A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
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INVESTIGATION OF THE ADHESION OF SCALE FORMING IN THE PROCESS OF STEEL CHARGE HEATING BEFORE PLASTIC WORKING

BADANIA PRZYCZEPNOŚCI ZGORZELINY POWSTAJĄCEJ W PROCESIE NAGRZEWANIA WSADU STALOWEGO PRZED PRZERÓBKĄ PLASTYCZNĄ

On the basis of the author's own testing results, the effect of heating process parameters on the adhesion of the scale layer to the steel substrate is discussed.

The tests were carried out using own adhesion measurement methods.

Mathematical relationships for the effect of heating temperature and furnace atmosphere composition on the magnitude of adhesion have been derived.

Technological aspects of scale adhesion in the process of heating steel charge before plastic working are discussed.

Na podstawie wyników własnych badań omówiono wpływ parametrów procesu nagrzewania na przyczepność warstwy zgorzeliny do podłoża stalowego.

Badania wykonano wykorzystując własne metody pomiarowe przyczepności.

Opracowano zależności matematyczne ujmujące wpływ temperatury nagrzewania i składu atmosfery pieca na wartość przyczepności.

Omówiono technologiczne aspekty przyczepności zgorzeliny w procesie nagrzewania wsadu stalowego przed przeróbką plastyczną.

A list of designations

$a, a_1, a_2, b, b_1, b_2, c_1, c_2$ – constant values,
A, B, C, D – constant values,
E – activation energy, J/kmol or J/kg,
F – specimen surface area, m^2,
k – speed of reactions constant,
$m_0 \div m_3$ – mass of the specimen in the successive stages of the test, kg,
P_m – scale adhesion for mass method, %
P_z – scale adhesion for cold method, MPa,
R – gas constant, J/(kmol·K) or J/(kg·K),
T, t – temperature, K, °C,
z – loss of steel for scale, kg/m^2,
α – value of combustion air excess ratio,
τ – time, s or h.

1. Introduction

The processes of heating steel charge before plastic working are inseparably accompanied by steel oxidation. As a result of this phenomenon, scale forms, whose presence poses a substantial problem both for the heating process and for the subsequent plastic working.

For a long time, the world's metallurgy has been pursuing the goal of reducing the heat consumption. An important issue related to this objective is the reduction of the amount of forming scale by selecting an appropriate heating technology. This problem has been widely covered in publications [1÷4].

Heating of charge before plastic working is done primarily in pusher and stepper furnaces that are contin-

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uous operation furnaces. Each shutdown of the operation of such a unit results in heat losses. These shutdowns are largely caused by the necessity of carrying out repairs and overhauls of furnace hearths that have been damaged by the action of scale falling down during heating. This constitutes a major problem for the manufacturers of both metal sheets and plates and sections.

After exiting the furnace and prior to rolling, the steel surface should be cleared of scale. However, if the adhesion of the scale is too high, it will not be wholly removed. As a consequence, laps will form in the plastic working process, whose removal will require a laborious and costly treatment. This, however, impairs the quality of products [5]. The problem of too high scale adhesion occurs also in the wire drawing process. Indeed, scale residues left on the wire rod are pressed into the material during wire drawing and give rise to an intensive wear of the drawing dies [6].

Thus, it can be concluded that the next stage in the improvement of the heating process should be developing a technology that minimizes steel loss, but, at the same time, guarantees such scale adhesion to the steel substrate that the scale will not come off the steel surface in the furnace and allow itself to be removed after leaving the furnace.

The paper demonstrates a set of testing stand. It presents a methodology for the measurement of scale adhesion to the steel substrate. It also summarizes testing results and analyzes the effect of heating parameters on scale adhesion.

2. Basis theoretical

One of the most important external factors that determine the process of oxidation is temperature. An increase in temperature, with the remaining heating conditions unchanged, increases the rate of oxidation reaction. The dependence of the reaction rate on temperature is normally exponential in character [7].

