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THERMODYNAMIC AND KINETIC ASPECTS OF THE REFINING OF Fe-Cr ALLOYS USING CALCIUM UNDER VERY LOW OXYGEN PARTIAL PRESSURE

TERMODYNAMICZNE I KINETYCZNE ASPEKTY RAFINACJI STOPÓW Fe-Cr ZA POMOCĄ WAPNIA PRZY BARDZO NISKICH CIŚNIENIACH CZĄSTKOWYCH TLENU

The removal of phosphorus and other elements, e.g. Sn, Pb, As from liquid iron alloys containing chromium through oxidation is not possible from the thermodynamic point of view. Under very strong reducing conditions, when oxygen partial pressure $p_{O_2} \leq 1 \cdot 10^{-17}$ atm and when alkaline earth metals, mainly calcium, are used as a reacting substance, the reaction proceeds according to the following scheme:

$$n \left| [Ca]_{Fe}, Ca_{(l)}, \{Ca\}_{(g)} \right| + m[X]_{Fe} \Leftrightarrow Ca_n X_m, \quad \text{where}: X = P, N, Sn, As, \dots \text{etc.}$$

The investigations concerning this type of reaction are the main subject of the present study.

It was found, that the characteristic minimum $[\%X]_{min}$ occurs on the curves $[\%X] = f(\tau)$, where τ — refining time. The thermodynamic-kinetic model and computer program have been developed to find out how the main physicochemical factors determine the location of the $[\%X]_{min}$. The program allows to determine simultaneously the changes of content of six elements, i.e. O, S, P, N, C and Ca vs. refining time for arbitrarily selected values of temperature, pressure, metal composition, calcium addition etc. As the refining substance, the solution of calcium in calcium fluoride, metallic calcium and hydride calcium have been tested. The investigations were carried out under argon pressure within the furnace elevated up to 1.0 MPa at 1743 and 1823 K, respectively, using the CaF_2–Ca equimolar solution. The good agreement between the experimental results and calculated curves $[\%X]_{Fe} = f(\tau)$ has been achieved.

Usuwanie fosforu oraz innych szkodliwych domieszek jak cyna, ołów, arsen i in. z ciekłych stopów żelaza zawierających chrom poprzez ich utlenianie nie jest możliwe z termodynamicznego punktu widzenia. W silnie redukcyjnych warunkach, jeśli

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ciśnienie cząstkowe tlenu $p_{O_2} \leq 1 \cdot 10^{-17}$ atm oraz przy zastosowaniu metali ziem alkalicznych, głównie wapnia w charakterze reagentów reakcje rafinacji przebiegają zgodnie z następującym schematem:

$$n \left| [\text{Ca}]_{\text{Fe}}, \text{Ca}_{(l)}, \{\text{Ca}\}_{(g)} \right| + m[X]_{\text{Fe}} \Leftrightarrow \text{Ca}_n X_m,$$
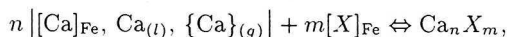
gdzie: X = P, N, Sn, As, ... itd.

Głównym celem niniejszej pracy były badania dotyczące w/w reakcji. Stwierdzono, że na krzywych typu $[\%X] = f(\tau)$, gdzie τ — czas rafinacji, występuje charakterystyczne minimum, $[\%X]_{\text{min}}$. Opracowano model termodynamiczno-kinetyczny i program komputerowy celem określenia, w jaki sposób główne czynniki fizykochemiczne determinują położenie minimum $[\%X]_{\text{min}}$. Program pozwala na określenie jednoczesnych zmian stężeń sześciu pierwiastków, tj. O, S, P, N, C oraz Ca w funkcji czasu rafinacji dla dowolnie wybranych wartości temperatury, ciśnienia, składu metalu, dodatku wapnia i in. W charakterze materiału rafinacyjnego testowano roztwór Ca w CaF₂, metaliczny wapń oraz wodorek wapnia CaH₂. Badania prowadzono w atmosferze argonu wewnątrz pieca, przy nadciśnieniu do 1,0 MPa, przy temperaturze 1743 i 1823 K, stosując równomolowy roztwór CaF₂–Ca. Uzyskano wystarczająco dobrą zgodność pomiędzy wynikami badań eksperymentalnych a krzywymi modelowymi typu $[\%X] = f(\tau)$.

