SANO, N., and KATAYAMA, H. Dephosphorization of stainless steels. *INFACON 6. Proceedings of the 1st International Chromium Steel and Alloys Congress, Cape Town.* Volume 2. Johannesburg, SAIMM, 1992. pp. 25–33.

Dephosphorization of Stainless Steels

N. SANO* and H. KATAYAMA†

**The University of Tokyo, Tokyo, Japan*
†Technical Development Bureau , Nippon Steel Corporation, Tokyo, Japan

After briefly describing the importance of the dephosphorization of stainless steels from the viewpoint of their corrosion resistance, as well as their production methods, the physicochemical principles of dephosphorization by oxidation and reduction are presented in more detail.

When phosphorus is removed by oxidation, the oxidation loss of chromium has to be curtailed. The prevailing oxygen partial pressure is limited by the $CaO–CaO.Cr_2O_3$ equilibrium if CaO-bearing slags are used. Therefore, highly basic slags have been developed that can function effectively under relatively lower oxygen pressures. Some examples of their use are shown.

Dephosphorization under reducing conditions is a new concept and is effective for alloys containing a large amount of chromium. Test data on the use of $Ca–CaF_2$ and $CaC_2–CaF_2$ fluxes are shown, and the importance of the post-treatment of spent fluxes is pointed out for environmental reasons.

Any dephosphorization step must satisfy the requirements of present processes for the production of stainless steel in terms of the carbon and chromium contents. The most efficient way of producing stainless steels of low phosphorus content is proposed.

Introduction

It is well known that the resistance to stress–corrosion of austenitic stainless steels is markedly improved by lower phosphorus contents. For example[1], the time to failure of 20Cr–20Ni steels in a boiling $MgCl_2$ solution at 143°C, subjected to a stress of 30 kg/mm^2, is increased from 5 hours to 250 hours by a decrease in the phosphorus content from 0,03 to 0,003 per cent[1]. This improvement in stress–corrosion resistance is the main impetus behind the development of a novel process for the removal of phosphorus from stainless steels.

Conventional dephosphorization of steels has been based on the oxidation of phosphorus, followed by the absorption of the product in suitable slags. However, this principle cannot be applied to the refining of stainless steel because chromium is oxidized in preference to phosphorus, so that a new concept in the physical chemistry of dephosphorization of molten steel had to be developed.

Traditionally, the following techniques have been employed to control the phosphorus content of stainless steels. Firstly, coke with a low phosphorus content should be selected for the reduction of the chromium ore. The specified phosphorus content of stainless steels can be as low as 0,01 per cent. Secondly, low-carbon ferrochromium or electrolytic chromium of low phosphorus content should be used but, if this is done, the production cost is very high. Thirdly, plain carbon steels should be thoroughly dephosphorized before the addition of ferrochromium. The phosphorus content of conventional stainless steels can be controlled at a level of 0,03 per cent by the use of these methods, but it is not possible to achieve a phosphorus content of less than 0,02 per cent in this way.

As described in more detail by Izawa *et al.* at this meeting, a new smelting–reduction technique has been developed in Japan for the reduction of chromium ore. One of the features of this technique is that coal, rather than electrical power, is used as an energy source for the reduction. The phosphorus content of the metal can be as high as 0,075 per cent if low-grade coal is used. This problem has further motivated the development of a new technique for the removal of phosphorus from chromium steels.

Physicochemical Principles of Dephosphorization

It is well known that phosphorus has two valencies, P^{5+} and P^{3-}. Figure 1 shows the stabilities of the phosphates and phosphides of calcium and barium as a function of temperature. Since the oxygen partial pressure prevailing in iron- and steel-making is always in the stability area of phosphates, the dephosphorization of steels has traditionally been based on the oxidation of phosphorus according to Equation [1] or [2]:

$$\underline{P} + \tfrac{5}{4}O_2 + \tfrac{3}{2}O^{2-} = PO_4^{3-} \quad [1]$$

$$\underline{P} + \tfrac{5}{4}O_2 + \tfrac{3}{2}CaO = \tfrac{1}{2}Ca_3(PO_4)_2. \quad [2]$$

However, as indicated earlier, dephosphorization of chromium steels has necessitated a method not based on oxidation, which has led to the unconventional use of P^{3-}. By this technique, phosphorus is removed by reduction to P^{3-}:

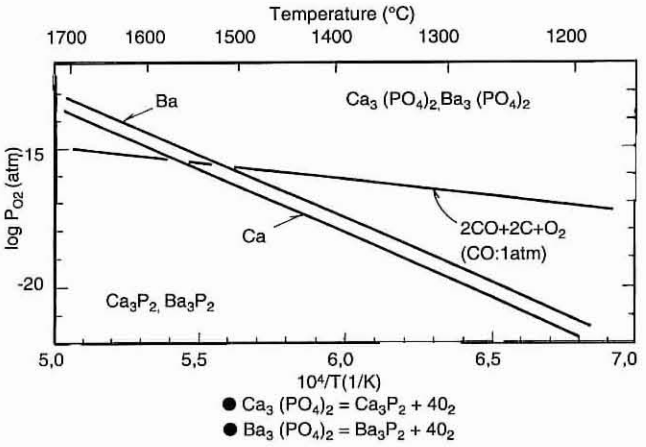


FIGURE 1. The solubility of phosphate and phosphide as a function of temperature and partial pressure of oxygen

$$\underline{P} + \tfrac{3}{2}O^{2-} = P^{3-} + \tfrac{3}{4}O_2 \qquad [3]$$

$$\underline{P} + \tfrac{3}{2}CaO = \tfrac{1}{2}Ca_3P_2 + \tfrac{3}{4}O_2. \qquad [4]$$

Figure 2 shows the phosphorus content of 41%CaO–59%Al_2O_3 melts at 1550°C, and at a partial pressure of phosphorus of 2,46 x 10^{-3} atm, as a function of the partial pressure of oxygen[2]. At a critical P_{O_2} value of $10^{-17,7}$ atm, the phosphorus content increases as the oxygen partial pressure is raised or lowered according to Equations [1] and [3]. This is in accordance with the trend shown in Figure 1. The dotted lines in Figure 2 show the expected slopes.

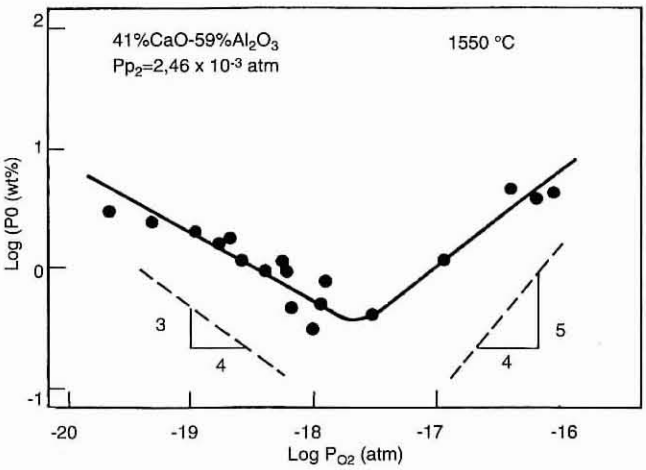


FIGURE 2. Variation of the phosphorus content of a CaO–Al_2O_3 melt with the partial pressure of oxygen

In the past decade, the two dephosphorization principles – oxidation and reduction – have been applied to the dephosphorization of stainless steels, and more details are given below.

