

# Investigations of the Dephosphorization of Liquid Iron Solution Containing Chromium and Nickel

MIROSLAW KARBOWNICZEK, ELZBIETA KAWECKA-CEBULA, and JAN REICHEL

The most up-to-date trends in stainless steel production—aiming at the reduction of production costs—consist of the substitution of steel scrap by hot metal, coming from the reduction of iron-chromium ores. This process requires a more extensive dephosphorization. The dephosphorization process, when applied to chromium steels, requires slag with high dephosphorization properties, as either chromium or chromium oxide entering the slag decreases distinctly the efficiency of the process. The results of laboratory investigations on the dephosphorization of liquid iron solutions containing chromium and nickel are presented. In particular, the study was focused on the selection of the optimal slag composition and the way the slag should be added. The slags based on calcium and fluorite with cryolite additions were considered. It was shown that the variables with the greatest impact on the dephosphorization process include chromium and nickel levels, temperature, and slag basicity. A statistical analysis was performed and regression equations were set. The results may be of use for the design of new methods of production of high-chromium steels.

DOI: 10.1007/s11663-011-9627-x

© The Author(s) 2012. This article is published with open access at Springerlink.com

## I. INTRODUCTION

THE problem of reducing the phosphorus level in iron solutions containing chromium and nickel has been studied by numerous investigators<sup>[1–13]</sup> because chromium steels may be produced using iron ores containing chromium compounds as charge materials. However, in such cases, the problem of removing phosphorus from the metal bath during the refining process arises. The dephosphorization of liquid iron in the presence of high Cr concentration is important not only for stainless steels but also for the production of low-phosphorus ferrochrome.

In conventional stainless steel technologies, the phosphorus problem is generally related not only to metallic charge materials, such as scrap or alloys, but also to the low quality of slag-forming materials, mainly lime. Independently of, sometimes problematic charge materials, new technological techniques coming into focus recently have solved the high phosphorus problems. In stainless steel technologies such as duplex, which comprises an electric arc furnace (EAF) and argon oxygen decarburization (AOD) converter, and triplex, which consists of an EAF and AOD-lance (AOD-L)/metal refining process-lance (MRP-L) converter and vacuum oxygen decarburization (VOD) plant, the phosphorus problem seems to be mainly caused by the quality of scrap and lime. But the most up-to-date trends in

stainless steel production—aiming at the reduction of production costs—substitute steel scrap by hot metal coming from the reduction of iron-chromium ores, which requires more extensive dephosphorization.

For the dephosphorization of a liquid iron solution containing chromium, the slag should exhibit good dephosphorizing properties, as either chromium or chromium oxides, which enter the slag during the refining process and decrease the dephosphorization efficiency of the process to an appreciable extent.

The best dephosphorizing properties cause slags to be formed on the base of oxides and halides of barium or calcium.<sup>[2–4,7–10,12]</sup> The phosphate capacity of the slags containing barium compounds is higher, so the dephosphorization becomes more effective. As barium compounds are more expensive, whereas those of calcium are more available, the slags based on CaO-CaF<sub>2</sub> are now mainly considered.

In most metallurgical processes, it is important to assure the low viscosity of slags to enable the rapid transport of mass and heat. One of the most common means of decreasing the viscosities of slags and their melting temperatures is the addition of some fluorite to the slag.<sup>[14]</sup> It is especially important for cases of the dephosphorization or desulfurization<sup>[15]</sup> of pig irons containing chromium to keep the process temperature low and to minimize chromium losses. In slags of high basicity with CaO, fluorite increases the phosphate capacity and stabilizes the slag, forming the following fluorophosphates: 3Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·CaF<sub>2</sub>.<sup>[16]</sup> Its action is based on decreasing the surface tension and its ability to dissolve oxides. Because of this special feature, CaF<sub>2</sub> is considered as an indispensable material in steelmaking technologies. Fluxes containing CaF<sub>2</sub>, however, are not used readily in metallurgical processes because of environmental problems, but they are characterized by

MIROSLAW KARBOWNICZEK, Professor, and ELZBIETA KAWECKA-CEBULA, Assistant Professor, are with the Department of Metal Engineering and Industrial Computer Science, AGH University of Science and Technology, Krakow 30-150, Poland. Contact e-mail: mkarbow@agh.edu.pl JAN REICHEL, Senior Researcher, is with SMS Siemag AG, Düsseldorf 40237, Germany.

Manuscript submitted October 11, 2010.

Article published online January 14, 2012.

excellent metallurgical properties, and they are cheap. CaF<sub>2</sub> technology transfer to industry thus must assure that regulations relating to environmental protection are adhered to.

This article analyzes the theoretical and experimental possibilities and conditions for dephosphorization of iron solutions when chromium is present. The laboratory investigations were carried out for iron solutions containing the following after melting: 2.07 to 3.66 pct C, 0.04 to 0.07 pct Si, 7.16 to 12.7 pct Cr, 1.25 to 3.25 pct Ni, and 0.078 to 0.155 pct P, as well as temperatures in the range of 1623 K to 1673 K (1350 °C to 1400 °C). To decrease the liquidus temperature and viscosity of the slags and to increase the slags' phosphate capacity, some additions of cryolite Na<sub>3</sub>AlF<sub>6</sub> were made. The study was focused on the selection of the optimal slag composition and the way the slag should be added.

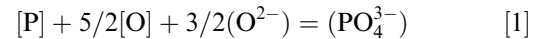
## II. DEPHOSPHORIZATION OF CHROMIUM STEELS

In electric stainless steelmaking, the phosphorus impurity comes mainly from scrap and ferroalloys. The presence of phosphorus considerably deteriorates steel quality. When steel solidifies, phosphorus segregates easily along grain boundaries, which leads to cold embrittlement, and the mechanical and anticorrosive steel properties are affected negatively. Therefore, for some grades of steel, low phosphorus levels are required, *i.e.*, below 0.01 pct. This refers particularly to steels used for low-temperature regions: marine steels, anti-hydrogen-induced cracking steels, and so on. To obtain such low phosphorus contents, two methods may be applied. The first consists of using expensive raw materials, mainly scrap or low-phosphorus ferroalloys. Another option is the use of significantly cheaper raw materials, but with higher phosphorus content. For such a case, however, it is necessary to decrease the phosphorus content to the target level either by dephosphorization of the hot metal in the electric furnace or by a special treatment such as dephosphorization, desiliconization, and desulfurization. Dephosphorization of hot metal with chromium or steel-containing chromium may be carried out in oxidative conditions at relatively high oxygen potential or also in reductive. In oxidative dephosphorization, the slags should have higher basicity and sufficient phosphate capacity.

