

Development and verification of the scale growth model during high temperature oxidation for S235 steel

Aleksandra Przyłucka^{1*} , Agnieszka Cebo-Rudnicka¹ , Marcin Rywotycki¹ ,
Joanna Augustyn-Nadzieja² , Zbigniew Malinowski¹ 

¹ AGH University of Science and Technology, Faculty of Metals Engineering and Industrial Computer Science, Department of Heat Engineering and Environment Protection, al. Mickiewicza 30, 30-059 Krakow, Poland.

² AGH University of Science and Technology, Faculty of Metals Engineering and Industrial Computer Science, Department of Physical and Powder Metallurgy, al. Mickiewicza 30, 30-059 Krakow, Poland.

Abstract

Every year rapid industrialization and the following urbanization fuel the global demand for steel. The use of steel products contributes to the sustainable development of society. The scale growth mechanism accompanies the high-temperature plastic working of metals and alloys. The article focuses on the thickness of the scale formed as a result of annealing steel samples in a furnace. Samples made of S235 (A283C) steel were heated at two temperatures, 1100°C and 1200°C, for 8 minutes. The amount of scale formed was determined on the basis of photos taken with a light microscope. The transformed equations of steel oxidation kinetics were used in the computational part. The scale thickness obtained numerically corresponded to the scale formed in real conditions. The aim of the research was to adjust the scale growth model on steel so that it gives correct results in relation to the actual thickness of the formed oxidized layer.

Keywords: scale, numerical simulation, model of oxidation

1. Introduction

The metallurgical industry of iron and its alloys is a top producer of semi-finished products and final products among all industries in the world. Demand for steel increases in line with global economic growth affecting both developed and developing countries. Manufacturers of steel products used in the automotive, rail, construction, and machinery industries aim to maintain steel as a versatile product without which modern society cannot grow sustainably. According to the report *2020. World Steel in Figures* prepared by World Steel Association (2020), world steel production in 2019 amounted to 1869 million tons, the corresponding amount of scale was estimated at 18–35 million tons (Farahat et al., 2010).

The scale is a layer of solid reaction product with a thickness exceeding 10 μm, and arises as a result of the oxidation of the surface of steel products during high-temperature plastic working processes, i.e., rolling, forging, or stamping. The scale contains a mixture of iron oxides of various oxidation states and oxides of other metals in trace amounts. The higher temperature and the longer product heating time result in a greater amount of oxidized products (Rostom Ali et al., 2012). Scale formation is an undesirable phenomenon because the oxidized metal is a waste of product, and the separating scale can lead to surface defects on the products, which in turn contributes to the deterioration of the surface quality. The paper presents the process of scale forming on a sample made of S235 (A283C) steel heated at high

*Corresponding author: aprzylucka@agh.edu.pl

ORCID ID's: 0000-0001-5210-3771 (A. Przyłucka), 0000-0003-3614-4287 (A. Cebo-Rudnicka), 0000-0002-0738-0339 (M. Rywotycki), 0000-0002-3614-0609 (J. Augustyn-Nadzieja), 0000-0003-2862-7588 (Z. Malinowski)

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temperatures. The performed experiment and calculations are preliminary research for a further doctoral dissertation.

2. High temperature oxidation

2.1. Mechanism of scale formation on steel

The mechanism of scale formation on metal alloys is a much less studied phenomenon than the oxidation of pure metals. Scale accumulating on the alloys is a multi-component system described by Hosemann et al. (2013), Pettit (2011), Więcek and Mróz (2014), and Xianglong et al. (2015). It usually consists of a heterophase mixture of compounds of specific alloy components together with the oxidant. Despite the mechanisms taking place at individual interfaces and inside the scale, there are also processes inside the metallic phase that significantly affect the oxidation process. The alignment of these differences depends on the diffusion rate of these components in the metallic phase. In most cases, this process takes place so leisurely that the alloy layer adjacent to the scales enriched with the slowest oxidizing components of the matter. Both this and the formation of an internal oxidation zone in the core lead to a more difficult oxidation process of alloys. Because of the complexity of the steel oxidation mechanism, it is impossible to apply one general theoretical solution for scale gain. The initial stage of the process is not parabolic due to the changing composition of the surface metal core layer during the course of the reaction. At a later period, the local concentration differences in the metallic phase are stabilized. The lowest subprocess determining the rate of scale formation is a diffusion of reactants in the metallic phase or in the reaction product. Scale formed in industrial conditions is accompanied by an environment of dry oxidizing gases. Essentially, these are exhaust gases consisting of: oxygen, carbon dioxide, carbon monoxide, sulfur dioxide, water vapor, nitrogen. The complicated nature of a mechanism leads to the use of theoretical generalizations for individual simplified cases. Knowledge of the process flow allows creating the theoretical model solutions in specific systems.

