OXIDATION OF ST55, LH15 AND AREMA STEELS AT HIGH TEMPERATURES IN AMBIENT AIR

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The results related to oxidation of ST55, LH15 and AREMA steel cylinders exposed to high temperatures in ambient air are reported. The oxidation temperatures are in the range from 940 to 1100 °C and the exposition time period, *t*, in the range from 0 to 500 h. It is shown that the steel oxidation can be well described by gas-filling cylindrical model. The classical Paidassi's model and saturation model are remembered. The obtained results are discussed from the point of view of steel compositions.

Key words: high temperatures, oxidation, steels, ambient air, influence of chemical composition

OXIDACE OCELÍ ST55, LH15 A AREMA PŘI VYSOKÝCH TEPLOTÁCH NA VZDUCHU

V příspěvku jsou uvedeny výsledky týkající se oxidace ocelí ST55, LH15 a AREMA při vysokých teplotách na vzduchu. Oxidační teploty leží v oblasti 940 až 1100 °C a doby oxidační expozice v oblasti 0 až 500 hodin. Průběh oxidace je možno dobře popsat pomocí modelu „nasycování vzorku plynem“. V článku je připomenut klasický Paidassiho parabolický model a novější saturační model. Získané výsledky jsou diskutovány z hlediska chemického složení ocelí.

1. Introduction

The materials chosen for oxidation experiments were ST55 (PN), LH15 (PN) and AREMA (ČSN) steels – PN stands for Polish Norm. Their compositions are presented in Table 1. The LH15 steel having higher content of carbon (0.90 wt.%) and of chromium (1.45 wt.%) is used in production of rolling contact bearings. ST55 is an alloyed carbon structural steel used in mechanical engineering. The AREMA steel is accepted as a rather pure iron, and it is used in electrical engineering [1].

The above-mentioned steels are similar in their chemical composition which makes it possible to compare their oxidation properties without difficulties.

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Table 1. Chemical composition of the experimental materials (wt.% and at.%)

Material		C	Si	Mn	P	S	Cr
ST55	wt.%	0.54	0.27	0.82	0.020	0.024	0.14
	at.%	2.455	0.525	0.815	0.035	0.041	0.147
LH15	wt.%	0.90	0.24	0.28	0.005	0.003	1.45
	at.%	4.039	0.461	0.275	0.009	0.005	1.503
AREMA	wt.%	0.026	0.015	0.260	0.016	0.028	0.035
	at.%	0.121	0.030	0.264	0.029	0.049	0.038

Material		Ni	Mo	Cu	Al	W	Co	Sn
ST55	wt.%	0.08	0.014	0.14	0.031	–	–	–
	at.%	0.084	0.008	0.120	0.063			
LH15	wt.%	0.13	0.020	0.16	0.014	–	–	–
	at.%	0.119	0.011	0.136	0.028			
AREMA	wt.%	0.020	0.005	0.045	0.027	0.005	0.010	0.004
	at.%	0.019	0.003	0.040	0.056	0.002	0.010	0.002

A lot of theoretical models describing the run of steel and alloy oxidation was proposed till now [2, 3, 4]. The classical Paidassi's model [3, 4] expresses well the initial stage of oxidation of some metallic materials by parabolic law

$$y(t) = kp\left(\sqrt{t} - \sqrt{\tau}\right), \tag{1}$$

where $y(t)$ is either the scale layer thickness $l(t)$, or any other quantity proportional to $l(t)$ as weight gain $\Delta w(t)$, etc., kp is the oxidation coefficient and t is the time. The parameter τ was introduced into Eq. (1) and subsequently into Eqs. (2), (3) with the aim to remove the discrepancies between the theory and experiment caused by drawbacks of the originally proposed theoretical model and by experimental errors. An extended application of the parabolic law was presented in our previous paper [5] dealing with the oxidation of steels heated at high temperatures in ambient air. The initial stages of oxidation were investigated in that work.

The parabolic law does not fit satisfactorily the data measured in long time periods of specimen oxidation (Fig. 1). It is visible in this figure that the deviation from the parabolic law starts at about $t = 70$ h.

A better agreement between the theory and data measured in long time experiments yields the saturation model [4] (Fig. 1). It reads in modified form

$$y(t) = A\left[1 - \exp\{-B(\sqrt{t} - \sqrt{\tau})\}\right] . \tag{2}$$

The constant A is a parameter obtained by fitting Eq. (2) to experimental data at $t \to \infty$, B characterizes the growth rate.

