DEPHOSPHORIZATION OF MANGANESE ALLOYS

J.Kr.Tuset* and A.N.Wærnes**

ABSTRACT

Dephosphorization of liquid manganese alloys is reviewed and discussed on the basis of thermodynamical data available from the literature. Two possibilities are concidered, either to remove phosphorus as a phosphate under oxidizing conditions or as a phosphide under reducing conditions. As the latter approch appears to be the most promising choice for high carbon ferromanganese alloys, this possibility was studied in a serie of laboratory experiments where magnesium at a defined partial pressure was used as the phosphide forming agent. It was found, however, that in equilibrium with a carbon saturated ferromanganese melt, the magnesium phosphide phase is not sufficiently stable to give a required degree of dephosphorixation at a reasonable pressure of magnesium. Similar experiments with calcium as the dephosphorization agent confirmed that calcium is not effective at all in carbon rich alloys due to calcium carbide formation, but was found to be quite effective in low carbon ferromanganese.

INTRODUCTION

Dephosphorization of liquid alloys rich in elements being less noble than the phosphorus itself is a difficult task and has been the subject of numerous publications over the last decade. Most of these studies, however, have focused on problems related to the dephosphorization of chromium-rich hot metal in the stainless steel industry where an economical and environmentally acceptable solution of this problem has been most persistently looked for. This has to do with the fact that product quality, f. inst. in terms of corrosion resistance, is significantly improved in ultra-low phosphorus stainless steels /1/, whereas the impurity level for phosphorus in chromium rich hot metal produced from recycled scrap, high carbon ferrochromium ore or obtained by direct smelting of chromium, tends to increase year by year.

Manganese-rich alloys are intermediate products usually used in diluted concentrations in steel, not valuable end products like chromium-rich steels. Thus, the incentive in the search for a dephosphorization process, deemed to be difficult and costly, has not been the same for manganese alloys as for chromium alloys. Less work has therefore been devoted to the phosphorus problem in the manganese industry, but data on thermochemical properties of slags and slag/metal equilibria gained from fundamental work on the dephosphorization of chromium alloys are applicable also on manganese-containing systems.

OPTIONAL METHODS

It has been experimentally verified /2,3/ that phosphorus dissolved in a liquid metal may either be removed by oxidation or by reduction.

In the oxidation process as used in steel refining where a slag is present, the dissolved phosphorus reacts and forms phosphate ions as expressed in Eq.[1].

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

Dephosphorization of the metal is here favoured by low temperature, a high oxygen potential and a high oxygen ion activity to phosphate activity coefficient ratio of the slag.

Under strongly reducing conditions and provided a slag is present , the phosphorus in the metal reacts with oxygen ions and forms phosphide ions according to Eq [2a].

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

or for a slag-free process, it may react with a dissolved alkali earth metal (Me) and form a solid phosphide as expressed in Eq [2b].

$$\underline{P} + \tfrac{3}{2}\underline{Me} = \tfrac{1}{2}Me_3P_2 \qquad [2b]$$

Dephosphorization proceeding according to these two reactions is favoured at high temperatures and in the case a slag is present, at a high oxygen ion activity to phosphide activity coefficient ratio.

When a slag is present, the transition from oxidative to reductive dephosphorization is controlled by an exchange reaction between phosphate and phosphide ions as given by Eq [3] obtained by subtracting Eq [2a] from Eq [1].

$$P^{3-} + 2O_2 = PO_4^{3-} \qquad [3]$$

* *J.Kr. Tuset, Professor, Institute of Metallurgy, Norwegian Institute of Technology*

** *A.N. Wærnes, Research Scientist, Division of Metallurgy, The Foundation of Scientific and Industrial Research at the Norwegian Institute of Technology (SINTEF)*

The phosphate to phosphide partition in the slag is then as expressed by Eq [4].

$$\frac{(\%PO_4^{3-})}{(\%P^{3-})} = K_{(3)} \cdot p_{O_2}^{2} \cdot \frac{f_{P^{3-}}}{f_{PO_4^{3-}}} \qquad [4]$$

showing dependence on temperature as defined by the equilibrium constant for reaction [3], the type of slag used as this affects the activity coefficients of phosphide and phosphate ions, respectively, and the oxygen potential, here expressed in terms of the partial pressure of oxygen.

Sano and co-workers /2,3/ have studied the phosphate to phosphide partition in $CaO-Al_2O_3$ and $CaO-CaF_2$ melts at various temperatures and partial pressures of oxygen. They found the phosphate to be predominant at $p_{O_2} > 10^{-18}$ atm in the oxide melt saturated on $CaO \cdot Al_2O_3$ and at $p_{O_2} > 10^{-16}$ in the fluoride melt saturated on CaO, both at 1550 °C. At oxygen pressures below these critical values, which decreases with decreasing temperature, the phosphide become the predominant specie. At this transition point the total phosphorus in the slag is at its minimum.

