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THE RATE OF METAL OXIDES REDUCTION FROM THE SLAG OF THE DIRECT-TO-BLISTER FLASH SMELTING PROCESS

KINETYKA REDUKCJI TLENKÓW METALI Z ŻUŻLI Z JEDNOSTADIALNEGO PROCESU OTRZYMYWANIA MIEDZI

A slag from the direct-to-blister flash smelting process, as well as the same slag modified by CaO and MgO additions, were reduced by powdered graphite. The rate of the oxygen removal from these slags was determined at 1523 K, 1573 K and 1623 K. It was found that, for the original slag and the slag modified by CaO and MgO additions with $x_{CaO} = 0.25$, and $x_{MgO} = 0.25$, the oxygen removal follows a reaction of the first order. For a higher concentration of the slag modifiers, the reduction process is controlled by mass transport.

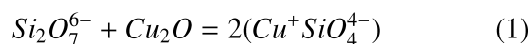
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Praca zawiera wyniki badań nad kinetyką otrzymywanego odmiedziowania żużla z procesu jednostadialnego Outokumpu za pomocą sproszkowanego grafitu. Badania przeprowadzono dla żużla otrzymanego bezpośrednio z pieca zawieszinowego oraz dla tego samego żużla modyfikowanego dodatkami CaO i MgO w temperaturach 1523K, 1573K i 1623K. Dla żużla wyjściowego oraz żużli modyfikowanych dodatkiem CaO ($x_{CaO} = 0,25$) lub dodatkiem MgO ($x_{MgO} = 0,25$) stwierdzono, że proces redukcji jest reakcją pierwszego rzędu. Dla żużli o większych stężeniach modyfikatorów ($x_{CaO} = 0,3$, $x_{MgO} = x_{CaO} = 0,25$) proces redukcji jest kontrolowany przez transport masy.

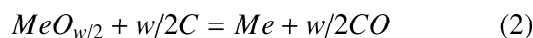
1. Introduction

The direct-to-blister process was commercially implemented in 1977, in Głogów, Poland. Because of its specific features, it did not gain a broad recognition in the copper industry, and nowadays it is only used in two locations. The second installation of this process is situated in Olympic Dam, Australia. The process requires high oxygen pressure and therefore is restricted to those smelting concentrates which mainly consist of minerals without iron (Cu_2S , CuS , Cu_9S_5) or with a small iron content (Cu_5FeS_4). As a consequence of the high oxygen pressure in an Outokumpu flash smelting furnace in the Głogów case the obtained slag contains 12-16% Cu. This is accounted for the approximately 1/3 of the copper content in the smelting concentrate. Therefore, a recovery of the copper from this slag has a practical importance and heavily influences the operational costs. The slag cleaning process is carried out in an electric furnace with coke and limestone additions. The limestone should modify the reduced slag in order to facilitate the process. However, slags are ionic liquids [1-5], and the copper exists in the slags as Cu_2O species and Cu^+ ions

associated with the silicate anions, according to the reaction:



Cu_2O is a basic oxide and the oxygen ion from it breaks the bridge in the Si-O network structure, which leads to the dissociation of the silicate anion complexes. During the reduction process, the situation becomes reverse. According to the model [6] it can be suggested that the dissolved copper is almost completely in the form of $(-Si-O^-Cu^+)$ species, for slags containing about 1 wt-% of copper. This can be taken as an explanation of the sluggishness of the copper recovery process, when it is close to completion, as the slag reduction proceeds according to the reactions:



where: w – is a metal valence,

$Me = Cu, Pb, Fe, \dots$

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The addition of limestone to the slag causes some of the copper ions Cu^+ to be replaced by Ca^{2+} ions and therefore, the number of (Cu_2O) species increases. In this paper, the influence of CaO and MgO additions to the slag obtained from the direct-to-blister flash smelting process on the rate of its reduction was investigated.