2.2. Models of metal oxidation at high temperatures

Most of the metals exposed to a oxygen-containing environment undergo the oxidation mechanism. Typically, the resulting reaction product is solid-state and accumulates on the surface of the reacting material.

The works by Dobrzański and Dobrzańska-Danikiewicz (2011), Jagadeeswara Rao et al. (2020), Mrowec (1982), and Surowska (2002) describe the basic methods of investigating the oxidation mechanism of metals and alloys, which concerns the measurement of the increasing reaction products. The oxidation process is a complex phenomenon consisting of many partial reactions. The most substantial chemical reactions take place at individual interfaces and pertain to the diffusion of the reactants in the layer of the reaction product. The solubility and diffusion of gases in metals depend on the chemical construction and structure of the materials. Metal absorption capacity and the value of the diffusion coefficient under certain conditions are affected by the presence of defects in the crystal structure such as dislocations, vacancies, or grain boundaries. The subprocesses belonging to interfacial chemical reactions include:

- transport of metal in the form of ions along with an identical sum of electrons to the crystal lattice of the oxidation product,
- chemisorption of the oxidizer in the form of ions on the surface of the layer, after the preceding splitting of molecules into atoms and taking the appropriate amount of electrons from inside the crystal lattice,
- embedding chemisorption anions of the oxidant into the crystal lattice of the reaction product.

However, the following processes are responsible for the transport of substances in the scale:

- diffusion of metal cations and electrons from the metal-scale interface to the surface of the layer through defects in the crystal lattice of the oxidation product,
- diffusion of oxidizer anions from the scale-oxidant interface to the metal surface and simultaneous diffusion of electrons in the opposite direction,
- commensurate anions and cations diffusion and electrons diffusion.

Depending on the pressure of the oxidizing background, the nature of the reaction product, and reaction time and temperature, one of the above-mentioned subprocesses may affect the rate and the manner of scale formation. At high temperatures, the chemical reactions of the formation of chemical compounds occur much faster than the diffusion of metal or oxidizer ions through the scale layer. This may result in determining the speed of the overall reaction beyond diffusion. The parallel course of the oxidation process is described by the dependence $\Delta m/q$, where Δm is defined as the ratio of the mass of the oxidant bound by a unit of the metal surface q to

the time t (Fig. 1). This dependency may have various character, resulting from the stage or conditions of the oxidation process. The most common types of metals and alloys oxidation rate reactions are described by the kinetic laws of oxidation at high temperatures.

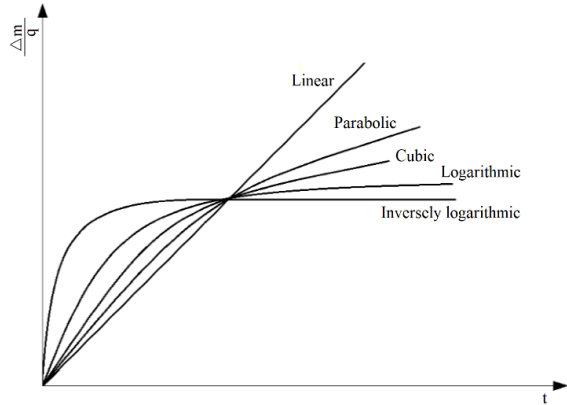


Fig. 1. Kinetic laws of metal and alloy oxidation

If no scale has formed on the oxidized metal or the resulting reaction product has a liquid form, so that the process of binding the oxidant on the surface of the material controls the rate of the chemical reaction taking place, the dependence of the metal loss thickness on the time is determined by the linear law (Mrowec & Werber, 1975):

$$\frac{dx_{Me}}{dt} = k_1 \quad (1)$$

$$x_{Me} = k_1 \cdot t + C \quad (2)$$

where: x_{Me} – thickness loss of the oxidized metal; t – reaction time [s]; k_1 – linear constant rate of oxidation; C – integration constant.

