DEPHOSPHORIZATION OF FERROMANGANESE ALLOY WITH FLUXES

KAZUAKI YAMAMURA

General Manager, Technical Department
Chuo Denki Kogyo Co., Ltd.

SHINICHI HOUNO

Assistant Manager, Technical Section
Chuo Denki Kogyo Co., Ltd.

TORU MIYASHITA

Assistant Manager, Technical Section
Chuo Denki Kogyo Co., Ltd.

YASUSHI KANNO

Staff, Technical Section
Chuo Denki Kogyo Co., Ltd.

(Speaker)

RYOHEI ISHIKAWA

Manager, Technical Section
Chuo Denki Kogyo Co., Ltd.

ABSTRACT

For the dephosphorization experiment of ferromanganese with CaC2-CaF2 Flux, medium and low carbon ferromanganese were melted at the specified temperature in a semi enclosed 10kg high-frequency induction furnace and in a 13t ladle.
The influences of temperature, CaC2 addition amount, atomosphere, metal [C] , and impurities in the flux were investigated.
As the result, with addition of 30kg CaC2/t-15kg CaF2/t to a 13t ladle, medium carbon ferromanganese with P 0.041% was obtained.

Introduction

In recent years, together with the tendency towards higher qualities for high Mn steel like high Mn nonmagnetic steel, structural steel for extremely cold regions, etc., the demand for low phosphorus ferromanganese has become stronger. Conventionally, there were the following five methods for the production of low phosphorus ferromanganese.

(1) Reduction of Mn ore with carbonaceous material and removal of phosphorus as spiegel for production of low phosphorus ferromanganese slag. By forther reduction of the obtained slag with low phosphorus carbonaceous material, low phosphor, high carbon ferromanganese is produced. *1

(2) Silicomanganese with a high[Si]content is treated with alkaline earth metal oxide-fluorite flux for production of low phosphorus, high[Si]silicomanganese. *2

(3) Low phosphorus ore is used as raw material, silicomanganese is produced by the normal process, and low phosphorus, medium carbon ferromanganese is produced by removing silicon from this material with low phosphorus ore.

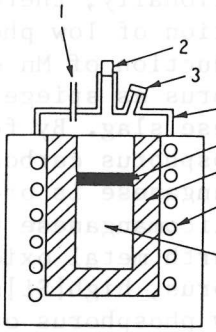
(4) Production of low phosphorus ferromanganese by reaction of the slag resulting from production of medium or low cartbon ferromanganese or silicomanganese in a reactor with ferrosilicon. *3

(5) Treatment of granular high carbon ferromanganese with Ca-CaCl2 type flux or Mg-MgCl2 type flux. *4

However, low silicon and low carbon in addition to low phoshorus are required for high grade steel. Accordingly,quality correspondence is not possible with method (1) for manufacture of high carbon ferromanganese, method (2) with high[Si]and method (3) with comparatively high phosphorus For method (4), the equipment costs are high and the productivity is low, while for method (5) realization is difficult in regard to productivity and processing expenses. Here, we have investigated a method with phosphorus removal for low carbon ferromanganese. As the result, we have confirmed that industrial production of low phoshorus, medium carbon ferromanganese with[P]0.05% or less is possible by processing with carbide-fluoride (CaC2-CaF2) type flux *5. In regard to phosphorus removal for ferroalloy by CaC2-CaF2 flux, there is the experiment report for ferrochrome by Nakamura et al., *6 but no research is to be found in regard to ferromanganese.

Experiment method

1. Experiments with a 10kg High-frequency induction furnance
Fig. 1 shows the experiment equipment. For the experiment, ferro-manganese was melted at the specified temperature in a semi-enclosed 10 kg high-frequency induction furnace in an argon atmosphere. Sampling of the melt was executed at specified intervals by sucking up with a quartz tube after flux addition to the melt. The quality of flux is shown in Table 1. CaC2 for ingot steel desulfurization with few impurities was used. Fluorite as the original mineral or mixed with refined fluorite according to the experiment conditions was used. The experiment conditions are shown in Table 2. The influences of temperature, CaC2 addition amount, atmosphere, metal [C], and impurities in the flux onto the dephosphorization were investigated.