In manganese refining, there is an upper limit in tolerable oxygen potential as defined by the reaction in Eq [5].

$$\underline{Mn} + \tfrac{1}{2}O_2 = MnO \qquad [5]$$

At 1400 °C and in the case liquid high carbon ferromanganese (HC FeMn) is subjected to refining, manganese oxide of unit activity will form at $p_{O_2} = 10^{-17}$ atm /4,5/. At $p_{O_2} = 10^{-18}$ atm, which is the phosphate to phosphide transition point for a CaO-saturated system at 1400 °C /3/, reaction [4] will in presence of such a slag proceed to the right until the activity of manganese oxide reaches a value of about 0.3, thus implying that serious oxidation losses of manganese may occur.

It is not expected, therefore, that a CaO - based slag system will be an adequate sink for phosphate ions in oxidative refining of manganese-rich ferroalloys. This has been confirmed experimentally by Parys /6/ and Maeda /7/ and coworkers who have studied dephosphorizaton of Fe-Mn-C-alloys in presence of CaO – or Na_2CO_3 - based fluxes /6/ as well as melts made up from K_2CO_3-KF, K_2CrO_4-KF and K_2CrO_4-KCl systems /7/ at 1350 and 1250 °C, respectively. They found that the degree of dephosphorization decreased with increasing manganese concentrations up to 20 - 26 %Mn. In the case of CaO - based slags, hardly no removal of phosphorus could be found in metal that initially contained 0.13 %P and 14.8 %Mn /6/. The situation was somewhat better in the potassium chromate systems where the phosphorus level dropped from 0.1 to 0.07 %P in metal initially containing 26 %Mn, but at the expense of losses in both manganese and carbon content /7/.

Fundamental studies on phosphorus in $BaO-BaF_2$ melts have shown that this system has a phosphate capacity which is larger by an order of magnitude than the equivalent CaO system, whereas the phosphide capacity is nearly the same/8/. This implies that the oxidation approach can be used at lower oxygen potentials when applying the oxide of barium in combinations with its low-melting halides as a flux instead of calcium or various alkali metals.

This knowledge has been utilized by Katayama and coworkers /9/ among others on high carbon Fe-Mn alloys. They used $BaCO_2$ and a 50/50 mixture of $BaCO_2$ and $BaCl_2$ as the dephosphorization agent at temperatures varying between 1300 - 1500 °C. For a 60 % Mn - alloy at 1300 °C they obtained a slag/metal distribution ratio for phosphorus of about 10 for the chloride flux and 20 for the oxide flux mainly consisting of BaO and MnO after reaction.

Water soluble barium compounds are toxic, however, and the environmental problems associated with the use of such materials as fluxing materials make them unattractive for industrial applications.

The alternative therefore, is to go for a reduction process where the phosphorus is removed either in the form of phosphide ions dissolved in a slag as already discussed, or as a solid phosphide where calcium or magnesium are the most appropriate reagents when considered in view of availability, toxicity and ability to form stable phosphides. The latter may, however, be a matter of discussion, as there appears to be considerable discrepancies in available data on the standard free energy of formation of the various phosphides involved.

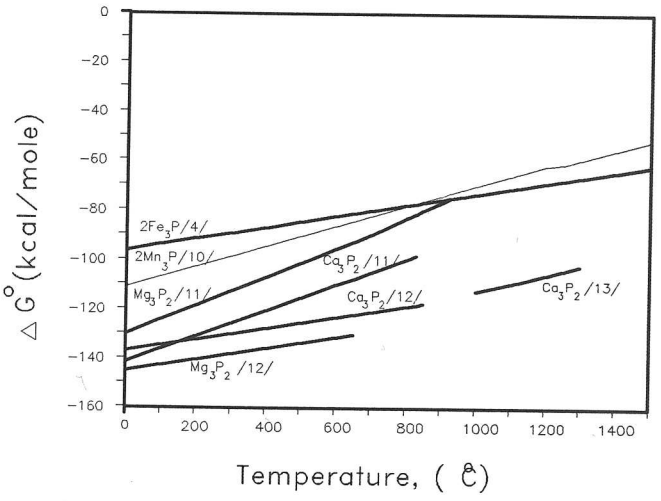

Fig.1. Standard free energy of formation of various phosphides as given by Kubaschewski/4/, Lee /10/, Barin and Knacke /11/, Ghosh /12/ and Min/13/.