A linear course of the oxidation process can also take place when a porous scale is formed. This causes such a rapid inflow of oxidant to the metal surface that the interfacial reaction becomes the slowest subprocess.

At high temperatures, a continuous, tight-knit scale forms on the oxidized metal, which separates the metal from the gaseous medium. This is the most common course of the reaction, called the parabolic law:

$$\frac{dx}{dt} = \frac{k'_p}{x} \quad (3)$$

$$x^2 = 2k'_p \cdot t + C \quad (4)$$

where: x – scale thickness; k'_p – parabolic constant rate of oxidation.

In this case, the slowest subprocess affecting the rate of scale formation is diffusion transport of the substrates through a continuous layer of the reaction product forming on the metal surface.

In the real system, additional phenomena that modify the course of the reaction take place during the ongoing oxidation process, which can be described using the cubic law:

$$x^3 = 3k'_c \cdot t + C \quad (5)$$

where k'_c – constant rate of oxidation.

3. Experimental tests

3.1. Measurements on an experimental stand

The first stage of experimental research required the preparation of a test stand and test samples. The experimental stand included an electric chamber furnace with a control system, which provided, i.a. recording temperature of the furnace atmosphere. Six samples made of S235 (A283C) constructional steel were prepared for the tests. Each of the samples had a cylindrical shape with a diameter of 10 mm and a height of 5 mm. In the axis of each sample, from the side of the lower face, a 5 mm deep hole was drilled in. A type N thermoelement with a diameter of 0.5 mm was placed in it. After installing the thermoelements, each sample was placed in a metal holder (Fig. 2), which was heated along with the sample in a chamber furnace. The holder ensured a stable position of a sample in the furnace. The thermoelements were connected to the temperature measuring system, which was connected to a PC.



Fig. 2. The sample in a metal holder

Tests were performed for two furnace atmosphere temperatures: 1100°C and 1200°C. Before starting the experiment, the initial temperature of each sample was measured. The temperature of the air in which the samples were to be cooled was also checked. The course of the experiment was as follows: the furnace was heated to the temperature of 1100°C or 1200°C, then a sample was placed in the furnace where it remained for 480 seconds at the given temperature. After this time, the sample was removed from the furnace, and fast cooled in air. The temperature change in time during the sample heating process in the chamber furnace to 1000°C is shown in Figure 3 and to the temperature of 1100°C in Figure 4. In both cases the sample temperature had risen rapidly for the first 200 seconds, after that, it stabilized at the level of 1000°C (Fig. 3) and 1100°C (Fig. 4).

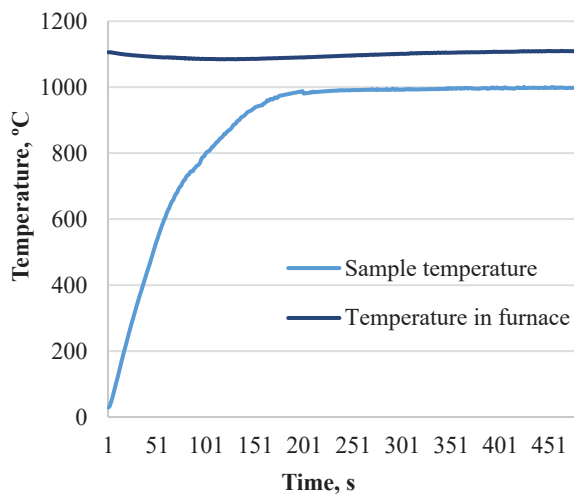


Fig. 3. Temperature change in time for the heating process to the temperature 1100°C

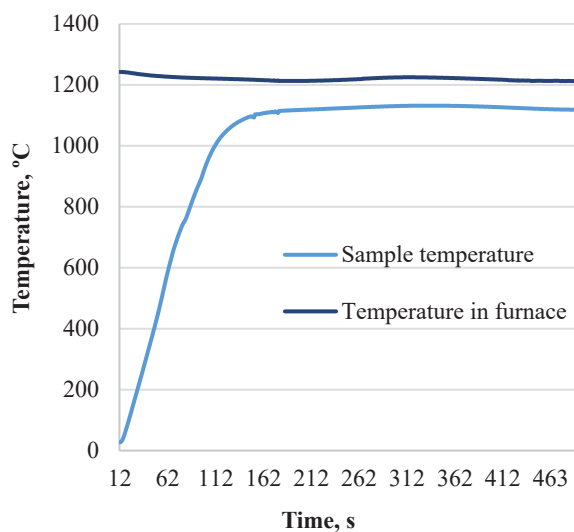


Fig. 4. Temperature change in time for the heating process to the temperature 1200°C