1) Argon gas entrance
2) Flux entrance
3) Window
4) Hood
5) Flux
6) Molten metal
7) MgO crucible
8) Induction coil

Fig. 1. Schematic diagram of experimental apparatus.

Table 1. Quality of flux

	CaC_2	CaF_2	SiO_2	CaO	Al_2O_3	P	S
CaC_2	83%	—	1.5%	11.5%	0.8%	0.02%	0.9%
Refined CaF_2	—	96.7%	0.5%	1.0%	0.2%	0.01%	0.02%
CaF_2	—	84.0%	14.0%	1.4%	0.4%	0.02%	0.02%

Table 2. Experimental conditions

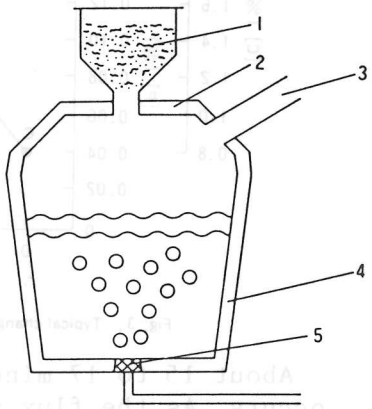
Items	Experimental conditions	
Initial component of melt	Mn	73.5 ~ 75.5 %
	C	1.0, 1.8, 3.4, 4.4, 5.2, 6.2 %
	Si	1.2 ~ 1.5 %
	P	0.14 ~ 0.17 %
Atomosphere	Air, Argon, Nitrogen	
Temperature	1450 ~ 1500°C	
CaC_2 amount	10, 20, 30, 50 Kg/t	
CaC_2/CaF_2	2.0	
SiO_2 in CaF_2	1.0, 5.0, 10.0, 14.0 %	

As the experiments were executed mainly at 1450 to 1500°C, the CaF2 amount was selected as a dissolvable ratio from the equilibrium state diagrams *7.

2. Actual equipment experiments

For the actual equipment experiments, melt tapped from a 6000 kVA 3-phase Heroult electric furnace was used. The production quantity per tap was 13 t. Ladle outline and dimensions are shown in Fig. 2. After slag removal for the melt tapped into a normal ladle, the melt was transfered to a ladle for dephosphorization. A magnesia porous plug was installed in the center of the bottom of the ladle for dephosphorization treatment. A ladle, for which the brick lining had been exchanged just before the experiment, was used to prevent flux pollution by slag.

Size	
Internal diameter	2 m
Depth of ladle	2 m
Depth of metal	1.6 m



1) Flux
2) Hood
3) To dust collector
4) Ladle (MgO-dromite brick)
5) Porous plug (MgO)

Fig. 2. Schematic diagram of operating apparatus

For the melt transferred into the treatment ladle, argon gas was blown through the porous plug for stirring, a hood was placed onto the ladle, and flux was added via the chute installed on the hood. For comparison, test was executed without gas stirring, where the flux was placed on the treatment ladle bottom and then the melt was poured in. And test also was executed with argon gas stirring in an air atmosphere.

Experiment results and investigations

1. High-frequency induction furnace

(a) Experiment situation

Directly after flux addition, white smoke was blown out from the gap of the hood and ladle. After several minutes, the white smoke started to burn with emission of a strong light. It is believed that CaC2 in the furnace was decomposed, that the resulting Ca was vaporized, blown out, and burned. The flame reached a maximum about 10 to 15 minutes after flux addition, and afterwards it decreased. The flame also decreased with increasing [C] content in the ferromanganese, and no flame was observed in the experiment where flux was added to high carbon ferromanganese.

