Oil Shale, Vol. 14, No. 3 Special
pp. 317-327

ISSN 0208-189X

CORROSION RESISTANCE OF FERRITIC ALLOYS 13 CrMo 44 AND 10 CrMo 910 IN CONDITIONS OF SUPER HEATERS OF PF OIL SHALE BOILER

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The laboratory and industrial tests of corrosion resistance of German ferritic alloys 13 CrMo 44 and 10 CrMo 910 are performed in the presence of chlorine-containing external deposits and the empirical kinetic equations are established. The X-ray structural analysis of oxide layers of these alloys and Russian pearlitic alloy 12Cr1MoV is executed. The comparative analysis of corrosion resistance of three alloys of superheaters of the PF oil shale boiler is presented.

INTRODUCTION

Recently the costs of boiler tubes needed for the repair of PF oil shale boiler on the eastern and western markets became practically equal. In this connection already some years ago it has arisen the necessity of estimation of corrosion resistance of western tube alloys, first of all made according to DIN, under the influence of deposits of oil shale ashes. To solve the problem, laboratory tests (duration till 1000 hours) and industrial examination (duration till 7000-13,000 hours) of the following two ferritic alloys were performed in TED of TTU:

13 CrMo 44	(Cr - 0.81%, Mo - 0.50%) and
10 CrMo 910	(Cr - 2.21%, Mo - 0.92%).

These alloys are used most frequently for manufacturing of superheaters.

The corrosion resistance of these alloys is compared to Russian pearlitic alloy 12Cr1MoV, of which the majority of superheaters of boilers on Estonian power plants are nowadays manufactured. The properties of alloy 12Cr1MoV are accepted on the data of the normative documents and our own researches [1,2].

CORROSION RESISTANCE OF ALLOYS 13 CrMo 44 AND 10 CrMo 910

The laboratory corrosion tests were performed using the standard technique [3] for temperatures 500, 540, 580 and 620°C. The fly ash from the electrostatic precipitator with the content of chlorine 0.46% was used for imitation of ash deposits. The industrial tests were performed using inserts into superheaters of two boilers of the Baltic Power Plant. Alloy 13 CrMo 44 was tested on the boiler TP-67 (plant No 23) and alloy 10 CrMo 910 on the boiler TP-17 (No 8). Average weighed temperature of outside surface of inserts was equal to 516°C on the boiler No 8 (test duration 13,000 hours), on the boiler No 23 temperature equalled to 495°C (test duration 7600 hours). The content of chlorine in external ash deposits on heating surfaces in these points of boiler by approximate estimations usually makes about 7%.

The results of corrosion tests of alloys 13 CrMo 44 and 10 CrMo 910 are presented in Figs. 1 and 2. Using regression analysis of the laboratory data, the kinetic equations were found in the following form:

$$\ln\Delta S = a - b\cdot T^{-1} + \left(c + d\cdot T\right)\ln\tau \qquad (1)$$

where:

ΔS - depth of corrosion, mm,

T - temperature of metal of a sample, K,

τ - duration of test, h,

a, b, c, d - empirical parameters of regression equation.

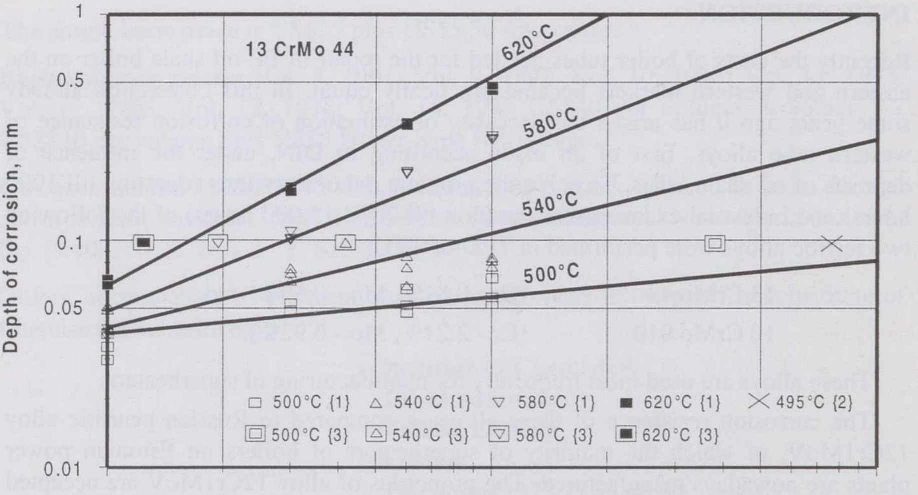

Figure 1. Experimental data and estimated lines of corrosion depth of alloy 13 CrMo 44. {1} - laboratory tests; {2} - industrial tests; {3} - equivalent times calculated on the data of industrial tests