This can be expressed by Arrhenius equation [8÷10]:

$$k = A\exp\left(-\frac{E}{RT}\right). \tag{1}$$

In general, the dependence of the reaction rate on temperature can be described by the following equation [11]:

$$k = A \cdot T^m \cdot \exp\left(-\frac{B}{T}\right) \tag{2}$$

which for:
m = 0 is Arrhenius equation,
m = 1 is Eyring equation,
m = -1 is Evans equation.

The reactions of iron oxidation in gaseous atmospheres follow the laws of thermodynamics, with these reactions being reversible. The direction of these reactions depends on the temperature and composition of combustion gas. Determining the conditions of equilibrium of the furnace atmosphere with the metal being heated is possible on the basis of the diagrams of equilibrium constants of the reactions under consideration as a function of temperature [12].

The relative thickness of layers is also a function of temperature. A certain regularity occurs, at the same time, whereby with increasing temperature the relative thickness of the inner layer, in which the metal occurs at the lowest oxidation state, rapidly grows to cover almost the whole scale with its scope [12, 13].

The existing results of experimental testing on the adhesion of scales are not consistent and serious doubts arise due to the lack of a reliable method for determining scale adhesion to the substrate at high temperatures. The first method for the quantitative determination of scale adhesion to the metallic substrate has been developed by Engell and Peters. It involves the measurement of the force needed for tearing the scale layer off the metallic core surface at ambient temperature, after stopping the oxidation process. This method essentially allows only the determination of the residual adhesion that has remained in spite of the thermal dilatation. Namely, the stresses associated with the difference in the thermal expansion of the metallic phase and the scale may considerably weaken the adhesion or even remove it completely. Nevertheless, the results obtained by Engell and Peters cast new light on the problems related to the adhesion of scales to the metallic substrate. The dependence of adhesion on temperature is complex in character, as initially it increases with increasing temperature and then, after reaching a maximum, it rapidly decreases. This is true above all for those cases, where the alloy addition oxides formed in the reaction precipitate on the core surface in the form of separate phases, or where these compounds come into reaction with vistite. Alloy additions of this type are aluminium and silicon, which substantially reduce the adhesion of scale to the substrate. Manganese, on the other hand, whose chemical affinity to oxygen is only slightly higher than that of iron, practically does not affect the scale adhesion to the substrate, since, owing to its good solubility in vistite, the manganese oxide will not precipitate on the core surface as a separate phase. In the case of iron-carbon alloys, the increase in carbon concentration usually causes a reduction in scale adhesion. This is likely to be associated with the formation of volatile carbon oxides at the scale-alloy interface, whose pressure counteracts the adhesion. On the other hand, it has been established that the adhesion of scale to the alloy containing 0.12% of carbon is higher than to pure iron. This probably results from the fact that, at low carbon contents of alloy, the formation of oxides at the scale-core interface occurs at a later stage of the reaction.

Adhesion, or the force of bond of the scale with the substrate, depends, among other things, on the composition of the gaseous atmosphere in the heating furnace.

The atmosphere in furnaces fired with gaseous fuels includes strongly oxidizing components, such as O_2, H_2O; less oxidizing components, such as CO_2; and reducing components, such as CO, H_2, CH_4. A component of the atmosphere is also the inert gas N_2, and if a high deficit of air occurs, solid particles in the form of carbon soot can be found in the atmosphere. In the case of the complete combustion of the fuel ($\alpha > 1.0$), the resultant combustion gas contains CO_2, O_2 and H_2O.

With the increase in the value of α, the concentrations of O_2 and N_2 increase, while the concentrations of CO_2, and H_2O decrease. Such a combustion gas composition is oxidizing in character, with the oxidizing properties of the combustion gas increasing with the increase in α (with increasing O_2 content of combustion gas). In the case of an air deficit, the combustion gas contains CO, H_2, often CH_4 and Csoot, as well as CO_2 and H_2O.

The composition of the furnace atmosphere during the combustion of fuel gases can most simply be defined by the value of excess air ratio [14]. When carrying out the tests under discussion, the adhesion was expressed as a function of this ratio.