As shown in Figure 1, there are two sets of free energy data available for the phosphides of calcium and magnesium, one given by Barin and Knacke /11/, the other by Ghosh and Hess /12/. In addition there are

the data on Ca_3P_2 appearing in a recent publication of Min and Sano /13/. Their data are nearly consistent with the data of Ghosh and Hess, especially if the temperature dependence is considered which is important as this defines a value for the standard entropy of formation for these types of compounds that looks reasonable. For these reasons most faith has here been given to the data of Ghosh and Hess also for the phosphide of magnesium.

Extrapolating the data of Ghosh and Hess, the phosphide of magnesium appears to be more stable than that of calcium up to 1200 °C which is about 100 K above the point where magnesium boils. This applies under standard conditions, however, and not for an open system where the magnesium may vaporize and easily get lost. This puts calcium in favour of magnesium as a dephosphorization agent for application in liquid ferroalloys under strongly reducing conditions. Magnesium, however, has the advantage of not forming a stable carbide as does the calcium. This discriminate the calcium from being a realistic option in the selection of a dephosphorization agent for ferroalloys rich in carbon, like HC FeMn.

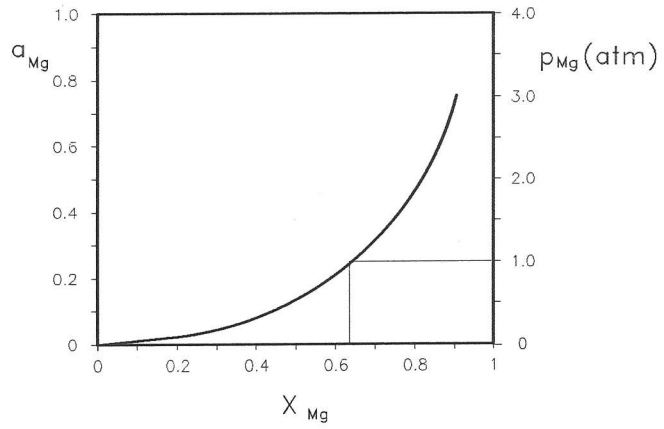

Fig. 2. Activity of magnesium in the system Sn-Mg recalculated to 1300 °C from data of Sharma /14/ and Sommer et Al /15/ and checked experimentally at one point.

DEPHOSPHORIZATION WITH MAGNESIUM

The potential of magnesium as a dephosphorization agent in manganese alloys is defined by the solubility product of the phosphide as expressed in terms of the concentration product given in Eq. [6]

$$K_{sp} = [\%Mg]^3 \cdot [\%P]^2 \qquad [6]$$

together with an equation that express how the concentration of dissolved magnesium in the liquid alloy is related to the partial pressure of magnesium.

Experimental method

A set of laboratory experiments were carried out in order to determine these relations for a selection of manganese alloys. Such a study has to be made by equilibrating the liquid alloys with or without presence of Mg_3P_2 under conditions were the temperature and the partial pressure of magnesium are defined. To be able to do this in a furnace designed for operation at atmospheric pressure at 1300 °C, where the vapour pressure of pure magnesium is about 4 atm /4/, alloys of the Sn-Mg system were used as the source of magnesium. These alloys are in the liquid state at 1300 °C, have a negligible vapour pressure of tin, and the activity of magnesium defining the magnesium pressure of the system varies with composition as given in Figure 2.

All the equilibrating experiments were done by using a closed crucible of graphite or mild steel acting as an isothermal box when heated under atmospheric pressure of argon to 1300 °C in a vertical graphite tube furnace. As sketched in Figure 3, this crucible was divided into two communicating compartments, the lower one loaded with a cylindrical disc of premelted and analysed Sn-Mg alloy, the upper one containing from one to three small crucibles of graphite or magnesia charged with premelted and crushed Fe-C, Mn-C, HC Fe80Mn or LC Fe80Mn. Some samples of the charging material was also deliberately contaminated on phosphorus and some charges were made up from mixtures of Mg_3P_2 and HC or LC FeMn. Slags were also added in some of the experiments. These starting materials were all made up from reagent grade chemicals.

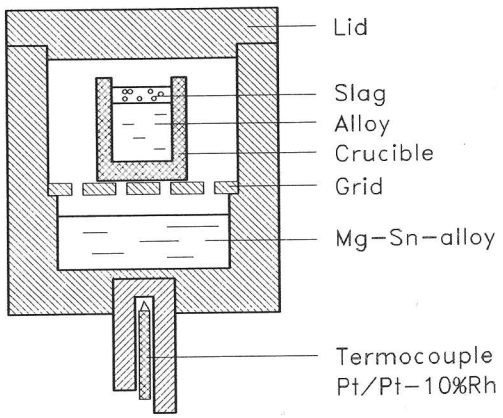

Fig. 3. Crucible assembly used for equilibrium tests.