2. Apparatus

A schematic diagram of the apparatus used in this study is shown in Figure 1. It consists of a furnace with Superkantall heating elements, powered by means of a transformer controlled by a Eurotherm controller, which is also connected to a controlling thermocouple Pt-PtRh10. The furnace temperature was maintained at $\pm 1\text{ K}$ and the maximum temperature variation in the hot zone was $\pm 2\text{ K}$. An alumina reaction tube was sealed at the top and the bottom by means of water cooled brass - heads and with use of rubber O-rings. The measuring thermocouple Pt-PtRh10 was situated close to the crucible containing investigated slag, and it measured the temperature of the sample with a Keithley's 2000 multimeter. The powdered graphite was placed in a metallic container, situated just under the upper cap of the reaction tube. The graphite container had a number of holes, which enabled a gas passage through the graphite powder. The bottom of the graphite container was made of copper foil, and it could be removed by an Al_2O_3 tube (I.D. 4 mm) by pushing it, when the experiment was started. This tube was then transferred into the slag and positioned about 5 mm above the bottom of the crucible.

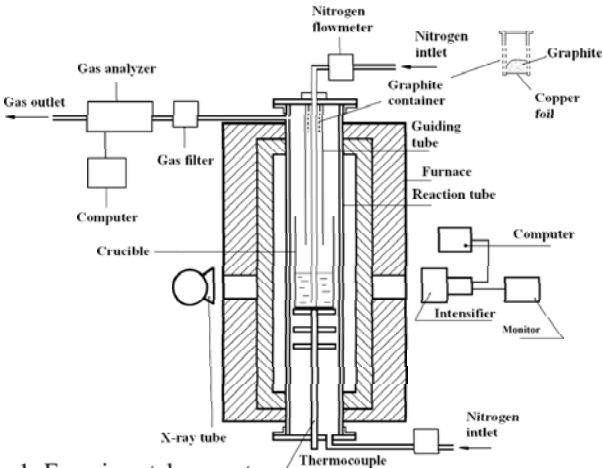


Fig. 1. Experimental apparatus

Purified nitrogen of $5\text{ dm}^3/\text{h}$ flow rate was allowed to pass through this tube and then by the graphite powder, before the experimental run, and through the slag – while the experiment lasted. A nitrogen stream of $20\text{ dm}^3/\text{h}$ flow rate was admitted into the reaction tube through its bottom head. Both nitrogen streams were controlled

with the use of electronic flow meters manufactured by Brooks. The gas train was made by means of steel tubing connected to Hooke's fittings and valves. During the experiments, gas composed of nitrogen and $\text{CO} + \text{CO}_2$ mixture, formed as a result of reactions between the graphite powder and slag, was analyzed by a gas analyzer for CO and CO_2 every 5 seconds, and the results were recorded by the computer. In addition, X-ray radiography was used for a direct observation of the reduced slag and the Cu-Pb-Fe alloy formation.

3. Calibrations of the gas analyzer

The infrared gas analyzer used in this study analyzed CO and CO_2 content in the gaz mixture. To speed up a passage of the reaction gas through the furnace, nitrogen of total $25\text{ dm}^3/\text{h}$ flow rate was admitted into the reaction tube. For this reason, the gas analyzer had to be calibrated. The calibration was carried out by allowing a passage of a gas mixture containing nitrogen of $25\text{ dm}^3/\text{h}$ flow rate with additions of predetermined flow rates of CO , CO_2 , and $\text{CO}+\text{CO}_2$. The flow rates of these gases were controlled by Brooks flow meters and corrected to 273 K . Consequently, the gas analyzer showed readings for CO and CO_2 , as can be seen in Fig. 2. The results were recorded by the computer. If the obtained reading of $\%\text{CO}$ and $\%\text{CO}_2$ did not change with time, then these values were taken as true values.

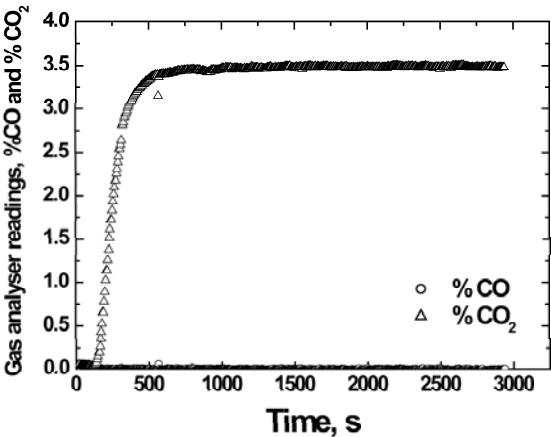


Fig. 2. Readings of the gas analyzer for CO_2 and CO , in the case when the mixture of nitrogen ($25\text{ dm}^3/\text{h}$) with carbon dioxide ($5\text{ dm}^3/\text{h}$) was passing through the experimental set up

Figure 3 shows the relation between the gas analyzer reading for CO , and the fraction of CO in the gas mixtures admitted into the reaction tube.