3. Measuring stand

To realize the objective of the study, a specialized laboratory has been built at the KPPiOŚ (Department of Industrial Furnaces and Environmental Protection). A set of testing stands is shown schematically in Fig. 1 [15].

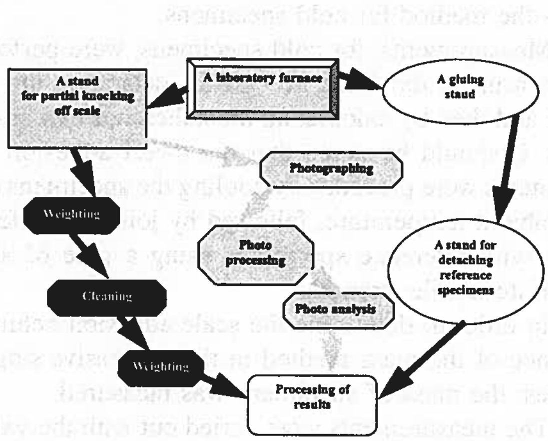

Fig. 1. Schematic diagram of testing stands

The basic element of the testing stand is an electric furnace, type KS 520. A combustion chamber with a gas burner are integrated with the furnace. The burner performs the role of a gaseous atmosphere generator. The temperature in the furnace is controlled by means of a TROL — 9090 regulator. The accuracy of temperature control is ±1.0K [16].

In order to determine the adhesion of scale, a scale knocking-off device was designed and constructed. The device is shown in Fig. 2.

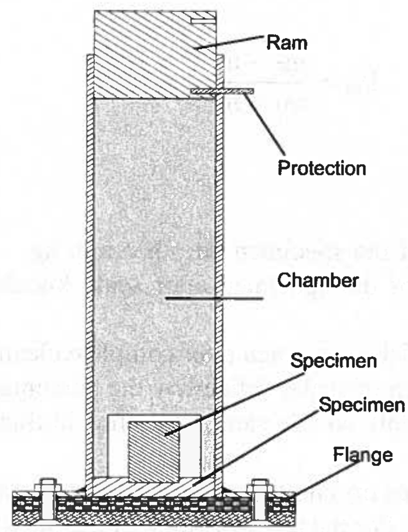

Fig. 2. A scale knocking off device

The instrument is composed of a round cross-section battering chamber, a ram with a safety lock, and a specimen stand. After releasing the safety lock, the free falling ram hits the specimen to chip off the scale. It became a very important problem for this instrument to establish the energy that the ram should hit the tested specimen with. At too high energy, the complete detachment of the scale may occur, irrespective of the force of its bond with the steel substrate. Too low energy, on the other hand, might not detach the scale at all. The essence of the measurement using the battering ram was to use such energy as to produce a partial detachment of scale for specimens heated within the full range of the thermo-chemical heating parameters under consideration. The energy with which the ram hits a specimen depends on the mass of the ram and on the height from which it falls.

4. Testing methodology

A methodology for the measurement of adhesion has been developed, for both cold and hot charge.

It was assumed that the degree of specimen surface cleaning after partial chipping off of the scale layer would be essential for the measurement for hot specimens. For the determination of scale adhesion, two methods have been developed: a mass method and a visual method.

The mass method of determining the adhesion of scale involves the weighting of specimens in the successive stages of the test.

The adhesion of a scale layer can be expressed by the ratio of the mass of scale left after knocking off to the entire mass of the scale. The value of so determined adhesion is defined by the following relationship:

$$P_m = \frac{m_2 - m_3}{m_1 - m_3} \cdot 100\%, \qquad (3)$$

where:
m_1 — mass of the specimen after heating, kg,
m_2 — mass of the specimen after scale knocking off, kg,
m_3 — mass of the specimen after complete cleaning, kg,
P_m — adhesion of scale, defined by the percentage fraction of scale left on the steel core after hitting by the ram, %.

The masses m_2 and m_3 are determined by weighting the specimens. For the determination of the mass m1, the following relationship is used:

$$m_1 = m_0 + \frac{z \cdot F}{0{,}74}, \qquad (4)$$

where: m_0 - mass of the specimen before heating, kg,
z - loss of steel for scale, kg/m^2,
F - specimen surface area, m^2.