The samples were usually kept at the reaction temperature of 1300 °C for a period of about 2 hrs before they were allowed to cool in the furnace. They were then carefully prepared for chemical analysis together with the Sn-Mg alloy. Tin and manganese were determined by titration, phosphorus by a colorimetric method, magnesium, calcium and iron by atomic absorption, and carbon by combustion according to the Leco method. To achieve equilibrium a holding time of 2 hrs turned out to be sufficient in most cases, but up to 6 hrs was used in some of the experiments as a check.

Magnesium solubility

Figures 4 and 5 present results of the solubility measurements. The straight lines drawn, representing the least squares fit to the experimental points given are expressed analytically in Table I.

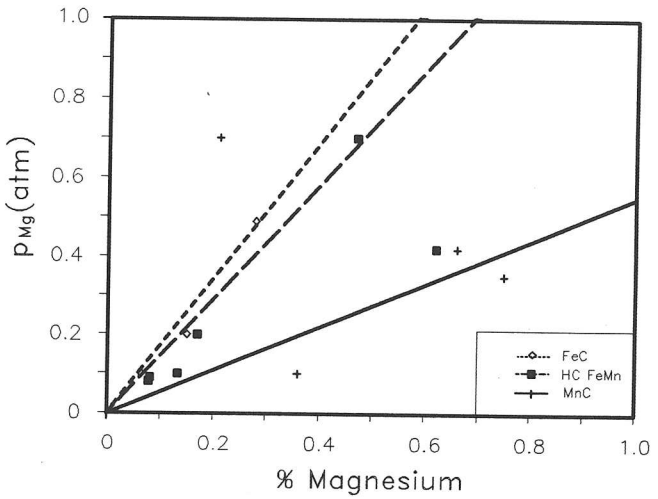

Fig.4. Concentration of magnesium dissolved in iron, manganese and Fe80Mn-alloys, all saturated on carbon at 1300 °C, as function of magnesium vapour pressure.

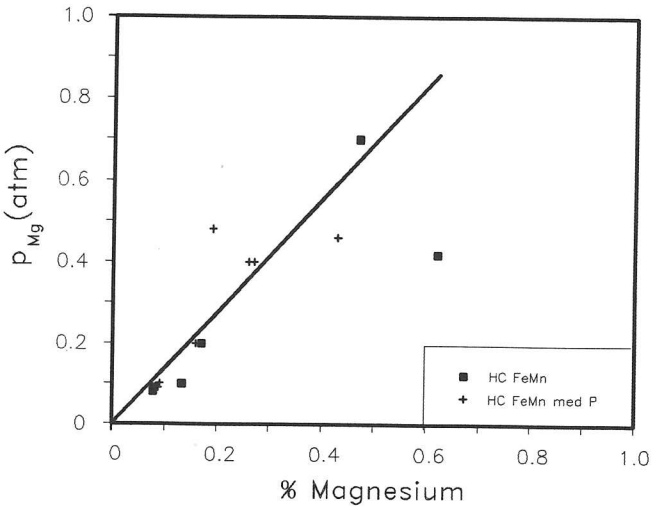

Fig.5. Concentration of magnesium in carbon saturated Fe80Mn-alloys without and with phosphorus as function of magnesium pressure at 1300 °C.

Table I. Solubility of magnesium vapour in various Fe-Mn-alloys at 1300 °C.

Alloy	
Carbon saturated manganese	$\%Mg = 1.6 \cdot p_{Mg}(atm)$
HC FeMn	$\%Mg = 0.72 \cdot p_{Mg}(atm)$
Carbon saturated iron	$\%Mg = 0.6 \cdot p_{Mg}(atm)$
LC FeMn	$\%Mg = 0.7 \cdot p_{Mg}(atm)$
Manganese	$\%Mg = 1.4 \cdot p_{Mg}(atm)$

The solubility of magnesium vapour as given for carbon saturated iron in Table I agree with data previously reported by Engh et al/16/, who used a different method and arrived to the expression $[\%Mg]_{Fe-C} = 0.56 p_{Mg}(atm)$, valid at 1260 °C. Magnesium vapour appears to be 2 - 3 times more soluble in manganese than in iron, and more so in carbon saturated manganese than in pure manganese. The effect of carbon is insignificant for the Fe80Mn-alloys, however, where the solubility is slightly higher than for iron, and where the presence of phosphorus (up to 0.3%P) does not seem to influence on the solubility of magnesium vapour in the liquid metal.

Solubility product of magnesium phosphide

Experiments meant to represent the situation where a three-phase equilibrium is established between FeMn (liq), $Mg_3P_2(s)$ and Mg(g) are referred to in Table II. In order to approach the equilibrium from both sides one set of experiments was made with mixtures of LC or HC FeMn and a surplus of Mg_3P_2 as the starting materials, whereas the other started with premelted alloys highly contaminated on phosphorus (2.3 - 2.6%P).