The efficiency of any dephosphorization process may be given by the following<sup>[17,18]</sup>:

- The distribution coefficient for phosphorus between the slag (P) and the metal phase [P] expressed by the phosphorus concentration in the slag:  $L_P = (\text{pct P})/[\text{pct P}]$  or by the phosphorus (*V*) oxide concentration in the slag:  $L_P = (\text{pct P}_2\text{O}_5)/[\text{pct P}]$
- The dephosphorization degree  $\eta_p$ , which is equal to the ratio of the phosphorus concentration removed from the metal  $[\Delta P]$  to the initial phosphorus concentration  $[P]_i$ :  $\eta_p = [\Delta \text{pct P}]/[\text{pct P}]_i$

Dephosphorization of a metal bath at oxidative conditions follows the reaction below:



In this reaction, phosphorus in the metal bath [P] reacts with oxygen dissolved in that phase [O], and with the oxygen ions of the slag phase (O<sup>2-</sup>), forming phosphate anions in the slag phase (PO<sub>4</sub><sup>3-</sup>). The equilibrium constant of this reaction is given by

$$K_{(1)} = \frac{a_{(\text{PO}_4^{3-})}}{a_{[\text{P}]} \cdot a_{[\text{O}]}^{5/2} \cdot a_{(\text{O}^{2-})}^{3/2}} \quad [2]$$

As to the extent of the phosphorus absorption by the slag, it may be estimated by the quantity named the phosphate capacity  $C_{\text{PO}_4^{3-}}$ . It was defined by Wagner<sup>[19]</sup> for the equilibrium between a liquid slag phase containing phosphate anions, (pct PO<sub>4</sub><sup>3-</sup>), a gas phase containing oxygen {O<sub>2</sub>}, and a phosphorus vapor {P<sub>2</sub>}, as follows:

$$C_{\text{PO}_4^{3-}} = \frac{(\text{pct PO}_4^{3-})}{p_{\text{P}_2}^{1/2} \cdot p_{\text{O}_2}^{5/4}} \quad [3a]$$

For metal/slag equilibrium, more useful is another form of the slag capacity—converted into the phosphorus content—called phosphorus capacity  $C_P$

$$C_P = \frac{(\text{pct P})}{a_{[\text{P}]} \cdot a_{[\text{O}]}^{5/2}} = \frac{L_P}{f_{[\text{P}]} \cdot a_{[\text{O}]}^{5/2}} \quad [3b]$$

where  $f_{[\text{P}]}$  is the activity coefficient of phosphorus in the metal bath. Both the capacities may be related to each other by the Eq. [4], which results from converting the mole masses of PO<sub>4</sub><sup>3-</sup> and of phosphorus, and by using the free energy of dissolution of oxygen<sup>[20]</sup> and phosphorus<sup>[21]</sup> in liquid iron

$$\log C_P = \log C_{\text{PO}_4^{3-}} - 1.8077 - \frac{21742}{T} \quad [4]$$

The dependence of the distribution coefficient for phosphorus on the parameters of the slag and of the metal phase may be obtained by transformation of Eq. [3b]

$$\log L_P = \log C_P + \log f_{[\text{P}]} + 2.5 \log a_{[\text{O}]} \quad [5]$$

Based on their own data and that in the literature, Sano and Katayama<sup>[7]</sup> elaborated on a plot that indicates the optimal type of dephosphorization, dependent on the dephosphorized melt's composition (Figure 1). The carbon stainless steels are dephosphorized at oxidative conditions by using the high alkaline mixtures of high-phosphorus capacity depending on the chromium content: for >20 pct Cr on the base of BaO, *e.g.*, BaO-BaCl<sub>2</sub> or for <20 pct Cr on the base of CaO. For economic reasons, it is recommended to dephosphorize the “crude” stainless steels before the AOD process when they contain less than 2 pct carbon. For oxidative conditions, one has to control the chromium losses. For any chosen flux type, its chemical composition, process temperature, and consumption per 1 kg of the metal, as well as the way it is added, should be established experimentally.

### III. INVESTIGATION METHODS

The experimental heats were run in an induction furnace with a capacity of 20 kg. The furnace was equipped with a pressed refractory lining made of a high-alumina refractory mass Rodarox mix 17, which had the following chemical composition: 84 pct Al<sub>2</sub>O<sub>3</sub> and 16 pct MgO. During the heat, the temperature of the metal bath was controlled by taking PtRh10/Pt (type S) thermocouple measurements. Both metal and slag samples were taken to analyze their chemical compositions.

In the course of the research, eight heats and two dephosphorization mixtures were used: M5 (25 pct of cryolite) and M6 (15 pct of cryolite). Previously, eight heats were run to select an adequate dephosphorization mixture and to establish the optimum way it is blown in. Initially, the powdered mixture was blown in using an argon-oxygen gas mixture. The metal charge (20 kg) used for the research consisted of pig iron, FeCr, and Ni<sub>met</sub>. The phosphorus concentration was supplemented with the addition of FeP, and the metal bath was carburized by adding graphite.