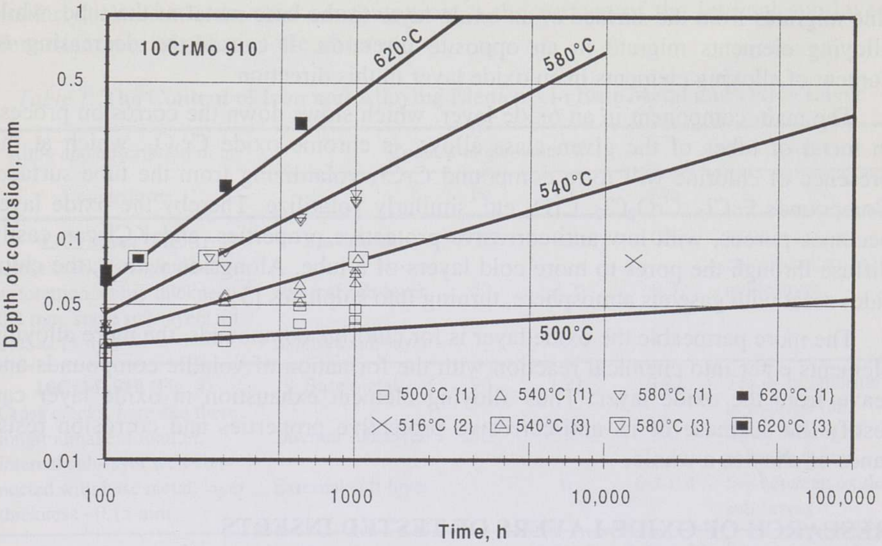

Figure 2. Experimental data and estimated lines of corrosion depth of alloy 10 CrMo 910. {1} - laboratory tests; {2} - industrial tests; {3} - equivalent times calculated on the data of industrial tests

For comparison of results of laboratory and industrial tests, the equivalent operating times of alloys for temperature conditions of laboratory tests are estimated. For equivalent time τ_{eq}, the operating time of alloy at given temperature T_g is accepted, during which the same depth of corrosion is reached as in industrial tests at temperature T and at duration τ. In accordance with [3,4], the equivalent time was determined using the equation:

$$\tau_{eq} = \tau^{\frac{c+d\cdot T}{c+d\cdot T_g}} e^{\left[\frac{b}{c+T_g}\cdot\frac{T_g-T}{T\cdot T_g}\right]} \qquad (2)$$

The parameters *a, b, c, d* are accepted in conformity with the kinetic equations (1).

PROPERTIES OF ASH DEPOSITS AND THE CORROSION RATE

Protective properties of deposits, arising on a surface of superheater, depend first of all on the content of alloying elements in an oxide layer, its porosity and presence of crack, and on the character of cohesion of a layer with the base metal. In general case alloying elements migrate from the base metal into oxide layer, and their content in a layer is correlated with its content in the base metal and metal face temperature, remaining constant along the thickness of oxide layer. However, when the metal of tubes of a superheater is operating in the environment of products of PF of oil shale, the external deposits contain chlorine compounds that essentially change the general picture of corrosion process. As the compounds of chlorine enter into chemical reaction both with chrome and with iron, a counter migration takes place, namely chlorine migrates from the surface of an oxide layer to the base metal of the tube, while alloying elements migrate in an opposite direction. It causes the decreasing of content of alloying elements in an oxide layer in this direction.

The main component in an oxide layer, which slows down the corrosion process in metal of tubes of the given class alloys, is chrome oxide Cr_2O_3, which at the presence of chlorine will form compound $CrCl_3$ volatilizing from the tube surface. Compounds $FeCl_3$, CrO_2Cl_2, CrO_3 etc. similarly volatilize. Thereby the oxide layer becomes porous, with low anti-corrosive protective properties, and KCl can easily diffuse through the pores to more cold layers of a tube. Alongside with it, the chlorides react with gaseous atmosphere, turning into sulphates [5].