The typical component behavior after flux addition is shown in Fig. 3. After flux addition, recarburizing progresses rapidly,

and dephosphorization progresses with this. The change of the [Mn] in the melt is small.

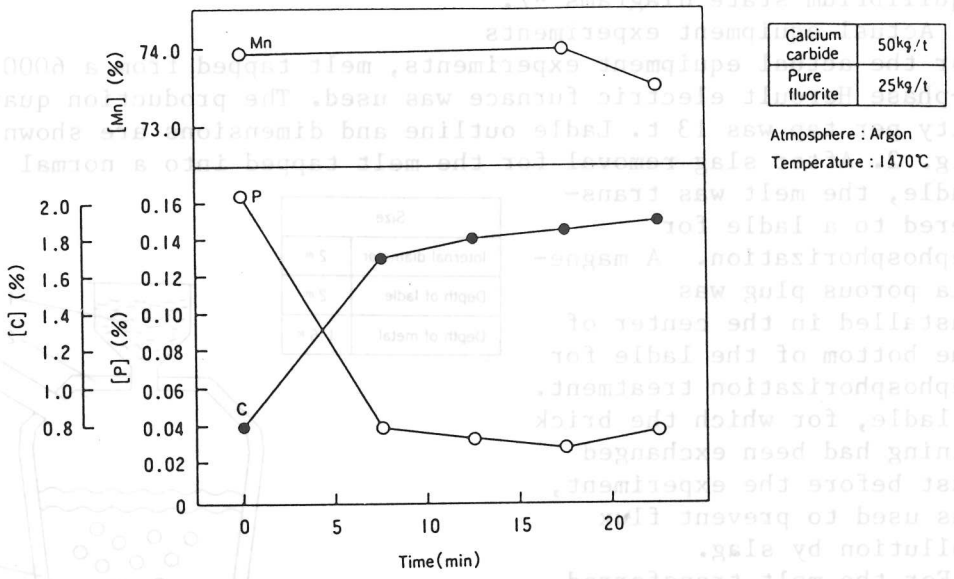


Fig. 3. Typical change in composition of molten Ferromangan

About 15 to 17 minutes after flux addition, rephosphorization occurs. As the flux after treatment shows a carbide smell, it is believed that dephosphorization with CaC2-CaF2 type flux occurs according to equation (1).

$$2\,\underline{P} + 3(CaC2) = (Ca3P2) + 6\,\underline{C} \qquad (1)$$

The standard free energy change ΔG° with this reaction is -40.2 kcal/mol for a process of 1900°K. However, $\Delta G^\circ\underline{P}$ = -37.9 kcal/mol *9, $G^\circ CaC2$ = -23.2 kcal/mol *9, and $\Delta G^\circ Ca3P2$ = -102.2 kcal/mol *10 shall be assumed.

(b) Influence of the CaC2 addition amount

Fig. 4 shows the influence of the CaC2 addition amount onto the dephosphorization behavior. With increasing CaC2 addition amount, the [P] percentage decreases. However, not melted flux remains with excessive addition, and an addition amount of about 50 kg/t is considered to be the limit. With addition of 50 kg CaC2/t (25 kg CaF2/t), [P] became 0.031%. Fig. 5 shows the relation between the CaC2 addition amount and the [C] percentage in the melt. The carbon resulting from decomposition of CaC2 is dissolved in the melt and the [C] percentage increases. The calculation values in the figure are the increases of the [C] percentage with complete dissolving of the carbon in the CaC2.

(c) Influence of the temperature

Fig. 6 shows the influence of the temperature onto the dephosphorization. The boiling point of metallic Ca is 1492°C, the Ca evaporation loss increases with increasing temperature, and the dephosphorization performance decreases.