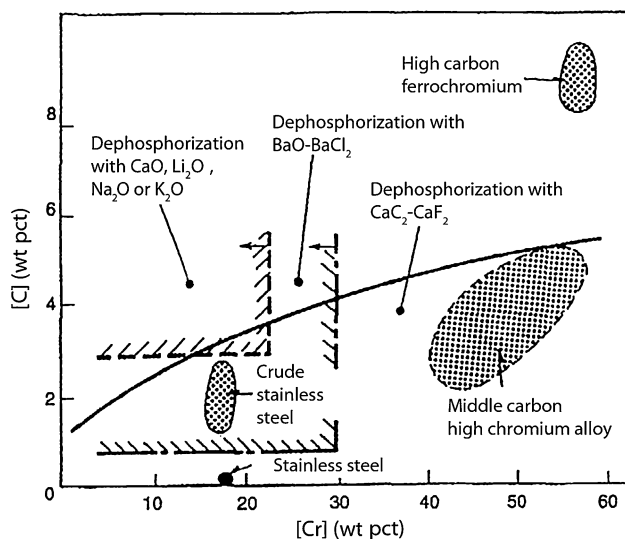


Fig. 1—Suitable metal compositions for various methods of dephosphorization.<sup>[7]</sup>

After the charge melted, an attempt was made to keep the temperature at the level of 1773 K (1500 °C). The next stage consisted of desiliconization of the liquid pig iron by adding the scale in amounts ranging from 1000 to 2000 g. Then, the formed slag was extracted and the alloy elements were added. When a temperature of approximately 1623 K (1350 °C) was achieved, the process of the metal bath dephosphorization was conducted by adding a dephosphorizing mixture.

In total 1.5 kg of the mixture was used per every heat with 100 g portions added every 1 minute. While the dephosphorizing mixture was being added, a jet of the gas mixture (oxygen and argon) was injected into the metal bath. The jet had a precisely set intensity of flow at the level of 10 dm<sup>3</sup>minute<sup>-1</sup>.

### IV. RESEARCH RESULTS

Table I presents the temperature, the chemical composition of the metal bath, and the dephosphorization degree  $\eta_p$  for all the heats. The added dephosphorizing mixtures were composed of CaO, CaF<sub>2</sub>, and Na<sub>3</sub>AlF<sub>6</sub>. The slag formed by the dephosphorization process contained, apart from the used mixture components, the products of the metals' oxidation, *i.e.*, FeO, Cr<sub>2</sub>O<sub>3</sub>, MnO, NiO, SiO<sub>2</sub>, and P<sub>2</sub>O<sub>5</sub>, and the products of dissolution of the lining, *i.e.*, MgO. The dephosphorizing mixture contains fluorite, so it should be present also in the slag. As far as the results from an analyzer are concerned, the entire amount of calcium in a sample was calculated automatically as CaO. Table II shows the slag composition corrected by calculating the concentrations of CaO and CaF<sub>2</sub> for their actual contents. The iron oxide at the process temperature should be present in the form of FeO. When the sample is cooled below 833 K (560 °C), FeO is subject to decomposition, and as a result, Fe<sub>2</sub>O<sub>3</sub> and metallic Fe are obtained. Taking into account the high-temperature process, one needs to consider the presence of mainly FeO. The analysis results do not include Na<sub>2</sub>O. Na<sub>2</sub>O concentration can be estimated based on an analysis of alumina in proportion to component of cryolite. It is clear that a certain amount of sodium will evaporate in the form of NaF or sodium vapors. Adding the amount of sodium oxide

Table I. Temperature, Chemical Composition of Metal Bath, and the Dephosphorization Degree  $\eta_p$

Heat Number	$T_i$ , K (°C)	$T_f$ , K (°C)	Chemical Composition (pct)										$\eta_p$ (pct)
			[C] <sub>i</sub>	[C] <sub>f</sub>	[Si] <sub>i</sub>	[Si] <sub>f</sub>	[Cr] <sub>i</sub>	[Cr] <sub>f</sub>	[Ni] <sub>i</sub>	[Ni] <sub>f</sub>	[P] <sub>i</sub>	[P] <sub>f</sub>	
9	1689 (1416)	1656 (1383)	3.27	2.78	0.07	0.053	12.7	10.5	1.65	1.41	0.096	0.062	35.66
10	1691 (1418)	1594 (1321)	3.66	3.19	0.04	0.050	9.72	8.59	1.31	1.27	0.110	0.056	49.09
11	1623 (1350)	1651 (1378)	3.41	3.04	0.05	0.057	9.52	8.82	1.25	1.29	0.120	0.066	44.58
12	1654 (1381)	1627 (1354)	3.26	2.87	0.06	0.058	7.87	8.23	1.25	1.70	0.114	0.061	46.58
13	1630 (1357)	1719 (1446)	2.29	1.54	0.05	0.049	7.71	7.78	1.98	2.98	0.110	0.064	41.82
14	1636 (1363)	1641 (1368)	2.82	2.41	0.05	0.046	7.19	7.43	2.64	2.93	0.155	0.062	60.06
15	1662 (1389)	1718 (1445)	2.07	1.62	0.05	0.043	7.16	6.85	2.93	3.40	0.068	0.036	46.22
16	1657 (1384)	1593 (1320)	3.14	2.64	0.07	0.057	11.1	11.2	3.25	3.41	0.078	0.0553	29.40

$f$ , final value of each parameter;  $i$ , initial value of each parameter.

Dephosphorization degree  $\eta_p = \text{Etap} = \frac{[P]_i - [P]_f}{[P]_i} 100$  pct.

**Table II. The Chemical Composition of Slag Corrected by Calculating the Concentration of CaO, CaF<sub>2</sub>, FeO, Na<sub>2</sub>O, and P<sub>2</sub>O<sub>5</sub> for Their Actual Contents**

Heat Number	Mixture	T <sub>f</sub> , K (°C)	Slag Composition (pct)										η <sub>p</sub> (pct)
			CaO	SiO <sub>2</sub>	FeO	MnO	Al <sub>2</sub> O <sub>3</sub>	MgO	Cr <sub>2</sub> O <sub>3</sub>	CaF <sub>2</sub>	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	
9	M5	1656 (1383)	24.36	6.90	19.15	0.76	4.99	0.58	14.33	24.41	9.08	0.04	35.66
10	M5	1594 (1321)	22.11	6.75	25.74	0.82	4.98	0.56	13.16	22.15	9.08	0.13	49.09
11	M5	1651 (1378)	25.14	4.46	17.31	0.54	5.13	0.46	11.89	25.19	9.34	0.68	44.58
12	M5	1627 (1354)	27.36	4.02	17.95	0.48	5.37	0.43	10.33	27.41	9.77	0.72	46.58
13	M6	1719 (1446)	25.28	2.79	19.53	0.73	4.05	0.47	13.58	25.33	7.37	0.28	41.82
14	M6	1641 (1368)	30.87	2.30	20.84	0.46	3.70	0.42	9.74	30.93	6.73	1.44	60.06
15	M6	1718 (1445)	28.45	2.25	19.46	0.65	2.78	0.41	12.84	28.50	5.06	0.32	46.22
16	M6	1593 (1320)	24.74	3.23	18.86	0.64	3.95	0.40	12.84	24.79	7.19	0.16	29.40