The more permeable the oxide layer is for chlorine compounds, the more alloying elements enter into chemical reaction with the formation of volatile compounds and leave from the oxide layer. Thus alloying element exhaustion in oxide layer can testify the decrease of its anti-corrosive protective properties and corrosion resistance of alloy as a whole.

RESEARCH OF OXIDE LAYERS OF TESTED INSERTS

For detailed elucidation of the reasons of distinction in protective properties of oxide layers of tested alloys a special research was undertaken. The test samples, containing an oxide layer and the base metal, were cut out from tubes passed through industrial tests in boiler. After grinding and polishing, the superficial layers of samples were investigated first of all under optical microscope MIKROPHOT FX (Japan). The portraits were read out by a video camera and entered in a graphic format on the PC. Then samples were studied under scanning microscope JXA 840A (Japan) with an accelerating voltage 20 kV. Line scans were read with the help of X-ray spectrometer AN 10000, the time of scanning of a spectrum made 20-3600 seconds depending on alloying element concentration*. Portraits of samples structure and distribution of particular elements in an oxide layer and the base metal are given in Figs. 3-5 and in Table 1. From each tube two samples were cut out and investigated.

The oxide layer of alloy 13 CrMo 44, Fig. 3a, consists from well connected with the base metal internal sub-layer and several exfoliated sub-layers, everyone having the thickness up to 0.1-0.3 mm. Here and there a layer contains cross cracks. The content of chrome in the base metal makes 0.8%, while in oxide layer, Fig. 3b, in the separate centres reaches 2.3-3.3%, that is 3-4 times higher than in base metal. The distribution of chrome is rather non-uniform beginning already from the surface of the base metal, and in superficial sub-layer in places is lower, than in metal. Similarly changes the content of molybdenum. However, its content in the internal sub-layer, that determines the anti-corrosive protective property of an oxide layer as a whole, is significantly less than in the base metal. In oxide layer chlorine practically is absent.

The oxide layer of alloy 10 CrMo 910 places is exfoliated on two sub-layers, Fig. 4a. Internal sub-layer is well connected with the base metal. The content of chrome in the sub-layer, Fig. 4b, is practically the same, as in the base metal. Chrome is homogeneously distributed up to border with external sub-layer, where its concentration at first jumps up to ~3% and then falls up to zero. Molybdenum is distributed

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* Measurements provided by Prof. U. Kallavus. Institute of materials, TTU.

similarly, also with elevated concentration at the surface of the internal sub-layer. Here the traces of chlorine are observed.

Table 1. **The Content of Iron and Alloying Elements in Base Metal and Oxide Layer**

Alloy and description of an oxide layer	Content of elements, %				Notes
		Fe	Cr	Mo	
13CrMo44 (Fig. 3) Cross cracks, longitudinal exfoliation, entire thickness 0.3 mm, some sub-layers till 0.08-0.13 mm	Base metal	97.7	0.8	0.5	Weak traces of chlorine in an oxide layer
	Internal sub-layer	50	2.3	0.3	
	External sub-layer		3.0	1.1	
10CrMo910 (Fig. 4) Cross cracks, here and there longitudinal exfoliation, internal sub-layer well connected with base metal, layer thickness ~0.15 mm	Base metal	96	2.21	0.92	Traces of chlorine in internal sub-layer, centres of chlorine in cavities between oxide sub-layers
	Internal sub-layer	50	3.0	3.0	
	External sub-layer		0	0.3-0.4	
12Cr1MoV (Fig. 5), industrial test $\tau>25\cdot10^3$ h, $t_m<540$°C Longitudinal exfoliation, entire thickness till 0.3 mm	Base metal		0.9-1.2	0.25-0.35	Strong traces of chlorine in an oxide layer
	Internal sub-layer		0.6	0.3	
	External sub-layer		0.3	0.2	

Presented in Fig. 5 data on alloy 12Cr1MoV are obtained for the samples, which have been cut out from a tube of the fifth step of superheater of the boiler TP-67 of Baltic Power Plant, operated more than 25,000 hours at average temperature below 540°C. Oxide layer is exfoliated here on two, in places on three sub-layers. Internal sub-layer has a much more porous structure. Alloying elements are distributed also a little differently, than in two previous cases, Fig. 5b, namely:

- chrome does not concentrate in an oxide layer, its content is continuously reduced towards the outside surface of the oxide layer,
- the content of molybdenum in an oxide layer practically does not vary, remaining on the same level, as in the base metal,
- strong traces of chlorine with concentration in the particular centres on border between two sub-layers of an oxide layer and in cavities are observed.