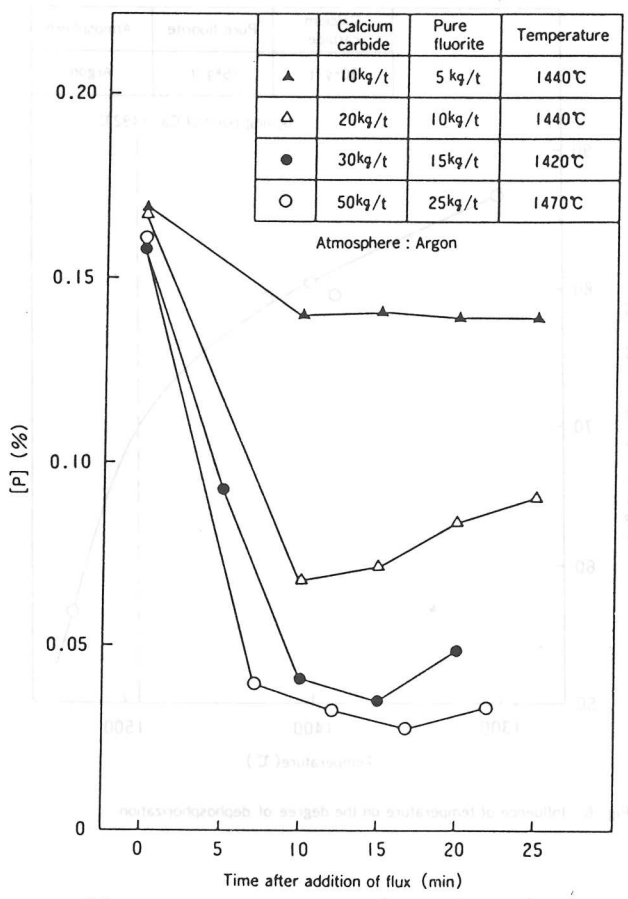


Fig. 4 . [P] change of Low carbon ferromangan

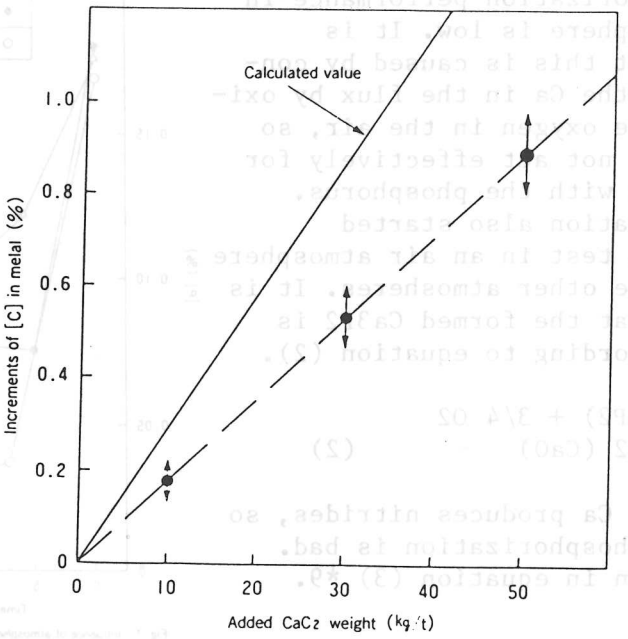


Fig. 5 . Relation with the increments of [C] and added CaC_2 weight

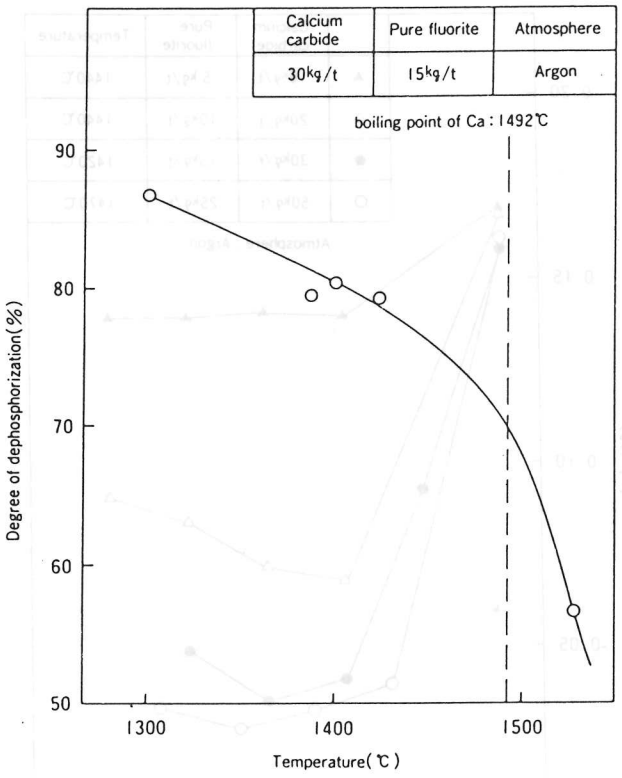


Fig. 6 . Influence of temperature on the degree of dephosphorization

(d) Influence of the atmosphere

Fig. 7 shows the influence of the atmosphere onto the dephosphorization. The dephosphorization performance in an air atmosphere is low. It is believed that this is caused by consumption of the Ca in the flux by oxidation by the oxygen in the air, so that it does not act effectively for the reaction with the phosphorus. Rephosphorization also started earlier with test in an air atmosphere than with the other atmosheres. It is estimated that the formed Ca3P2 is oxidized according to equation (2).

$$1/2\ (Ca_3P_2) + 3/4\ O_2 = \underline{P} + 3/2\ (CaO) \qquad (2)$$