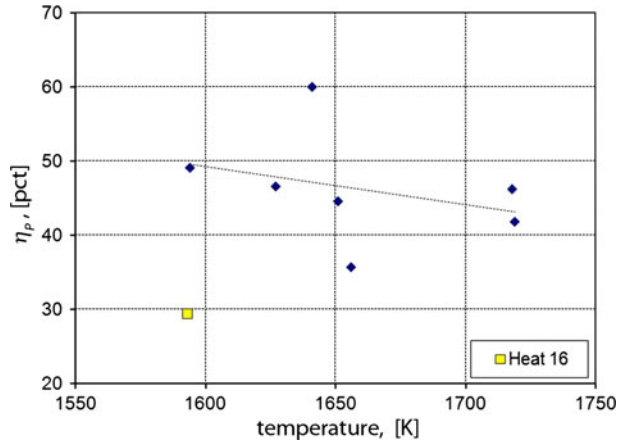


Fig. 2—The effect of temperature on the dephosphorization degree η<sub>p</sub>.

together to slag would make the sum (pct) of all the slag components in excess of 100 pct. This mainly stems from neglecting the Na<sub>2</sub>O losses. It can be assumed that the Na<sub>2</sub>O and other slag components complement each other and form 100 pct. The final chemical composition of slag is presented in Table II.

The basicity of the analyzed slag can be presented as the ratio between the sum of the basic oxides' concentration (pct): CaO, MgO, FeO, and MnO, as well as the acidic and amphoteric oxides concentration (pct): SiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, Cr<sub>2</sub>O<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub>. The oxide of chromium (III) exhibits, similarly to aluminum oxide, amphoteric properties. In above slags, depending on their basicity (B), chromium cations Cr<sup>2+</sup> (for B < 2) or chromate anions CrO<sub>3</sub><sup>3-</sup> (for B > 2) are present.<sup>[22]</sup> One might neglect the minor oxides present such as MgO or MnO. As Table II shows, these oxides do not have any major impact on the value of basicity.

## V. ANALYSIS OF THE RESULTS

The relations that were found on the basis of the conducted analysis are shown in Figures 2 through 12.

Figures 2 and 3 present the dephosphorization degree η<sub>p</sub> vs temperature T plots. The data confirm the advantageous effect of a temperature decrease on the

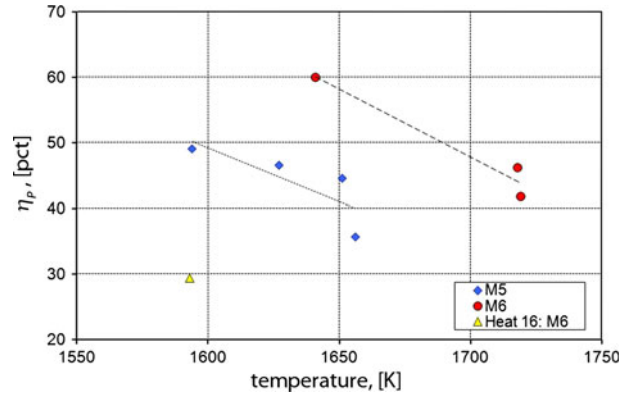


Fig. 3—The dephosphorization degree η<sub>p</sub> vs temperature, dependent on the dephosphorizing mixture (M5 or M6) used.

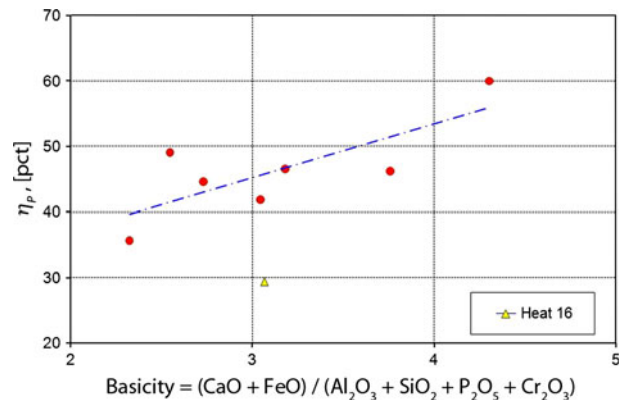


Fig. 4—The dephosphorization degree η<sub>p</sub> vs the slag basicity (the ratio of the basic oxides to the acidic and amphoteric oxides).

dephosphorization degree. It obeys, for all the experimental data, independently of the chromium level of the metal and the composition of the dephosphorizing mixture. The mixture M5 of higher cryolite content is less effective than M6 (Figure 3). An exception is the heat 16, which deviates from the preceding general tendency (attained the degree of dephosphorization: η<sub>p</sub> = 29.45). This follows from the highest content of Cr in this heat, 11.2 pct and Ni, 3.41 pct (total Cr + Ni = 14.6 pct) and 0.078 pct P (initial) compared

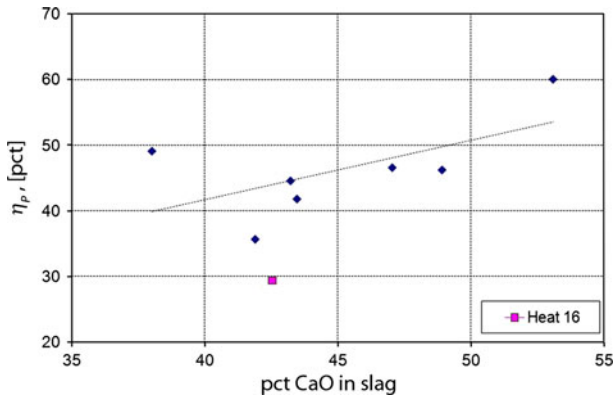


Fig. 5—The dephosphorization degree  $\eta_p$  vs CaO content of the slag.

