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Effect of CaO on Phosphate Capacity of Deoxidation Slag for Effective Utilisation of Phosphorus in Steel

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Recent proposal of utilisation of impurities in steel requires preservation of phosphorus in molten steel during its refining process. To know the phosphorus absorbing ability of deoxidation by-product slag having CaO, the phosphorus partition has been investigated between the $MnO-SiO_2-Fe_tO-CaO-MgO-P_2O_5$ slag and molten iron in this study. The phosphate capacities ($C_{PO_4^{3-}}$) for the present slag has been determined as a function of temperature and optical basicity has follows;

$$\log C_{PO_4^{3-}} = (11\,300\,\Lambda + 54\,560)/T + 18.30\,\Lambda - 27.43$$

CaO was found useful to improve phosphate capacity of this system to some extent.

Key words: steel scrap; utilisation of impurities; deoxidation; phosphate capacity;

1. Introduction

Nowadays, the environmental problem such as waste emission arises as a matter of urgency. In the steelmaking process, use of degraded iron ore with high phosphorus will be inevitable in near future due to a depletion of high quality ores, resulting in the increment of refining slag amount.

As a countermeasure to this problem, utilisation of impurities attracts more attention recently. Some favourable results have been reported on microstructure refining and improvement of steel property[1]. If the detrimental problems of impurities disappear by well controlled processes, only the preferable effect of each element will be eminent. With regard to phosphorus, as-cast austenite grain size in steel greatly reduces by the presence of phosphorus. The mechanism involves a segregation of phosphorus to condense in the inter dendritic region retarding the ferrite/austenite transformation during cooling by a pinning effect [2-4]. To preserve phosphorus in steel during deoxidation process, elements having high deoxidising and low dephosphorising abilities are suitable for use such as manganese and silicon. One of authors has previously investigated the phosphate capacity for the $MnO-SiO_2-Fe_tO$ system[5] and showed very low phosphorus distribution ratios between the slag and molten iron. However, there may be an optimal value of phosphorus content in steel since too high phosphorus will bring about the welding problem and so on. Therefore, control of the phosphorus content to some extent would be necessary. Addition of CaO will be a good candidate to control phosphorus content during deoxidation; however, the thermodynamic property of phosphorus is not available for the manganese-silicon deoxidation system having CaO.

Accordingly, the present work aims to evaluate phosphate capacities as an index of dephosphorising ability for the $MnO-SiO_2-Fe_tO-CaO-MgO$ system by measuring phosphorus partition between the slag and molten iron and to estimate phosphorus distribution ratio in practical operations.

2. Experimental

2-1. Preparation of premelted slag

Raw material for the present slag was a mixture of CaO and MnO calcined from $CaCO_3$ (99.9 % in purity) and $MnCO_3$ (99.9 % in purity), SiO_2 powder (99.9 % in purity), dehydrated 2MgO・P_2O_5, and FetO precedently prepared by melting Fe(99.99 % in purity) and Fe_2O_3 (99% in purity) powder in an iron crucible. The purpose of addition of iron oxide is to control oxygen partial pressure in main experiments. Table 1 gives nominal composition of the slag and Figure 1 shows these compositions plotted on the CaO-MnO-SiO_2 pseudo-ternary system[6]. The CaO content varies with incremental steps up to 22 mass% on the composition line with MnO/SiO_2 ratio of 2. After complete mixing, the powders were melted in an iron crucible (26-mm in outer diameter, 20-mm in inner diameter, and 70-mm in length) for 1 h at 1673 K in an argon atmosphere. After taking out and quenching the sample, it was subject to the main experiments.

Table 1 Nominal composition of master slags in mass%

Component	CaO	MnO	SiO_2	FeO	MgO	P_2O_5
Slag 1	5.0	61	31	2.0	0	1.0
2	11	57	29	2.0	0	1.0
3	16	54	27	2.0	0	1.0
4	22	50	25	2.0	0	1.0

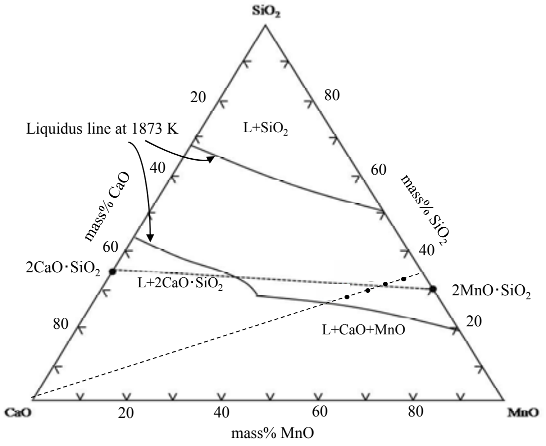

Fig. 1 Initial composition of master slag projected on the CaO-MnO-SiO_2 pseudo ternary system at 1873 K[6]. The compositions are on mass% basis.