The visual method of adhesion testing relies on the computer analysis of the specimen surface after the scale has been chipped off. It enables the determination of the ratio of the area of scale that has not come off as a result of ram action to the entire area of scale covering the steel core. The image source was a digital camera operating with a computer unit.

Tests were carried out to determine the adhesion of scale using the visual method. It was found that the accuracy of the quantitative determination of scale adhesion by the visual method was little precise. It allows the graphical representation of specimen surfaces after chipping off of the scale and the visual determination of the degree of adhesion for different heating conditions. Fig. 3 shows examples of photographs of specimens for different heating conditions, illustrating, respectively, high and low scale adhesion.

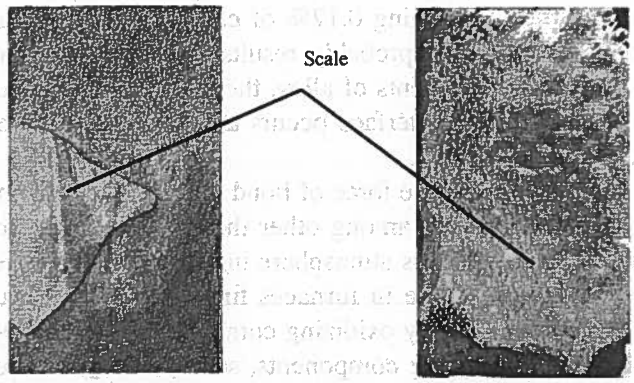

Fig. 3. Specimens pictures big and little scale adhesion demonstrate for differents heating parameters

Specimens „cooled down" to ambient temperature were subjected to adherence tests. In this case, the examined quantity was the tensile force which allows the scale to be detached from the steel core by reference specimens glued to the face walls of specimens tested [15, 17].

The method applied to the testing of scale adhesion to the cold charge is a quantitative method allowing the numerical determination of the force that bounds the scale with the steel core.
The value of force needed for detaching the scale layer from the steel surface was measured by using a TC-FR100TL.A4K testing machine.

5. Results of adhesion measurements

On the basis of the preliminary tests carried out it was established that the two methods would be used for further measurements:
- the mass method,
- the method for cold specimens.

Measurements, for cold specimens, were performed by measuring the force needed for detaching the scale layer and then by calculating the adherence expressed in MPa. It should be noted that the direct adhesion measurements were preceded by cooling the specimens down to ambient temperature, followed by joining the formed scale with reference specimens using a glue of an appropriate tensile strength.

In order to determine the scale adhesion behind assistance of the mass method in the successive stages of the test the mass of specimens was measured.

The measurements were varied out with the value of combustion air excess ratio of $\alpha = 0.6 \div 1.4$. Results of scale adhesion measurements are summarized in Table 1 and Table 2.

TABLE 1

Results of scale adhesion measurements for cold method

Value of combustion air excess ratio α	Temperature t, °C				
	1000	1100	1200	1300	1330
	Scale adhesion P_z, MPa				
0,6	0,430	0,784	1,126	2,664	3,478
0,7	0,361	0,528	0,986	2,444	3,156
0,8	0,215	0,361	0,833	1,674	2,139
0,9	0,187	0,324	0,632	0,967	1,425
1,0	0,158	0,272	0,521	0,778	1,032
1,1	0,134	0,228	0,320	0,518	0,724
1,2	0,111	0,167	0,278	0,472	0,527
1,3	0	0,027	0,062	0,127	0,158
1,4	0	0	0	0	0

TABLE 2

Results of scale adhesion measurements for mass method

Value of combustion air excess ratio α	Temperature t, °C				
	1000	1100	1200	1300	1330
	Scale adhesion P_m, %				
0,6	15,97	20,25	28,53	33,64	35,41
0,7	14,06	18,02	24,72	30,13	31,74
0,8	12,21	15,38	19,02	24,87	26,32
0,9	10,89	12,76	16,64	20,59	23,08
1,0	9,32	11,74	14,67	17,71	18,93
1,1	7,12	8,72	10,54	14,27	16,26
1,2	5,61	6,88	9,06	13,48	15,42
1,3	3,55	4,62	6,89	9,07	12,88
1,4	1,64	2,28	3,64	5,66	7,88

6. Comparison between the cold and the mass methods

As the thermal expansion of a scale layer is much lower than that of steel, the adhesion measurement for cold specimens may be burdened with a significant error. For this reason, tests for hot specimens were also carried out using the mass method.