Dephosphorization to Phosphate by Oxidation

According to Equation [1], dephosphorization can be enhanced by the use of a higher partial pressure of oxygen, more basic slags, and lower temperatures because of the exothermic nature of Equation [1]. However, thermodynamically, the oxygen partial pressure is fixed by Equation [5] and, at a higher P_{O_2} than this critical value, which is determined by the chromium content of the metal and the slag composition

$$\tfrac{4}{3}Cr + O_2 = \tfrac{2}{3}Cr_2O_3, \qquad [5]$$

chromium rather than phosphorus is oxidized. Equation [5] indicates that, as the chromium content is increased, the prevailing oxygen partial pressure decreases, rendering dephosphorization more difficult. Furthermore, the activity coefficient of phosphorus in iron is lowered by chromium. The interaction parameter, e_P^{Cr}, has a value[3] of -0,018. This is a further factor militating against the efficient removal of phosphorus from stainless steels. For these reasons, highly basic slags have been developed, which should, from a theoretical point of view, be effective even at lower oxygen partial pressures .

When CaO-bearing slags are used, Equation [6], instead of Equation [5], should be considered because of the formation of $CaO.Cr_2O_3$:

$$\tfrac{4}{3}Cr + O_2 + \tfrac{2}{3}CaO = \tfrac{2}{3}CaO.Cr_2O_3 \qquad [6]$$

$$\log PO_2\,(\text{atm}) = -\tfrac{4}{3}\log a_{cr} - \frac{47{,}000}{T} + 12{,}0. \qquad [7][4]$$

Suppose molten, carbon-saturated, 13%Cr–Fe (a_{cr}= 0,041) is dephosphorized by CaO-saturated slags at 1300°C, the oxygen partial pressure, calculated from Equation [7], is 9,5 x 10^{-17} atm. Phosphorus in stainless steels has to be removed at a partial pressure of oxygen below this critical value by the use of highly basic slags.

The ability of a slag to contain phosphorus is expressed by the phosphate capacity, which is defined by reference to Equation [1] as

$$C_{PO_4^{3-}} = \frac{(\%PO_4^{3-})}{PO_2^{5/4}\,P_{P_2}^{1/2}} = K_1 \frac{a_{O^{2-}}^{3/2}}{f_{PO_4^{3-}}}, \qquad [8]$$

where $a_{O^{2-}}$ is the activity of free oxide ions and can be regarded as a measure of the basicity of the slag; $f_{PO_4^{3-}}$ is the activity coefficient of PO_4^{3-} and depends on the slag composition; and K_1 is the equilibrium constant of Equation [1] and increases as the temperature is lowered. Equation [8] indicates that $C_{PO_4^{3-}}$ is increased as $a_{O^{2-}}$, or the slag basicity, is increased.

Traditionally, dephosphorization has been expressed by Equation [9] using molecular formalism:

$$2\underline{P} + \tfrac{5}{2}O_2 = (P_2O_5). \qquad [9]$$

By definition, $C_{PO_4^{3-}}$ is inversely proportional to the square root of $\gamma_{P_2O_5}$, the activity coefficient of P_2O_5.

Generally speaking, slags having larger phosphate capacities are more effective for dephosphorization. Figure 3 shows the phosphate capacities of a variety of basic slags, which were determined experimentally by the present authors. BaO-bearing slags clearly have larger $C_{PO_4^{3-}}$ values than CaO-bearing slags, and the temperature dependence of $C_{PO_4^{3-}}$ is fairly significant.

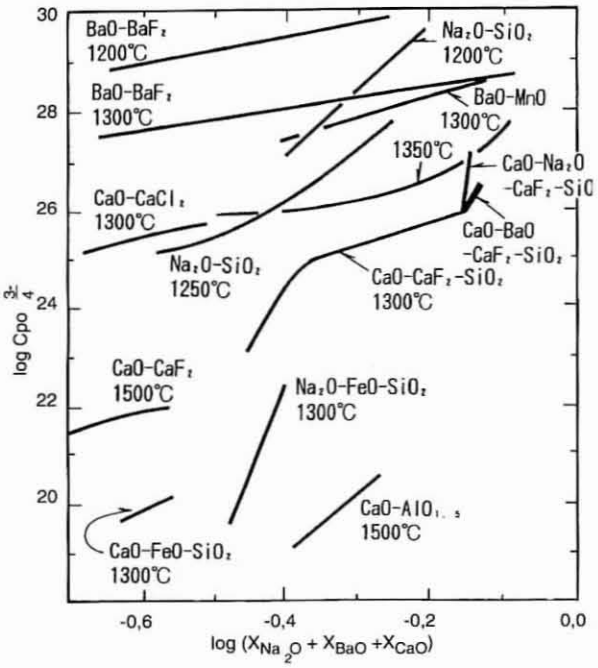


FIGURE 3. Phosphate capacities of various flux systems

Figure 4 shows the phosphorus partition ratio, *Lp*, between $CaO–CaF_2–SiO_2$ melts doubly saturated with CaO and $3CaO.SiO_2$ with a phosphate capacity of $10^{25.7}$, and carbon-saturated iron as a function of the chromium content[4]. The solid line with solid circles applies to the case of 1 atm of P_{CO}, indicating that the *Lp* decreases with increasing chromium content because of a negative value of e_P^{Cr}. The solid curve shows the calculated *Lp* subject to the condition that the partial pressure of oxygen is controlled by Equation [6]. Since the phosphate capacity of this slag is not large enough, the *Lp* value for a 16%Cr–C Fe alloy is too low for practical dephosphorization, suggesting the need for a slag with a higher phosphate capacity. The dotted line refers to a conceptual slag with a phosphate capacity of 10^{27}. Such a slag possesses a sufficiently high phosphate capacity for the efficient removal of phosphorus, as indicated by the phosphorus-distribution ratio, *Lp*.

