Arch. Metall. Mater., Vol. 61 (2016), No 1, p. 301–306

DOI: 10.1515/amm-2016-0057

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THE EFFECT OF SLAG ON THE EFFECTIVENESS OF PHOSPHORUS REMOVAL FROM FERROUS ALLOYS CONTAINING CARBON, CHROMIUM AND NICKEL

The aim of this study was to determine the impact of slag composition on phosphorus removal from ferrous solutions containing carbon, chromium and nickel. Additions of cryolite, Na_3AlF_6, were applied for better fluxing and higher phosphate capacity of the slag. An X-ray analysis of final slags formed during dephosphorization of ferrous solutions containing chromium and nickel with CaO-CaF_2 or CaO-CaF_2-Na_3AlF_6 mixtures of different chemical compositions was carried out. The equilibrium composition of the liquid and the solid phase while cooling the slags from 1673K to 298K was computed using FactSage 6.2 software. The performed equilibrium computations indicated that the slags were not entirely liquid at those temperatures. The addition of cryolite causes a substantial increase of the liquid phase of the slag. It also has a favourable effect on the dephosphorization grade of hot metal. The obtained results were statistically processed and presented in the form of regression equations.

Keywords: dephosphorization, slag, dephosphorization grade

1. Introduction

Stainless steel production includes a stage of phosphorus removal from the metal bath containing carbon, chromium, nickel, and other elements. An effective lowering of the phosphorus content in such conditions is one of the most difficult steelmaking tasks. Phosphorus should be oxidized, while it is important to limit the oxidation of chromium as well.

In order to establish advantageous conditions for decreasing the phosphorus content in ferrous solutions containing higher levels of chromium and nickel, more systematic investigations of the effects of the method of slag formation, as well as the effects of qualitative and quantitative chemical and mineralogical slag composition on the effectiveness of dephosphorization of such ferrous solutions were carried out. The main task was to get the optimum reduction of the phosphorus level while minimising the loss of chromium [1÷10]. The final slag mineralogical composition after dephosphorization of the ferrous solution containing chromium and nickel with mixtures of CaO-CaF_2 and CaO-CaF_2-Na_3AlF_6 of various compositions was determined. The equilibrium slag compositions, both in the liquid and solid phase, were computed with the FactSage 6.2 program. Additions of cryolite Na_3AlF_6 were applied to increase the fluidity of the slag and its phosphate capacity.

2. Experimental investigations

38 test heats were made in order to study the dephosphorization process of liquid metal in an induction furnace with a capacity of 20 kg [1]. A high chromium pig iron containing 2÷4% of carbon, 2÷18% of chromium, 1÷3% of nickel and 0.04÷0.16% of phosphorus was used. The dephosphorization process was carried out at low temperatures, within the 1473÷1673K range. Two types of desulphurization mixtures were applied:

- mixture „1": CaO-CaF_2 (30 heats)
- mixture „2": CaO-CaF_2 with a cryolite Na_3AlF_6 addition (4 heats with 25% of cryolite – denoted 2a, and 4 heats with 55% of cryolite – denoted 2b).

The dephosphorization mixture was applied on the metal surface in portions of 100 g each, every 1 min., 1.0÷1.5 kg/heat, i.e. below 0.075 kg/kg of hot metal. Simultaneously, in order to enhance the contact of the dephosphorization mixture with the metal bath and to ensure good oxidation conditions, a blow of gaseous oxygen and argon mixture of invariable flow intensity was applied for about 10÷15 min. During the heats preparation, the bath temperature was monitored, and samples of metal and slag were taken for chemical and mineralogical analyses.

The dephosphorizing properties of slags depend on their mineralogical composition. Therefore, a diffraction X-ray phase analysis by means of a HZG-4 diffractometer was performed and the equilibrium computations of the slag composition with the FactSage 6.2 program were executed within a temperature range from room temperature up to the process temperature, i.e. 1673K. Filtered Co-kα radiation was used for the x-ray examination. For the analysis, three samples of the slag after dephosphorization were taken for the addition of the CaO-CaF_2 mixture, and the same number of samples were taken for the addition of the CaO-CaF_2-Na_3AlF_6 mixture.