List of symbols

A	— area of the metal-slag interface,
f_X	— activity coefficient of the component X in the metal,
J_X	— molar flux of the component X,
K_X	— equilibrium constant of reaction (1),
$M_{\text{Ca}_n X}$	— molar mass of the component X,
n	— stoichiometric coefficient or index of the power,
$\sum n_s$	— sum of the number of moles of particular slag components,
V_m	— liquid metal volume,
$[\%X]_0$	— concentration of the removed element in the metal for the time $\tau = 0$,
$[\%X]_\tau$	— concentration of the removed element for the time $\tau \neq 0$.

Greek symbols:

$\beta'_X, \beta'_{\text{Ca}_n X}$	— modified mass transfer coefficient of reagent in the metal and slag phases, respectively,
$\gamma_{\text{Ca}_n X}$	— activity coefficient of the component X in the slag,
ρ_m, ρ_s	— density of metal and slag, respectively.

Other symbols:

$[\,], (\,), \{\,\}$	— metal, slag, and gaseous phases, respectively,
$(*)$	— concentrations of reagents at the metal–refining-slag phase interface,
subscript (b)	— the concentration in the bulk.

1. Introduction

Removal of phosphorus and the majority of elements of the IVa and Va groups from the liquid iron alloys in the presence of chromium by their oxidation during the steel-making process, is impossible without substantial chromium losses. In order to find out whether there is any range of the concentration of chromium and phosphorus within broad limits of the concentration of these elements in iron solutions, in which, from a thermodynamic point of view, it would be possible to oxidize the phosphorus in the presence of chromium, a number of calculations has been performed for a hypothetical liquid Fe-Cr(0-20%)–Ni(8%)–P(0-3.0%) solution at the temperatures 1773 and 1873 K. The results of those calculations for the range of chromium contents from 8.0 up to 20.0 wt.% are shown in Fig. 1.
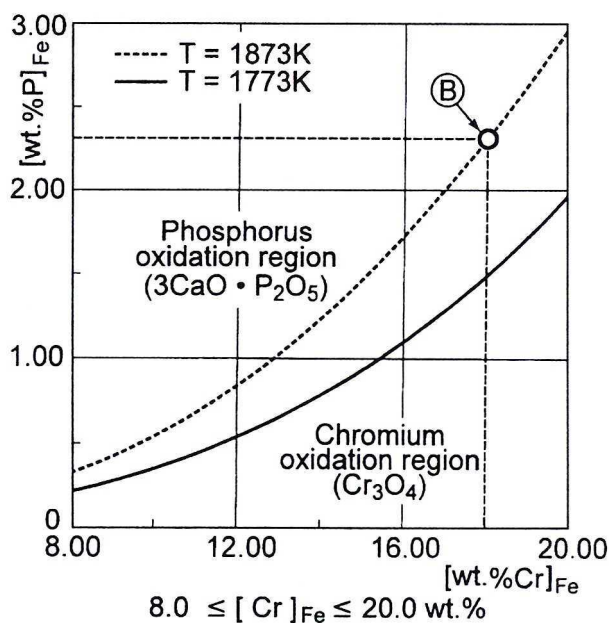

Fig. 1. Isotherms of the oxidation of phosphorus and chromium in the Fe-Cr-P alloy at the temperatures 1773 and 1873 K

Results of these calculations indicate that at the temperature 1873 K, in the liquid metal containing 0.035 wt.% P, the reaction of chromium oxidation with the formation of $FeO \cdot Cr_2O_3$, Cr_2O_3 or Cr_3O_4 will prevail for any chromium content greater than 1.25 wt.%. Similarly, with a chromium content of 18 wt.% and at the temperature 1873 K, (point B, Fig. 1) the oxidation of phosphorus would be possible, if the phosphorus content in the liquid metal was 2.36 wt.%.