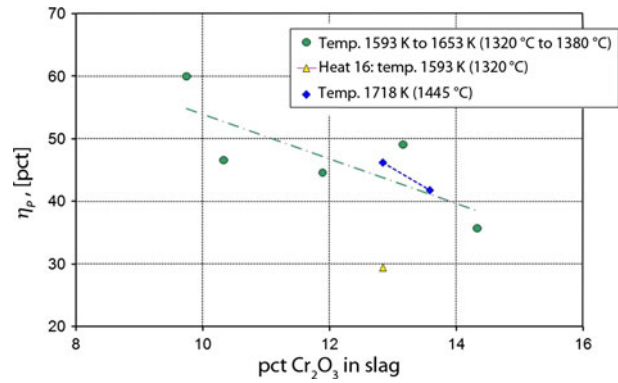


Fig. 8—The dephosphorization degree  $\eta_p$  vs  $\text{Cr}_2\text{O}_3$  content of slag for different temperatures.

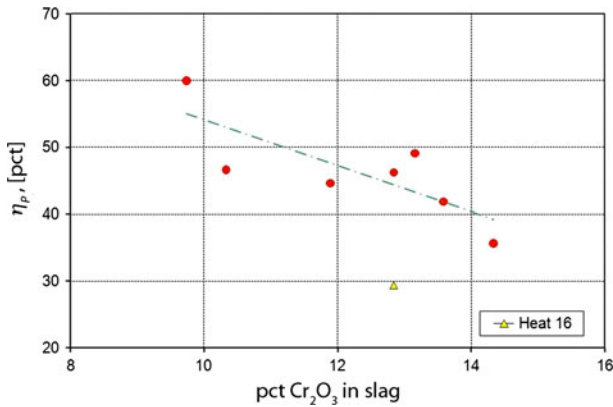


Fig. 6—The dephosphorization degree  $\eta_p$  vs  $\text{Cr}_2\text{O}_3$  content of the slag.

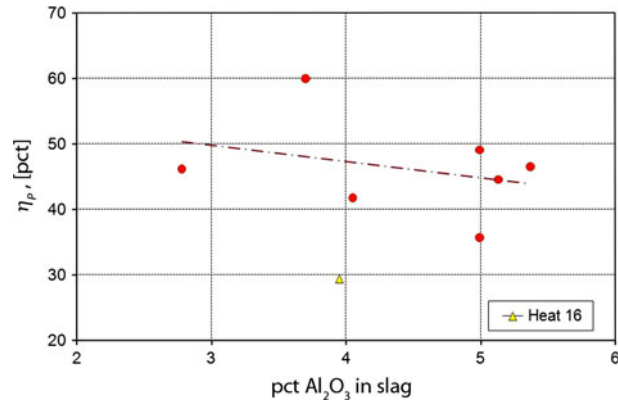


Fig. 9—The dephosphorization degree  $\eta_p$  vs  $\text{Al}_2\text{O}_3$  content of the slag.

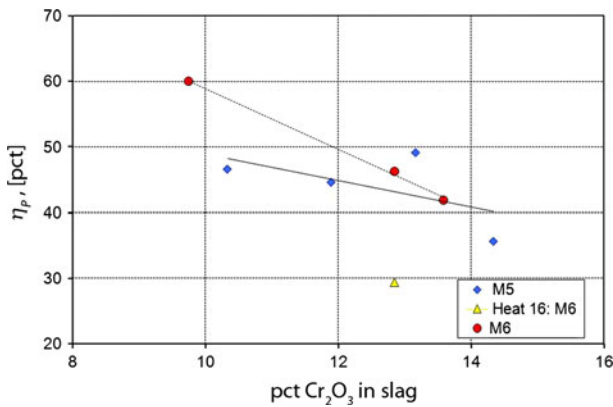


Fig. 7—The dephosphorization degree  $\eta_p$  vs  $\text{Cr}_2\text{O}_3$  content of slag, dependent on the dephosphorizing mixture (M5 or M6) used.

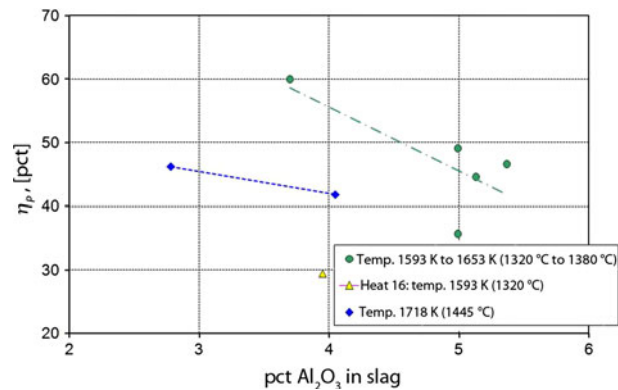


Fig. 10—The dephosphorization degree  $\eta_p$  vs  $\text{Al}_2\text{O}_3$  content of the slag for different temperatures.

with other heats. A small degree of dephosphorization was also obtained for heat 9:  $\eta_p = 35.66$ . This heat is characterized by similar, although advantageous from the dephosphorization viewpoint, contents of Cr = 10.5 pct and Ni = 1.4 pct (total Cr + Ni = 11.9 pct) and 0.096 pct P (initial). A higher phosphorus content in the metal promotes dephosphorization on account of the favorable activity coefficient  $e_P^P = 0.062$ .<sup>[23]</sup> Oxygen

$e_P^O = 0.13$ ,<sup>[23]</sup> carbon  $e_P^C = 0.126$ ,<sup>[23]</sup> silicon  $e_P^{\text{Si}} = 0.118$ ,<sup>[23]</sup> and sulfur  $e_P^S = 0.028$ <sup>[23]</sup> have a similar influence. Nickel, however, to a lesser extent, and chromium decrease strongly the activity of phosphorus in the metal. Depending on the author, the value  $e_P^{\text{Ni}}$  is proposed to be 0,<sup>[23]</sup>  $-0.004$ ,<sup>[24]</sup> and  $-0.006$ <sup>[25]</sup>;  $e_P^{\text{Cr}}$  lies between  $-0.016$  and  $-0.030$ .<sup>[13]</sup> In the ternary system

