleaning procedures.

Predictions of the steel X8CrNiNb16 13 corrosion depth made by Equation (2) for destruction period $\tau_0 = 240$ hour, $\xi = 0.35$ and $\xi = 1$ are presented in Fig. 4. Average temperature of field tests was 511 °C, but maximum may be 580 °C due to thermal irregularity along superheater surfaces. Temperature

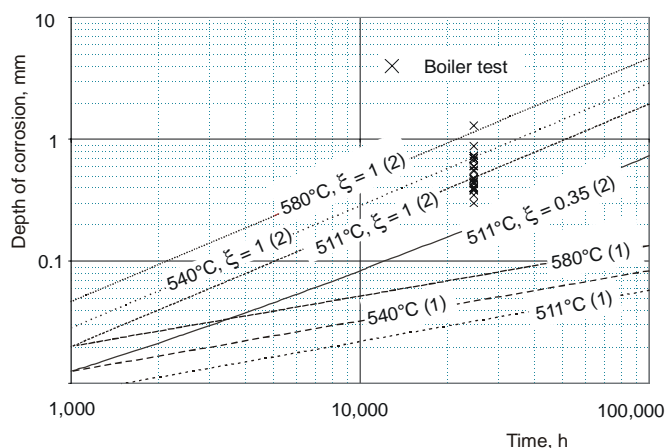


Fig. 4. Corrosion of steel X8CrNiNb16 13 in oil shale boiler (average temperature 511 °C, test duration 24,700 h) and its prediction by Equations (1) and (2) for $\tau_0 = 240$ h

increase drastically accelerates predicted depth of corrosion providing good coincident with the field data (boiler test). Shortening of the destruction period gives the same result (these curves are not shown in Fig. 4).

The validity of such shortening as well as assumption $\xi = 1$ was proved by examination of tube base metal and oxide layer under electron microscope (Fig. 5). Oxide layer entire thickness is $\delta \approx 50\text{--}70\ \mu\text{m}$, the layer seems to be loose and porous. It is clearly seen that oxide layer separates into some sub-layers that may be easily removed even under the weight of deposits leading to shortening of the destruction period and to further increase in corrosion intensity. Oxide layer high porosity means that such layer is unavailable to prevent intensive counter-migration – Cl toward base metal and alloying elements toward layer outer boundary – and to diminish corrosion intensity. According to oxide layer appearance and corrosion intensity determined in field testing, the corrosion exponent b of this steel should be much higher than the prediction made on the basis of laboratory tests ($b = 0.42$, Table 1). Prediction made according to this steel Ni/Cr ratio by using power correlation (Fig. 2) gives the value $b \approx 0.58$ that seems much more realistic.

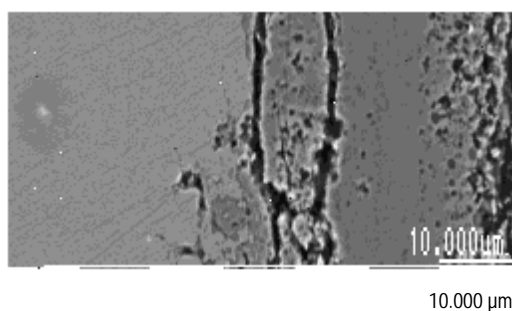


Fig. 5. On-tube oxide layer of steel X8CrNiNb16 13 after 24,700 h testing in boiler TP-101 No. 3A of Estonian Power Plant

Steel B-407 that had shown in laboratory tests the corrosion resistance very close to steel X8CrNiNb16 13 was tested in boiler TP-17 No. 3 of Baltic Power Plant. Test duration was 5,300 hours, average temperature $503\ ^\circ\text{C}$. Total amount of tube test sections was 4, average measured corrosion depth was 0.014 mm (Figs 6 and 7).