Growing demand for 18/8 type steels of enhanced purity required that theoretical and experimental studies on a new type of refining, the so-called *reduction refining*. The concept of this refining was developed and tested on a technical

scale in 1976 by Y. N a k a m u r a [1]. It is based on the possibility of involving phosphorus, nitrogen, arsenic, tin, and other elements into chemical reaction by means of the alkaline-earth metals under the conditions of very low oxygen partial pressures of the order of $1 \cdot 10^{17}$ atm. in the reaction zone.

The subject of this study is contained in the field of so-called *calcium metallurgy* and relates to the reduction refining of liquid alloys under very low oxygen partial pressures and in hyperbaric conditions.

2. Refining of Cr(18)Ni(8) Alloy — Characteristics of the Simulation Model

If calcium is used as a reagent, then the reaction of calcium with elements to be removed can be written as follows:

$$n \left| Ca_{(l)}, \, [Ca]_{Fe}, \, \{Ca\}_{(g)} \right| + [X]_{Fe} \Leftrightarrow (Ca_n X). \tag{1}$$
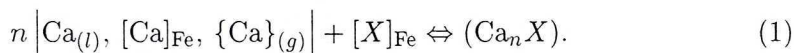
It is advisable in this case to find out for which of the three forms of calcium the thermodynamic conditions are the most favorable for the course of the reaction according to scheme (1). Thus, comparison of the changes of the standard Gibbs free energy was made for possible reactions of calcium with phosphorus. The results of calculations are shown in Fig. 2.
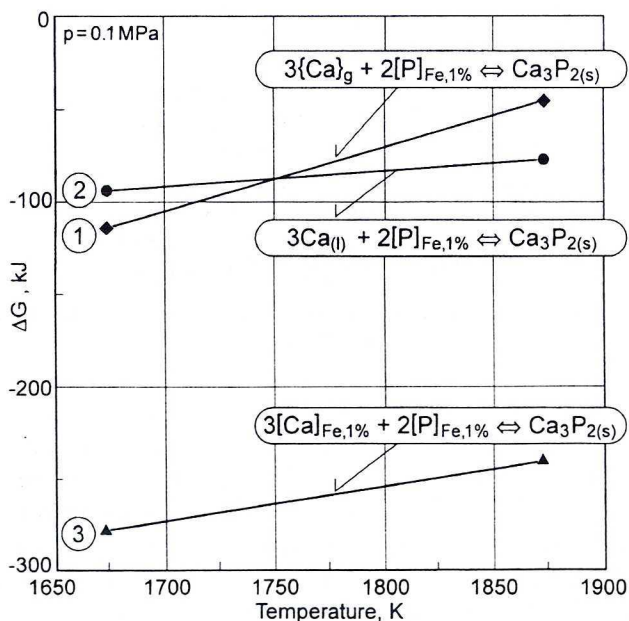

Fig. 2. Change of the Gibbs free enthalpy of the reaction of calcium with phosphorus as a function of temperature

It results from Fig. 2 that the reactions of phosphorus dissolved in liquid metal will proceed, above all, with the participation of dissolved calcium, $[Ca]_{Fe}$, since the straight line representing the relationship $\Delta G^0 = f(T)$ lies, for this form of calcium, in the range of the most negative values of ΔG^0. Because of the fact that the solubility of calcium both in the liquid iron and its alloys with a high chromium content is very low (approx. 0.032 wt.% Ca), reaction "3" (Fig. 2) may have a limited range in many cases of temperature, pressure and the chemical composition of liquid metal. In the processes of reduction removal of phosphorus, (as well as other harmful admixtures), the participation of reaction "2" may thus play an important role, in spite of the fact that this reaction is heterogeneous.

More comprehensive information concerning the intensity of calcium evaporation from CaF_2-Ca liquid solutions is contained in the author's own study [2].