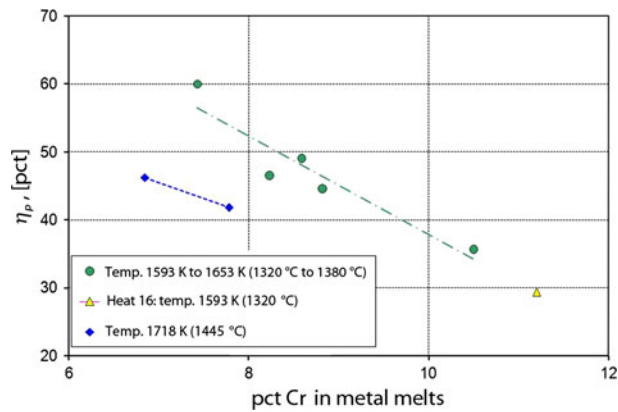


Fig. 11—The dephosphorization degree  $\eta_p$  vs Cr content of metal for different temperatures.

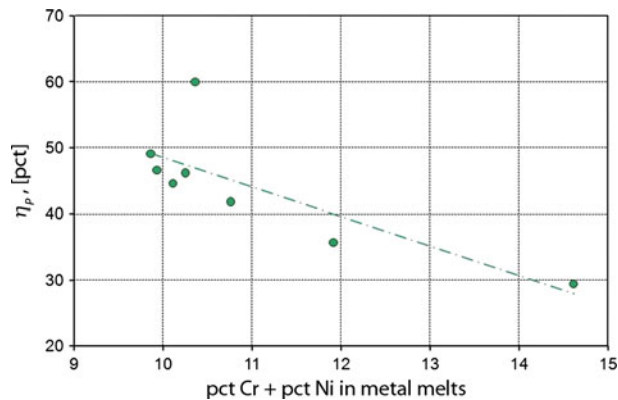


Fig. 12—The dephosphorization degree  $\eta_p$  vs the total Cr + Ni content of metal.

Fe-Cr-P, a strong intermolecular reaction of a covalent nature, occurs between Fe and P atoms, as well as between Cr and P. The Fe-Cr solution, however, approaches the ideal with a tendency to positive deviations from Raoult's law. In the liquid state, in the solution Fe-Cr-P, binary complexes can form as follows: FeP, Fe<sub>3</sub>P, Fe<sub>3</sub>P, CrP, Cr<sub>2</sub>P, Cr<sub>3</sub>P, Cr<sub>3</sub>P<sub>2</sub>, and ternary, *e.g.*, FeCrP.<sup>[13]</sup> The presence of nickel favors decreasing of the activity of phosphorus in the metal. The marked point (heat 16) deviates from the dependence found for M6. The metal sample of heat 16 has the highest content of nickel and chromium when compared with the analyzed samples numbers 9 through 15.

The dephosphorization degree  $\eta_p$  related to the slag basicity, as defined as the ratio of the basic oxides content to the sum of the contents of the acidic and amphoteric oxides, is presented in Figure 4. Aluminum oxides as well as chromium oxides are amphoteric. When present in a basic slag, they exhibit more acidic properties; for instance, they will form AlO<sub>3</sub><sup>3-</sup>. By increasing the slag basicity, one gets better dephosphorization independently of temperature, chromium content, and composition of the dephosphorizing mixture.

Figures 5 through 10 present the effects of particular slag components on the dephosphorization degree. Figure 5 presents the effect of CaO taken from the

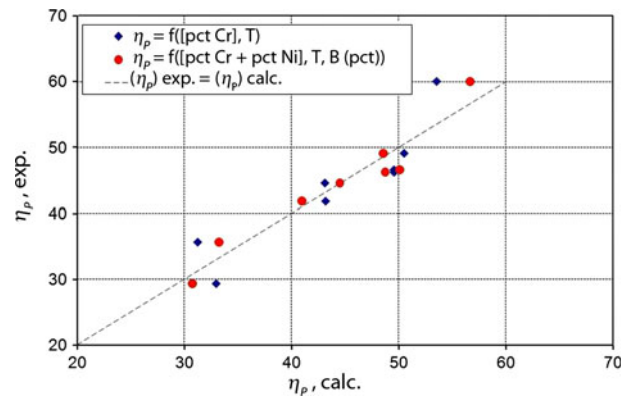


Fig. 13—Comparison of the dephosphorization degrees and experimental data with those computed with regression Eqs. [6] and [7].

chemical analysis. Independent of the variable parameters of the process, every increase of CaO content in the slag effects an increase of the dephosphorization degree as it increases the phosphorus capacity of the slag. Taking into account that CaF<sub>2</sub> is in the slag, one achieves close dependence (with a lower slope of the straight line plot).

Figures 6 through 8 present the effect of the chromium oxide content of the slag on the dephosphorization degree. By increasing Cr<sub>2</sub>O<sub>3</sub> of the slag, the dephosphorization decreases independently of the other parameters (Figure 6). The mixture M6 gives better dephosphorization with low Cr<sub>2</sub>O<sub>3</sub> content (Figure 7), which is a result of the higher basicity for this case. Heat 16 deviates from the other results for the mixture M6. The effect of the Cr<sub>2</sub>O<sub>3</sub> content on the dephosphorization is more apparent than that of temperature (Figure 8). Heat 16 deviates significantly from the others for 1593 K (1320 °C).

Increasing alumina in the slag decreases the dephosphorization properties of the slag to a small extent, which is shown in Figure 9. The high scatter of the found data and the use of mixtures containing various amounts of Al<sub>2</sub>O<sub>3</sub> (M5: approximately 5 pct Al<sub>2</sub>O<sub>3</sub>; M6: approximately 3 to 4 pct Al<sub>2</sub>O<sub>3</sub>) do not allow subsequent conclusions. The data presented in Figure 10 confirm the considerable effect of temperature. For a given Al<sub>2</sub>O<sub>3</sub> content, increasing the temperature affects the dephosphorization process negatively (Figure 10).