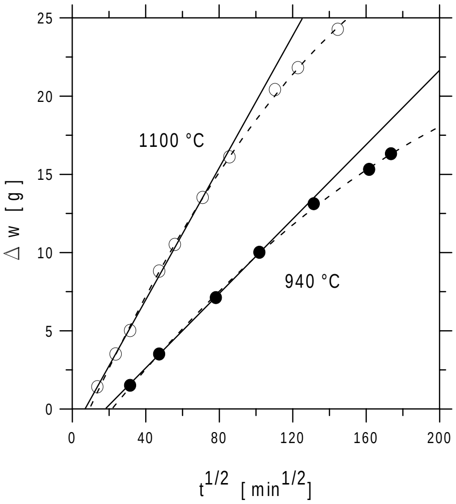

Fig. 1. An example of experimental data fitted by Eq. (1), parabolic law (solid line), and by Eq. (2), saturation effect (dashed line), steel AREMA, $\phi = 20$ mm, $L = 30$ mm, $T = 1100$ and 940 ℃.

The saturation model (2) does not give any information on the physical basis of metal oxidation. However, this information is, at least partially, contained in the gas-filling model developed for explanation of weight gain of cylindric specimens [6]. It has the following form:

$$\Delta w(t) = \Delta w_{\max}\left[1 - \frac{32}{\pi^2}\sum_{m=1}^{\infty}\frac{1}{r_m^2}\exp\left\{-\frac{r_m^2}{a^2}D_{\text{eff}}\,(t-\tau)\right\}\cdot \right. \\ \left. \cdot\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left\{-\frac{(2n+1)^2}{L^2}\pi^2 D_{\text{eff}}\,(t-\tau)\right\}\right], \tag{3}$$

$\Delta w_{\max}$ is the maximal weight gain for $t \to \infty$, r_m are the roots of Bessel function $J_0(r_m) = 0$, a is the specimen radius, L is its length, and D_{eff} is the effective coefficient which characterizes the oxidation course of the given material.

The interpretation of the values D_{eff} as effective diffusion coefficients is based on Arkharov-Agapova work [7], which have proposed that scaling at high temperatures may be attributed to the outward diffusion of Fe across the entire scale layer and to inward diffusion of O_2 into the metal.

The aim of the present paper is a presentation of:

i) application of Paidassi's and saturation model to experimental data;

ii) the fit of Eq. (3) to experimental data;

iii) effective diffusion coefficients obtained from experimental data analysis.

2. Experimental

The chemical composition of materials used in our work is introduced in Table 1. The dimensions of cylindric specimens made of these materials are ø = 10 mm, $L = 15$ mm (ST55, LH15) and ø = 20 mm, $L = 30$ mm (AREMA). The produced specimens were polished by abrasive papers, purged in alcohol and afterwards oxidized in the furnace FCF-16H in ambient air. At the end of the individual oxidation anneals, the specimens were taken out from the furnace and cooled down in air. These cooled specimens were used for metallographic observation and for weight gain $\Delta w(t)$ measurements; $w(t)$ means the specimen weight after oxidation run and $w(0)$ before it; $\Delta w(t) = w(t) - w(0)$. The values $w(0)$, $w(t)$ were found by the analytic balance WA-33.

3. Results and discussion

An example of a scale layer formed on LH15 steel surface is shown in Fig. 2. It is visible in this figure that the scale layer is rather heterogeneous and that it contains many cracks and cavities. This structure enables the ambient air to penetrate the scale layer in the course of oxidation run and to oxidize the metal specimen. The oxidation coefficient kp (Eq. (1)) amounts to 0.0295 mm/min$^{1/2}$ in the given case.

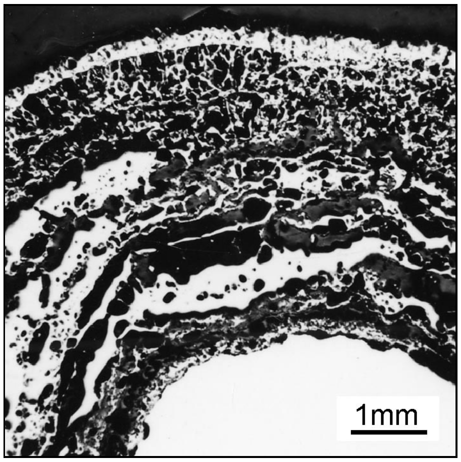

Fig. 2. The scale layer formed on the surface of LH15 steel; $T = 980\,°\mathrm{C}$, $t = 31350$ min, scale layer thickness $l = 4.31$ mm.