For the thermodynamic and kinetic description of the refining process, the following assumptions are made:

(I) — the process of chemical reaction occurs at the metal–refining-slag phase interface,

(II) — the rate limiting step of the process is the diffusion of reagents in the reacting phase,

(III) — at the metal–refining-slag phase interface, the reacting system reaches the state of local thermodynamic equilibrium.
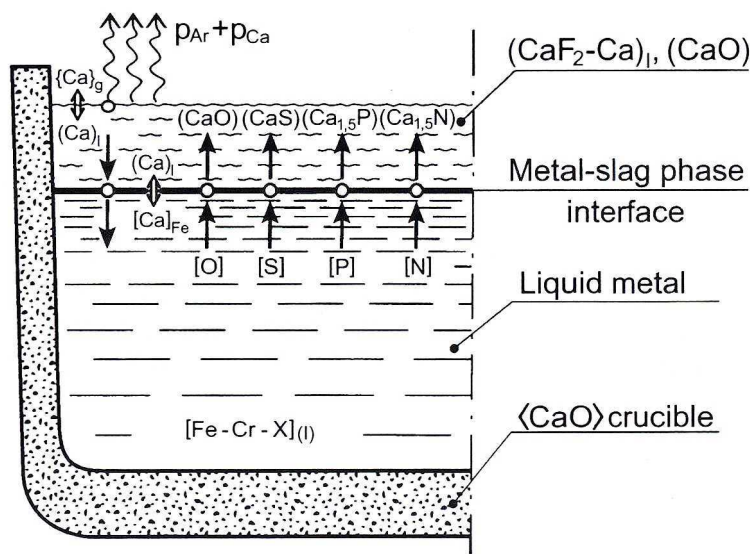

Fig. 3. Schematic diagram of the reduction refining using calcium

A general scheme of the described process is shown in Fig. 3. A kinetic model of the refining process has been developed, which is similar to that proposed by Ohguchi and Robertson [3] for the removal of sulphur and phosphorus from

liquid pig iron. Considering assumptions (I–III), the following expression for the so-called *formal equilibrium constant* can be written for reactions that proceed according to scheme (1):

$$K'_{(X)} = \frac{(\%Ca_nX)^*}{[\%X]^* \cdot a_{Ca(l)}^{*n}}. \tag{2}$$

A similar expression, called *effective equilibrium constant*, was employed in work [3]. The values of reagent concentrations and calcium activity in equation (2) are unknown, therefore a necessity arises of having such a notation of equilibrium constants that they can be expressed and calculated through known values. After making appropriate substitutions and transformations, we obtain:

$$K'_{(X)} = \frac{(\%Ca_nX)^*}{[\%X]^* \cdot a_{Ca(l)}^{*n}} = \frac{K_X \cdot M_{Ca_nX} \cdot \Sigma n_s \cdot f_X}{\gamma_{Ca_nX}}. \tag{3}$$

Let us define the flux of reagents considered in the described system as:

$$J_X = \beta'_X \{[\%X]_b - [\%X]^*\} = \beta'_{Ca_nX} \{(\%Ca_nX)^* - (\%Ca_nX)_b\}. \tag{4}$$

The modified mass transfer coefficients are related to the commonly used mass exchange coefficients, β_X or β_{Ca_nX} in the following manner:

$$\beta'_X = \frac{\beta_X \cdot \rho_m}{100 \cdot M_X}, \tag{5a}$$

$$\beta'_{Ca_nX} = \frac{\beta_{Ca_X} \cdot \rho_s}{100 \cdot M_{Ca_nX}}. \tag{5b}$$

By combining equations (2)–(5), the values of $[\%X]^*$ or $(\%Ca_nX)^*$ can be determined as a function of several unknown quantities and one known quantity, i.e. $[\%X]^* = f(a_{Ca(l)}^{*n})$ or $(\%Ca_nX)^* = f(a_{Ca(l)}^{*n})$. The calculation of the values of $[\%X]^*$ or $(\%Ca_nX^*)$ is possible after writing down the equation for the mass balance of calcium used in the reactions, evaporated calcium, and calcium delivered with the refining-slag phase. In such a case, the balance of calcium fluxes will take the form:

$$1.5J_P + J_O + J_S + 1.5J_N + 0.5J_C + J_{\{Ca\}} - J_{Ca(l)} = 0. \tag{6}$$

Assuming that the described refining reactions are 1st order we obtained:

$$\frac{V_m}{A} \cdot \frac{d[\%X]}{d\tau} = \beta_X \{[\%X]^* - [\%X]_b\}. \tag{7}$$

Integrating equation (7) for the time τ, and after substituting $\beta_X \, A/V_m = \beta_{E,X}$, we obtain after suitable transformations the following formula:

$$[\%X]_\tau = \exp(-\beta_{E,X} \cdot \tau) \{[\%X]_0 - [\%X]^*\} + [\%X]^*. \tag{8}$$

Relationship (8) constitutes the basic kinetic equation, based on which changes of the removed element concentrations can be calculated, together with the elapsed refining time. By utilizing this relationship, a computer program has been developed, which enables changes in the concentrations of O, S, P, N, C and Ca to be determined as a function of refining time for any arbitrary initial conditions.