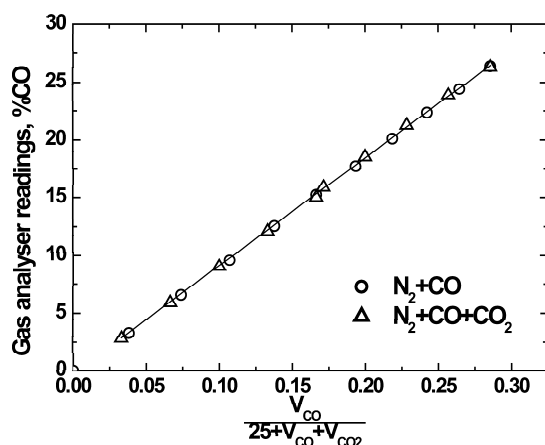


Fig. 3. The correlation between the reading of the gas analyzer for CO and the carbon oxide fraction in the gas mixture passing through the reaction tube of the furnace

A similar correlation was obtained for CO₂. Using the last square method, the following relations were found:

$$\%CO = 92.01 \frac{V_{CO}}{25 + V_{CO} + V_{CO_2}} \quad (4)$$

$$\%CO_2 = 96.43 \frac{V_{CO_2}}{25 + V_{CO} + V_{CO_2}} \quad (5)$$

where: %CO, %CO₂ are the analyzer readings for CO and CO₂, respectively,

V_{CO} , V_{CO_2} are the flowrates of CO and CO₂ in [dm³/h].

Relations (4) and (5) were used for the determination of the CO and CO₂ volumes formed during the reduction process between two consecutive readings of the gas analyzer.

4. Experimental procedure

A slag produced by the Głogów direct-to-blister flush smelter was used in this study. The main constituents of this master slag are listed in Table 1.

TABLE

Composition of the Głogów direct-to blister flush smelter slag

Components	Cu	Fe	Pb	Zn	SiO ₂	MgO	CaO	Al ₂ O ₃
wt- %	11.41	11.23	2.62	0.85	33.22	4.13	12.87	9.22

The rate of the slag reduction determinations was measured for the master slag as well as for the master slag modified by CaO and MgO additions. The masses of the added components were calculated to obtain the selected mole fractions of these components ($x_{CaO} = 0.25$, $x_{CaO} = 0.30$, $x_{MgO} = 0.25$, and $x_{CaO} = x_{MgO} = 0.25$).

The crucible with the chosen slag (about 130 g), was placed in the reaction tube of the furnace. In the upper brass- head of the reaction tube a graphite container and a port for alumina tube (I.D. 4 mm) were situated. Through the alumina tube, the nitrogen of 5 dm³/h flow rate was allowed to flash the graphite powder. Another nitrogen stream of 20 dm³/h flow rate was introduced to the reaction tube of the furnace, through its bottom cap. After a few hours (5-7 hrs) the furnace was switched on and the temperature controller adjusted to 573 K. The furnace was kept under these conditions for approximately 12 hours. Next, the temperature of the furnace was increased to the selected value (1523 K, 1573 K or 1623 K). The sample was kept for one hour at the selected temperature, and then the alumina tube was transferred to the position in which the end of the

orifice was immersed into the slag and positioned 5 mm above the bottom of the crucible.

Next, the bottom of the graphite container was punctured and it allowed the graphite powder to fall down on the slag surface. The passage of the graphite powder to the crucible was secured by an alumina tube of 20 mm diameter, which end was close to the slag surface.