The second part of the experiment was to measure the thickness of a scale formed on the surface of the heated samples. The oxidized layer of metal oxides on the surface of each sample was visible to the naked eye, as shown in Figure 5. After complete cooling, the samples were taken from holders and disconnected from the thermoelements. In order to facilitate further preparation, the samples were embedded in acrylic and the solidified research material was cut. Due to the high brittleness of the scale, the cutting process was complicated to implement. The resulting metallographic specimens were examined with a light microscope being the equipment of the Department of Physical and Powder Metallurgy. Received photographs of a sample heated at 1100°C were taken with 10× and 20× (Fig. 6) magnification objectives. While photographs of the scale formed in 1200°C were taken with 5× and 10× magnification lens (Fig. 7).

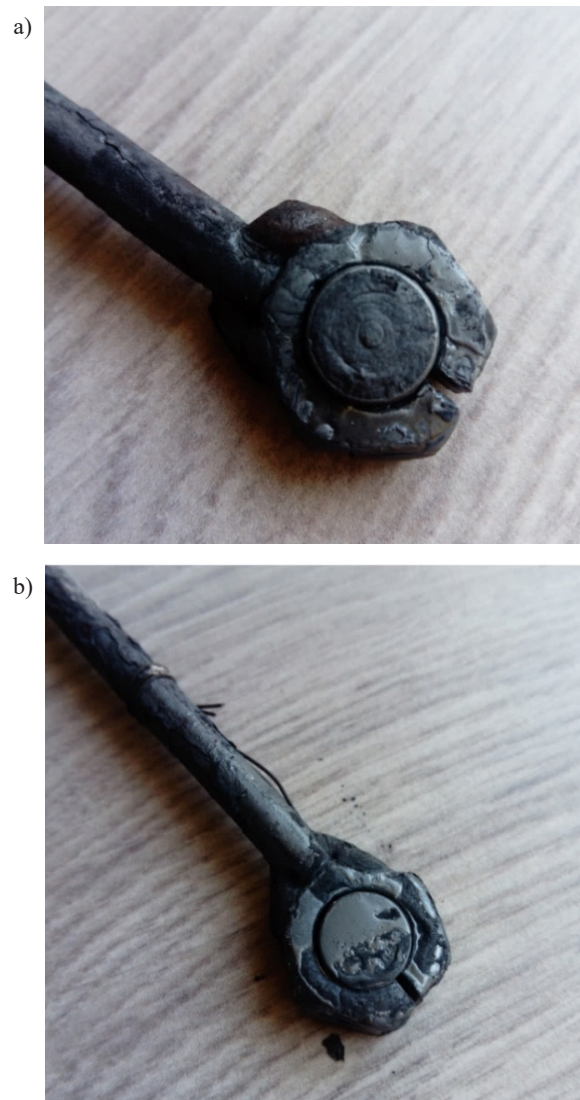


Fig. 5. Samples with a scale layer heated at: a) 1100°C; b) 1200°C

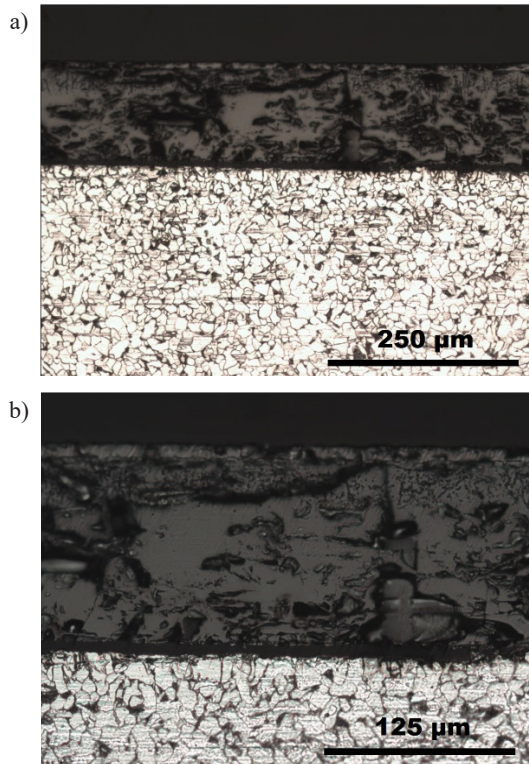


Fig. 6. Cross-section of a sample heated at 1100°C with magnification: a) 10×; b) 20×