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3. Results of investigations

Table 1 presents the initial and final chemical compositions of the metal bath and the dephosphorization temperatures of the selected six heats, for which X-ray analyses were performed. The chemical compositions of the slags were determined by means of an Oxford Instruments Twin-X, an X-ray fluorescent spectrometer with energy dispersion. The chemical compositions of the slags – corrected for the estimated fluorine and sodium content – are presented in Table 2.

The phosphorus content in the slag is low, below 1% (converted into oxide: max. 1.6% P_2O_5), which could be referred to the maximum content of ca. 4% of calcium and sodium phosphates combined. Not every X-ray picture allows us to identify phosphorus compounds, as the required concentration for univocal identification of any specific compound is 5% at least. It is also worth mentioning, that complex compounds, formed of simple oxides at different proportions are also difficult for univocal differentiation. Their maximum peaks often correspond to very close, or sometimes even the same values of Θ angle, while their contents are close to the detectability threshold.

The performed X-ray analyses of the slags formed after the dephosphorization process allowed us to identify the main compounds of those slags, as follows:

- in either type of slags: CaO, CaF_2, Fe_2O_3, $Fe_{0.98}O$, $CaFe_2O_4$, $(Fe_{0.6}Cr_{0.4})_2O_3$, $FeCr_2O_4$, $CaSiO_3$,
- in the slags coming from the heats with mixture “1”: $CaCr_2O_4$, $FeSiO_3$, Fe_2SiO_4,
- in the slags coming from the heats with mixture “2”: $Ca_{12}Al_{14}O_{33}$, $Ca_{12}Al_{14}O_{32}F_2$, $NaCaPO_4$, $Ca_{10}Na(PO_4)_7$, NaF, $Na_2Cr_2O_4$, $NaAl_{11}O_{17}$.

For the slags from the heats with mixture “1”, no phosphates were found due to their very low content in the slag.

For the slags, coming from the heats without cryolite addition, which contained more silica, simple calcium and iron silicates, such as $CaSiO_3$; $FeSiO_3$, Fe_2SiO_4 were detected. On the X-ray pictures for those slags, one can notice a specific change in the nature of iron oxides, depending on the iron content in the slag. The slag samples from heats A and B, with

TABLE 1

Compositions of the metal baths for heats before and after dephosphorization

Heat	Deph. mixture	Stage of dephosphorization	T, K (°C)	Metal composition, %							ηP %
				C	Cr	Ni	Si	Mn	P	S	
dephosphorizing mixture CaO-CaF											
A	1	before	1561 (1288)	3.97	4.98	2.53	0.024	0.08	0.046	0.005	
		after	1540 (1267)	3.41	4.60	2.50	0.025	0.05	0.020	0.001	56.52
B	1	before	1521 (1248)	4.12	4.42	2.66	0.026	0.15	0.105	0.006	
		after	1485 (1212)	3.72	4.13	2.64	0.025	0.11	0.050	0.003	52.38
C	1	before	1588 (1315)	3.23	18.2	2.95	0.026	0.10	0.069	0.011	
		after	1569 (1296)	2.40	17.4	2.90	0.025	0.08	0.040	0.017	42.65
dephosphorizing mixture $CaO-CaF_2-Na_3AlF_6$											
D	2a	before	1654 (1381)	3.26	7.87	1.25	0.06	0.09	0.114	0.015	
		after	1627 (1354)	2.87	8.23	1.70	0.06	0.13	0.060	0.009	47.37
E	2b	before	1636 (1363)	2.82	7.19	2.64	0.05	0.12	0.155	0.018	
		after	1641 (1368)	2.41	7.43	2.93	0.05	0.16	0.060	0.008	61.29
F	2b	before	1662 (1389)	2.07	7.16	2,93	0.05	0.16	0.068	0.009	
		after	1718 (1445)	1.62	6.85	3.40	0.04	0.22	0.040	0.008	41.18