Presented data allow to assume, that dense, well connected with the base metal and the chrome rich oxide layer of alloy 10 CrMo 910 has, in conditions of the PF oil shale boiler, higher anti-corrosive protective properties and is much less sensitive to concentration of chlorine in external deposits, than oxide layers of two other alloys. Largely it is confirmed by the diagrams of Figs. 1 and 2. The equivalent times of alloy 13 CrMo 44, Fig. 1, are essentially displaced to the left from kinetic lines at the same temperatures, while the equivalent times of alloy 10 CrMo 910, Fig. 2, well coincide with kinetic lines. Let us remind, that in laboratory experiments the content of chlorine made in this case 0.46%, in industrial tests by approximate estimations it was about 7%

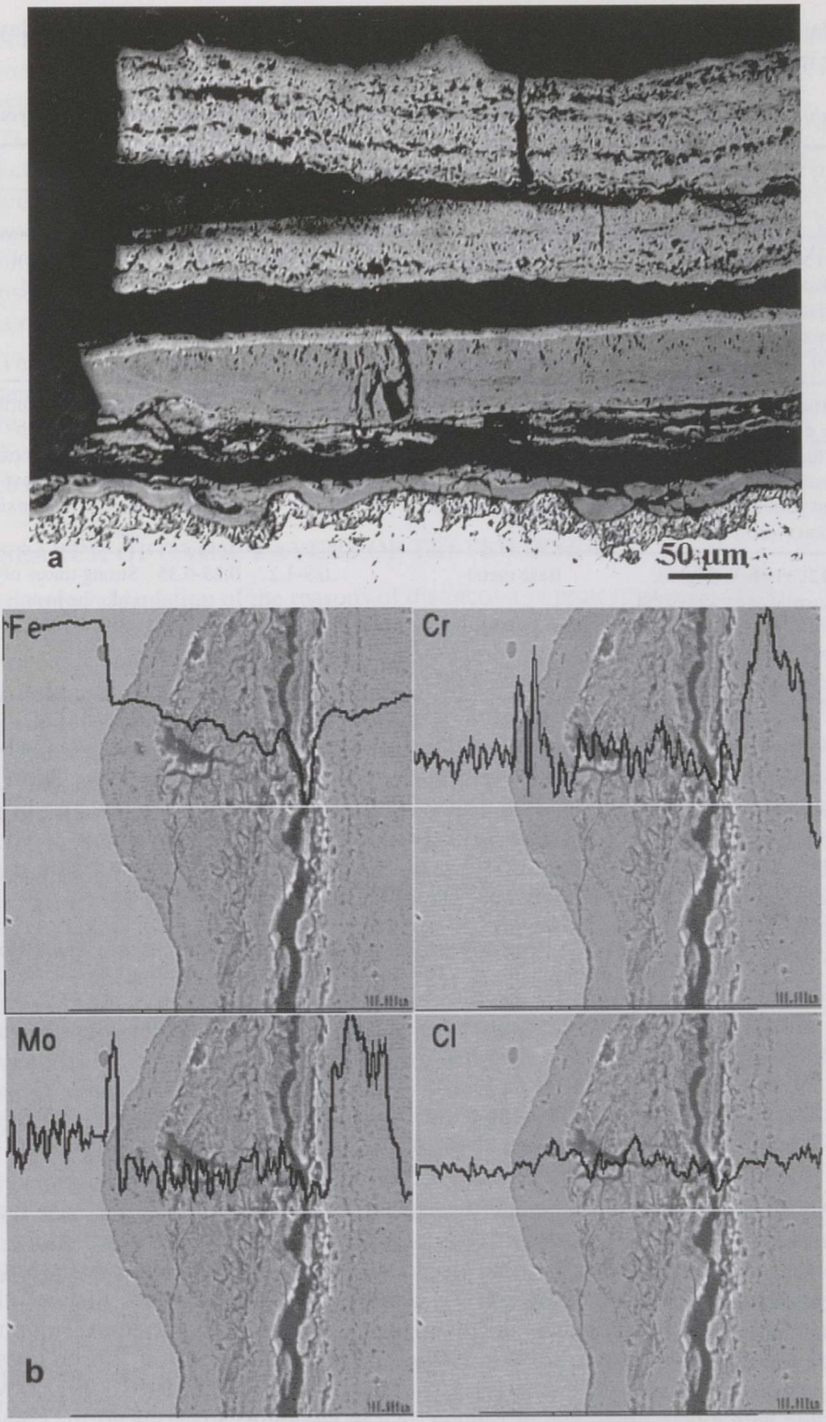

Figure 3. Structure of oxide layer of alloy 13 CrMo 44 (a) and distribution of iron, chrome, molybdenum and chlorine in base metal & oxide layer (b)