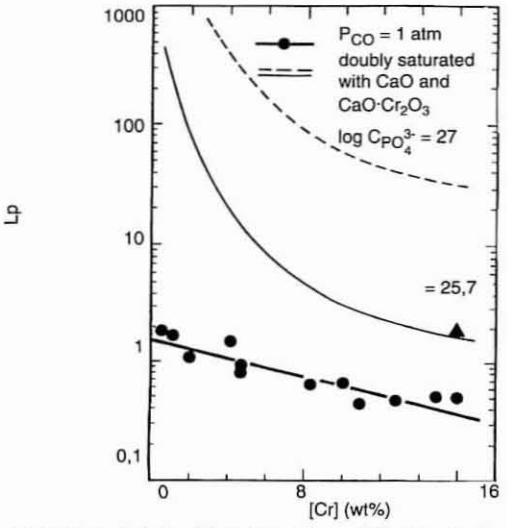


FIGURE 4. Relationship between *Lp* and Cr content of carbon-saturated iron at 1300°C equilibrated with $CaO–SiO_2–CaF_2$ melts saturated with CaO and $3CaO.SiO_2$

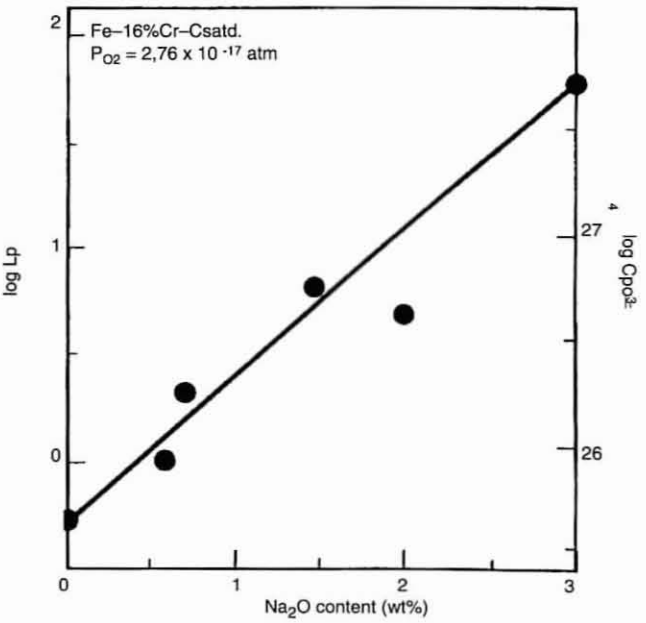


FIGURE 5. Relationship between log *Lp* and the Na_2O content of $CaO–SiO_2–CaF_2$ slag at 1300°C (CaO, $3CaO.SiO_2$ saturated)

According to Figure 3, $BaO–BaF_2$, $Na_2O–SiO_2$, and $CaO–SiO_2–CaF_2–Na_2O$ systems are candidate slags for the successful dephosphorization of stainless steels. Figure 5 shows that a small addition of Na_2O to the $CaO–SiO_2–CaF_2$ slag has a significant effect on dephosphorization[4]. With an Na_2O addition of 3 per cent, the *Lp* is expected to be as high as 200 for carbon-saturated 16%Cr iron at 1300°C at an oxygen partial pressure of $2{,}7 \cdot 10^{-17}$ with the coexistence of CaO and $CaO.Cr_2O_3$.

Although some oxidation of chromium is unavoidable, the chromium oxide content of the slag should be kept as low as possible. Figure 6 shows the solubility[5,6] of Cr_2O_3 and $CaO.Cr_2O_3$ in a $CaO–SiO_2–CaF_2$ melt at 1500°C. The Cr_2O_3 content at a double saturation of CaO and $CaO.Cr_2O_3$ is approximately 2 per cent. The value of *Lp* at this slag

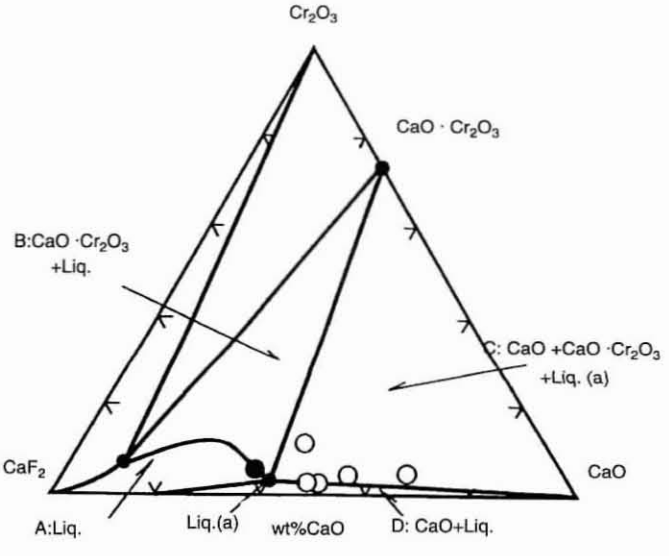


FIGURE 6. Iso-thermal sections of the phase diagrams of the system $CaO–CaF_2–Cr_2O_3$. The plotted data show the slag composition given in Figure 7

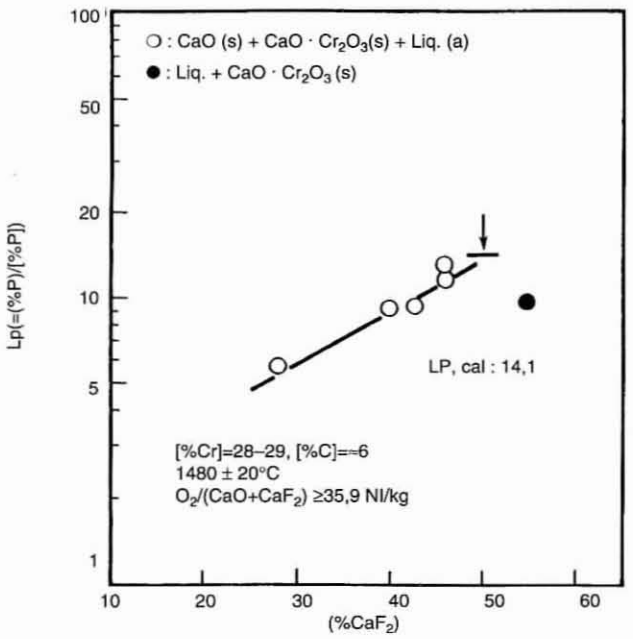


FIGURE 7. *LP* as a function of (%CaF_2)

composition obtained by flux injection – described in detail in Figure 7 – is in excellent agreement with the thermodynamic estimation based on Equation [7] and the $C_{PO_4}^{3-}$ value for the CaO–CaF_2 system shown in Figure 3.

The oxidant for the removal of phosphorus with CaO–CaF_2 slags is usually chromium ore. If Ca–CrO_4 is used instead, the performance is improved[7], indicating that dephosphorization proceeds preferentially to chromium oxidation. The recovery of phosphorus occurs towards the end of the treatment as a result of the attainment of equilibrium for both chromium and phosphorus between the metal and the slag. Accordingly, the injection of slag may be effective in that a fresh slag is supplied continuously. For example, CaO–CaF_2 slags were injected into 300 kg of an Fe–Cr–C melt with an O_2–Ar mixture as the carrier gas, yielding good dephosphorization, as shown[8] in Figure 8 and Table I.