TABLE 2

Corrected compositions of the slags

Heat	Deph. Mixture	Slag composition, %									
		CaO	CaF_2	FeO	Cr_2O_3	SiO_2	P_2O_5	MnO	MgO	Al_2O_3	Na_2O
dephosphorizing mixture $CaO-CaF_2$											
A	1	31.60	31.60	23.01	7.21	9.94	0.74	0.21	0.59	1.44	-
B	1	37.50	37.50	16.92	4.96	6.27	1.59	0.03	0.60	0.40	-
C	1	25.45	25.45	14.31	17.24	13.89	0.14	0.62	0.33	0.97	-
dephosphorizing mixture $CaO-CaF_2-Na_3AlF_6$											
D	2a	27.36	27.41	17.95	10.33	4.02	0.72	0.48	0.43	5.37	9.77
E	2b	30.87	30.93	20.84	9.74	2.30	1.44	0.46	0.42	3.70	6.73
F	2b	28.45	28.50	19.46	12.84	2.25	0.32	0.65	0.41	2.78	5.06

higher FeO contents (23% and 16.9% respectively), show high peaks for $CaFe_2O_4$ ferrate, while for the slag from heat C with the lowest FeO content (14.3%), a very tiny peak for $CaFe_2O_4$ was detected. However, for the slag containing low amounts of FeO, peaks for ferrous chromates and silicates are significantly bigger.

By using the FactSage 6.2 program, the equilibrium compositions of the slags in liquid and solid state were computed. The results for examples of compositions of the liquid and solid states for slags without (heat B) and with cryolite (heat E) are presented graphically in Fig. 1÷2. A completely solidified slag without cryolite occurs at temperatures below 1313K (Fig. 1a and 1b), while slags with cryolite solidify totally only below 473K (Fig. 2a and 2b).

Fig. 1a

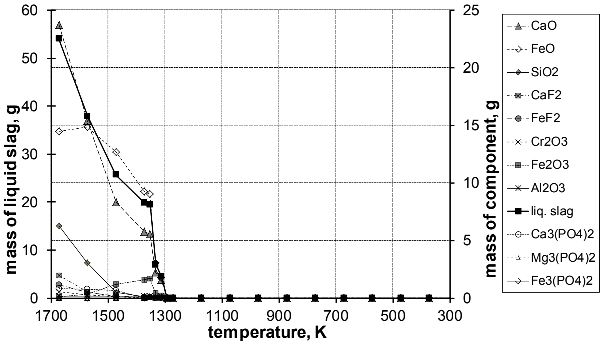

Fig. 1b

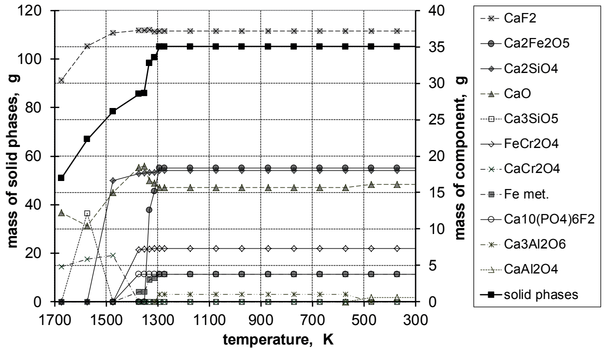

Fig. 1. The course of changes of the mass of the: a) liquid phase; b) solid phase of slag "B" (without cryolite), during solidification of a 105g slag sample from a temperature of 1673K down to 298K. At 1673K, the mass of the liquid phase in the slag is equal to ca. 54g and the solid phases in the slag is equal to ca. 51g