Using the results of adhesion measurements, computer simulations were performed, based on which functions describing the correlation between the cold and the mass methods have been derived [15]. From among the generated functions, three have been selected, which most accurately describe the correlation between the two methods.

The derived functions describing the correlation between the methods take on the form of:

- a linear equation

$$P_z = -a + b \cdot P_m \tag{5}$$

- a multinomial equation

$$P_z = a_1 + b_1 \cdot P_m + c_1 \cdot P_m^2 \tag{6}$$

- an exponential equation

$$P_z = a_2 + b_2 \cdot \exp(c_2 \cdot P_m) \tag{7}$$

where:

P_z - scale adhesion for cold method, MPa,

P_m - scale adhesion for mass method, %,

$a, a_1, a_2, b, b_1, b_2, c_1, c_2$ - constant values.

Figs. 4÷6 show the correlation between the mass method and the cold method, and the values of statistical errors, respectively, for relationships (5), (6) and (7).

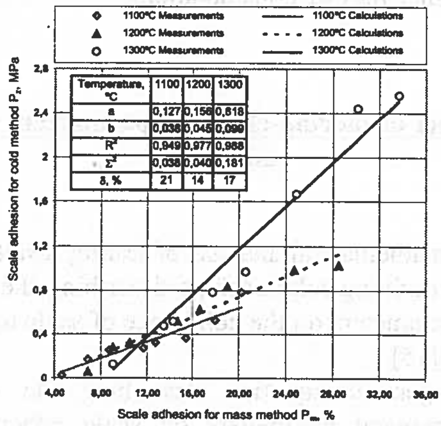

Fig. 4. Correlation among mass and cold method of measurement of scale adhesion (relationship5)

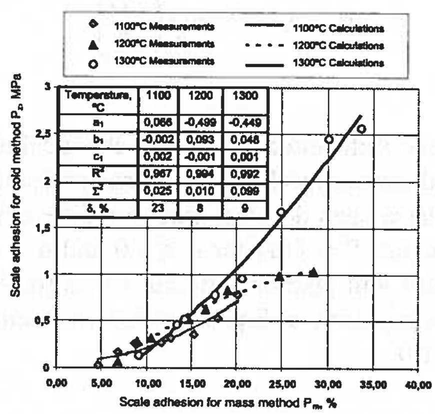

Fig. 5. Correlation among mass and cold method of measurement of scale adhesion (relationship6)

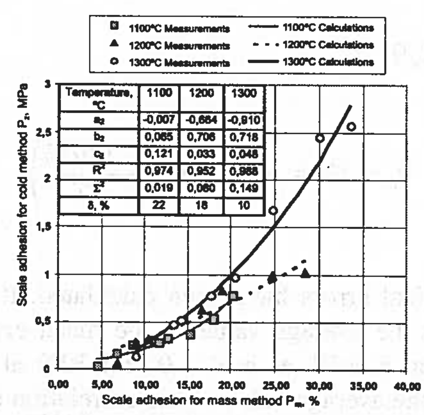

Fig. 6. Correlation among mass and cold method of measurement of scale adhesion (relationship7)

Obtaining the mathematical relationships between the discussed methods of scale adhesion measurement confirms the correctness of the developed methodology and enables the verification of correctness of testing results. The existence of the above-mentioned correlation allowed reference to be made only to the cold method in the further part of considerations.

7. Effect of thermo-chemical parameters on the adhesion

The mathematical analysis of testing results was reduced to deriving relationships describing the effect of heating parameters on the adherence of scale to the steel substrate [15].