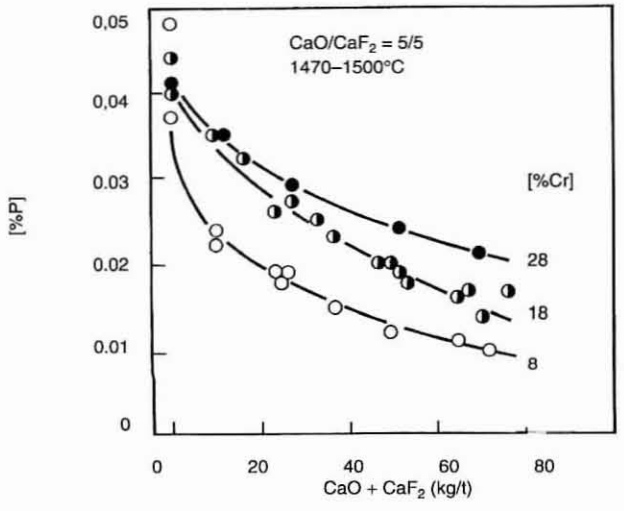


FIGURE 8. Influence of chromium content on dephosphorization

TABLE I
CONDITIONS FOR THE DEPHOSPHORIZATION OF Fe–C–Cr MELTS BY THE INJECTION OF CaO–CaF_2 FLUXES

Metal	300 kg
Chemical compositions	[Cr] : 8–28% [P] = [S] : ≈ 0,040 % [C] : ≈ 6 %, [Si] : tr
Flux	CaO–CaF_2 CaO/CaF_2 = 7/3–4/6
Injection feed rates	Flux: ≈1,5 kg/min O_2 : 60– 175 Nl/min (O_2/Ar=2/l)
Temperature	1470–1500°C

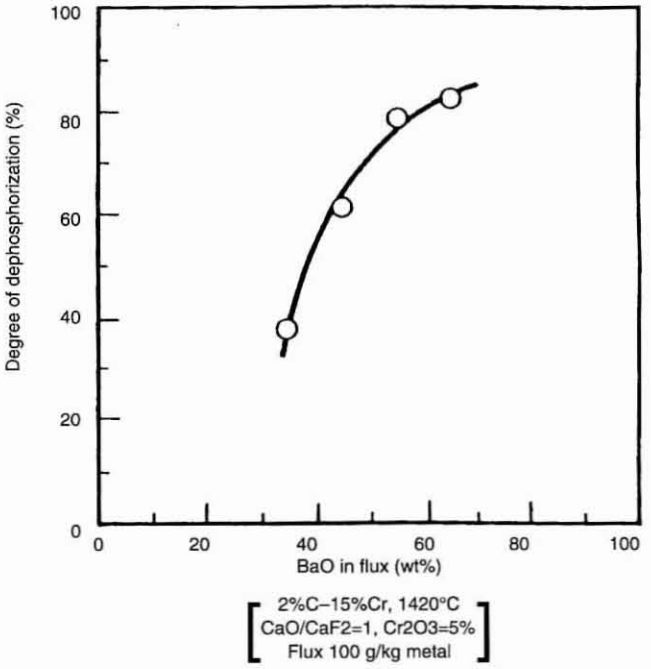


FIGURE 9. Effect of (BaO) on dephosphorization with a CaO–BaO–CaF_2–Cr_2O_3 flux

Barium oxide is more basic than CaO so that an improvement in dephosphorization is expected from its addition to CaO-bearing slags, as shown[9] in Figure 9.

Figure 10 shows the activity of P_2O_5 in the BaO–BaF_2–$BaCl_2$–CaO system. BaF_2 and CaO are more effective than $CaCl_2$ and CaO, respectively[10]. However, if the slag is kept saturated with CaO when BaO is replaced by CaO, the dephosphorization capability will not deteriorate, as expected from the recent measurement by the authors of the sulphide capacity of the BaO–BaF_2–CaO saturated system.

Figures 11 and 12 show thermodynamic and kinetic aspects in the dephosphorization of Fe–Cr–C melts by the BaO–BaF_2 system[11,12]. The BaO–$BaCl_2$ flux has been used in practice to dephosphorize crude stainless steels. Although

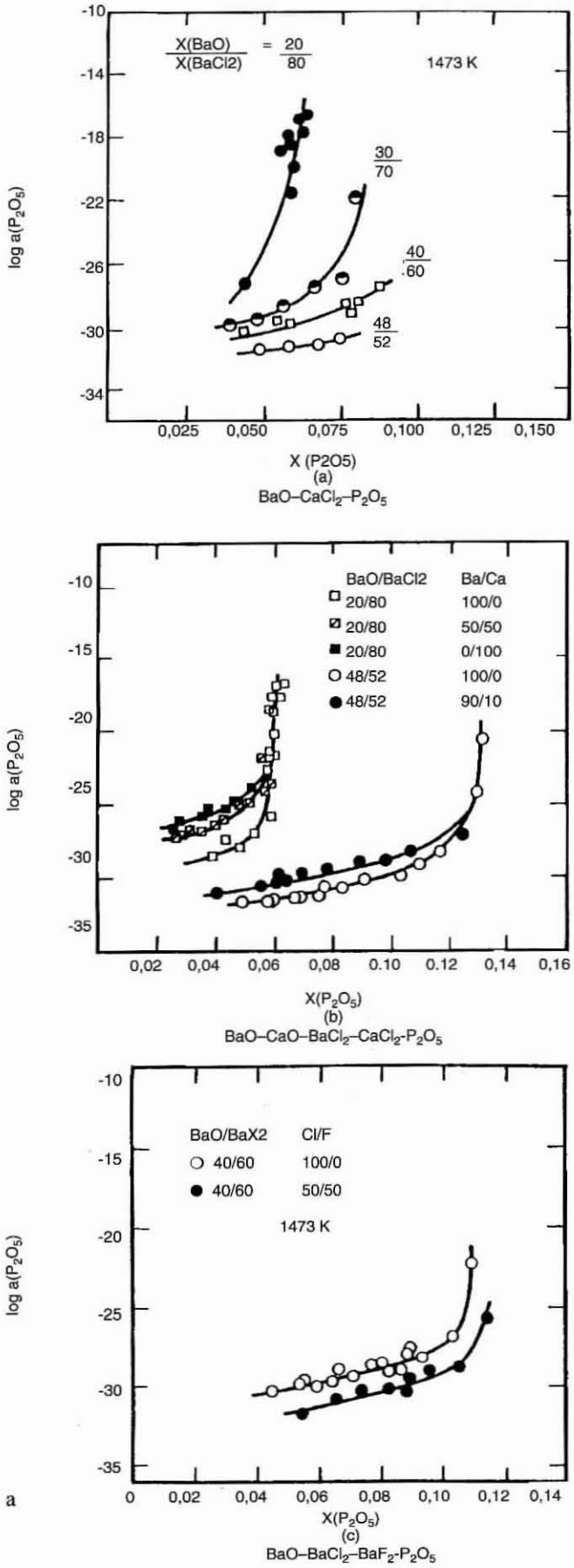


FIGURE 10. Activities of P_2O_5 in BaO–$BaCl_2$–BaF_2–$CaCl_2$–P_2O_5 melts

relatively large consumption of flux is needed, efficient dephosphorization at low carbon content (1 to 2 per cent) and high chromium content (up to 25 per cent) was attained by strong agitation of the metal bath in an AOD vessel[12].