Fig 2a

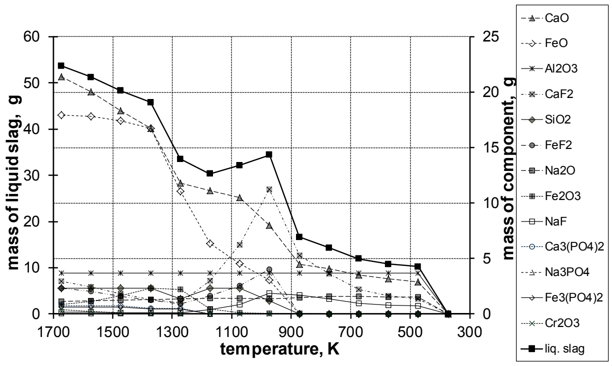

Fig. 2b

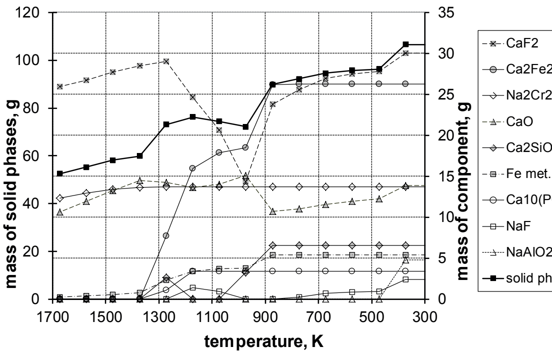

Fig. 2. The course of changes of the mass of the: a) liquid phase; b) solid phase of slag "E" (with cryolite), during solidification of a 106.5g slag sample from a temperature of 1673K down to 298K. At 1673K the mass of the liquid phase of the slag is equal to ca. 54g and the solid phases in the slag is equal to ca. 52.5g

The equilibrium computations for solid state conditions at a temperature of 298K, for the slags dephosphorized with the CaO-CaF_2 and CaO-CaF_2-Na_3AlF_6 mixtures, indicate the presence of the following compounds: CaO, CaF_2, $Ca_2Fe_2O_5$, Ca_2SiO_4, $CaAl_2O_4$, $Ca_{10}(PO_4)_6F_2$, Fe_{met}. For various types of mixtures one gets different compounds for chromium and sodium combinations. When the CaO-CaF_2 mixture was used, the chromium was bound in the form of $FeCr_2O_4$ and $CaCr_2O_4$, while for the CaO-CaF_2-Na_3AlF_6 mixture, the final slag product contained $Na_2Cr_2O_4$. For higher sodium contents, the slag contained free sodium fluoride, NaF, and instead of calcium aluminate, $CaAl_2O_4$, it contained sodium aluminate, $NaAlO_2$. For slags without cryolite, small amounts of magnetite, Fe_3O_4, may occur in the solid state.

At a temperature of 1673K, both slags after dephosphorization with CaO-CaF_2 and CaO-CaF_2-Na_3AlF_6 are not entirely liquid. The liquid phase, for the heats with no cryolite, constitutes about 40÷70%, while for those with cryolite it takes about 50÷65% of the overall mass of the slag. It consists of simple oxides, sulphides, fluorides and phosphates. At that temperature, the compounds are dissociated into metal cations and the following anions: sulphide S^{2-}, silicate SiO_4^{4-}, fluoride F^-, phosphate PO_4^{3-}, aluminate AlO_2^-. In the liquid slag, the phosphorus occurs in the form of phosphates, mainly calcium and iron phospates, and less sodium phospates, depending on the slag composition. The solid phase contains predominantly CaF_2, noticeably less CaO and small amounts of silicates Ca_3SiO_5 or Ca_2SiO_4, and chromates $CaCr_2O_4$, $MgCr_2O_4$, while for slags with cryolite, also contains sodium chromate, $Na_2Cr_2O_4$.