In N2 gas, Ca produces nitrides, so that the dephosphorization is bad. This is shown in equation (3) *9.

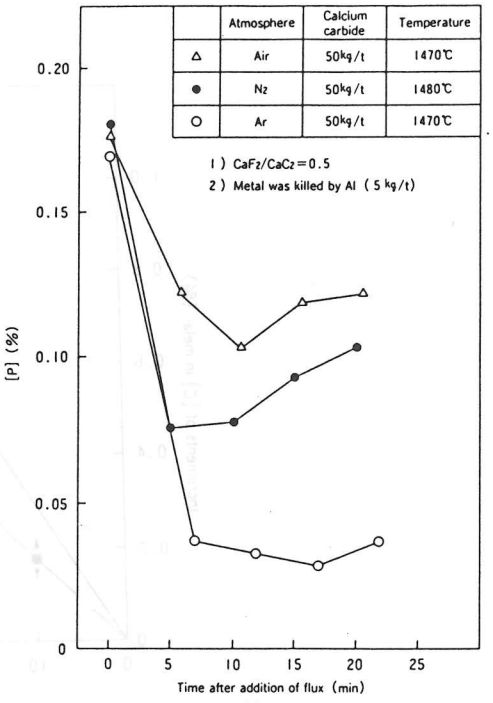


Fig. 7 . Influence of atmosphere on [P] behavior

$$3\,Ca\,(g) + N_2\,(g) - Ca_3N_2\,(1) \qquad (3)$$

$$\Delta G^\circ = -219{,}500 + 117{,}55\,T\ (cal/mol)$$

The standard free energy at 1900°K is -3.8 kcal/mol.

(e) Influence of the impurities in the flux

Fig. 8 shows the influence of (SiO2) in the fluorite onto the dephosphorization ratio. Adjustment of (SiO2) was executed by mixing of refined fluorite and fluorite mineral at specified ratios. The dephosphorization ratio decreases notably with increasing (SiO2). It is believed that the reason for this is the oxidation consumption of Ca according to equation (4).

$$(SiO_2) + 2\,(CaC_2) = 2(CaO) + \underline{Si} + 4\,\underline{C} \qquad (4)$$

The reaction equations for (MnO) from the ferromanganese slag and (MgO) from the refractory as further possible impurities are shown in equations (5) and (6).