The break of the bottom of the graphite container was taken as the beginning of the experiment. However, the first signal of the reduction process was detectable after about 60 seconds from that moment. The gas leaving the reaction tube was analyzed for the CO and CO₂ content every 5 seconds by the gas analyzer, and the results were recorded by the computer. It was assumed that the reduction would take place on the graphite/slag interface and that its area was equal to the surface of the cross section of the crucible (15.2 cm²). The mass of the graphite powder needed for the covering of the slag surface was determined from the mean size of the powder (0.15 mm) and the powdered graphite density (0.278 g/cm³). It was also assumed that this mass could be bigger because of the packing factor; however, it should not exceed the computed values (0.063 g) more than twice.

In each experiment, the mass of the used graphite powder

was about 1.5 g, and this means that during almost the whole experimental run, the reaction surface was equal 15.2 cm^2 .

An example of the obtained results is shown in Figure 4.

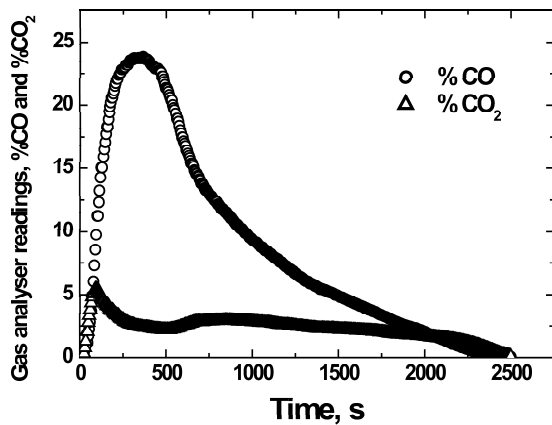


Fig. 4. The results obtained for the oxygen reduction from the slag with $x_{CaO} = 0.25$ at 1573 K

Observed decrease of the CO and CO₂ contents results from the decreasing of the Cu₂O, PbO, FeO, etc concentrations in the reduced slag and after some time, also because of the decrease of the graphite/slag interface. Taking into account equations (4) and (5), the volumes CO and CO₂ evolved (dm³/h) can be determined from the analyzer readings (%CO and %CO₂):

$$V_{CO} = \frac{25 \times (\%CO)}{92.01 - (\%CO) - 0.956 \times (\%CO_2)}, \quad [\text{dm}^3/\text{h}] \quad (6)$$

$$V_{CO_2} = \frac{23.897 \times (\%CO_2)}{92.01 - (\%CO) - 0.956 \times (\%CO_2)}, \quad [\text{dm}^3/\text{h}] \quad (7)$$

As the analyzer readings were adjusted to 0 °C, the numbers of the CO and CO₂ moles produced per one second can be calculated from the relations:

$$n_{CO} = \frac{V_{CO}}{22.4 \times 3600} \quad (8)$$

$$n_{CO_2} = \frac{V_{CO_2}}{22.4 \times 3600} \quad (9)$$

The corresponding number of oxygen moles removed from the slag during a period of 5 seconds was determined from the relation:

$$n_O^i = \frac{n_{CO}^i + n_{CO}^{i+1}}{2} \times 5 + 2 \times \frac{n_{CO_2}^i + n_{CO_2}^{i+1}}{2} \times 5, \quad (10)$$

where: n_{CO}^i, n_{CO}^{i+1} – the number of the CO moles formed during the reduction process per one second, recorded in two consecutive measurements,

$n_{CO_2}^i, n_{CO_2}^{i+1}$ – the number of CO₂ moles formed during the reduction process per one second, recorded in two consecutive measurements.

By the summation of the n_O^i values, the equation ($n_O = f(t)$) describing the oxygen removed from the slag as a function of the reduction time was determined. In a similar way, the mole number of the carbon consumed in the process ($n_C = g(t)$) can be estimated. Figure 5 shows an example of such functions. It is worth mentioning that the masses of the consumed carbon calculated by this method were slightly lower than the masses of the graphite used in the experimental runs. The differences were in the order of 0.8 to 1.5%, and this fact can be taken as an evidence for the correctness of the implemented method.