Alkaline metal oxide is highly basic and is expected to be an efficient additive to CaO-bearing slags, as described earlier with reference to the Na_2O additions in Figure 5. However, Na_2O is too basic in the sense that it is easily reduced by co-existing chromium or carbon to form sodium vapour before reacting with the phosphorus. Therefore, thermodynamically, Li_2O is a more realistic additive because it is less basic than Na_2O.

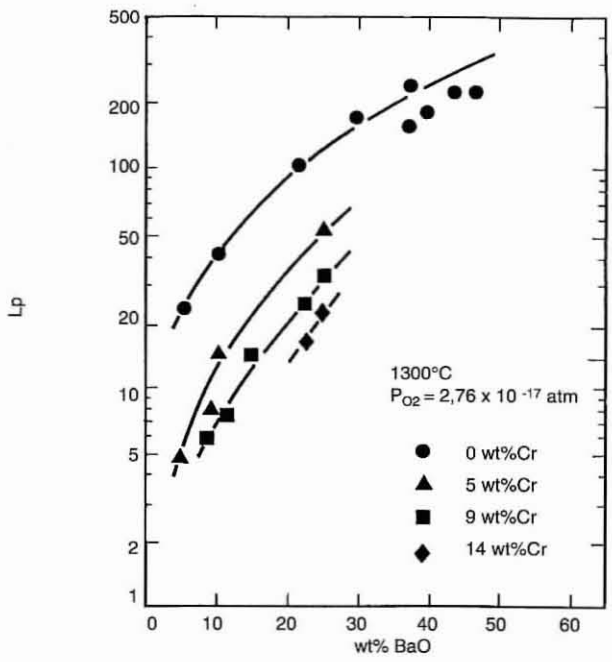


FIGURE 11. Phosphorus partition ratio between Fe–Cr–C $_{satd}$ alloy and BaO–BaF_2 melts as a function of the BaO content at 1300°C

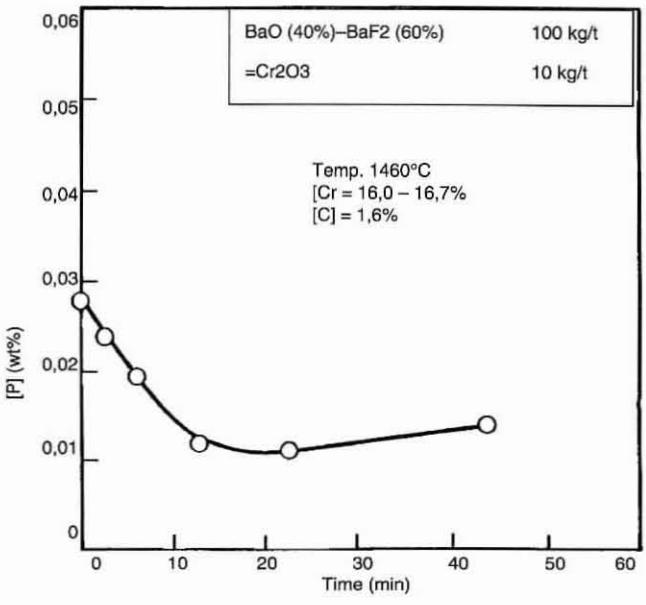


FIGURE 12. Dephosphorization of crude stainless steel with BaO–BaF_2–Cr_2O_3 flux

Figure 13 shows the results of dephosphorization of Fe–C–Cr melts by a 1%Li_2CO_3–14%CaO–47%CaF_2–29%FeO slag[13]. For an 18%Cr–6%C–Fe alloy, 60 per cent of the phosphorus was removed by the use of 70 kg/t of this flux. The Na_2SiO_4–NaF, Na_2CO_3–NaCl, $CaCl_2$, $FeCl_2$, K_2CO_3–KCl, and KF systems have been evaluated extensively for the removal of 60 to 80 per cent of the phosphorus. A typical example of dephosphorization by an Na_2SiO_4–NaF flux is shown[14] in Figure 14. The major disadvantage of these fluxes is their high cost.

Slags used for dephosphorization by oxidation are a combination of oxides (CaO, BaO, Na_2O, Li_2O etc.), halides (CaF_2, $CaCl_2$, $BaCl_2$, BaF_2, NaF, etc.), and oxidants (Cr_2O_3, $CaCrO_4$, Fe_2O_3, etc.). The functions of the halides are to lower the melting point of the slag and the activity coefficient of P_2O_5, and to raise the activity coefficient of Cr_2O_3.

The reasons for the recent success of the dephosphorization of stainless steels by oxidation is as follows. Firstly, the carbon content is increased to between 2 and 4 per cent, corresponding to the metal composition prior to being charged to an AOD furnace, resulting in less oxidation of chromium and an increased activity coefficient of phosphorus. Secondly, highly basic oxides such as BaO and Na_2O are used. Thirdly, some halides are added. The key to further success would be to avoid the contamination of the slags by refractory materials such as SiO_2 and Al_2O_3, and to keep the temperature at which the treatment is done as low as possible.

Dephosphorization by the Reduction of Phosphide

In the application of Equation [3] in practice, molten calcium and CaC_2–(CaF_2) fluxes have been used to keep the partial pressure of oxygen sufficiently low, as expressed by Equations [10] and [11]:

$$Ca(1) + {}^1/_2\, O_2 = CaO \qquad [10]$$

$$CaC_2 + {}^1/_2\, O_2 = CaO + 2\underline{C}\,. \qquad [11]$$

Accordingly, Equation [3] can be rewritten

$$\tfrac{3}{2}\underline{Ca} + \underline{P} = \tfrac{3}{2}Ca^{2+} + P^{3-}. \qquad [12]$$

Figure 15 shows the phosphorus content of molten iron as a function of its calcium content for various fluxes at 1600°C, satisfying the relationship[15] expected by Equation [12].

A pioneering test was successfully carried out by Nakamura *et al.*, who employed an ESR technique in the remelting of stainless steels using a Ca–CaF_2 flux, which lowered the vapour pressure of calcium[16]. Table II demonstrates a significant refining effect for impurities belonging to groups IV, V, and VI in the Periodic Table, including phosphorus.