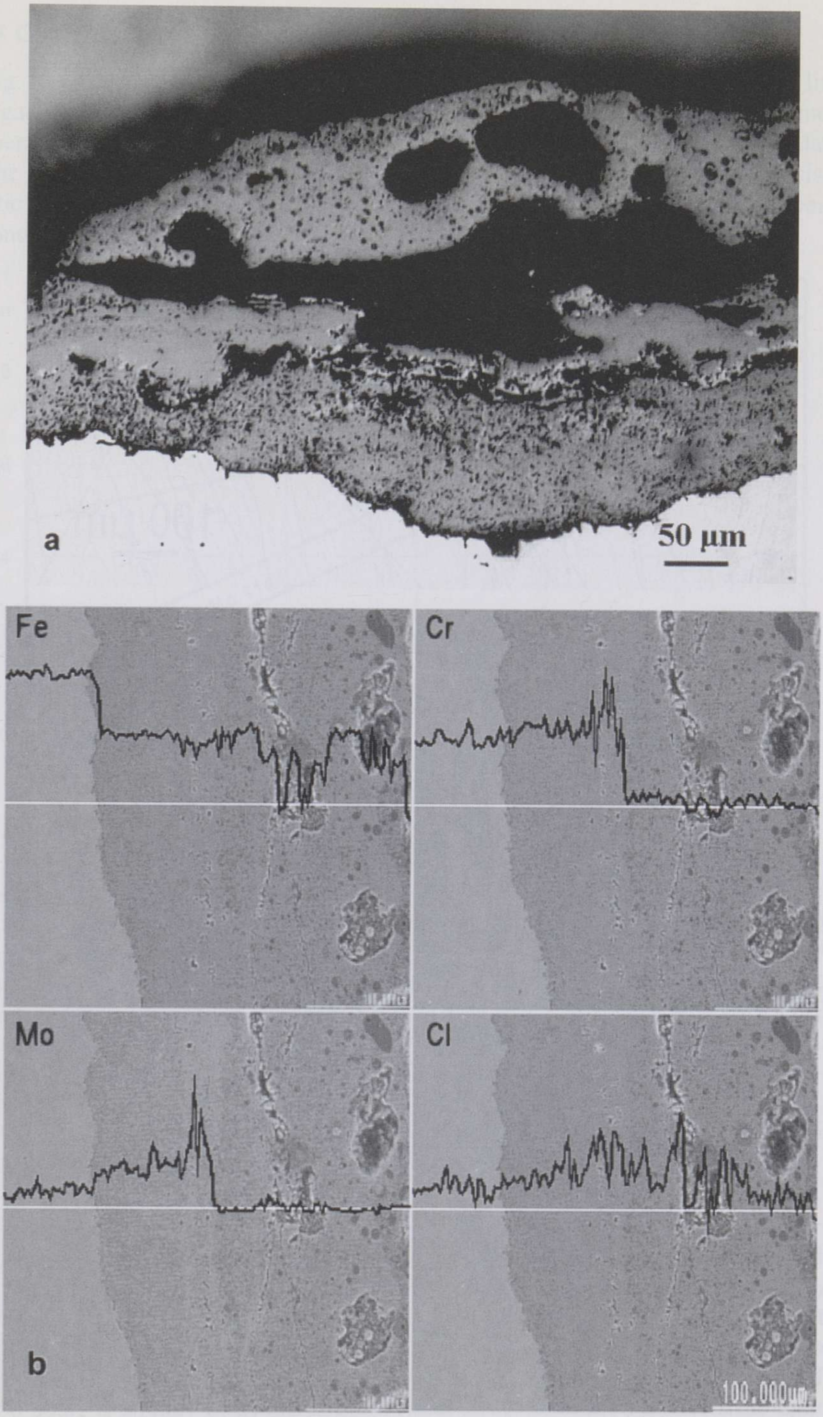

Figure 4. Structure of oxide layer of alloy 10 CrMo 910 (a) and distribution of iron, chrome, molybdenum and chlorine in base metal & oxide layer (b)