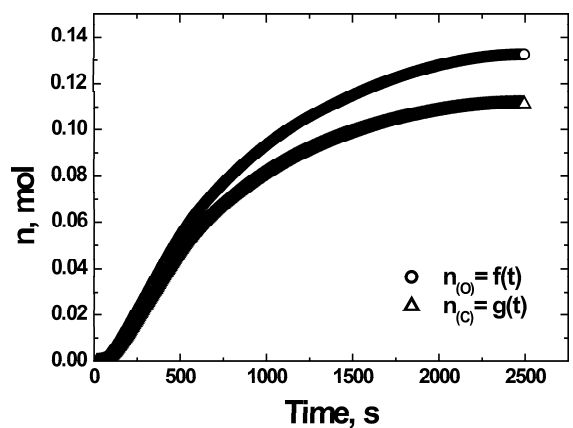


Fig. 5. A relation between the removed oxygen from the master slag as well as consumed carbon and the reduction time at 1523 K

Taking into account the ionic theory of slags, the process of the oxygen removal from the slag, can be written schematically:



If we assume that the oxygen removal from the investigated slag is a reaction of the first order, then, under a fixed reaction surface and with the mole number of the oxygen (n_O^0) which can be removed from the slag by carbon, the following relation can be written:

$$-\frac{dn_O}{dt} = kn_O \quad (12)$$

where: k – is the rate of the reduction process,

$n_O = n_O^0 - n_O(t)$ is the number of oxygen moles in the slag, which can be removed under experimental conditions at a given time (for $t = \tau$),

N_O^0 – the initial number of the oxygen moles which can be removed from the slag under experimental conditions (for $t = 0$),

$n_O(t)$ – the number of oxygen moles removed in

the time period $t = \tau$.

Integrating the equation (11), the following relation can be obtained:

$$-\ln\left(1 - \frac{n_O(t)}{n_O^0}\right) = -\ln(1 - X_O) = kt \quad (13)$$

where: $X_O = n_O(t)/n_O^0$.

Utilizing the relation $n_O = f(t)$ (Fig. 5) and the equation (12), the rate constant k of the overall reduction process can be determined if the value of n_O^0 is known. The value of n_O^0 can be determined in the same experiment if the mass of the used carbon is in excess to the stoichiometric requirements of the reactions involved. In general, the k constant has to be normalized and referred to the surface unit, and n_O^0 should be referred to the volume unit of the reduced slag.

5. Results

Experiments were carried out for the master slag of the composition given in Table 1, and the same slag modified by CaO, MgO and CaO + MgO additions. The masses of the added oxides were adjusted to obtain their concentration in the slag of 0.25 and 0.30 mole fractions. Figure 6 illustrates the results for the master slag at 1523 K.

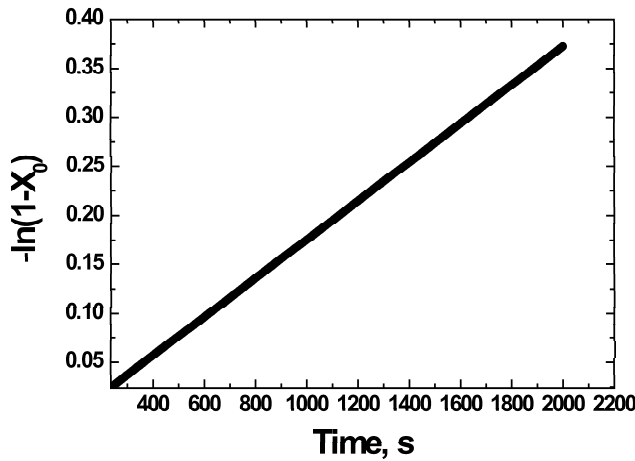


Fig. 6. Relation of $-\ln\left(1 - \frac{x_O(t)}{x_O^0}\right) = f(t)$ for the master slag at 1523 K

The first few points were cut off because they show a remarkable deviation from the trend of the majority of points. This phenomenon can be explained by the much lower temperature of the falling graphite powder than the temperature of the slag surface. Utilizing the equation (12), the rate constant k of the process of oxygen removal can be estimated. Figure 7 shows the temperature dependence of the rate constant for the master slag.