3. Experimental

The subject of investigations were five alloys, the composition of which are given in Table 1. The alloys were prepared in a vacuum induction furnace (VIF) using *Armco* iron and chromium (99.8 wt.% Cr) and nickel (99.9 wt.% Ni) metals.

TABLE 1

Chemical composition of Fe-Cr-Ni alloys used in the investigations

Alloy type	Content of elements, wt.%						
	C	P	S	Cr	Ni	N	O
S 1	0.020	0.011	0.005	17.7	7.69	0.0089	0.0203
S 2	0.020	0.029	0.007	17.0	7.22	0.0107	0.0171
S 3	0.021	0.380	0.007	17.9	7.83	0.0123	0.0142
S 2-A	0.029	0.028	0.006	17.1	7.13	0.0092	0.0087
S 2-B	0.037	0.028	0.006	17.0	7.32	0.0088	0.0039

The alloy ingots melted in the VIF were hot forged into Ø 26 mm-diameter round bars from which metal samples of a mass of 0.15 – 0.18 kg were turned to obtain the shape as shown in Fig. 4. Crucibles used in the investigation were made of sintered CaO. The refining agent was a CaF_2-Ca mixture in the molar ratio 1:1, and the amount of 1.5% of the metal weight was recalculated for pure calcium. The top slag (25 wt.% CaO–75 wt.% CaF_2), that was added after the complete melting of the metal sample, was prepared from analytically pure components[1]. The crucible containing an alloy sample was placed inside the pressure resistance furnace with a graphite tube as the heating element (Fig. 5). After closing up the furnace, the air was pumped out, and then the furnace was filled with purified argon up to the working pressure of 0.6 MPa. The tests were carried out at 1743 and 1823 K. A constant temperature was maintained within the furnace with an accuracy of ±3 degrees. The duration time of a particular test at a given temperature was varied from 1 to 20 minutes with one-minute steps. After the required time had elapsed, the sample was rapidly removed from

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[1] The mass of CaF_2 introduced with the refining material was taken into account in the slag amount.
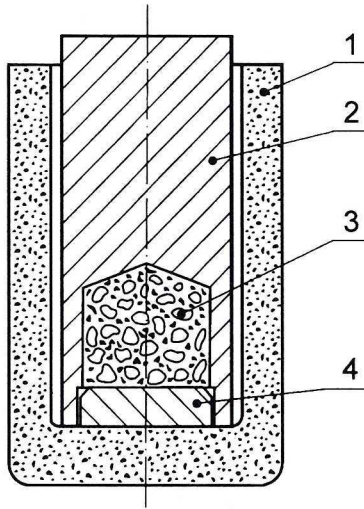
Fig. 4. Sketch of the metal sample; 1 – CaO-crucible, 2 – metal sample, 3 – CaF$_2$-Ca refining agent, 4 – metal plug
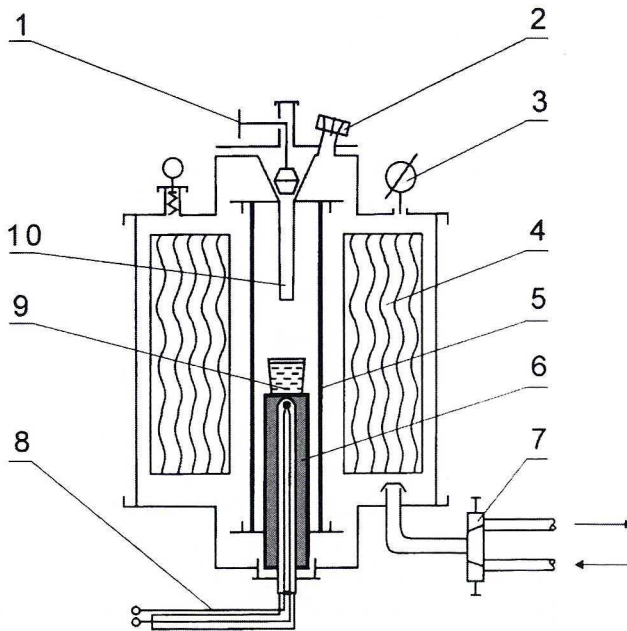