2-2. Experimental procedure

Five grams of the pre-melted slags and 3 g of electrolytic iron (99.95 % in purity) were set in a fused MgO crucible(21-mm in outer diameter, 17-mm in inner diameter, and 30-mm in length). The crucible was placed in the centre of an alumina tube (70-mm in outer diameter, 60-mm in inner diameter, and 1000-mm in length) set in an $MoSi_2$ electric resistance furnace having a proportional-integral-differential(PID) controller with Pt-Pt/6 pct Rh thermocouple. After heating up, the temperature was controlled within ±2 K in the temperature uniform zone over a length of 50mm and maintained from 1843 to 1923 K for equilibration of molten slag and molten iron. The equilibrium time was determined to be 6 h by the preliminary experiments.

2-3. Degrees of freedom in the present system

A system in a thermodynamically unique state should have the degree of freedom of zero. The Gibbs phase rule is helpful for this understanding;

$$F = C - P + 2 \qquad (1)$$

where F is the degree of freedom, C is the number of the components and P is the number of the phases, respectively. In the present system, we have equilibrated liquid MnO-SiO_2-Fe_tO- CaO-MgO-P_2O_5 slag and molten iron in an MgO crucible in an argon atmosphere. Therefore, the components present on element basis are calcium, manganese, silicon, iron, magnesium, phosphorus, oxygen and argon, giving the value of C to be 8. The phases present are liquid slag, molten metal, crucible material and gas, giving the value of P to be 4. The total atmospheric pressure and temperature are externally fixed. Accordingly, the degrees freedom is 4. Thus, the degrees of freedom for this system become zero by determining the initial content ratio of the slag components among MnO, SiO_2, Fe_tO CaO and P_2O_5, having degrees of freedom of 4. Therefore, the present system can attain the equilibrium as long as the slag composition does not change and remains in a steady and constant state through the experiments.

2-4. Sample analysis

After equilibration, the crucible was quickly removed from the furnace and cooled in a jetting argon gas. The slag and metal were separated each other from the sample. The slag was magnetically selected to eliminate the contamination of metallic iron. Then, they were subject to chemical analyses. Containing SiO_2, the sample was dissolved into aqueous solution of hydrochloric acid and nitric acid with addition of small amount of hydrofluoric acid. Then, the content of manganese, silicon, iron, calcium, magnesium and phosphorus in the slag and metal were measured by Inductively Coupled Plasma Optical Emission Spectrometry(ICP-OES). The oxygen content of the metal was determined with a LECO* oxygen analyser.

*LECO is a trademark of Leco Corporation, St. Joseph, MI.

3. Results and Discussion

3-1. Preliminary experiments

Figures 2 shows the change in content of each component in slag with the holding time for the system of 10CaO-52MnO-26SiO_2-10Fe_tO-2$Mg_2P_2O_7$ slag (on mass basis) and molten iron in an MgO crucible in an argon atmosphere at 1873 K. The content of each component shows constancy after about 4 h; thus, the holding time has been determined to be 6 h for equilibration combining the results for those in metal . In addition, the constancy in the slag composition confirms the attainment of equilibrium state in the present system.

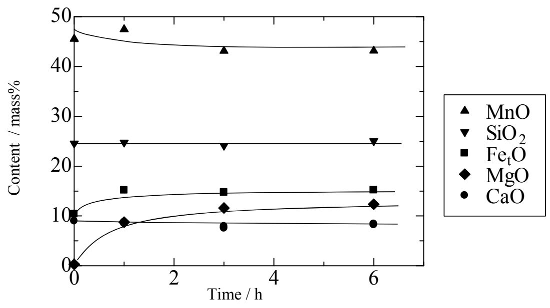

Fig.2 Content change of components in slag against time at 1873 K.