The general equation describing the effect of thermo-chemical parameters on scale adherence has been reduced to the following form:

$$P = A \cdot \alpha^{C} \cdot \exp\left(-\frac{D}{T}\right). \tag{8}$$

The analysis of the effect of thermo-chemical parameters on scale adherence has been performed and suitable relationships have been derived. Due to a different behavior of the function $P = f(\alpha)$ for $\alpha \leqslant 1.0$ and $\alpha > 1.0$, these relationships will take on different forms [6, 7].
The following forms of Equation (8) have been obtained:
- for $\alpha \leqslant 1.0$

$$P_z = 1507 \cdot \alpha^{-1,9} \cdot \exp\left(-\frac{11646}{T}\right) \tag{9}$$

- for $\alpha > 1,0$

$$P_z = 1764 \cdot \alpha^{-5,1} \cdot \exp\left(-\frac{12013}{T}\right). \tag{10}$$

Statistical errors have been calculated. It has been found that the average value of the mean error of approximation is 14% at $\alpha \leqslant 1.0$ and 30% at $\alpha > 1.0$. Whereas, the average value of the correlation coefficient is $R^2 = 0.959$ for $\alpha \leqslant 1.0$ and $R^2 = 0.939$ for $\alpha > 1.0$.

Figure 7 shows the relationship of adherence against the value of combustion air excess ratio, determined for the "cold" method with the use of Equations (9) and (10).

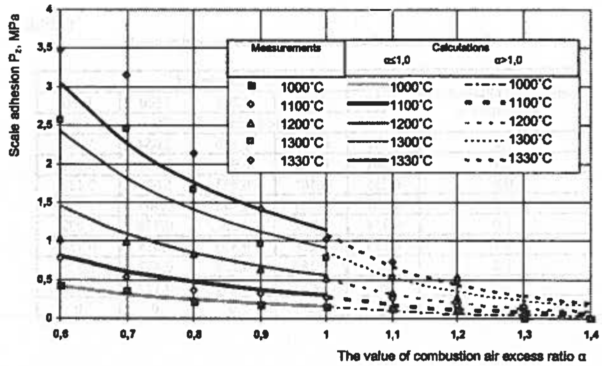

Fig. 7. Relationship of adherence vs. thermo-chemical parameters for measurements and calculations

8. Technological aspects of scale adhesion to the steel substrate

The problem of scale adhesion to the substrate is of paramount technical importance. Scales of low adhesion to the substrate allow the attacking gas to access the core surface or the adjacent reaction product layers. Under these conditions, the scale has no protective properties. On the other hand, though, a weak adhesion of scale is advantageous, where a necessity exists to remove it from the metal surface after heat treatment done in an oxidizing atmosphere. A good adhesion and compactness of scale reduces losses resulting from the oxidation of the charge. However, it makes the removal of oxides from the metal surface difficult, as it is often a complicated operation from the technological point of view [18].

The performed tests and analyses suggest that, in the aspect of heating technology, the adhesion of scale should be considered within some ranges of its values, as shown in Fig. 8.

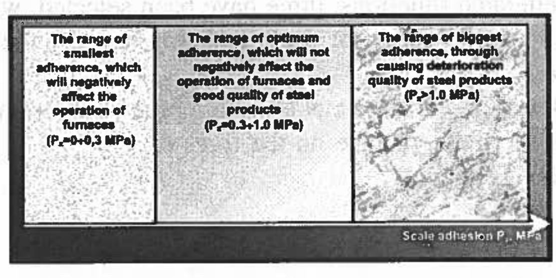

Fig. 8. The ranges of scale adherence as guidelines for the realizing of technology guaranteeing correct work of heating furnaces and good quality of steel product

9. Findings and conclusions

The performed theoretical analysis and the laboratory tests carried out allow the following conclusions to be drawn:

1. Heating parameters have an essential effect on the adhesion of scale to the steel substrate.
2. Scale adhesion decrease with increasing value of combustion air excess ratio.
3. The correlation between heating parameters (temperature and the value of combustion air excess ratio) can be described by mathematical relationships; however, a different behaviour of these relationships for aŁ1.0 and for a¿1.0 should be taken into account.
4. On the basis of the analysis of measurement results, the range of optimum adherence can be determined (P=0.3÷1.0 MPa), which will not negatively affect the operation of furnaces and good quality of steel products.
5. The performed investigation of the effect of heating parameters on the adherence of scale can form guidelines for the technology of heating steel charge before plastic working.