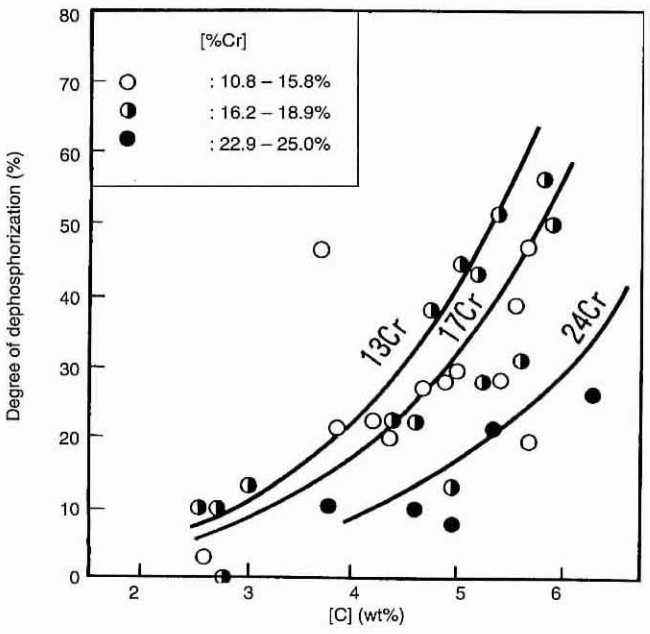
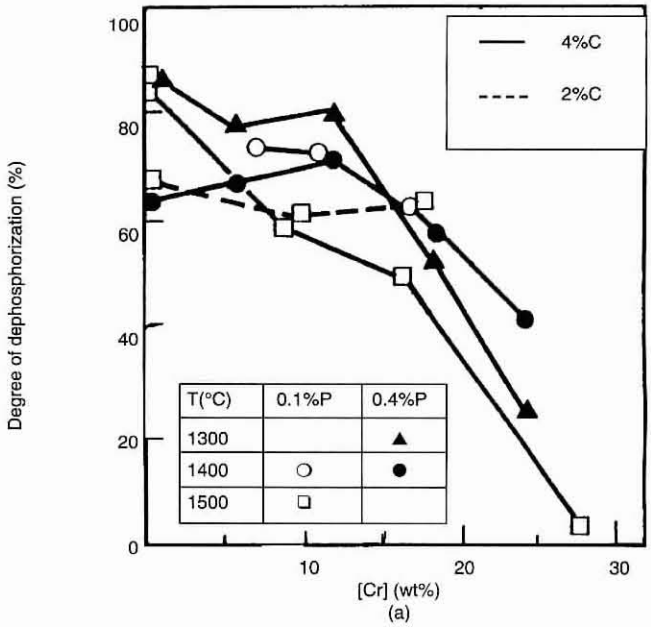


FIGURE 13. Effect of [%C] on dephosphorization with Li_2O–CaO–CaF_2–FeO flux
(Flux:70 g/kg of metal, 1490–1520°C)



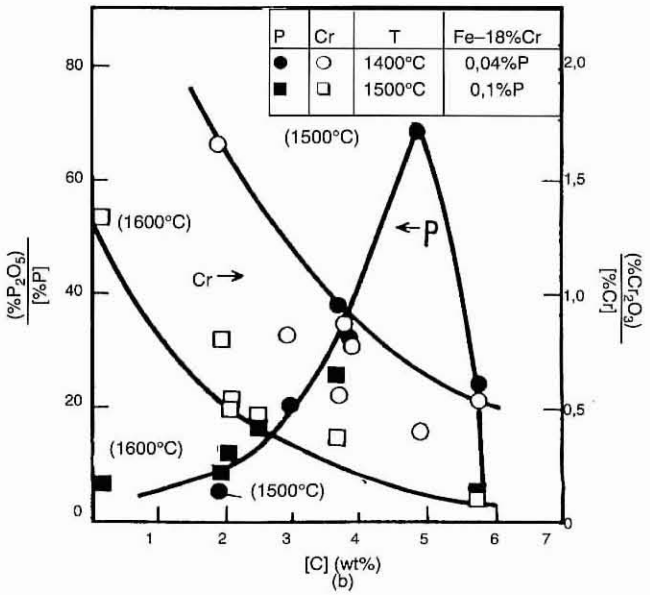


FIGURE 14. Effect of [%Cr] and [%C] on dephosphorization with Na_4SiO_4–50% NaF (30 g/300 g of metal)

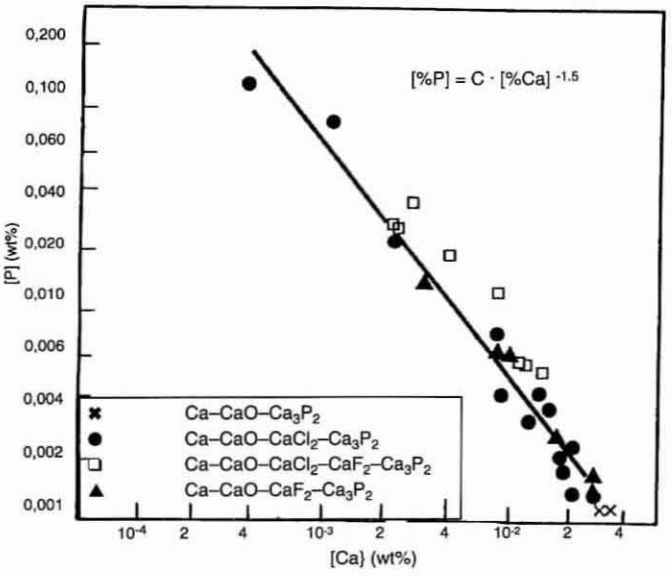


FIGURE 15. Equilibrium diagram of iron-melt dephosphorization with Ca [1600°C, P_{Ar}=10 bar, (%Ca_3P_2) : 1–2%]

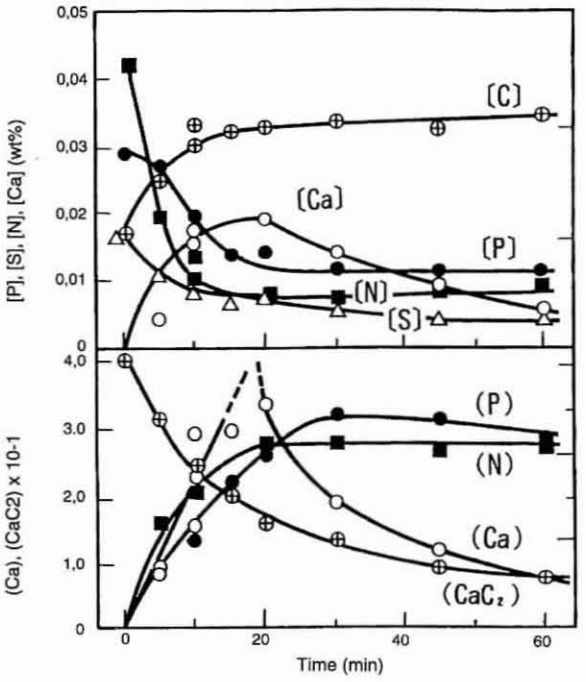


FIGURE 16. Change of composition after the addition of 50CaC_2–50CaF_2 flux on 18%Cr–8%Ni–0,5% steel with a rotating crucible

In practice, CaC_2 has been used instead of calcium for economic reasons. Figure 16 shows the removal of phosphorus, sulphur, and nitrogen, and the build-up of carbon in crude stainless steels[17]. The calcium content of the CaC_2–CaF_2 melt increased as the CaC_2 dissociated and then decreased as a result of the oxidation of impurities or evaporation.