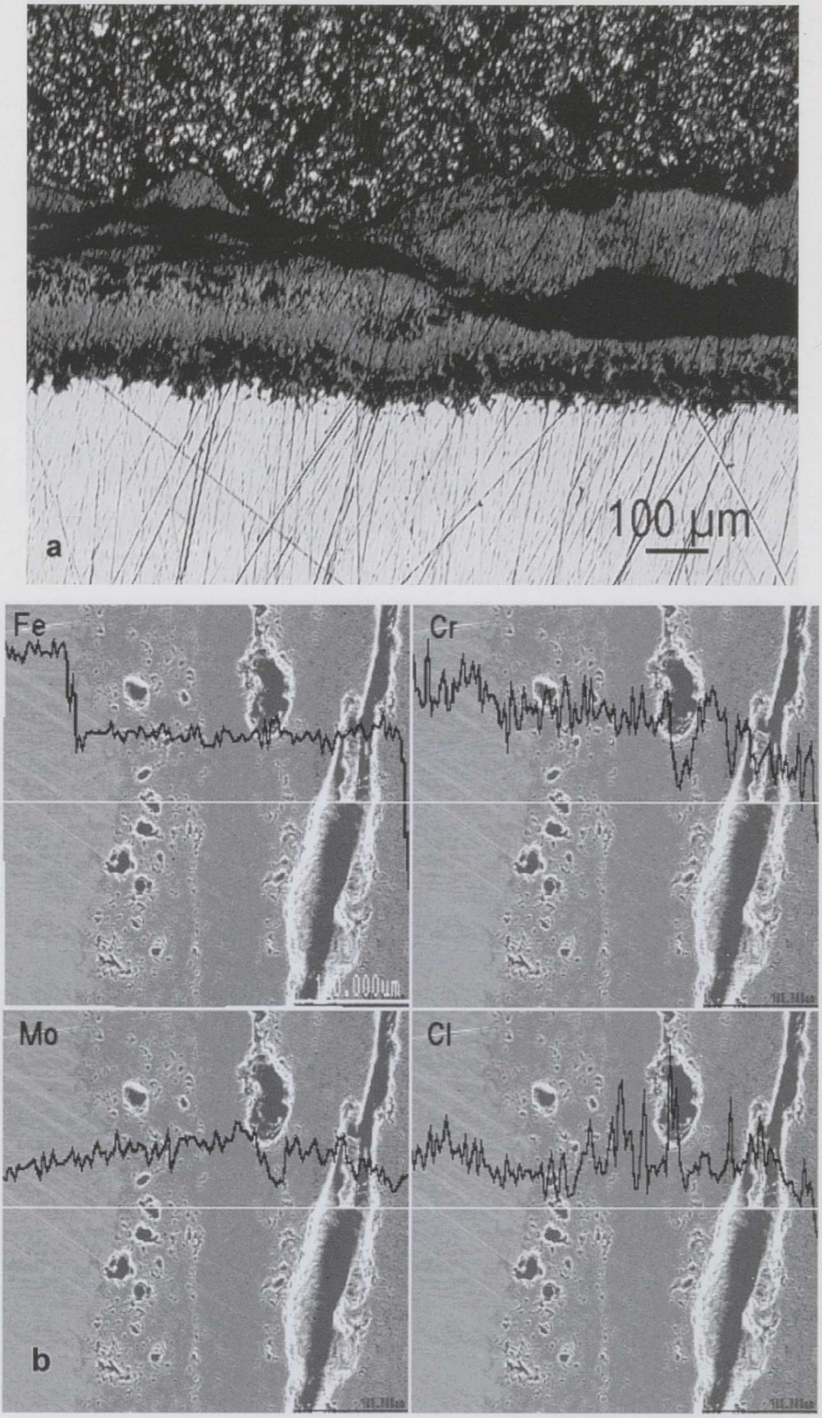

Figure 5. Structure of oxide layer of alloy 12Cr1MoV (a) and distribution of iron, chrome, molybdenum and chlorine in base metal & oxide layer (b)

THE COMPARATIVE ANALYSIS OF CORROSION KINETICS

In Fig. 6 the metal oxidation exponent *n*, describing an inclination of corrosion lines in logarithmic co-ordinates i.e. the corrosion rate, are presented depending on metal temperature. The parameter *n* of alloys 13 CrMo 44 and 10 CrMo 910 is calculated on the basis of equation (1). For alloy 12Cr1MoV *n* is calculated on the basis of kinetic equations [2], confirmed to the content of chlorine 0.46% (that corresponds to conditions of laboratory tests of alloys 13 CrMo 44 and 10 CrMo 910).