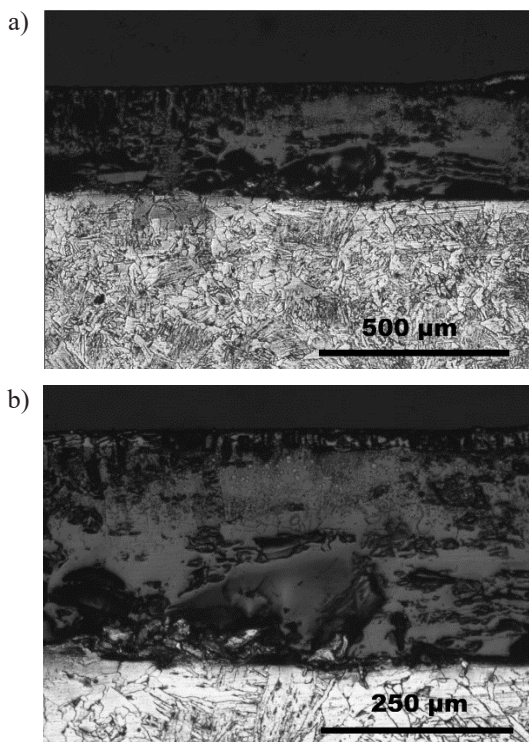


Fig. 7. Cross-section of a sample heated at 1200°C with magnification: a) 5×; b) 10×

Based on the obtained photographs (Figs. 6 and 7), the thickness of the formed scale was measured. For each sample, the average scale thickness was determined on

the basis of 20 measuring points distributed over the entire surface of an oxidized layer formed. The obtained measurement results are presented in Table 1. The average thickness of the scale formed on the sample surface which was heated at 1100°C was 156 µm. The scale formed on the surface of a sample heated at 1200°C had a thickness of 320 µm. The presented measurements show that the temperature difference of 100°C had a significant effect on formed oxidation layer thickness. As a result, the layer of scale formed at 1200°C was twice as thick as that formed on the sample heated at 1100°C.

Table 1. Measured scale thickness values on a sample heated at 1100°C and 1200°C

No.	Scale thickness [µm]	
	1100°C	1200°C
1	161.21	350.51
2	164.14	322.22
3	165.56	295.96
4	155.05	324.24
5	161.62	332.33
6	160.61	319.18
7	138.89	321.21
8	142.93	328.27
9	144.95	335.35
10	149.59	361.62
11	149.75	313.64
12	157.42	315.15
13	165.15	278.79
14	166.41	302.02
15	167.78	275.76
16	164.78	331.31
17	138.38	301.52
18	139.99	317.68
19	162.47	328.79
20	161.71	343.94
Average	155.92	319.98

Calculations of scale formation

In the case of the oxidation of steel in pure oxygen and at air temperatures higher than 400°C, it is commonly assumed that the process follows the parabolic law (Mrowec & Werber, 1975). A computer program developed at the Department of Heat Engineering & Environment Protection was used to simulate the process of scale increase. This program is used to simulate, i.a. heating processes to determine the temperature distribution in heated charge. Based on research presented by Vashchenko et al. (1972) in the numerical

codes, the general equation of the steel oxidation kinetics is implemented. These equations allow the determination of the thickness of a scale layer formed during the heating process. In the research conducted by Chen et al. (1993), Opel' et al. (1974), and Sachs and Tuck (1967), it is usual to express oxidation data in terms of the gain in weight per unit area of the oxidizing metal. Based on the results of the above-mentioned works, a general equation was developed in the form:

$$Z = A \exp\left(-\frac{B}{T}\right) \tau^C \quad (6)$$

where: Z – weight gain of the scale [g/m^2]; T – sample surface temperature [K]; τ – time after sample left furnace [s].