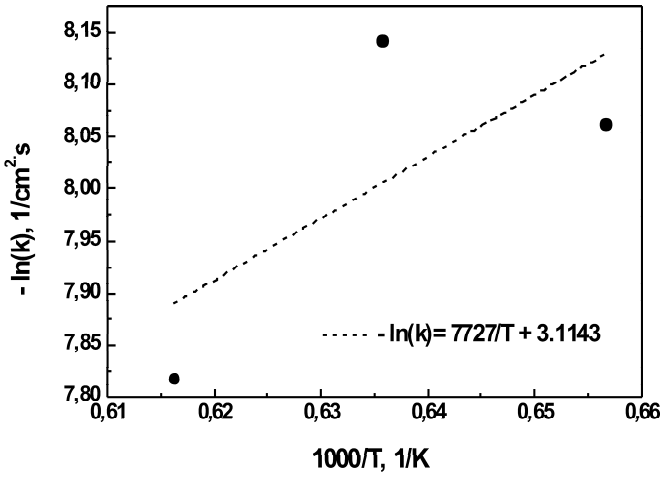


Fig. 7. A function of $-\ln\left(1 - \frac{x_O(t)}{x_O^0}\right) = f(t)$ for the master slag

The estimated activation energy (76.3 kJ/mol) should be regarded as an approximate value because of the narrow experimental temperature range. A similar relation (Fig.8) was obtained for the master slag modified by CaO with mole fraction $x_{CaO} = 0.25$.

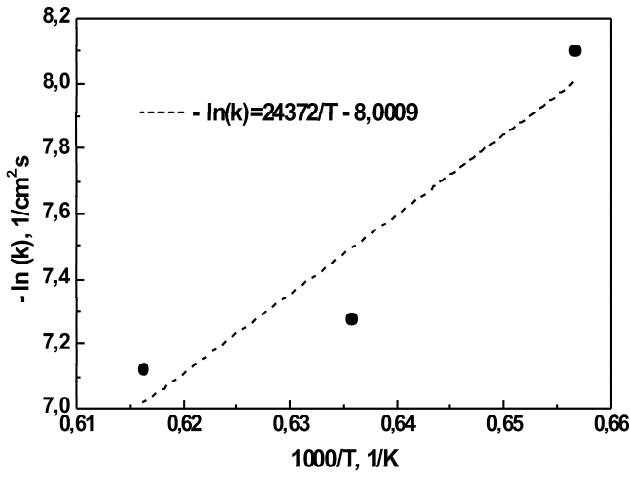


Fig. 8. A function of $\ln k = f\left(\frac{1000}{T}\right)$ for the slag modified by CaO addition with $x_{CaO} = 0.25$

In the case of the master slag modified by CaO with $x_{CaO} = 0.3$, the function $-\ln(1 - X_O) = f(t)$ does not follow a linear relation(Fig.9).

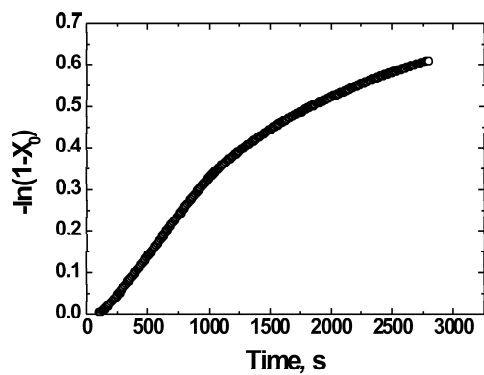


Fig. 9. The plot of the function $-\ln\left(1 - \frac{x_{O(t)}}{x_O^0}\right) = f(t)$ for the master slag modified by CaO addition with $x_{CaO} = 0.30$ at 1523 K

A similar relation $-\ln(1 - X_O) = f(t)$ was obtained for 1573 K and 1623 K. For this reason, the rate constants for this slag could not be determined. A possible explanation for this phenomenon can be associated with the mass transport of Cu_2O , PbO and FeO from the bulk to the slag/graphite interface. In other words, the 5 l/h flowrate of nitrogen stream passing through the slag did not secure the homogeneity of the melt, in the case when the reduction rate exceeded a certain level.

5.1. Experimental results for master slag modified by MgO addition

An addition of MgO to the master slag very increases rapidly its melting temperature and for this reason, the experiments were limited to the slag composition with $x_{MgO} = 0.25$. The results obtained in this case were described by relation (12), and the example of such correlation is given in Fig 10.