Table II. Experimental results used in calculating the solubility product of Mg_3P_2 in LC and HC FeMn at 1300 °C.

Starting materials	Equilibrated metal %Mg	%P	$[\%Mg]^3 \cdot [\%P]^2$	$p_{Mg}(atm)$	Expected Mg-solubility
$HC\,FeMn + Mg_3P_2$	0.43	1.02	0.083	0.50	0.36
	0.32	2.45	0.203 *	1.00	0.72
	0.90	2.62	0.005	0.18	0.13
$HC\,FeMn(2.3\%P)$	0.25	2.20	0.76	1.00	0.72
	0.09	2.26	0.004 *	0.31	0.15
$LC\,FeMn + Mg_3P_2$	0.31	1.67	0.083	0.50	0.36
	0.15	2.86	0.028	0.12	0.086
$LC\,FeMn(2.6\%P)$	0.02	2.84	$6.4 \cdot 10^{-5}$ *	0.19	0.14

* Values excluded in calculating a mean value for the solubility product as there are reasons to believe that the phosphide has not been formed in two of the samples and that the third is contaminated on phosphide.

The two first columns of Table II list the concentrations of magnesium and phosphorus, respectively, as analysed in metal samples carefully cleaned from surplus phosphide contaminating the metal surface. These data were used in calculating the concentration products listed in the third column. The next two columns list the expected vapour pressure of magnesium of the system at the temperature of reaction, as defined by the final compositions of the Sn-Mg alloys used, as well as the corresponding equilibrium concentration of magnesium in the manganese alloys as calculated from the expressions in Table I.

The agreement between the magnesium values given in the first and last column of Table II are not excellent, but satisfying in view of the analytical uncertainties involved. Such uncertainties, multiplying in the concentration product, explain the scatter in the resulting values given in the third column.. Taking the arithmetic mean of these, one arrive to 0.055 as a reasonable value of the solubility product of Mg_3P_2 in LC and HC FeMn at 1300 °C.

Using available thermodynamic data such as an extrapolated value for the free energy of formation of Mg_3P_2 based on the data of Ghosh and Hess/12/, the free energy of the transformation from gaseous to liquid phosphorus as given in a paper of Lee/10/ and his expression for the activity coefficient of phosphorus at infinite dilution in liquid manganese, one can for a temperature of 1300 °C arrive to a theoretical value for the equilibrium constant of the reaction represented by Eq [7].

$$3Mg(g) + 2\underline{P}_{Mn} = Mg_3P_2(s) \qquad [7]$$

$$K_{1300^oC} = \frac{a_{Mg_3P_2}}{p^3_{Mg} \cdot [\%P]^2} = 221.5$$

Inserting for the unit activity of Mg_3P_2 and for $p_{Mg} = [\%Mg]/0.7$ as given in Table I, this gives a semitheoretical value for the solubility product of Mg_3P_2 as expressed in Eq [8].

$$K_{sp(theo.)} = [\%Mg]^3 \cdot [\%P]^2 = 1.55 \cdot 10^{-3} \qquad [8]$$

A graphical presentation of this equation appears as a straight line with the slope -3/2 in the diagram of Figure 6, also showing a plot of the experimental results of Table II. The most reliable of these are grouped around the dashed line representing the experimental value:

$$K_{sp}(\exp.) = 0.055$$

If the difference in the free energies associated with these constants is attributed to the stability of the magnesium phosphide alone, this implies that the free energy of formation of Mg_3P_2 at 1300 °C should be about 45 kJ/mole less negative than indicated by the data of Ghosh and Hess in Figure 1.

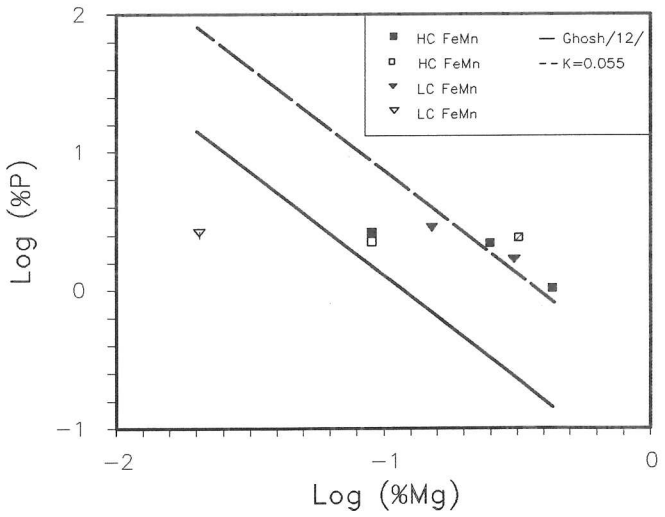

Fig.6. Equilibrium concentration of phosphorous and magnesium in LC FeMn and HC FeMn in presence of Mg_3P_2, experimental and calculated results. Open symbols are regarded as unsertain.