The results[18] of an industrial-scale trial are shown in Figure 17. Figure 18 shows the effect of the carbon content of the metal on dephosphorization[17]. As expected from Equation [11] and shown in Figure 17, dephosphorization is decreased as the carbon content of the metal is increased[19]. The function of CaF_2 is to dissolve the CaC_2 so as to maintain a molten flux and to dissolve the calcium as a dissociation product of CaC_2, thereby avoiding its violent

TABLE II

REFINING EFFECTS OF Ca–CaF_2 FLUXES (HEAT 1) IN COMPARISON WITH THOSE OF Ca–CaF_2 FLUXES (HEAT 2) IN AN ESR PROCESS

	Electrode Position* mm	Transition element, %			I-b	II-b	III-b	IV-b group			
		Cr	Mn	Ni	Cu p.p.m.	Zn p.p.m.	Al p.p.m.	C %	Si %	Sn p.p.m.	Pb p.p.m.
		17,03	1,30	7,80	770	84	20	0,051	0,39	220	152
Heat 1	30	-	-	-	710	80	70	-	-	73	35
	120	-	-	-	710	77	<20	-	-	55	35
	210	17,08	1,30	7,74	710	78	<20	0,053	0,43	78	35
Heat 2	30	-	-	-	730	79	40	-	-	250	143
	120	-	-	-	770	80	<20	-	-	250	146
	210	17,08	1,25	7,78	770	73	<20	0,054	0,42	250	143

	Electrode Position* mm	V-b group, p.p.m.					VI-b group, p.p.m.				II-a
		N	P	As	Sb	Bi	O	S	Se	Te	Ca p.p.m.
		76	30	52	20	160	211	130	110	86	25
Heat 1	30	26	10	<20	<5	3	36	<50	40	12	80
	120	33	5	<20	<5	4	40	<50	40	11	110
	210	56	10	<20	<5	4	34	<50	<30	10	150
Heat 2	30	81	45	52	5	81	87	90	30	75	10
	120	80	35	52	5	78	83	130	80	74	10
	210	77	35	56	5	90	76	130	90	78	10

* Distance measured from the ingot bottom

evaporation. Figure 19 shows that CaF_2 additions up to 25 per cent are favourable because of an increasing calcium content in the flux. However, beyond that value, calcium reacts preferentially with the refractories or evaporates, so that the efficiency of dephosphorization drops drastically[17].

The major disadvantage of this process is that hazardous PH_3 is generated when the slag is exposed to moisture in the air. To solve this problem, the phosphide in the flux has to be oxidized to phosphate by the addition of iron ore or by the injection of oxygen. Figure 20 shows typical results of oxygen blowing. Most of the phosphide is oxidized to phosphate[18]. For industrial application of this process, a complete post-treatment of slags is most important for environmental reasons.

Summary

Although the dephosphorization of stainless steels was considered to be impossible in the past, it has been achieved in the past decade by the adoption of new physicochemical concepts. In the assessment of various techniques of dephosphorization, it is very important for one to determine whether the metal composition satisfies the requirements for the conventional stainless-steelmaking processes. Figure 21 is a summary of the various techniques in terms of carbon and chromium contents, and the optional products of the three stages of dephosphorization are apparent:

(1) high-carbon ferrochromium,

(2) medium-carbon stainless steels before decarburization

(3) low-carbon stainless steels before casting.

It has not been found possible to dephosphorize ferrochromium. The second possibility may be an option by the use of BaO or modified CaO-bearing slags for the oxidation of phosphorus. Alternatively, CaC_2–CaF_2 fluxes can be used under reducing conditions, and can be applied to high-chromium metal, followed by mixing with low-

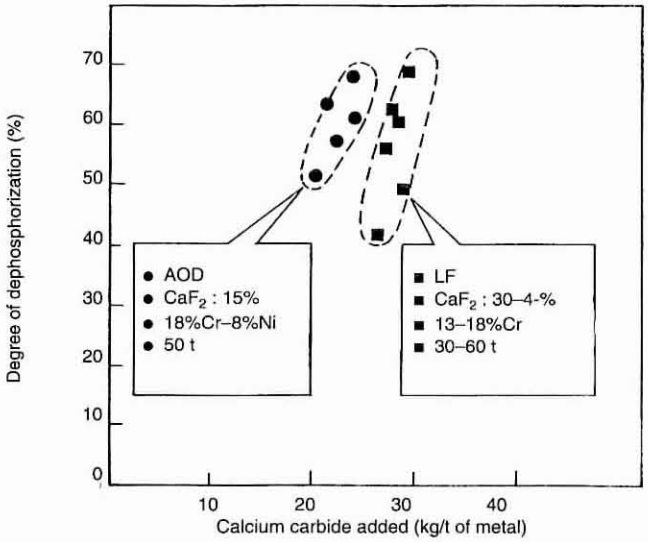


FIGURE 17. Dephosphorization with CaC_2–CaF_2 flux in a plant

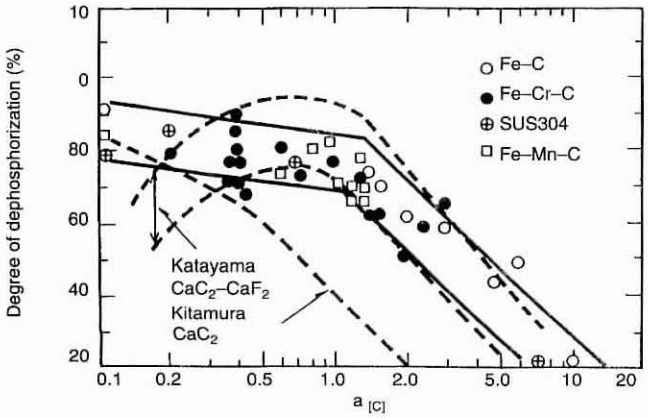


FIGURE 18. Influence of the activity of carbon in the metal on the dephosphorization (plots : experiment with 50 per cent CaC_2–50%CaF_2 flux in a rotating crucible)