3-2. Experimental results

Table 2 gives all the results for the equilibrium experiments. The slags after experiment keeps the intended composition ratios among major components, MnO, SiO_2, FeO and CaO, with exception of considerable amount of MgO originating from the crucible. Iron ion may be present in the form of both divalent and trivalent cation. However, the present slag coexisted with molten iron and contained the limited amount of CaO as strongly basic oxide up to 20 mass%; thereby, the valency of iron ion could be shifted to two. Accordingly, all the iron ion has been treated as FeO in the calculation. On the basis of these experimental data, thermodynamic properties of each component in the slag have been elucidated in the following paragraphs. Table 3 lists the interaction parameters necessary for evaluation of the activity coefficient of each element in molten iron.

Table 2 Experimental results for the present system.

No.	Temp. / K	Chemical composition of slag / mass%						Impurity contents in iron / mass %		
		CaO	MnO	SiO_2	FeO	MgO	P_2O_5	P	O	Mn
1	1843	4.74	47.6	26.1	8.14	13.1	0.130	0.318	0.0272	0.443
2		10.4	46.1	26.6	7.82	8.53	0.237	0.287	0.0301	0.459
3		15.9	44.4	25.1	8.38	5.62	0.335	0.215	0.0285	0.491
4	1873	5.02	43.6	27.8	8.77	15.0	0.125	0.317	0.0386	0.426
5		10.3	43.0	26.6	8.43	11.4	0.219	0.289	0.0375	0.487
6		15.6	41.9	25.3	9.27	7.34	0.306	0.196	0.0406	0.509
7		19.7	40.4	24.5	8.88	5.64	0.699	0.218	0.0360	0.473
8	1923	4.92	44.2	26.6	7.41	16.7	0.0646	0.376	0.0353	0.706
9		10.7	41.6	26.1	6.94	14.9	0.119	0.318	0.0352	0.803
10		16.1	42.9	24.7	8.12	8.49	0.230	0.282	0.0447	0.812
11		19.6	41.4	23.5	8.27	6.57	0.551	0.395	0.0394	0.780

Table 3 Interaction coefficients between i and j, e_i^j at 1873 K[7]

	Mn	O	P
Mn	0.0034	-0.083	-0.0035
O	-0.021	$-1750/T+0.76^{8)}$ (1823-1923 K)	0.07
P	0	0.13	0.053

3-3. Activity coefficient of P_2O_5 in the MnO-SiO_2-Fe_tO-CaO-MgO-P_2O_5 system

Equation (2) defines the phosphorus distribution between slag and metal;

$$L_P \equiv (mass\%P)/[mass\%P] \qquad (2)$$

where (mass%P) and [mass%P] are phosphorus content in slag and iron on mass basis. The distribution ratio of phosphorus, L_P, increases with an increase in CaO content, indicating attracting force between P_2O_5 and CaO supported by the fact that the former is acidic oxide and the latter is basic one. The L_P decreases with an increase in temperature, indicating the fact that the formation of phosphorus oxide is an exothermic reaction.

Phosphorus and oxygen in molten iron react to form P_2O_5 in the present system according to the following equation;

$$2\underline{P}(\text{mass\% in Fe})+5\underline{O}(\text{mass\% in Fe})=P_2O_5(l) \qquad (3)$$

$$\Delta G_{P2O5}^{\circ} = -781100+557T[J/mol][9] \qquad (4)$$

Hence, there appears activity coefficient of P_2O_5 in the slag in the Raoultian standard, γ_{P2O5}, in ΔG° for Reaction (3) as Eq. (5);

$$\Delta G_{P2O5}^{\circ} = -RT\ln\{(\gamma_{P2O5} \cdot X_{P2O5})/(f_P^2[mass\%P]^2 \cdot f_O^5[mass\%O]^5)\} \qquad (5)$$

where X_{P2O5} is the molar fraction of P_2O_5, f_P is the activity coefficient of phosphorus relative to 1 mass % Henrian standard derived from the interaction parameters in Table 3. The obtained activity coefficient,γ_{P2O5},from Eq.(5) was multiply-regressed as functions of temperature and content of CaO, MnO and MgO to be Eq.(6) . Figure 3 shows the regression lines at each temperature.