Figures 11 and 12 present the effects of metal bath composition on dephosphorization. Figure 11 shows that increasing chromium in the metal deteriorates dephosphorization. The data show also that temperature affects dephosphorization negatively. Heat 16, with its relatively high chromium content, fits well with the other results for the lower temperature region. An increase in chromium seems to affect the process more than the composition of the dephosphorizing mixture. Increasing the total chromium and nickel in the metal bath, as noted previously, because of the negative activity coefficients on phosphorus, deteriorates the dephosphorization process significantly (Figure 12).

The presented plots confirm the influence of temperature, slag basicity, CaO, and Cr<sub>2</sub>O<sub>3</sub> contents of the slag, as well as of total chromium and nickel content of the metal

on the effectiveness of dephosphorization. Furthermore, they allow a more precise quantitative approach.

A statistical analysis was performed by the authors to find quantitative relationships of the dephosphorization degree factor as a function of temperature; chromium content of the metal; CaO, Cr<sub>2</sub>O<sub>3</sub>, FeO, and Al<sub>2</sub>O<sub>3</sub> contents of the slag; and the slag basicity. The slag basicity was defined as the ratio of the content (in wt pct) of the basic components (CaO, without CaF<sub>2</sub> and FeO) to the content (in wt pct) of the acidic (SiO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub>) and amphoteric (Cr<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>) components.

The *F* test, at 0.95 confidence level, indicates the correlation between the dephosphorization degree and the two variables: chromium content and temperature. *F* is equal to 11.94 with limiting value  $F_{\min}(2,5) = 5.79$ . The model equation for this case is given by

$$\eta_p = -0.1023 \cdot T - 6.754 \cdot [\text{pct Cr}] + 271.63 \quad [6]$$

where variance  $S = 4.48$  for squared correlation coefficient  $R^2 = 0.83$ .

Statistically important regressions were not obtained when three variables were considered:  $\eta_p = f(\text{temp.}, [\text{pct Cr}], (\text{pct CaO}))$ ;  $\eta_p = f(\text{temp.}, [\text{pct Cr}], (\text{pct Cr}_2\text{O}_3))$ ;  $\eta_p = f(\text{temp.}, [\text{pct Cr}], (\text{pct Al}_2\text{O}_3))$ ; and  $\eta_p = f(\text{temp.}, [\text{pct Cr}], B(\text{pct}))$ .

Statistical computations were also performed for three variables selected from total chromium and nickel content of the metal and the slag basicity or one of the slag oxides. A statistically important correlation was found only for the total content of chromium and nickel of the metal, temperature, and slag basicity. For this condition, it was  $F = 18.61$  by limiting the value  $F_{\min}(3,4) = 6.59$ . The model equation for this case is given by

$$\eta_p = -0.052 \cdot T - 4.45 \cdot [\text{pct Cr} + \text{pct Ni}] + 11.78 \cdot B + 153.35 \quad [7]$$

where variance  $S = 3.11$  for squared correlation coefficient  $R^2 = 0.93$ .

As the number of the heats was low, as well as was the scope of variability of the parameters, the effects of a greater number of the parameters were not analyzed.

A comparison of the experimental dephosphorization degree data  $\eta_p$  with the model ones is shown in Figure 13. The correlations are satisfactory, in particular, the Eq. [7].

Additionally, attempts were made to estimate how the carbon of the metal affects the dephosphorization process; however, because of the high scatter of the data, no conclusions were derived. It seems that carbon does not affect the process. A variation of the carbon content with a constant chromium content should affect the oxidation degree of chromium. And vice versa, a constant carbon content with varying chromium should produce an almost constant content of chromium oxide in the slag.

With too low a carbon content (for instance, <2 pct), chromium losses to the slag get higher. Moderate increase of carbon content enhances dephosphorization as it allows lowering of temperature of the process (decreases the melting point of metal). However, when carbon content is too high, dephosphorization process

becomes less effective, as carbon decreases the oxygen activity in the metal. No statistically important correlation (because of the low number of heats) was found between Cr<sub>2</sub>O<sub>3</sub> content of slag and final carbon, chromium, lime contents and process temperature:

$$(\text{pct Cr}_2\text{O}_3) = 0.41 \cdot [\text{pct Cr}] - 0.85 \cdot [\text{pct C}] + 0.015 \cdot T_f - 0.46 \cdot (\text{pct CaO}) - 1.34 \quad [8]$$

where variance  $S$  is 0.80 and  $R^2$  is 0.89 with test  $F(4,3) = 6.18$  and with  $F_{\min}(4,3) = 9.12$ , for  $\alpha = 0.05$ .

However, although few data points were used, a statistically important correlation was found for chromium losses to the slag and the contents of chromium, lime, iron oxide, and the process temperature:

$$(\text{pct Cr}_2\text{O}_3) = 0.88 \cdot [\text{pct Cr}] + 0.29 \cdot (\text{pct FeO}) + 0.033 \cdot T_f - 0.25 \cdot (\text{pct CaO}) - 49.77 \quad [9]$$

where variance  $S = 0.43$  and  $R^2 = 0.97$  with test  $F(4,3) = 22.95$  and with  $F_{\min}(4,3) = 9.12$ , for  $\alpha = 0.05$ .

This finding indicates that any increase of chromium content, temperature, and oxidation of slag results in an increase of chromium losses. Any increase of CaO in the formed slags, however, decreases chromium losses. Calcium chromates were not found in the samples; however, iron and sodium chromates were present. The behavior of the slag components will be the subject considered in a subsequent publication. X-ray analyses of slag samples will allow the determination of mineralogical composition of each slag.