Practical implications

The practical implication of this is that the magnesium is less effective as a dephosphorization agent than expected from the most optimistic data given in Figure 1, but much more effective than indicated by the most pessimistic one. For magnesium phosphide of unit activity to form in ferromanganese containing 0.1%P at 1300 °C, the magnesium concentration in the bath has to exceed 1.7% Mg if the experimental value of the solubility product applies at this concentration, whereas the semitheoretical value in Eq [8] gives 0.54 %Mg as the upper limit. The magnesium pressures corresponding to these two figures are 2.6 and 0.8 atm, respectively.

Table III. Magnesium and phosphorus in metal equilibriated with CaO-saturated chloride slags at 1300 °C.

Experiment no	[%Mg]	[%P]	$[Mg]^3 \cdot [\%P]^2$
1.	0.23	0.66	0.005
2.	0.28	0.48	0.005

Presence of a slag acting as a solvent for the phosphide lowers the required concentration product as expressed in Eq [9]

$$[\%Mg]^3 \cdot [\%P]^2 = 0.055 \cdot a_{Mg_3P_2} \qquad [9]$$

This effect is shown in Table III where the results of two experiments using a CaO-saturated $CaO-CaCl_2$ slag are reported. As seen, the concentration product of the metal is lowered by a factor of 10, but the phosphorus content of the slag is low, less then 1%P.

This implies that refining down to 0.1%P in ferromanganese can be achieved at a level of 0.8 %Mg, which corresponds to a magnesium pressure of 1.1 atm, but the quantity of slag needed is high, minimum 220 kg per ton of metal if the initial phosphorus content is as high as 0.3 %P.

DEPHOSPHORIZATION WITH CALCIUM

The aim of the experimental work and the methods used in the present study on calcium, were the same as those for magnesium. The major experimental alteration made was that pure calcium metal was used as a replacement for the Sn-Mg alloys. Furthermore, it was found necessary to protect the graphite container with an inner lining of molybdenum sheets in order to ensure that the calcium pressure was defined by the calcium itself and not by the equilibrium between calcium carbide and graphite. The best solution to this problem, however, as used in a few experiments, was to replace the graphite with a similar container of mild steel.

Calcium solubility

Results of the solubility measurements together with some literature data discussed in the following are summarized in Table IV. The values related to the ferromanganese alloys are plotted in Figure 7 also showing a tentative curve drawn on these bases.

Table IV. Results of solubility measurements on calcium at 1300 °C as compared with available data.

	This work			Litterature data	
Alloy	Without C	1.2 %C	Saturated on C	Without C	Saturated on C
Iron			0.02	-	0.036/17/
Manganese	0.4		0.02	0.55/18/	-
Ferro-manganese	0.17 *	0.1	<0.06	-	-

* Mean value of three independent experiments with a calcium content of 0.25, 0.18 and 0.072 resp.

In order to discuss these results, reference is first made to the boundary system Fe - C - Ca reproduced from the comprehensive studies of Schürmann and Jacke /17/ in Figure 8. As shown, the solubility of calcium in liquid iron is low, 0.035 %Ca at 1600 °C, but as carbon is added it increases up to a point where calcium carbide forms as a stable phase. Additions beyond this point lowers at first the calcium solubility, which is now controlled by the activity product of calcium carbide, i.e. by the expression in Eq [10]

$$K = a_{Ca} \cdot a_C^2 \qquad [10]$$

The solubility product derived from this equation increases with increasing carbon content due to the mutual interaction between calcium and carbon in liquid iron. This interaction is responsible for the observed increase in calcium solubility both at low and high levels of carbon and brings the calcium concentration up to 0.067 %Ca at carbon saturation at 1600 °C. According to Figure 8 this value drops to 0.036 %Ca at 1300 °C, which agree quite well with the present figure of 0.02 %Ca given in Table IV for carbon saturated iron.