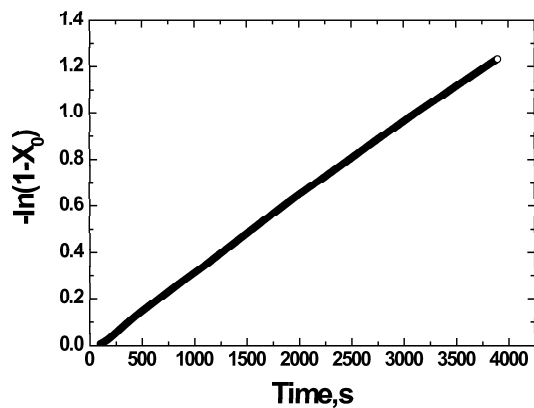


Fig. 10. A function of $-\ln\left(1 - \frac{x_{O(t)}}{x_O^0}\right) = f(t)$ for the master slag modified by MgO addition with $x_{MgO} = 0.25$ at 1523 K

In this case, similar relations were obtained for 1573 K

and 1623 K. The estimated rate constants for all three experimental temperatures allows to find its temperature dependence, which is given in Fig. 11.

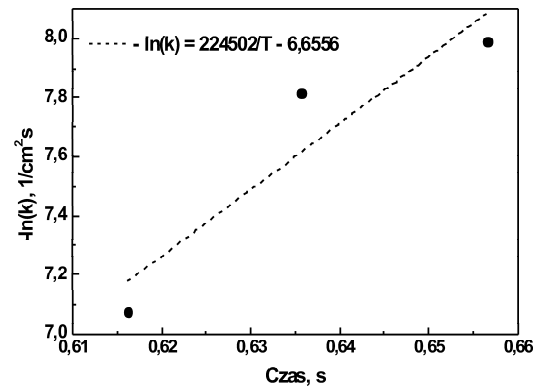


Fig. 11. The relation of $\ln k = f\left(\frac{1000}{T}\right)$ for the master slag modified by MgO addition with $x_{MgO} = 0.25$

5.2. Experimental results for master slag modified by CaO and MgO additions

In this case, the master slag was modified by additions of CaO and MgO in such quantities that the mole fractions of these oxides were equal to 0.25. An attempt to describe the obtained results by the linear relation in the $(-\ln\left(1 - \frac{x_{O(t)}}{x_O^0}\right), t)$ axes failed, as it can be seen in Figure 12.

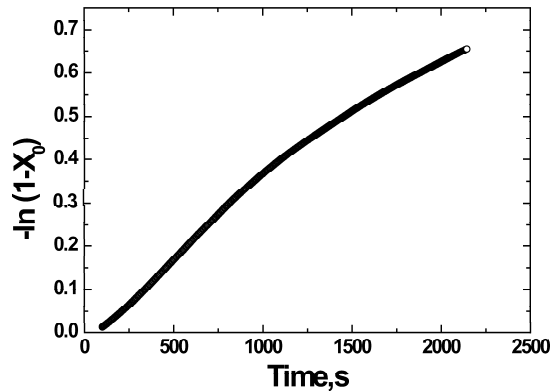


Fig. 12. The function of $-\ln\left(1 - \frac{x_{O(t)}}{x_O^0}\right) = f(t)$ for the master slag modified by CaO and MgO additions with $x_{CaO} = 0.25$, $x_{MgO} = 0.25$ at 1523 K

6. Conclusions

The kinetics of the oxygen removal from the slag produced in the direct-to-blister flush smelter in Głogów, Poland, can be described by the relation for the reaction of the first order for the master slag, and the master slag

modified by CaO and MgO additions -with $x_{CaO} = 0.25$, and $x_{MgO} = 0.25$. Estimated activation energy for the slag reduction is approximately equal to about 1/3 of the value reported for the fayalite slag [7,8]. The increasing content of CaO ($x_{CaO} = 0.3$) and ($x_{CaO} = x_{MgO} = 0.25$) leads to a curvilinear dependence $-\ln(1 - X_O) = f(t)$. A possible explanation of such a behavior may be an increase of the reduction rate, and therefore, the process begins to be controlled by mass transport in the liquid slag. This obstacle can be overcome by vigorous stirring of these slags.

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