Equations (1) and (2) were applied to evaluation of experimental data of Δw shown in Fig. 1 and in the all others related to the ST55, LH15, AREMA steels oxidized at the temperatures $T = 940$, 980, 1020, 1060, 1100 ℃. The evaluated oxidation coefficients, $kp(t, T)$, are temperature dependent and satisfy the Arrhenius plot $kp = kp_\mathrm{o} \exp(-Q/RT)$. The parameters kp_o and Q obtained in the quoted evaluation are presented together with previously introduced parameters kp_o, Q [5] in Table 2. It is visible that the presented values kp_o, Q, kp(1000 ℃), especially the oxidation energies Q, do not differ considerably from the previous data [5]. The discrepancy between Q(LH15) in the present work and Q(LH15) in Ref. [5] may be explained by slightly higher content of alloying elements C, Si, Mn, Cr, Ni in the LH15 steel [5]. The values $\sqrt{\tau}$ vary, as the case may be, randomly and their mean values read for the individual steels: $\sqrt{\tau}$(ST55) = 1.5, $\sqrt{\tau}$(LH15) = 3.3, $\sqrt{\tau}$(AREMA) = 10.3 min$^{1/2}$.

Table 2. Parameters kp_{o} and Q characterizing the parabolic growth of weight gain $\Delta w(t)$ of oxidized steels, values $kp(1000\,^{\circ}\text{C})$, mean values of the improving fitting parameters $\sqrt{\tau}$, and dimensions ϕ and L of specimens

Material	ϕ [mm]	L [mm]	kp_{o} [$\text{g}\cdot\text{cm}^{-2}\cdot\text{min}^{-1/2}$]	Q [kJ/mol]	$kp(1000\,^{\circ}\text{C})$ [$\text{mg}\cdot\text{cm}^{-2}\cdot\text{min}^{-1/2}$]	$\overline{\sqrt{\tau}}$ [$\text{min}^{1/2}$]	Refer.
ST55	10	15	131.4	109.2	4.34	1.5	[pw]
LH15	10	15	52.0	99.9	4.14	3.3	[pw]
AREMA	20	30	1.553	59.5	5.65	10.3	[pw]
ST55	10	15	201.9	115.5	3.74	0	[5]
LH15	10	15	419.4	125.5	2.97	0	[5]

Table 3. Values A_{o}, $Q(A)$, B_{o}, $Q(B)$ characterizing the saturation course of steels oxidation (Eq. (2)) in dependence on temperature; illustration data $A(1000\,^{\circ}\text{C})$, $B(1000\,^{\circ}\text{C})$; $\overline{\sqrt{\tau}}$ is the improving fitting parameter (mean value), ϕ, L are the dimensions of specimens

Material	ϕ [mm]	L [mm]	A_{o} [$\text{g}\cdot\text{cm}^{2}$]	$Q(A)$ [kJ/mol]	$A(1000\,^{\circ}\text{C})$ [$\text{g}\cdot\text{cm}^{-2}$]	B_{o} [$\text{min}^{-1/2}$]	$Q(B)$ [kJ/mol]	$B(1000\,^{\circ}\text{C})$ $\times 10^{3}$ [$\text{min}^{-1/2}$]	$\overline{\sqrt{\tau}}$ [$\text{min}^{1/2}$]
ST55	10	15	15.00	31.84	0.741	7.247	71.41	8.51	8.0
LH15	10	15	28.68	38.72	0.739	2.585	61.36	7.85	8.8
AREMA	20	30	7.36	16.53	1.544	0.193	40.01	4.40	11.8

The knowledge of oxidation coefficient kp enables to calculate the oxidation rate of the investigated materials, which is given by the equation

$$V(\text{oxid}) = \frac{\mathrm{d}\Delta w(t)}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\left(kp\sqrt{t}\right) = \frac{kp}{2\sqrt{t}} = \frac{kp_\mathrm{o}\exp(-Q/RT)}{2\sqrt{t}}. \tag{4}$$

Taking, for the sake of simplicity, $t = 1$ min and $T = 1000$ °C, we get for the individual steels: V(oxid, ST55) = 2.17, V(oxid, LH15) = 2.07, V(oxid, AREMA) = 3.83 mg·cm^{-2}·min^{-1}. The greatest initial oxidation rate is possessed by the steel AREMA followed by ST55 and LH15. It follows from Eq. (4) that the oxidation rate decreases with increasing oxidation time t to the limiting value $V(\text{oxid}) \to 0$ at $t \to \infty$.