$$(MnO) + (CaC_2) = (CaO) + \underline{Mn} + \underline{C} \qquad (5)$$

$$(MgO) + (CaC_2) = (CaO) + \underline{C} + Mg\ (g) \qquad (6)$$

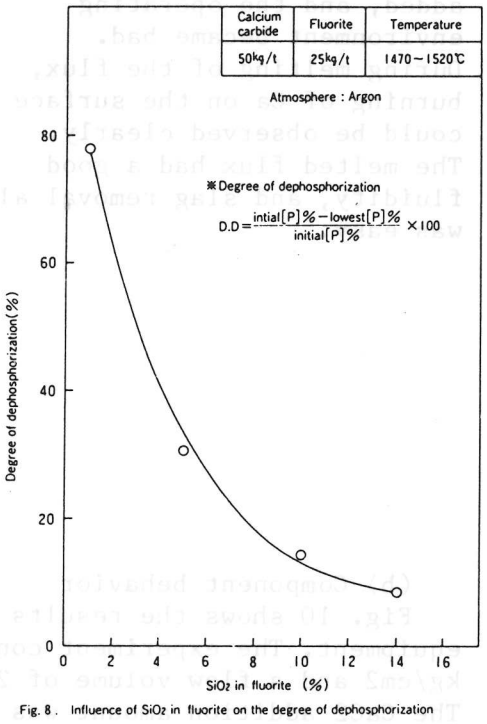


Fig. 8. Influence of SiO_2 in fluorite on the degree of dephosphorization

(f) Influence of the carbon saturation ratio in the ferromanganese

Fig. 9 shows the influence of the degree of carbon saturation ratios in the ferromanganese onto the dephosphorization. The degree of carbon saturation is the ratio with the degree of dissolution for saturated carbon in high carbon ferromanganese. The samples for the experiments were obtained by mixing low carbon ferromanganese and high carbon ferromanganese at specified ratios.

The dephosphorization improves with decreasing degree of carbon saturation, and for high carbon ferromanganese, dephosphorization by CaC2 becomes nearly impossible.

2 Actual equipment

(a) Experimint situation

In the experiment where a hood was placed onto the ladle, the occurring dust was collected by a dust collector, and the amount blown to the outside of the hood was small. In the experiment without a hood, a considerable amount of dust occurred when the flux was added, and the operating environment became bad. During melting of the flux, burning of Ca on the surface could be observed clearly. The melted flux had a good fluidity, and slag removal also was easy.

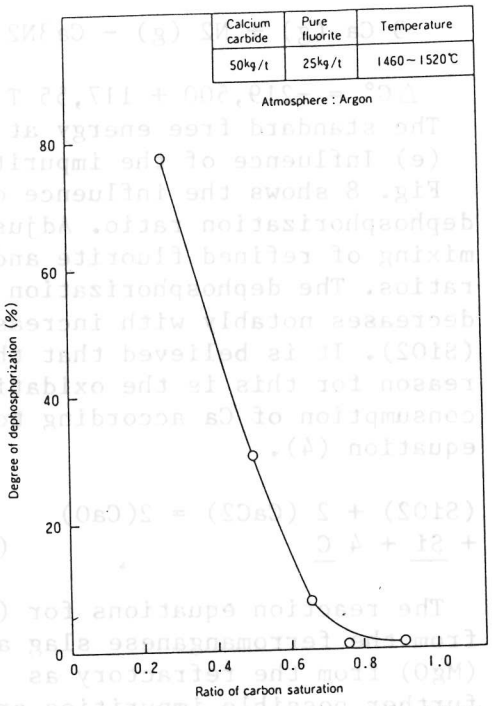


Fig. 9. Influence of carbon saturation ratio on the degree of dephosphorization

(b) Component behavior

Fig. 10 shows the results of the experiments with actual equipment. The experiment conditions were an Ar gas pressure of 5 kg/cm2 and a flow volume of 200 1/min.
The CaC2 addition amount was 30 kg/t. The reason for this was the fact that unmelted flux remained in some cases with addition of 50 kg/t in the high frequency induction furnace experiments. The flux melting with actual equipment was better than that with high frequency induction furnace.