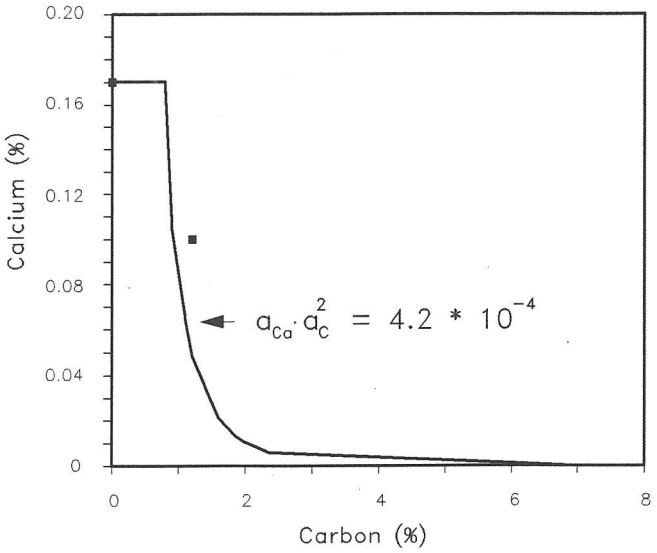

Fig.7. Calcium solubility in liquid ferromanganese as function of carbon content at 1300 °C, tentative curve.

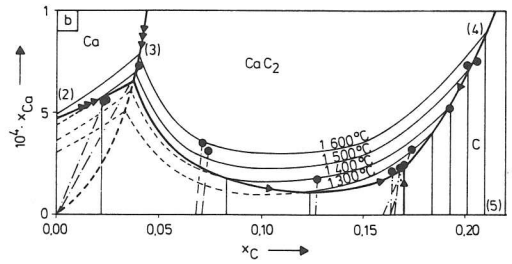

Fig.8. Thermodynamic evaluation of the calcium and calcium carbide saturation line for iron melts. Ref.Schürmann and Jacke/17/

Similar to iron, manganese does not mix with calcium neither in its liquid or solid state, but the mutual solubilities are somewhat higher in the Mn-Ca system than in the equivalent iron system/18/. From the phase diagram one may read a value as high as 0.55 %Ca for the calcium solubility in liquid manganese at 1300 °C, whereas the experimental value in Table IV is 0.4 %Ca.

Manganese in liquid steel does not influence on the solubility of calcium when present at low concentrations, but tends to increase the solubility at concentrations in the range of 10 - 20 %Mn/19/. Thus, a value of 0.17 %Ca as arrived to for carbon free ferromanganese in the present work looks reasonable.

The tentative curve of Figure 7 suggests that the calcium solubility in ferromanganese remains unaffected by presence of carbon up to the point where calcium carbide forms. This happens when the activity

product in Eq[10] is equal to $K = 4.2 \cdot 10^{-4}$ at 1300 °C, as calculated from the standard free energy of formation of CaC_2 given by Kubaschewski and Alcock/4/. This corresponds to a carbon activity of about 0.02 for a metal being in equilibrium with calcium of unit activity. The calcium activity at higher activities of carbon decreases according to the expression in Eq [11]

$$a_{Ca} = 4.2 \cdot 10^{-4} \cdot a_C^{-2} \qquad [11]$$

Inserting for $a_{Ca} = \frac{1}{0.17} \cdot [\%Ca]$ and neglecting that calcium and carbon interacts in these melts, one can with some modifications, use the activity data for carbon as given by Ohtani/20/ and calculate a solubility curve for calcium up to the saturation on carbon as done in Figure 7. As shown, the lower limit for carbide formation appears at about 0.8 %C.

The solubility product of calcium phosphide

Results of experiments aiming for the solubility product of Ca_3P_2 in LC and HC Fe80Mn at 1300 °C are summarized in Table V.

Table V. Experimental results used in calculating the solubility product of Ca_3P_2 in LC and HC FeMn at 1300 °C.

Alloy	%Ca	%P	$K = [\%Mg]^3 \cdot [\%P]^2$
$HCFeMn + Ca_3P_2$	0.006	1.86	$7.5 \cdot 10^{-7}$
	0.980	1.10	1.14
$HCFeMn(2.3\%P)$	0.030	2.13	$1.2 \cdot 10^{-4}$
$HCFeMn(0.35\%P)$	0.017	0.33	$5.4 \cdot 10^{-7}$
$LCFeMn + Ca_3P_2$	0.009	1.44	$1.5 \cdot 10^{-6}$
	0.028	0.87	$1.7 \cdot 10^{-5}$
$LCFeMn(2.6\%P)$	0.011	2.06	$5.6 \cdot 10^{-6}$
$LCFeMn(0.46\%P)$	0.172	0.09	$4.1 \cdot 10^{-5}$

The obtained concentration products listed in Table V are consistent for LC FeMn, i.e. for alloys with < 0.3 %C and 80 - 84 %Mn, only, but not for the carbon-saturated alloys. The LC FeMn-alloys are therefore believed to be in equilibrium with solid Ca_3P_2, and the mean value of the 4 experiments listed is hereby defined as the solubility product of this compound, as expressed in Eq [12]

$$K_{sp} = [\%Ca]^3 \cdot [\%P]^2 = 1.6 \cdot 10^{-5} \qquad [12]$$

The metal has in one of these 4 experiments only, reached to an equilibrium with the gaseous phase. It is easily understood that this may take some time for samples that are initially high in phosphorus, but it is less easy to understand for samples initially made up from mixtures of LC FeMn and Ca_3P_2. One has to remember, though, that Ca_3P_2 is soluble to a considerable extent in liquid calcium, up to 65 % at 1550 °C /13/. Saturated Ca-vapour may therefore condense on the phosphide and form a liquid of low activity of calcium, consequently the concentration of calcium in metal being in close contact with this liquid will be lowered. In both types of experiments a short reaction time, as used in the present experiments, will increase the chances for the phosphide to survive as a solid phase.