To obtain the scale thickness, it is necessary to transform the above equation. For this purpose, the following formula is used:

$$x = \frac{Z}{d} \quad (7)$$

where: x – scale thickness [mm]; d – scale density [kg/m^3].

The next stage of the research was to determine the parameters of the Z function. In the numerical model used, these parameters were adjusted on the basis of experimental measurements of the scale formed depending on time and temperature. On the basis of the analysis, the following equation of kinetics reaction was obtained for a sample heated at the temperature of 1100°C . Satisfactory results have been obtained using the following equation:

$$Z = 9.75 \exp\left(-\frac{9000}{T}\right) \sqrt{\tau} \quad (8)$$

And for the sample heated at 1200°C :

$$Z = 10.75 \exp\left(-\frac{9000}{T}\right) \sqrt{\tau} \quad (9)$$

The numerical model uses the finite element method to calculate sample temperature and scale thickness. To describe the surface of the sample, a set of 1088 nodes has been used. The two-dimensional discretization of the steel sample used is shown in Figure 8.

The calculation results included i.a. sample temperature variation during the heating process in the furnace. The program generated a temperature profile along the axis of tested samples. The temperatures generated by the program were calculated on the basis of the model presented in Hadała (2013) work. It is a 2D model that allows determining the temperature field in the nodes shown in Figure 8.

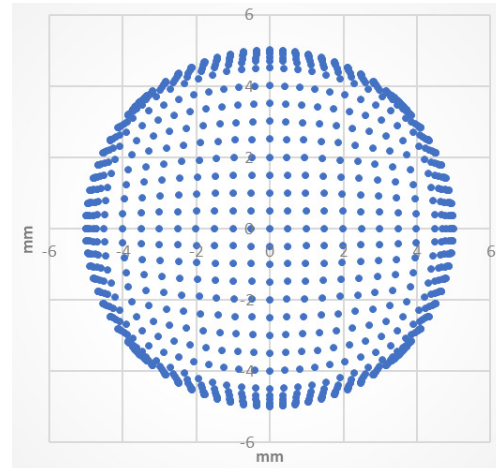


Fig. 8. Set of nodes of the sample top surface used in calculations

The calculated temperature was compared with the temperature measured by thermoelements. Figures 9 and 10 show a comparison of temperatures obtained in the experimental stand and calculated ones. The results of the comparison indicate that the experimentally measured temperatures in time are consistent with the values determined by numerical calculations.

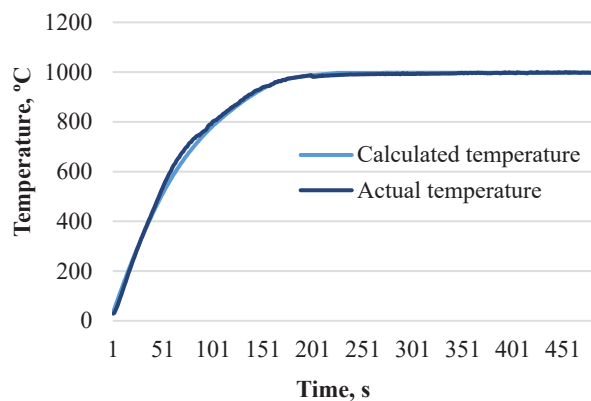


Fig. 9. Comparison of the measured and calculated sample temperatures in the furnace heated to 1100°C

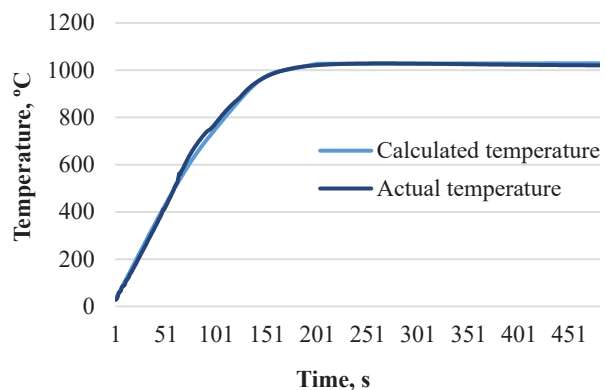


Fig. 10. Comparison of the measured and calculated sample temperatures in the furnace heated to 1200°C

Using the formula (6), equations (8) and (9) were transformed in order to obtain the calculations results of the increase in scale thickness on the sample surface. The obtained calculations results show that due to the rapid sample temperature drop, the steel oxidation process after the sample was removed from the furnace was insignificant. The increase in scale thickness during heating of the samples at 1100°C and 1200°C is shown in Figures 11 and 12.