In this case prediction made by Equation (1) is much closer to the field test than made by Equation (2). It means that the oxide layer of this steel was formed in the same way as under stable deposits. Examination of oxide layer under electron microscope (Fig. 7) shows that the oxide layer seems to be very dense and well adhered with base metal, so periodical cleaning from ash deposits most probably does not remove it. Such oxide layer has good protective properties against chlorine corrosion.

Steel X8CrNiMoNb16 16 was tested in boiler TP-67 No. 25 of Baltic Power Plant. Test duration was 7,480 hours, average temperature $517\ ^\circ\text{C}$. Average corrosion depth measured was 0.027 mm (Fig. 8).

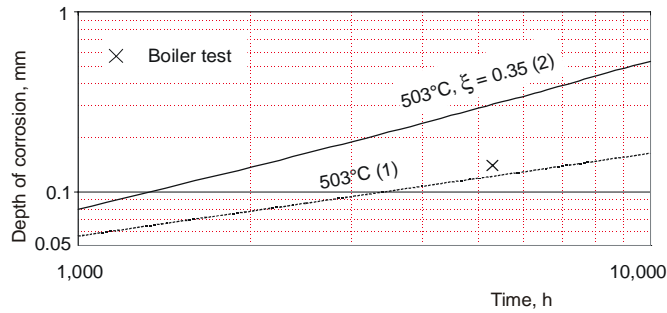


Fig. 6. Corrosion of steel B-407 in oil shale boiler (average temperature 503 °C, test duration 5,300 h), and its prediction by Equations (1) and (2) for $\tau_0 = 240$ h

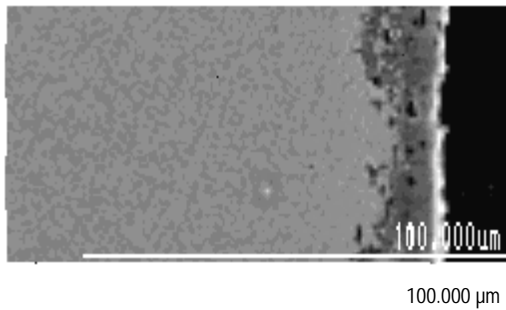


Fig. 7. On-tube oxide layer of steel B-407 after 5,300 h testing in boiler TP-101 No. 3A of Estonian Power Plant

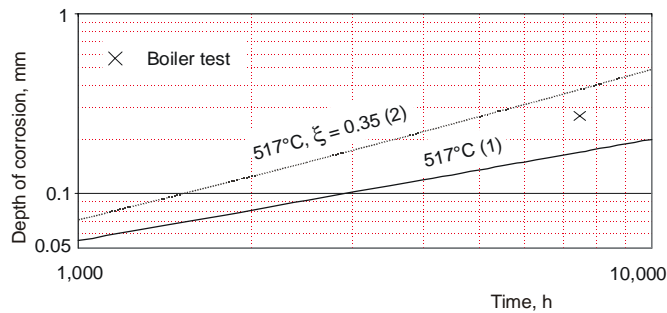


Fig. 8. Corrosion of steel X8CrNiMoNb16 16 in oil shale boiler (average temperature 517 °C, test duration 7,480 h), and its prediction by Equations (1) and (2) for $\tau_0 = 240$ h

Two tubes from steel 12Ch1MoV with protective coating were tested in oil shale boiler at average temperature 513 °C, tests durations were 5,300 and 11,318 hours. Test results and prediction of corrosion depth estimated for protective coating and tube base metal 12Ch1MoV are presented in Fig. 9. The result of the shorter test is close to the prediction made for coating taking into account periodical ($t_0 = 240$ h) partial ($\xi = 0.35$) removal of the oxide layer.

The protective layer is quite dense and well cohered both with the base metal and with oxide layer (Fig. 10). Some non-metal insertions in protective layer, caverns between it and base metal, and porosity of the oxide layer do not decrease its protective ability. In the second case the test result was closer to corrosion of the base metal. Unfortunately, we do not have appropriate metallographic sample from this tube to make a final conclusion, but it seems that in this case protective layer was, after definite operational period, partially or entirely destroyed, and further corrosion intensity was equal to the value of the steel 12Ch1MoV corrosion intensity.