## VI. SUMMARY

The removal of phosphorus out of the liquid iron solutions containing chromium and nickel is important for theoretical and practical reasons. The dephosphorization process, when it is to be run effectively, needs the thermodynamic data relating to the chemical reactions. Even more important are the parameters of the process, in particular the limits of fluctuations of the process parameters. The former are as follows: the equilibrium rates of the all the reactions that occur, the interaction coefficients of solutes for the temperature region of the dephosphorization process, *i.e.*, 1623 K to 1723 K (1350 °C to 1450 °C). The latter are as follows: the material extracting phosphorus, the way it is added into the liquid metal, optimum temperatures, the composition, flow intensity, and pressure of carrier gas.

The article presents results of experimental investigations for dephosphorization of liquid iron solutions containing chromium and nickel. The study was focused on selection of the effective dephosphorizing mixture. Mixtures based on lime and fluorite with cryolite additions were considered. The process parameters such as the chemical composition of the dephosphorizing mixture, the formed slag, the metal bath, and the

temperature were analyzed to establish their impact on the effectiveness of the dephosphorization process.

It was found that the key factors for effective dephosphorization of the iron solutions containing chromium and nickel are the content of chromium and nickel of the metal, the temperature, and the slag basicity. Relevant model equations, derived by statistical regression methods, are also presented.

It was shown that CaO-CaF<sub>2</sub>-Na<sub>3</sub>AlF<sub>6</sub> mixture may be used effectively for dephosphorization of chromium-nickel pig iron. A 15 pct addition of cryolite is sufficient for dephosphorization of pig iron containing approximately 6 to 10 pct Cr. When the cryolite level is higher, the dephosphorizing effect becomes lower as it decreases slag basicity.

The conclusions drawn by the authors may be useful for the design of new methods of production of high-chromium steels, in particular, of those that apply as charge material pig iron produced from iron ores containing chromium compounds as well as for production of low phosphorus ferrochrome. The most up-to-date trends in stainless steel production—aiming at the reduction of production costs—consist of the substitution of steel scrap by hot metal, coming from the reduction of iron-chromium ores. This process requires a more extensive dephosphorization. The dephosphorization process, when applied to chromium steels, requires slag with high dephosphorization properties, as either chromium or chromium oxide entering the slag decreases distinctly the efficiency of the process.

#### ACKNOWLEDGMENT

The Polish Ministry of Science and Higher Education is acknowledged for its financial support by Grant 11.11.110.930 from Project AGH.

#### OPEN ACCESS

This article is distributed under the terms of the Creative Commons Attribution Noncommercial License which permits any noncommercial use,

distribution, and reproduction in any medium, provided the original author(s) and source are credited.

#### REFERENCES

1. M. Kowaka and H.J. Fujikawa: *J. Jpn. Inst. Met.*, 1970, vol. 34, pp. 1047–50.
2. R. Inoue, H. Li, and H. Suito: *Trans. ISIJ*, 1988, vol. 28, pp. 179–85.
3. S. Inoue, T. Usui, K. Yamada, and K. Takahashi: *Trans. ISIJ*, 1988, vol. 28, pp. 192–97.
4. Y.E. Lee: *Iron Steelmaker*, 1993, pp. 41–49.
5. L.F. Li, M.F. Jiang, C.J. Jin, W.Z. Wang, and Z.P. Chen: *Metall. Mater. Trans. B*, 1999, vol. 30B, pp. 451–57.
6. Y. Nakajima and M. Mukai: *ISIJ Int.*, 1993, vol. 33, pp. 109–15.
7. N. Sano and H. Katayama: *1st Int. Chromium Steel and Alloys Congress*, Cape Town, South Africa, vol. 2, SAIMM, Johannesburg, South Africa, 1992, pp. 25–33.
8. Z. Tian, K. Cai, L. Zhang, T. Wang, H. Shi, X. Yin, L. Zhu, and J. Zheng: *AISTech 2004 Proc.*, vol. I, pp. 719–25.
9. Y.D. Yang and J.O. Edstrom: *Scand. J. Metall.*, 1992, vol. 21, pp. 202–10.
10. O. Wijk: *Scand. J. Metall.*, 1993, vol. 22, pp. 130–38.
11. N. Masumitsu, K. Ito, and R.J. Fruehan: *Metall. Mater. Trans. B*, 1988, vol. 19B, pp. 643–48.
12. T.K. Inouye, H. Fujiwara, E. Ichise, and M. Iwase: *Metall. Mater. Trans. B*, 1994, vol. 25B, pp. 695–701.
13. A.I. Zaitsev, B.M. Mogutnov, and N.E. Shelkova: *Metall. Mater. Trans. B*, 1998, vol. 29B, pp. 155–61.
14. L. Wu, J. Gran, and D. Sichen: *Metall. Mater. Trans. B*, 2011, vol. 42B, pp. 928–31.
15. M. Karbowniczek, E. Kawecka-Cebula, K. Pytel, and J. Reichel: *Steel Res. Int.*, 2003, vol. 74 (10), pp. 610–16.
16. W.H. van Niekerk and R.J. Dippenaar: *Metall. Mater. Trans. B*, 1998, vol. 29B, pp. 147–53.
17. F.D. Richardson: *Physical Chemistry of Melts in Metallurgy*, vol. 1, Academic Press, London, 1974.
18. B.O. Mysen, F.J. Ryerson, and D. Virgo: *Am. Mineral.*, 1980, vol. 65, pp. 1150–57.
19. C. Wagner: *Metall. Trans. B*, 1975, vol. 6B, pp. 405–09.
20. Y. Kawai, R. Nakao, and K. Mori: *Trans. ISIJ*, 1984, vol. 24, pp. 509–14.
21. Y. Yang, A. McLean, and I.D. Sommerville: *Steel Res.*, 1995, vol. 66, pp. 103–09.
22. Y. Okabe, I. Tajima, and K. Ito: *Metall. Mater. Trans. B*, 1998, vol. 29B, pp. 131–36.
23. G.K. Sigworth and J.F. Elliot: *Met. Sci. J.*, 1974, vol. 8 (9), pp. 298–310.
24. S. Ban-ya, N. Maruyama, and Y. Kawase: *Tetsu-to-Hagane*, 1984, vol. 70 (1), pp. 65–72.
25. K. Jukio: *Tetsu-to-Hagane*, 1982, vol. 68 (11), p. S890.