REFERENCES

[1] F. Neumann, Metallurgische Betrachtungen zum Oxydationsverhalten von Stahl bein Erwarmen, Harterei-Tech. Mitt. 3, 198-207 (1971).

[2] P. Wawrzyk, P. Wessely, Bezzgorzelinowe nagrzewanie stali w piecach grzewczych, Śląsk, Katowice 1973.

[3] J. Szargut, J. Kozioł, E. Majza, Zasady poprawy eksploatacji pieców grzejnych, Zeszyty Naukowe Pol. Śl., Energetyka z. 106, Gliwice 1989.

[4] M. Kieloch, Energooszczędne i małozgorzelinowe nagrzewanie wsadu stalowego, Prace naukowe Wydziału Inżynierii Procesowej, Materiałowej i Fizyki Stosowanej, Seria Metalurgia nr 29, Częstochowa 2002.

[5] R.L. Higginson, B. Roebuck, E.J. Palmiere, Texture development in oxide scales on steel substrates, Scripta Materialia 47, 337 - 342 (2002).

[6] B. Golis, J.W. Pilarczyk, Z. Błażejowski, Druty stalowe, Politechnika Częstochowska, Prace dydaktyczne, Seria Metalurgia nr 35, Częstochowa 1991.

[7] S. Mrowec, Zarys teorii utleniania metali. Śląsk, Katowice 1971.

[8] N.Ju. Tajc, V.M. Olszanskij, Metodika rasczieta okislenija metalla. Metall Koksochim. 23, 163 - 166 (1970).

[9] A.N. Lebedev, S.I. Kazancev, S.I. Ginkul, Okalinoobrazovanie uglerodistych stalej v atmosfere vozducha. Izv. VUZ, Czern. Metall. 10, 155 (1985).

[10] V.M. Olszanskij, L.A. Guzov, N.Ju. Tajc, A.N. Minaev, Nagrew metalla s minimalnym okisleniem. Metall. Gorn. Prom. 3, 47-50 (1970).

[11] L. Filar, T. Filar, Praktyczna metoda obliczenia utleniania wsadu w procesie jego nagrzewania. W: Materiały XI Zjazdu Termodynamików. Cz.l. Szczecin-Świnoujście, 93-96 (1981).

[12] S. Mrowec, Kinetyka i mechanizm utleniania metali. Wydaw. „Śląsk", Katowice 1982.

[13] M. Kieloch, Technologia i zasady obliczeń nagrzewania wsadu. Skrypt Politechniki Częstochowskiej, Częstochowa 1995.

[14] M. Kieloch, Strata stali w piecach grzewczych przy zmiennej temperaturze nagrzewania, Politechnika Częstochowska, Seria Monografie nr 22, Częstochowa 1991.

[15] J. Boryca, Przyczepność warstwy zgorzeliny powstałej w procesie nagrzewania wsadu stalowego, Praca doktorska, Politechnika Częstochowska, Częstochowa 2005.

[16] J. Boryca, M. Kieloch, The adhesion of scale to the steel substrate in the process of heating the charge before plastic working, Acta Metallurgica Slovaka 8, 20 - 28 4/2002.

[17] M. Kieloch, J. Boryca, Ł. Piechowicz, Przyczepność zgorzeliny w procesie nagrzewania wsadu stalowego, Hutnik 1, 7 - 12 (2005).

[18] J. Boryca, M. Kieloch, Technologiczne aspekty przyczepności zgorzeliny do podłoża stalowego, Nowe technologie i osiągnięcia w metalurgii i inżynierii materiałowej, Seria Metalurgia nr 39, Częstochowa, 130 - 133 (2004).

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