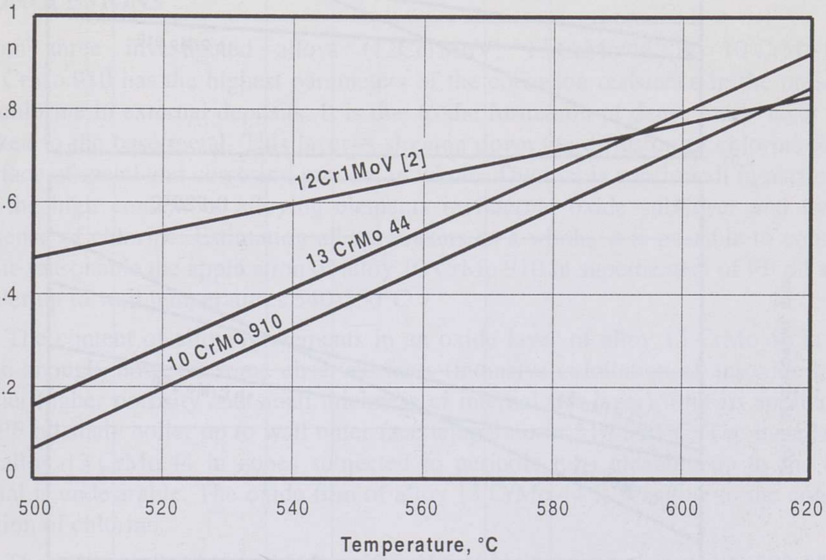

Figure 6. Dependence of metal oxidation exponent on temperature

In the investigated range of temperatures, the parameter *n* of alloys 13 CrMo 44 and 10 CrMo 910 grows much faster with increase of temperature than *n* of alloy 12Cr1MoV, exceeding estimations of *n* of alloy 12Cr1MoV in the range 590-610°C. In general case it is considered that parameter *n* characterises protective properties of oxide layer. The layer does not protect metal if $n=1$, the corrosion process occurs in this case with the same rate, as on a clean metal surface. However, in our case such process is possible only at temperatures laying outside of the scope of practical interest. In interesting us temperature range (up to 540-550°C), the oxide layers of alloys13 CrMo 44 and 10 CrMo 910 have obviously higher protective properties, than those of alloy 12Cr1MoV. The same conclusion follows from the analysis of Figs. 3-5 as well.

The comparative prognosis of corrosion depth of examined alloys for large terms of operation, received on the basis of appropriate kinetic equations, are presented in Fig. 7. The inclination of ΔS lines of 12Cr1MoV is significantly more abrupt than at alloys 13 CrMo 44 and 10 CrMo 910, especially at lower temperatures. At initial stage of the corrosion process, the depth of corrosion of alloys 13 CrMo 44 and 10 CrMo 910 is little bit higher, than at alloy 12Cr1MoV, but approximately after 10,000 hours is already observed a return ratio. In all cases the prognosis of depth of external corrosion for 100,000 hours does not exceed normalised in [1] limit that is equal to 1 mm.