At the process temperature, for the slags coming from the heats with no cryolite, the phosphorus occurs in calcium and ferrous (II) phosphates, yet for the heats with cryolite, apart from calcium and ferrous (II) phosphates, small amounts of sodium phosphates or possibly magnesium phosphates are formed. When cooling the slag within the temperature range of 1400÷1200K, the phosphates are transformed into calcium fluoro-orto-phosphate, $Ca_{10}(PO_4)_6F_2$. The latter was not detected by the mineralogical analysis, probably due to the fast rate of the cooling process, which did not allow the new phase to form, additionally due to its level below the detectability threshold (about 5%).

4. Effect of the slag chemical composition on dephosphorization of metal

The slag from the dephosphorization process is composed of products formed by oxidation of metal bath components by the blown-in oxygen, including products of phosphorus oxidation, slag residues from hot metal desiliconization, dissolving components of the dephosphorizing mixture, and finally products of dissolution of the furnace crucible refractory lining. The share of the dephosphorizing mixture in the slag mass may be estimated on the basis of the alteration of the CaO content in the slag as compared to the dephosphorizing mixture (all CaO comes from the mixture only). In the conducted heats, the share of the dephosphorization mixture was only from ca. 47%, to ca. 75% of the slag mass at the most. With no metal oxidation products, the dephosphorizing mixture alone would not be able to form any liquid slag. The equilibrium computations point out that at the process temperature the slag consistency is pasty, as only ca. a half of the slag is in a liquid state.

The slag features a high fluorine content coming from fluorite, which is one of the main components of the mixtures used for dephosphorization. As shown by the equilibrium computations, the slag is saturated with fluorite, and only a small amount of fluorite is dissolved in the liquid slag. Thus, the mass of the fluorite used for dephosphorization is too large, so the surplus fluorite forms a separate phase. As for the liquid phase, most of the fluoride ions form loosely bound complexes Ca^{2+}-$2F^{-}$. Fluoride ions lower the slag viscosity, however they do not change the amount of NBO and BO oxygen atoms, which means that no depolimerization of the silicate structure occurs [11].

The slag is characterised by a relatively high content of iron oxides (ca. 17÷25% for slags from the heats with cryolite, while for the other slags even 14.3÷ 64.5% , when converted into FeO). At high temperatures, mainly divalent iron occurs in the slags in the form of cations, accompanied by small amounts of Fe_2O_3 (according to the equilibrium computations there should be 10 times less Fe_2O_3 than FeO) forming anions, for instance FeO_2^{-}. FeO is not stable below ca. 833°K and – when cooled – it disintegrates into Fe_2O_3 and Fe. In basic slags, iron may be a component of anions, coming from the amphoteric oxide Fe_2O_3, e.g., $CaFe_2O_4$, $Ca_2Fe_2O_5$.

The dephosphorization process occurs by binding the phosphorus in the liquid slag in the form of calcium phosphates: $Ca_3(PO_4)_2$, iron (II) phosphates: $Fe_3(PO_4)_2$ and sodium phosphates: Na_3PO_4, $NaPO_3$. As sodium phosphate forms easier than calcium phosphate, the presence of sodium from cryolite should enhance the dephosphorization process. In the solidified slag, the phosphorus should be in the form of $Ca_{10}(PO_4)_6F_2$.

In liquid slags formed with no cryolite additions, metal oxides and a small amount of Cr_2O_3 occur. Most of the chromium at the process temperature, ca. 1473÷1673K, is bound in the form of solid calcium chromate: $CaCr_2O_4$. For temperatures corresponding to the solidification of slag, the calcium chromate transforms into ferrous (II) chromate, $FeCr_2O_4$. Dephosphorization mixtures 2a and 2b contain cryolite, so sodium cations appear in the slag, partially substituting calcium cations. For type “2” slags, the liquid phase containing a small amount of Cr_2O_3 is accompanied by a solid phase of sodium chromate, $Na_2Cr_2O_4$, which at temperatures below ca.1473K binds all the chromium. Both calcium chromates and sodium chromates at the process temperature do not dissolve in the liquid slag (Fig. 1a and 2a), forming separate solid phases. The mixtures with cryolite should enhance dephosphorization by binding phosphorus, however they can be detrimental by increasing chromium losses to the slag. Slags containing cryolite begin to melt at much lower temperatures (ca. 673K) than other slags (>1573K).