Rephosphorization occurred in the experiments without a hood, but it did not occur in the experiments in a semi-enclosed Ar gas atmosphere, and there is the possibility that dephosphorization progresses still further. However, as the melt temperature became about 1400°C and trouble was caused for the casting the experiment was stopped after 40 minutes.

The ferromanganese obtained with the experiment with a semi-enclosed Ar gas atmosphere was [Mn] 75.2%, [C] 1.6%, and [P] 0.041%.

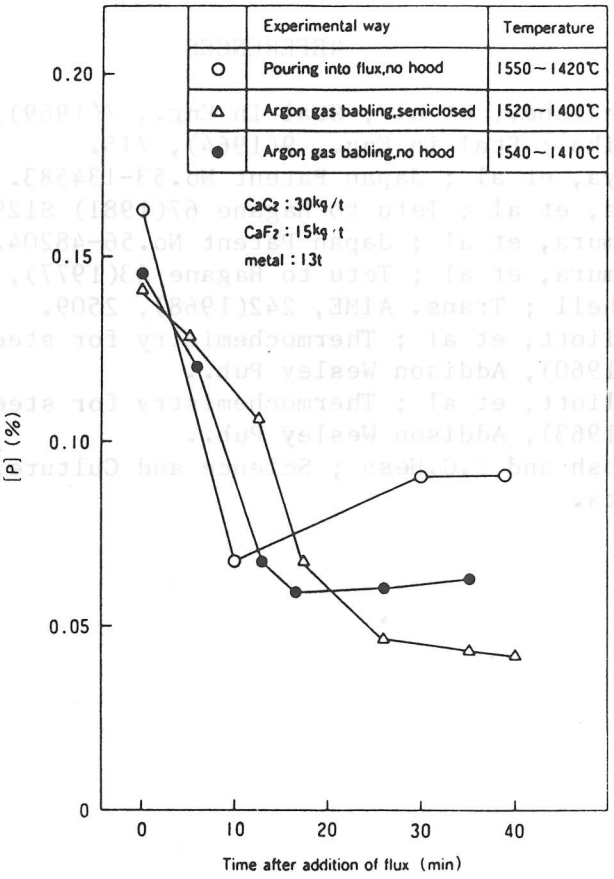


Fig.10. Example of [P]change of Low carbon ferromangan

Conclusion

As the result of dephosphorization experiments for medium and low carbon ferromanganese in a 10 kg high-frequency induction furnace and in a 13 t ladle, it was found that dephosphorization is possible in an Ar gas atmosphere by treatment with CaC2-CaF2 type flux. With addition of 30 kg CaC2/t (15 kg CaF2/t) to a 13 t ladle, medium carbon ferromanganese with [P] 0.041% was obtained.

For the future, cost reduction by design of mass production equipment with improved CaC2 reaction is planned to meet the demands of the iron and steel industry.

REFERENCES

1) N.P.Lyakishev, et al ; Stal in Eng., 7(1969), 642.
2) V.P.Zaiko ; Stal in Eng., 9(1964), 715.
3) A.Nagoya, et al ; Japan Patent No.53-134583.
4) T.Ikeda, et al ; Tetu to Hagane 67(1981) S129.
5) K.Yamamura, et al ; Japan Patent No.56-48204.
6) T.Nakamura, et al ; Tetu to Hagane 63(1977), 2287
7) A.Mitchell ; Trans. AIME, 242(1968), 2509.
8) J.F.Elliott, et al ; Thermochemistry for steelmaking, vol.1(1960), Addison Wesley Pub..
9) J.F.Elliott, et al ; Thermochemistry for steelmaking, vol.2(1963), Addison Wesley Pub..
10) P.C.Chosh and E.G.Hess ; Science and Culture, 28(1962), 386, Calcutta.