The application of Eq. (2) in evaluation of experimental data yields, in contrary to Eq. (1), the limiting weight gains A achieved at $t \to \infty$. The evaluated constants A are temperature dependent and satisfy, as well as the constants B, a quasi-Arrhenius relation. The respective characteristics A_o, $Q(A)$, B_o, $Q(B)$ are given together with the final maximum weight gains A(1000 °C) in Table 3.

The knowledge of these parameters yields the possibility to express the oxidation rate of the steels, i.e.,

$$V(\text{oxid, steel}) = \frac{AB}{2\sqrt{t}}\exp\left\{-B\left(\sqrt{t}-\sqrt{\tau}\right)\right\} . \tag{5}$$

Taking for simplicity $T = 1000$ °C, $t = 1$ min, $\tau = 0$, we get for the corresponding steels: V(oxid, ST55) = 3.2, V(oxid, LH15) = 2.9, V(oxid, AREMA) = = 3.4 mg·cm^{-2}·min^{-1}.

Equation (1) – parabolic law [3] – and (2) – saturation model [4] – were obtained on the basis of empirical treatment. Equation (3) was developed by a correct solution of differential equations in [6]. Its important value resides in the fact that it yields, besides the maximal weight gain Δw_max, the effective coefficient D_eff.

Table 4. The diffusion constants D_o, H expressing the temperature dependence of diffusivities D_eff, Eq. (3); Δw_max is the maximal weight gain for $t \to \infty$, illustration data D_eff(1000 °C), $\overline{\tau}$ is the improving parameter (mean value), ϕ, L are the dimensions of specimens

Material	ϕ [mm]	L [mm]	D_o [cm^2·s^{-1}]	H [kJ/mol]	Δw_max [g·cm^{-2}]	$10^8 \times D_\mathrm{eff}$(1000 °C) [cm^2·s^{-1}]	$\overline{\tau}$ [min]
ST55	10	15	126.4	233.4	0.630	3.350	224
LF15	10	15	79.2	230.6	0.629	2.733	246
AREMA	20	30	2.34×10^{-3}	117.0	1.269	3.707	372

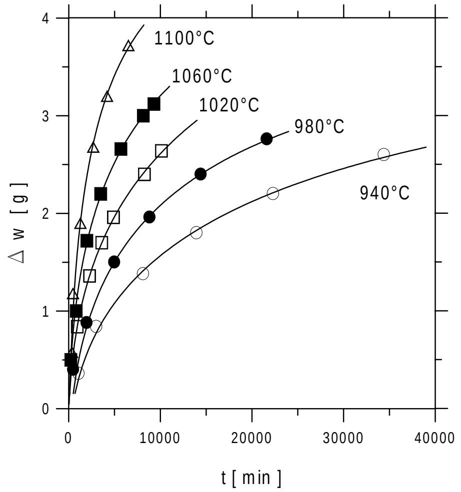

Fig. 3. The weight gain $\Delta w(t)$ measured on LH15 steel specimens at the temperatures from 940 to 1100 °C, fitted by Eq. (3).

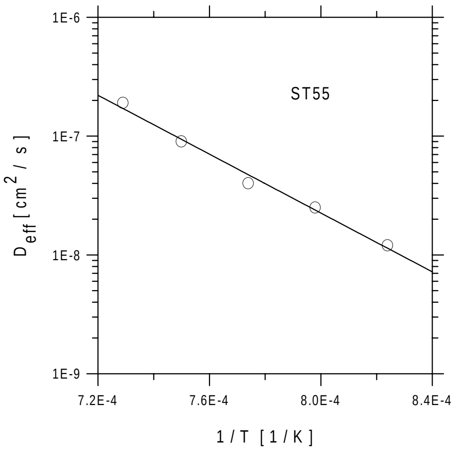

Fig. 4. An example of Arrhenius plot $D_{\mathrm{eff}} = f(1/T)$ for ST55 steel.