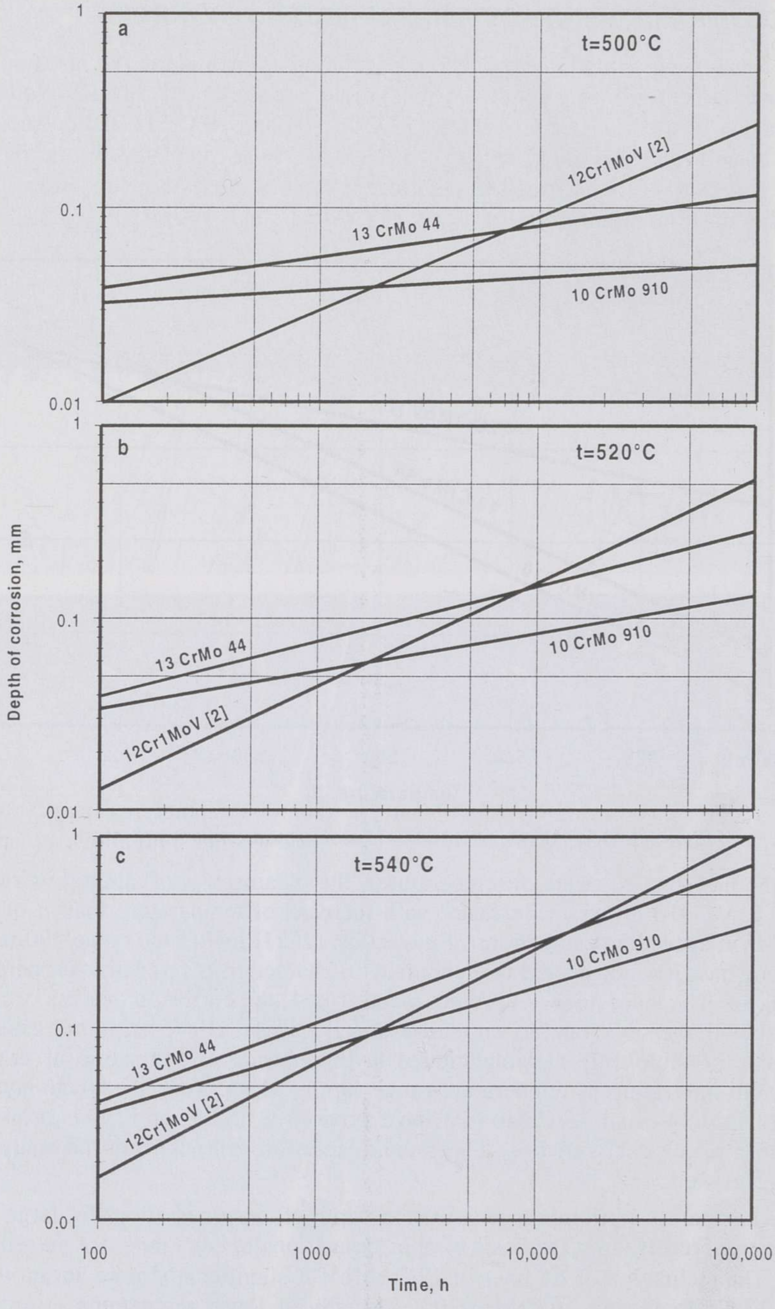

Figure 7. Prognosis of corrosion depth of tested alloys at various temperatures

On the basis of the presented data it is possible to confirm that the application of alloys 13 CrMo 44 and 10 CrMo 910 in superheaters of PF oil shale boiler up to wall outer face temperature of 540°C is quite reasonable. It is important to note, that the rather high corrosion depth of alloys 13 CrMo 44 and 10 CrMo 910 at the initial stage of operation, see Fig. 7, specifies expediency of use of these alloys first of all at those parts of superheaters, which are not subjected to periodic cleaning that causes periodic destruction of oxide layer. The application of periodic cleaning of a surface up to the base metal can essentially change the behaviour of kinetic lines and negatively affect the corrosion resistance of tubes from alloys 13 CrMo 44 and 10 CrMo 910.

CONCLUSIONS

From three investigated alloys (12Cr1MoV, 13 CrMo 44 & 10 CrMo 910) 10 CrMo 910 has the highest parameters of the corrosion resistance in the presence of chlorine in external deposits. It is due to the formation of dense oxide layer well linked to the base metal. This layer is slowing down the diffusion of chlorine to the surface of metal and corrosion process in whole. The fact is confirmed, in particular, by the high content of alloying elements in internal oxide sub-layer and by the absence of chlorine. Estimating all parameters as a whole, it is possible to consider quite reasonable the application of alloy 10 CrMo 910 in superheaters of PF oil shale boiler up to wall temperatures 540-550°C.

The content of alloying elements in an oxide layer of alloy 13 CrMo 44 is also high enough, however some observed facts (intensive exfoliation of an oxide layer, rather higher porosity and small thickness of internal sub-layer) limit its application in PF oil shale boiler up to wall outer face temperatures 510-520°C. The installation of alloy 13 CrMo 44 in zones subjected to periodic tube cleaning up to the base metal is undesirable. The oxide film of alloy 13 CrMo 44 is sensitive to the concentration of chlorine.

The corrosion resistance of alloy 12Cr1MoV in the temperature range 500-550°C in conditions of superheaters of PF oil shale boiler concedes with alloys 13 CrMo 44 and 10 CrMo 910 practically in all parameters.

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Presented by A. Ots
Received March 17, 1997