$$\log \gamma_{P_2O_5} = -29.3(X_{CaO} + 0.88X_{MgO} + 0.61X_{MnO}) - 37200/T + 19.8 \quad (6)$$

More strictly, the logarithm of activity coefficient of P_2O_5 should be described by using four terms, that is, composition term, inverse temperature term, their cross term, and constant term according to the regular solution model[10]. In this part, the form of Eq.(6) is adopted due to insufficiency of data to determine each modulus for four terms. However, each modulus of content term in Eq. (6) is close to the optical basicity value listed in Table 4, presumably showing each contribution to the tendency of the slag to accept P_2O_5. At any rate, this formula is useful for the prediction of the activity coefficient of P_2O_5 by the content of each oxide component and temperature; thereby, industrially meaningful.

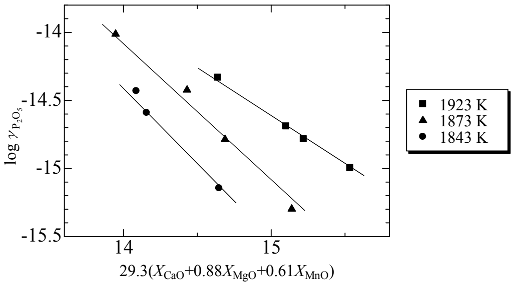

Fig.3 Relationship between log γ and content of CaO, MgO and MnO

Table. 4 Optical basicity of pure oxide[11]

Component	CaO	MnO	SiO_2	FeO	MgO	P_2O_5
Optical basicity, Λi	1.0	0.59	0.48	0.51	0.78	0.40

3-4. Phosphate capacity for the MnO-SiO_2-Fe_tO-CaO-MgO system

Equation (7) expresses the phosphate ion formation reaction from the gaseous phosphorus, oxygen and oxide ion in the slag;

$$1/2P_2(g)+5/4O_2(g)+3/2(O^{2-})=(PO_4^{3-}) \quad (7)$$

Wagner[12] has proposed phosphate capacity to evaluate the phosphate absorbing ability of a slag as follows;

$$C_{PO_4^{3-}} \equiv (mass\%PO_4^{3-})/(P_{P_2}^{1/2} \cdot P_{O_2}^{5/4}) = K_7 \cdot a_{O^{2-}}^{3/2}/f_{PO_4^{3-}} \quad (8)$$

where $(mass\%PO_4^{3-})$ is the content of phosphate ion on mass basis, P_i is the partial pressure of species i, K_7 is the equilibrium constant of Reaction (7), $a_{O^{2-}}$ is the activity of oxide ion and $f_{PO_4^{3-}}$ is the activity coefficient of phosphate ion relative to 1 mass % Henrian standard. The right-hand side of Eq. (8) describes the nature of a slag, each term of which cannot be determined separately. However, measurable values in the middle can give the value for phosphate capacity. To know the partial pressure of phosphorus and oxygen, one requires the standard Gibbs energy for the Reactions of Eqs. (9) and (11) and the experimental contents of phosphorus and oxygen in iron.

$$1/2P_2(g) = \underline{P}(\text{mass\% in Fe}) \quad (9)$$

$$\Delta G_P^\circ = -155\,700 + 5.4\,T\ [\text{J/mol}][13] \quad (10)$$

$$1/2O_2(g) = \underline{O}(\text{mass\% in Fe}) \quad (11)$$

$$\Delta G_O^\circ = -117\,110 - 3.39\,T\ [\text{J/mol}][14] \quad (12)$$

The phosphorus content in the slag provides the mass content of phosphate, (mass% PO_4^{3-}). Then, the phosphate capacity can be calculated from the data experimentally obtained. Figure 4 shows the phosphate capacity as functions of CaO content for each temperature level, together with the data for the slag without CaO[5]. The phosphate capacity increases with an increase in CaO content and decreases with an increase in temperature. This result confirms that the addition of CaO is effective to improve the phosphate absorbing ability of the present system.