The phosphorus slag capacity is determined mainly by the slag’s basicity. The examined slags were basic. Due to small amounts of acidic oxides in those slags, the basicity of the slag was defined as the ratio of percentage contents of basic oxides to acidic and amphoteric ones:

$$Basicity = B = \frac{CaO + Na_2O + FeO}{SiO_2 + Al_2O_3 + Cr_2O_3 + P_2O_5} \tag{1}$$

Fig. 3 presents the dephosphorization effectiveness, η_P as a function of basicity defined as above, for all heats. Although the slags with cryolite appeared to have a higher basicity, the dephosphorization effectiveness was similar to the slags with no cryolite. The graphs of dephosphorization effectiveness as a function of basicity for both types of slags are similar, yet a slightly better effectiveness may be noticed for slags with cryolite. The dephosphorization with cryolite was run at temperatures ca. 100 degrees higher than for the mixtures with no cryolite (Tab.1). As an increase in the temperature affects dephosphorization, the foregoing results indicate better dephosphorization properties of the slags with cryolite.

Fig. 3

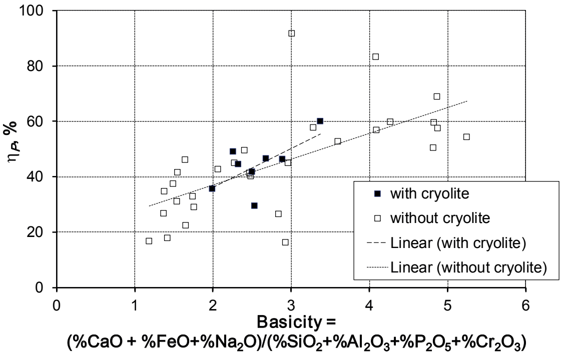

Fig. 3. Dephosphorization effectiveness, η_P, as a function of the slag basicity for all heats

The following regression correlations of dephosphorization effectiveness as a function of temperature, chromium and nickel content in the metal and the basicity B for both types of slags were obtained:

- slags with cryolite:

$$\eta_P = -0.0437 \cdot T - 4.28 \cdot (pctCr + pctNi) + 11.60 \cdot B + 133.5 \tag{2}$$

where S=3.3 and R^2=0.92, at the test value F(3,4)=16.22 and F_{lim}(3,4)=6.59 for α=0.05,

- slags with cryolite:

$$\eta_P = +0.0493 \cdot T + 0.029 \cdot (pctCr + pctNi) + 10.07 \cdot B - 60.7 \tag{3}$$

where S=14.2 and R^2=0.46, at the test value F(3,26)=7.32 and F_{lim}(3,26)=2,60 for α=0.05.

A comparison of the actual dephosphorization effectiveness to the one predicted by Eqs. (2) and (3) is presented in Fig. 4. A much better forecast is obtained for the slags with cryolite. Fig.5 presents experimental dependences of dephosphorization effectiveness, η_P, on the chromium oxide content in the slag.

Fig. 4

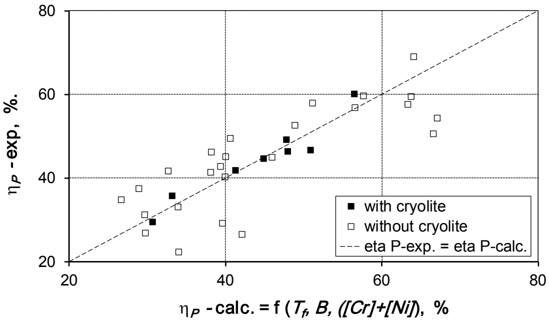

Fig. 4 . A comparison of the experimental data of dephosphorization effectiveness with those computed with regression Eqs. (2) and (3)