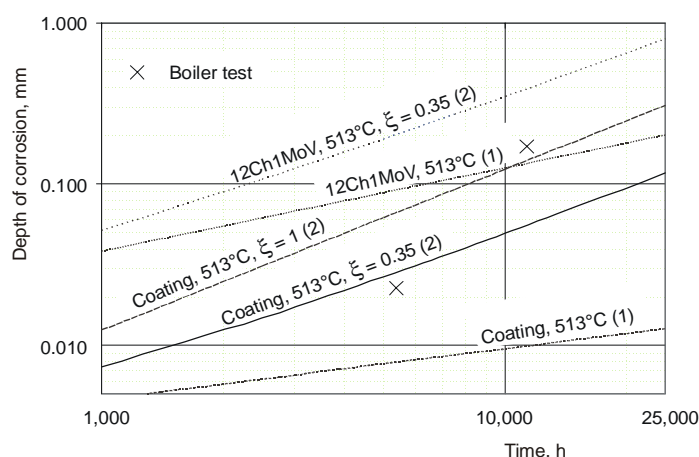


Fig. 9. Corrosion of steel 12Ch1MoV with protective coating Ni73Cr16 in oil shale boiler

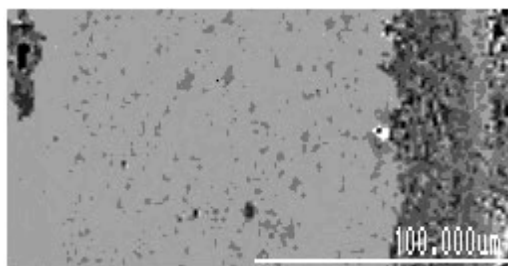


Fig. 10. Coating Ni73Cr16 on the tube of steel 12Ch1MoV and its oxide layer after 5,300-h operation in oil shale boiler at an average temperature of 513 °C

Conclusions

- To avoid intensive high-temperature corrosion under the impact of Cl, the Cr content of perlitic-ferritic steels operating at temperatures 500–520 °C should be at least 1.2–1.5% and at least 2.0–2.5% at temperatures 520–540 °C.

- The ratio Ni/Cr in austenitic steels operating at temperatures $>540\text{ }^{\circ}\text{C}$ should be >1.0 to warrant good resistance against high-temperature corrosion under the impact of chlorine, but the price of austenitic steel tubes depends mostly on Ni content, and therefore the use of perlitic-ferritic tubes coated by protective layer with high Ni content has good prospects. It also gives the opportunity to recover the locally corroded part of the tube of boiler heating surfaces *in situ* and without its entire replacing. The only problem is to get high quality of the protective layer that means its uniformity, the absence of porosity and perfect cohesion with the base metal, but it is solely the problem of coating technology.
- Protective properties of any oxide layer are specified by its density, porosity, and trend to exfoliation that depend, first of all, on the content of alloying elements and may be preliminarily predicted by using Fig. 2 (for operation in similar environment). The effect of other factors (steel preparation, tube manufacturing technology, etc.) could not be, unfortunately, predicted with satisfactory accuracy, so each new steel should be tested in conditions similar to oil shale boiler before making final conclusion about its convenience for oil shale boiler superheater.

REFERENCES

1. *Ots, A.A.* Corrosion and Fret of Boiler Heating Surfaces. – Moscow : Energoatomizdat, 1987 [in Russian].
2. *Tallermo, H., Klevtsov, I.* High-temperature corrosion of steels 12 Ch 1 MF, 13 CrMo 4 4 and 10 CrMo 9 10 in SF boilers at metal temperatures up to $540\text{ }^{\circ}\text{C}$ // VGB PowerTech. 1998. No. 8. P. 94–100.