Fig. 5. Schematic diagram of the pressurized laboratory furnace: 1 – charge equipment, 2 – viewfinder, 3 – manometer, 4 – Al$_2$O$_3$ fibre, 5 – graphite heating tube, 6 – graphite pin, 7 – magnetic valve, 8 – thermo-couple, 9 – CaO crucible, 10 – chute tube

the furnace and cooled down in a stream of argon. Upon the completion of metal refining, the phosphorus, sulfur, calcium, nitrogen and oxygen contents of metal were determined. The oxygen and sulfur contents were determined using LECO analyzers, whereas the remaining elements of those mentioned above — by the AAS method.

4. Results and discussion

The selection of the calcium carrier used as a refining material was made on the basis of test results which are shown graphically in Fig. 6. The suitability of the following materials for reduction dephosphorization has been evaluated: – metallic calcium, equimolar solution of Ca in CaF_2, and calcium hydride, CaH_2, used as a reducing agent in metallurgy of vanadium and uranium [5]. This is a ionic crystalline substance with the melting temperature 1115 K and the decomposition temperature 1302 K [6], which dissolves in liquid calcium and is highly hygroscopic. Considering the test results shown in Fig. 6, the following facts speak in favour of using CaF_2-Ca solution as a refining agent:

— the use of CaH_2 as a refining agent does not produce the expected results; the maximum relative degree of dephosphorization reached the value 39%, and
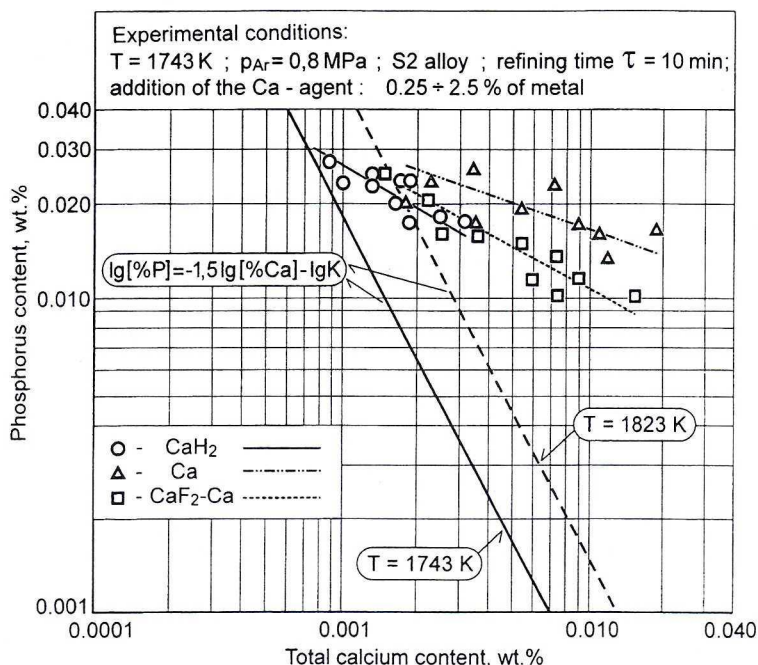

Fig. 6. Change of the phosphorus and calcium content in the S2-alloy for the Ca-carriers using in the experiment

the final concentration of total calcium in the refined metal was much lower as compared with the remaining refining agents;

— the lowest final concentrations of phosphorus in the metal were attained using the CaF$_2$-Ca refining agent, at comparable concentrations of total calcium found after refining using metallic calcium.