Fig. 5

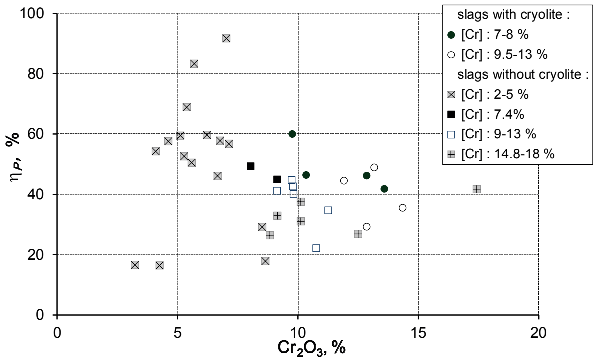

Fig. 5. The experimental data of dephosphorization effectiveness, ηP, as a function of chromium oxides contents in the slag for various chromium content in the metal bath

The influence of the chromium oxide content on dephosphorization also indicates that the dephosphorizing effectiveness, η_P , goes down when Cr_2O_3 content in the slag goes up. η_P is related to Cr_2O_3 content for the slags formed in the heats with mixtures with and without cryolite, as shown in Fig. 5, for various chromium contents in the metal bath. The dephosphorization efficiency is higher for similar chromium contents in metal when mixtures containing cryolite are used, see Fig. 5. Probably, an increase in basicity of slag with cryolite for moderate chromium contents prevails over reduction of basicity caused by the formation of solid calcium or sodium chromates which are insoluble in the slag.

5. Conclusions

1. X-ray analyses of the slags and the equilibrium computations for slags formed after dephosphorization of ferrous solutions containing chromium and nickel with dephosphorizing mixtures of $CaO-CaF_2$ or $CaO-CaF_2-Na_3AlF_6$ of different compositions were performed. X-ray pictures prove that solid phases are present in slags in the form of compounds that initially precipitated from the liquid phase and had no time to achieve real equilibrium. It concerns complex compounds formed from the same oxides but at different proportions. In both type of slags the following were found: CaO, CaF_2, $x CaO \cdot Fe_2O_3$, $x CaO \cdot SiO_2$, Fe_xO_y, Fe_{met}. Depending on the added dephosphorizing mixtures, different chromium and sodium compounds occur:
   - in the slags with $CaO-CaF_2$: $FeCr_2O_4$ and $CaCr_2O_4$; also $x FeO \cdot SiO_2$, and for the equilibrium (FactSage) - $Ca_{10}(PO_4)_6F_2$. No phosphates were detected by the X-ray analysis due to the low content of phosphates in these slags,
   - in the slags with $CaO-CaF_2-Na_3AlF_6$: $Na_2Cr_2O_4$ and $x CaO \cdot y Al_2O_3(F_2)$, and $x Na_2O \cdot y Al_2O_3$, for the equilibrium conditions (FactSage) $Ca_{10}(PO_4)_6F_2$, while X-ray measurements show $Na_xCa_y(PO_4)_z$.
2. The results of the X-ray analysis show different phase compositions of the solidified slag than the equilibrium FactSage computations. These differences are attributed mainly to the fact that equilibrium was not achieved during rapid cooling of the slag.
3. The results of computations made by the FactSage program indicate some surplus fluorite in the slag, which when appearing in solid state does not enlarge the liquid phase range.
4. It was established that regression correlations for the dephosphorization effectiveness depended on the temperature, chromium and nickel content in metal, and the slag basicity for both types of slags applied, i.e., those with and without cryolite.
5. For analogous chromium contents in metal, the dephosphorization effectiveness is higher in the case of the dephosphorization mixtures with cryolite.

Acknowledgement

The Polish Ministry of Science and Higher Education is acknowledged for its financial support by Grant 11.11.110.225 from Project AGH

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Received: 10 March 2015.