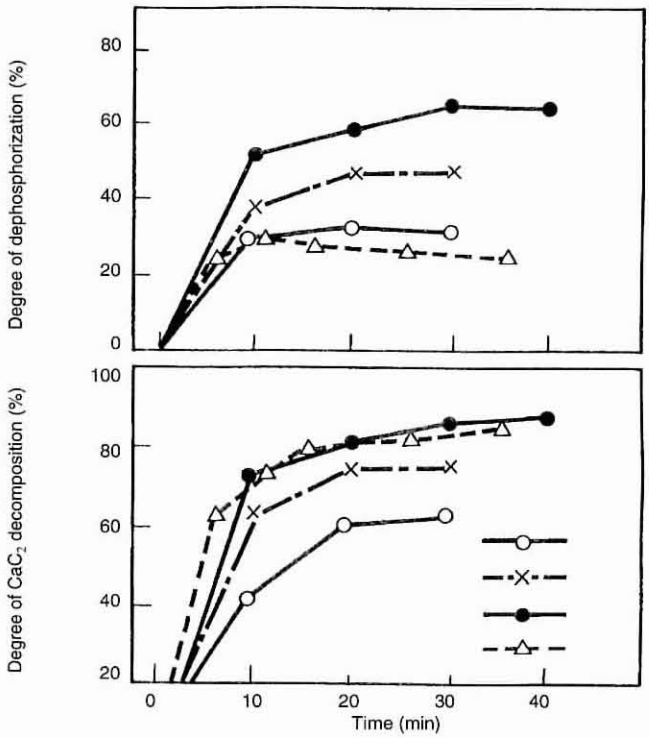


FIGURE 19. Influence of (%CaF_2) on the decomposition of CaC_2 and on the degree of dephosphorization in experiments of 600 kg scale with the top addition of flux

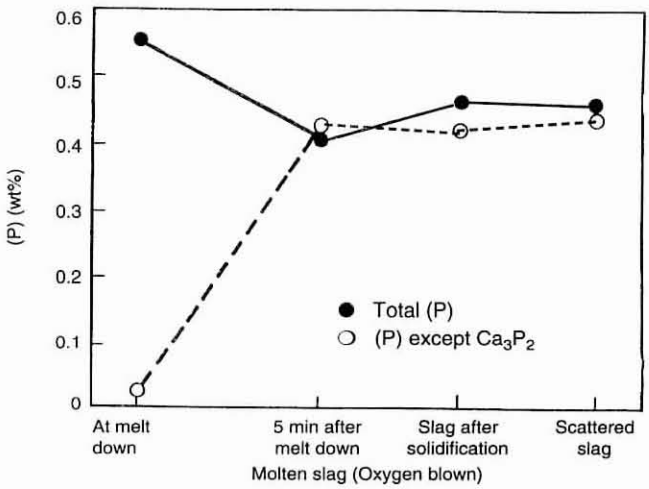


FIGURE 20. Results of oxygen blowing

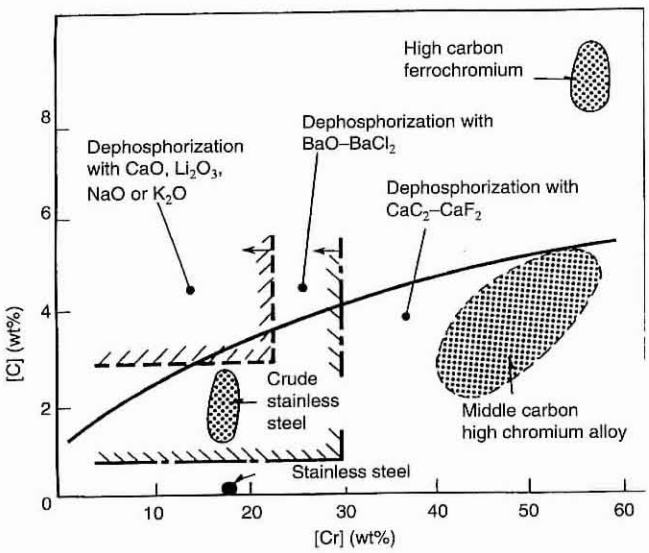


FIGURE 21. Suitable metal compositions for various methods of dephosphorization

carbon steels. The third case may be realized only by the use of Ca–CaF_2 fluxes.

In conclusion, it is believed that, for economic reasons, the most realistic approach is to dephosphorize crude stainless steels containing approximately 2 per cent carbon, which are supplied to the AOD process, by the use of CaO-bearing slags and some efficient additives such as Na_2O, BaO, etc. At the same time, the oxidation loss of chromium must be contained.

References

1. Kowaka, M., and Fujikawa, H. J.(1970). *Japan Institute of Metals*, 34, 1047.
2. Momokawa, H., and Sano, N. (1982). *Metall. Trans.* 13B, p. 643.
3. *Steelmaking data sourcebook.* (1988). The Japan Society for the Production of Science, 19th Committee on Steelmaking. Gordon and Breach.
4. Takiguchi, S., and Sano, N. (1988). *Tetsu-to-Hagané,* 74, p. 809.
5. Iwase, M. (1988). Text for the 122, 123rd Nishiyama Memorial Lecture Series, p. 87.
6. Nakajima, Y. (1991). *CAMP-ISIJ 4*, p. 50.
7. Nakao, R., Fukumoto, S., Takeuchi, H., and Tokuda, M. (1987). *Tetsu-to-Hagané*, 73, p. S.235.
8. Nakajima, Y. (1989). *CAMP-ISIJ 2*, p. 1120.
9. Inoue, S., Usui, T.,Yamada, K., and Kitagawa, T. (1986). *Tetsu-to-Hagané 72*, p. S.945.
10. Iwase, M., Fujiwara, H., Ichise, E., Ashita, K., and Akizuki, H. (1988/1990). *I & S 5*, p. 69, 6 and 51.
11. Hara, T., Tsukihashi, F., and Sano, N. (1990). *Tetsu-to-Hagané 76*, p. 352.
12. Matsuo, T., Ikeda, T., Kamekawa, K., and Sakane, T. (1986). *Tetsu-to-Hagané*, 79, p. A.33.
13. Yamauchi,T., Hasegawa, M., and Maruh-Ashi, S. (1981/1982). *Tetsu-to-Hagané,* 67, pp. S.188, 68. . S.291.
14. Kunisada, K., and Iwai, H. (1984). *Tetsu-to-Hagané*, 70, p. S.138.
15. Köhler, M., and Engel, H.J. (1984). *Proceedings of the 2nd International Symposium on Metallurgical Slag and Flux.* Fine, H.A., and Gaskell D.R. (eds.). AIME, p. 483.
16. Nakamura, Y., Tokumitsu, N., Harashima, K., and Segawa, K. (1976) *Trans. ISIJ*, 16, p. 623.
17. Harashima, K., Fukuda, Y., Kajioka,H., Nakamura, Y. (1986). *Tetsu-to-Hagané*, 72, p. 1685.
18. Katayama, H., Harashima, K., Kuwabara, M., and Fujita, M. (1986). *Tetsu-to-Hagané*, 72, p. A.41