For the total understanding of the contribution of all the oxide components, the optical basicity would be helpful since the basicity of the slag may be major factor essential to the phosphate absorbing ability. The following formula evaluates the theoretical value of optical basicity for a given slag with a certain composition;

$$\Lambda = \Sigma X_i n_i \Lambda_i / \Sigma X_i n_i \quad (13)$$

where X_i is molar fraction of component i, n_i is the number of oxygen atoms which belong to each oxide and Λ_i is the optical basicity of component i. Table 4 gives the values used in the calculation. Figure 5 shows the relationship between optical basicity and the phosphate capacity. Much better linearity than shown in Fig. 4 confirms the reasonability of expressing phosphate absorbing ability by way of optical basicity. Moreover, the phosphate capacity derived here was multiply-regressed as functions of temperature and optical basicity as Eq. (14). Figure 6 shows the regression lines at each level of optical basicity as functions of temperature.

$$\log C_{PO_4^{3-}} = (11\,300\Lambda + 54\,560)/T + 18.30\Lambda - 27.4 \quad (14)$$

Accordingly, the phosphate capacity for a given system could be evaluated by optical basicity and temperature at least within the composition range of the present system.

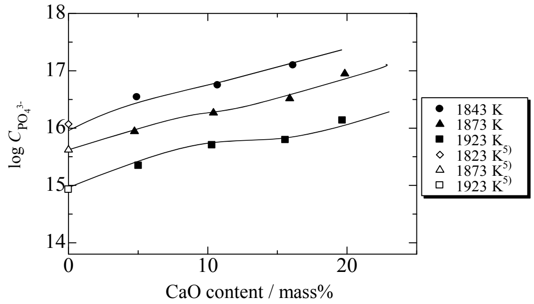

Fig. 4 Phosphate capacity for the CaO-MnO-SiO_2-MgO system against CaO content

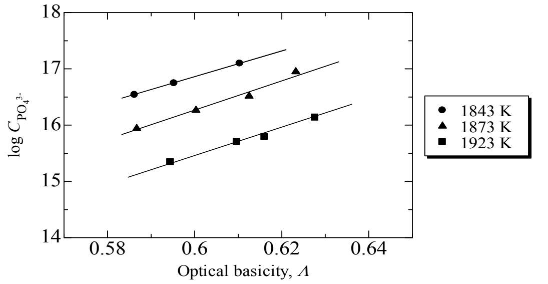

Fig. 5 Phosphate capacity for the CaO-MnO-SiO_2-MgO system against optical basicity.

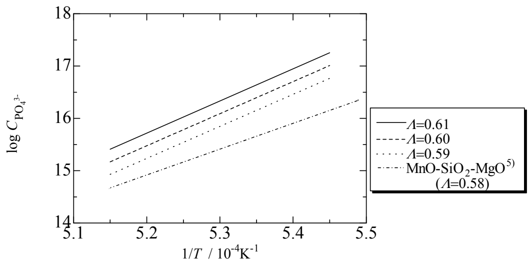

Fig. 6 Temperature dependence of phosphate capacity for the CaO-MnO-SiO_2-MgO system

3-5. Dissolution enthalpy of phosphorus oxide into the MnO-SiO_2-Fe_tO- CaO-MgO system

Equation (15) expresses the phosphate formation reaction including dissolution reaction into the slag. The equilibrium constant of the reaction is Eq. (16).

$$1/2P_2(g) + 5/4O_2(g) = (PO_{2.5}) \qquad (15)$$

$$K_{PO_{2.5}} = f_{PO_{2.5}}\ (mass\%PO_{2.5})/(P_{P_2}{}^{1/2} \cdot P_{O_2}{}^{5/4}) \qquad (16)$$

The van't Hoff equation relates the temperature dependence of equilibrium constant and enthalpy change for this reaction as follows;

$$\partial \ln K_{PO_{2.5}} / \partial (1/T) = -⊿H_{15} /R \qquad (17)$$

It should be noted that the equilibrium constant of left-had side is essentially identical with phosphate capacity expressed by Eq. (8). Then, assuming that the activity coefficient of phosphorus oxide, $f_{PO_{2.5}}$ does not change by temperature, Eq.(17) can be rearranged as Eq. (18) by using phosphate capacity, $C_{PO_4^{3-}}$,

$$\partial \log C_{PO_4^{3-}} / \partial (1/T) = -⊿H_{15}/2.303R \qquad (18)$$

The value for the left hand side of this equation can be easily derived from Eq. (14), leading the enthalpy change for the reaction of Eq.(15) as function of optical basicity expressed by Eq. (19).