Figure 6 shows also two straight lines that describe a hypothetical equilibrium state (an expression for the equilibrium constant) of the reaction:

$$1.5[\text{Ca}]_{\text{Fe}} + [\text{P}]_{\text{Fe}} = (\text{Ca}_{1.5}\text{P})_{(s)}. \tag{9}$$
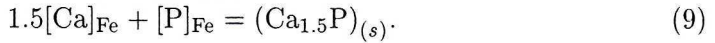
The investigations which are carried out enabled the experimental verification of the course of the refining processes as obtained through computer simulation for different initial conditions. Figure 7 shows a distribution of experimental points illustrating the variation of phosphorus and nitrogen concentrations for the alloy S1 refined at the temperature $T = 1743$ K as set against the characteristics of appropriate curves drawn based on the model developed.
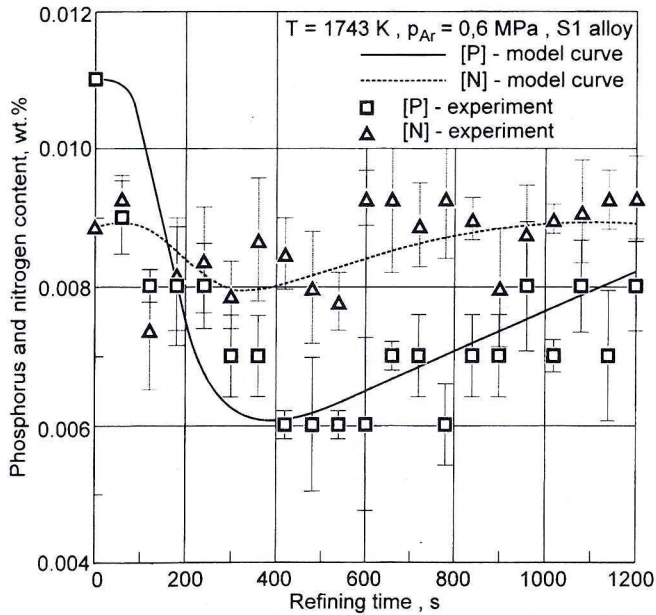

Fig. 7. Variation of P and N concentration in S1-alloy vs. refining time

Minimums occur on these curves, beyond which the phosphorus and nitrogen contents of the refined metal systematically increase. This is a consequence of the change in the direction of reaction (1), which results in partial decomposition of the reactions products, i.e. Ca$_3$P$_2$ and Ca$_3$N$_2$, caused by the depletion of the active calcium mass in the reacting system. The confirmation of this observation can be the results of studies by Masumitsu [4] concerning the Ca-CaF$_2$-Ca$_3$P$_2$

system. The deviations of experimental points from the model curves might result, among other things, from the assumption that reactions proceeding at the interface of reacting phases may reach the state of thermodynamic equilibrium. For the real experimental conditions, on the other hand, the course of reaction within the time interval examined was characterized by a specific deviation from the equilibrium condition. One of the causes of the deviation of experimental points from the model curves may be, for example, the arbitrarily made assumption on the identical values of the mass transfer coefficient of slag components, the constant value of the surface area of the liquid metal–refining-slag phase interface, etc. A substantially different pattern of concentration variations as a function of refining time can be observed for oxygen and calcium (Fig. 8). The curves shown in Fig. 8, and predicted from the model, indicate that the concentration of dissolved oxygen decreases systematically from the initial value down to limitedly low values as a result of the reaction of calcium with oxygen.
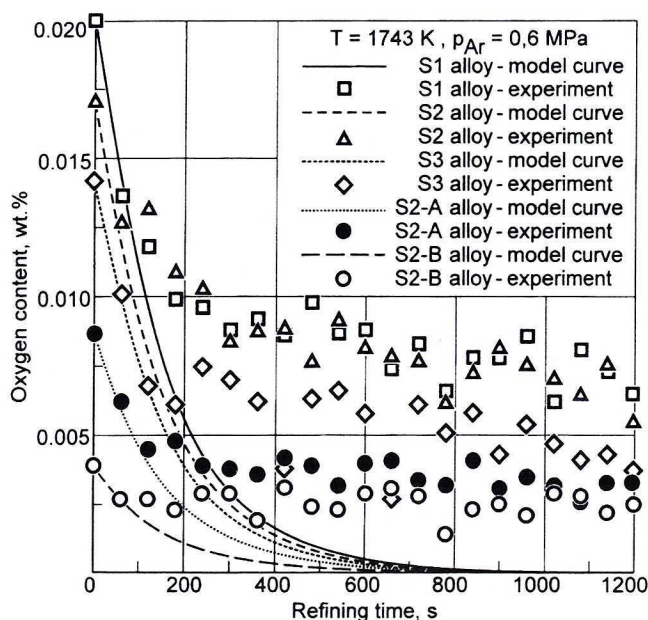