This quantity characterizes the gist of the oxidation processes in steels. The diffusivities D_{eff} obtained by computer fitting to experimental data $\Delta w(t)$, e.g. Fig. 3, are temperature dependent and satisfy the Arrhenius plot (Fig. 4). The diffusion characteristics D_{o} and H corresponding to the individual steels are introduced in Table 4 together with $D_{\mathrm{eff}}(1000\,^{\circ}\mathrm{C})$, and the mean values τ increase, similarly as in Tables 2 and 3, from the ST55 to AREMA steel. The values $\Delta w_{\max}$ were estimated approximately as 43 % of the original specimen weight ([4] p. 111).

The oxidation rate V(oxid, steel) resulting from Eq. (3) reads

$$\begin{aligned}\frac{\mathrm{d}\Delta w(t)}{\mathrm{d}\,t} = \frac{32\Delta w_{\max} D_{\mathrm{eff}}}{\pi^2} \Bigg[& \sum_{m=1}^{\infty} \frac{1}{a^2} \exp\left\{-\frac{r_m^2}{a^2} D_{\mathrm{eff}}(t-\tau)\right\} \cdot \\ & \cdot \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left\{-\frac{(2n+1)^2}{L^2}\pi^2 D_{\mathrm{eff}}(t-\tau)\right\} + \\ & + \sum_{m=1}^{\infty} \frac{1}{r_m^2} \exp\left\{-\frac{r_m^2}{a^2} D_{\mathrm{eff}}(t-\tau)\right\} \cdot \\ & \cdot \sum_{n=0}^{\infty} \frac{\pi^2}{L^2} \exp\left\{-\frac{(2n+1)^2}{L^2}\pi^2 D_{\mathrm{eff}}(t-\tau)\right\} \Bigg] .\end{aligned} \tag{6}$$

Taking, identically as in the previous cases, $T = 1000\,^{\circ}\mathrm{C}$, $t = 1$ min, $\tau = 0$, we get for the corresponding steels: V(oxid, ST55) = 2.7, V(oxid, LH15) = 2.4 and V(oxid, AREMA) = 2.8 $\mathrm{mg \cdot cm^{-2} \cdot min^{-1}}$.

4. Summary and conclusions

Three methods can be used for the investigation of iron and steel oxidation at high temperatures in ambient air.

i) Paidassi's method denoted as "parabolic law" (Eq. (1)). This method is suitable for evaluation of not too long measurements. It yields the values of oxidation coefficient kp, Table 2, which characterize the growth of weight gain of oxidized steels.

ii) The method of saturation model (Eq. (2)). This method can be well applied for evaluation of long time measurements. It gives, besides the oxidation coefficient B, the limiting value A, achieved at $t \to \infty$ (Table 3). The most accurate results can be obtained in such a case when the measured quantity $y(t)$ is the weight gain $\Delta w(t)$. Both the methods, i) and ii), have a semiempirical character.

iii) The gas-filling model (Eq. (3)) is physically motivated. It makes it possible to get, besides of maximum weight gain $\Delta w_{\max}$, the effective diffusion coefficient D_{eff} which shows that the run of metal oxidation has its origin in metal and O_2 diffusion in metallic matrix [7].

iv) A well satisfactory information on steel oxidation can be obtained from the values of oxidation rates V(oxid) of oxidized steels (Table 5). It is visible that the oxidation rate depends on the chemical composition of the steels:

a) The increased content of the elements C, Cr, Mn, Ni, Si [5] decreases the oxidation rate of steels (Tables 1, 5).

b) Oxidation rate V(oxid) is indirectly proportional to carbon content in steels (Tables 1, 5).

c) V(oxid) is decreasing function of oxidation time t (Table 5).

d) The methods (1), (2) and (3) yield approximately the same initial values of V(oxid), (Table 5).

Table 5. Oxidation rates V(oxid) of the individual steels ST55, LH15, AREMA calculated by the use of Eqs. (4), (5), (6); $T = 1000\,^{\circ}\mathrm{C}$, $t = 1$ and 4 min, $\tau = 0$; ϕ, L are the dimensions of specimens

Material			V(oxid, 1000 °C) $[\mathrm{mg \cdot cm^{2} \cdot min^{-1}}]$					
	ϕ	L	$t = 1$ min, $\tau = 0$			$t = 4$ min, $\tau = 0$		
	[mm]	[mm]	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (4)	Eq. (5)	Eq. (6)
ST55	10	15	2.17	3.13	2.68	1.09	1.55	1.33
LH15	10	15	2.07	2.88	2.41	1.04	1.43	1.20
AREMA	20	30	2.83	3.38	2.84	1.42	1.68	1.42

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