$$⊿H_{15} = -216.0\,\Lambda - 1044 \text{ [kJ/mol]} \qquad (19)$$

The enthalpy change decreases with an increase in optical basicity, proving that the phosphorus oxide can exist more stably in the slag with higher optical basicity. The standard enthalpy of formation reaction of phosphorus oxide, without dissolution, is known as Eq. (21);

$$P_2(g) + 5/2O_2(g) = P_2O_5(l) \qquad (20)$$

$$⊿H_{P_2O_5} = -1\ 534\ 000 \text{ J/mol[15]} \qquad (21)$$

Accordingly, subtraction of the value by Eq. (21) from that by Eq. (19) gives the enthalpy change including only the dissolution reaction of phosphorus oxide into the slag as follows;

$$PO_{2.5}(l) = (PO_{2.5}) \qquad (22)$$

$$⊿H_{PO_{2.5}} = -216.0\,\Lambda - 277.0 \text{ [kJ/mol]} \qquad (23)$$

Extrapolation of this relation to the region where the Λ value is 0.58 gives us the ΔH value of −402 kJ/mol, which show a large discrepancy with the ΔH value of −166 kJ/mol for the MnO-SiO_2-MgO system[5] having the same Λ value of 0.58. This comparison shows us the system containing CaO is much more capable of absorbing phosphorus oxide than the system without CaO.

3-6. Estimation of phosphorus distribution in a practical process

The experimentally obtained phosphate capacities can predict the phosphorus distribution ratio between slag and metal which is the direct indicator of the refining degree in the practical process. For instance, consider a weak deoxidation in a ladle furnace during a secondary refining process at 1873 K assuming the final oxygen content of the molten iron to be 40 ppm. Figure 7 shows the phosphorus distributions ratio derived from the empirical phosphate capacities on the basis of Eq. (24) for the present system along with CaO content at various temperatures.

$$L_P = (mass\%P)/[mass\%P] = (M_P/M_{PO_4^{3-}})C_{PO_4^{3-}} \cdot f_P f_O^{5/2}[mass\%O]^{5/2}\exp\{(\Delta G_P^\circ + 5/2\,\Delta G_O^\circ)/RT\} \quad (24)$$

where M_i denotes atomic or molecular mass of component i. The phosphorus distribution ratio varies from 0.0003 to 0.008 showing about one and a half order difference; however, the value is not large enough to remove a significant amount of phosphorus from steel. Therefore, more addition of CaO would be necessary to control the phosphorus content in the steel, in particular, originating from iron resource with high phosphorus contamination. Further investigation will be expected in higher CaO content region for the similar deoxidation slag systems.

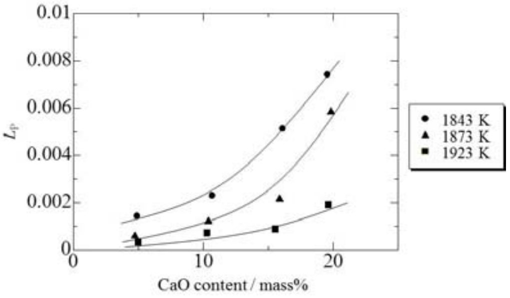

Fig. 7 Calculated value of distribution ratio of phosphorus

4. Conclusions

Effect of CaO on absorbing ability of phosphorus for the $MnO-SiO_2-Fe_tO-CaO-MgO$ system has been investigated by a chemical equilibration technique. The phosphorus distribution ratio has been estimated in a practical condition. The findings are summarised as follows;

・The phosphate capacities for the present system with CaO content from 4.73 to 19.6 mass% have been determined to be from 2.22×10^{15} to 1.25×10^{17} at temperatures from 1843 to 1923 K and obtained as functions of optical basicity and temperature;

$$\log C_{PO_4^{3-}} = (11\,300\Lambda + 54\,560)/T + 18.30\Lambda - 27.43$$

・The enthalpy change for the dissolution reaction of P_2O_5 has been obtained as functions of optical basicity;

$$\Delta H = -216.0\Lambda - 277.0 \text{ [kJ/mol]}$$

・Estimated phosphorus distribution ratio between the present slag and molten iron varies from 0.0003 to 0.008 by adding CaO in a moderate deoxidation condition. Addition of CaO improves dephosphorising ability of this system to some extent.

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