Fig. 8. Variations of oxygen concentrations during refining of Fe-Cr-Ni alloys

Experimental points, on the other hand, represent the total oxygen concentration, therefore the magnitude of the distance of those points from the model curves may constitute an approximate measure of the contents of non-metallic oxide inclusions left in the refined metal. A substantially different pattern of variations in the concentrations of phosphorus (as well as nitrogen) as a function of refining time can be noted for the sequential feeding of the refining agent, as compared to the curves shown in Fig. 7 during one-off addition (Fig. 9). If refining
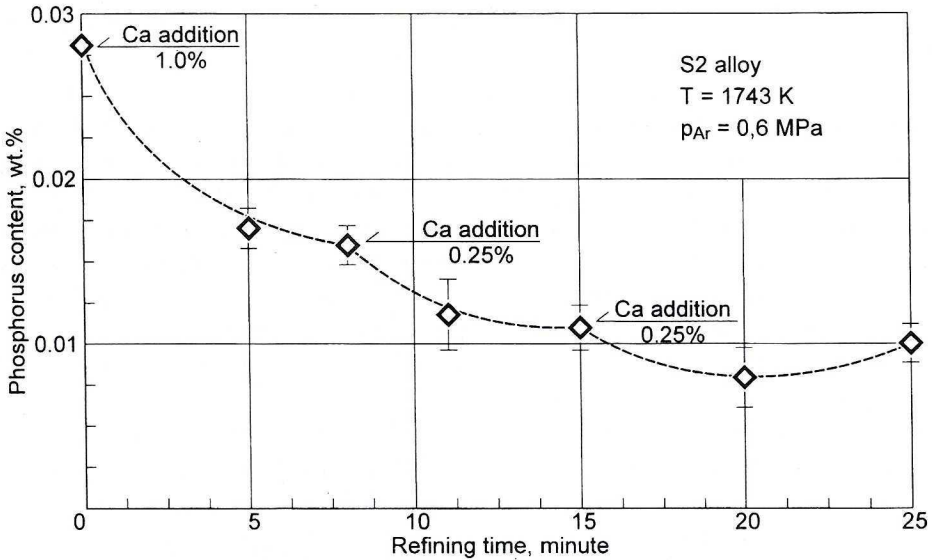
Fig. 9. Variation of phosphorus concentration in the S2 alloy as a function of the refining time

agent addition is repeated at the moment where the phosphorus concentration reaches the values close to the minimal ones, then the refining process extends in time, simultaneously inhibiting reverse reactions and restraining the increment of phosphorus concentration. The cycle of this type may be repeated by the addition of successive batches of calcium, however with systematically decreasing effect.

5. Final remarks

The information obtained from the simulation of various refining conditions performed using the developed model enables the following conclusions to be drawn:

• the thermodynamic-kinetic model and the computer program elaborated in this work enable to establish how the main physicochemical factors may determine a location of the minimum on the $[\%P, \%N] = f(\text{time})$ curves,

• the program allows to determine the simultaneous changes of six elements (O, S, P, N, C and Ca) vs. refining time for arbitrarily selected values of temperature, pressure, metal composition, calcium addition etc.,

• good enough agreement between the experiment result and the model curves of the type $[\%X]_{\text{Fe}} = f(\text{time})$ has been obtained,

• as the refining material, the solution of calcium in its compounds, such as CaF_2, should be used, which is more advantageous as compared to metallic calcium,

• the amount of the refining agent added should be made dependent, among other things, on the method of its addition — either in a one-off or sequential manner (preferred), and either with or without the stirring of the liquid metal during refining,

• the refining of liquid metal is recommended to be conducted in an inert gas atmosphere within the reaction space, under overpressure in the range of $0.4 - 0.6\,\mathrm{MPa}$.

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