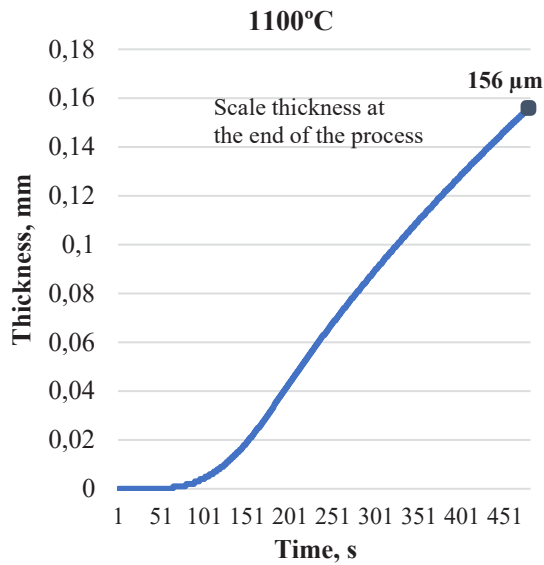


Fig. 11. Scale thickness increase with time at 1100°C

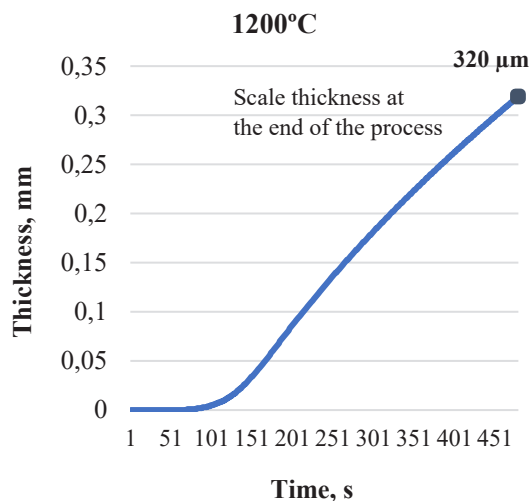


Fig. 12. Scale thickness increase with time at 1200°C

The results obtained using equations (8) and (9) show that the process of scale formation followed the parabolic law of steel oxidation. According to calculations, the final thickness of a scale formed on steel, which is marked by the black points in Figures 11 and 12 is the same as the ones measured by a light microscope. The final thickness of the scale layer for steel heated

at 100°C for 480 seconds was 156 μm. A calculated oxidized layer formed on a sample heated for 480 seconds at 1200°C had a thickness of 320 μm. The obtained results show that the calculation model gave correct results in comparison with the experimental part of the research.

Discussion

Constant technological development around the world would be impossible without the production and use of steel elements. The indisputable influence of steel on economic growth has been achieved through high standards of production of metallic alloy products, ensuring high quality of semi-finished and final products of the iron and steel industry. However, steel production entails the undesirable phenomenon of scale formation, which as a semi-product is not only disadvantageous due to the economic issues of steel production and material losses but also may contribute to surface defects of the resulting products with negative effects.

The above article presents a detailed description of the mechanism of scale formation in high-temperature processes. Scale formation on the surfaces of metals and alloys is conditioned by the atmosphere of a process. The rate of scale formed on steel increases with temperature. Scale formation described by the presented model requires the determination of constants in the equations describing its formation. For this purpose, a methodology for determining these constants was developed. This methodology is based on the tests carried out on the experimental stand, scale thickness measurements, and numerical calculation by using a self-made numerical program. The scale formed on the samples at temperatures of 1100°C and 1200°C had different thicknesses. The scale thickness which was determined experimentally was 156 μm for the sample heated at 1100°C and 320 μm for the sample at 1200°C. The equations of steel oxidation kinetics used in this work allowed to calculate the scale increment in time on the surface of the tested samples. The coefficients selected for the equations of kinetics allowed us to obtain the same scale thickness as experimental measurements. On this basis, it can be concluded that the developed methodology for modeling scale formation indicates the high correctness of the obtained results.

Acknowledgement

Scientific study financed from the regular activity of the Faculty of Metals Engineering and Industrial Computer Science of AGH University of Science and Technology. Work no. 16.16.110.663.

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