The phosphide added to the samples of HC FeMn has apparently not survived as an equilibrium phase in the experiments listed in Table V. The obvious reason is that the fraction of phosphide added has not been sufficiently high to establish the equilibrium for the reaction given in Eq [13]

$$Ca_3P_2(s) + 6\underline{C} = 3CaC_2(s) + 2\underline{P} \qquad [13]$$

The equilibrium constant for this reaction which controls the phosphorus level of the metal within the stability range of the carbide, has the following value at 1300 °C

$$K_{13} = 1.8 \cdot 10^7$$

if calculated from the data of Min/13/ for Ca_3P_2, Kubaschewski/4/ for CaC_2 and Lee/10/ for $P_2 = 2\underline{P}$. The equilibrium concentration of phosphorus in the metal as derived from this constant is strongly dependent on the carbon activity as expressed in Eq[14].

$$[\%P] = 4.2 \cdot 10^3 \cdot a_C^3 \qquad [14]$$

Inserting in this equation for $a_C = 0.02$ at 0.8 %C which is given as the lower limit for carbide formation in ferromanganese in Figure 7, one arrive to a value of 0.034 %P. The equivalent figure obtained by inserting for $[\%Ca] = 0.17$ in the solubility product for Ca_3P_2 given in Eq[12] is 0.057 %P.

Eq[12] combined with the solubility data in Figure 7 as well as Eq[14] agree on the point that ferromanganese containing less than 1 %C can be dephosphorized to a level of 0.1 %P by use of calcium or calcium carbide as reagents and under formation of Ca_3P_2 of unit activity. The use of slags as a solvent for the phosphide may extend this possibility to slightly higher levels of carbon. Interesting fluxes to be chosen for this purpose are the chloride and fluoride of calcium combined with its oxide.

The thermodynamics of these systems with the phosphide added have been studied by several, most recently by Masumitsu, Ito and Fruehan/21/. Calcium is soluble to an appreciable extent in both systems, but its effect on the activity coefficient of calcium phosphide has been found to be slightly lower for the chloride than for the fluoride system. It is therefore concluded that the chloride system is marginally better than the other for phosphorus removal.

It is possible from the given activities of the system $Ca - CaCl_2 - Ca_3P_2$ at 1400 °C/21/, to calculate how the phosphorus concentration of the slag varies with its calcium content at equilibrium with ferromanganese containing 0.1 %P. The results of such calculations

based on two different ways of calculating the phosphorus activity in the ferromanganese are shown in Figure 9. Line 1 refers to calculations based on data of Lee/10/ and applies for liquid manganese, while line 2 refers to calculations based on accepted interactions parameters for liquid steel.

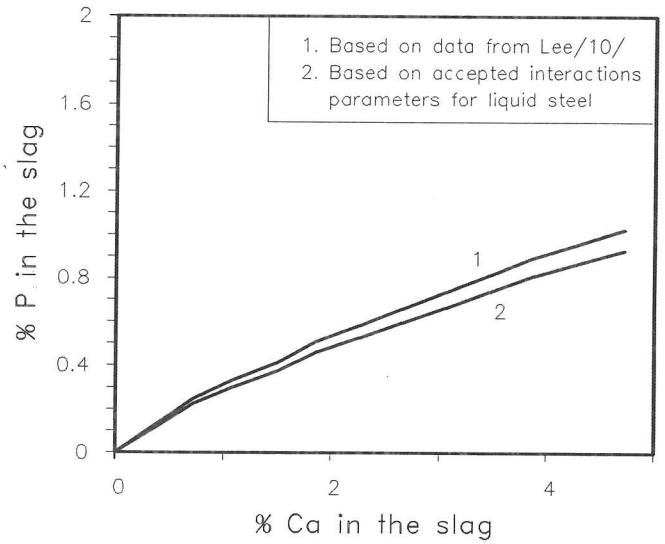

Fig.9. Calculated variations of the concentration of phosphorus with calcium content in $Ca-CaCl_2-Ca_3P_2$ slags at 1400 °C and at equilibrium with ferromanganese with 0.1 %P. Line 1 and 2 applies for different values of f_P.

Considering now the removal of 1 kg P from 1 ton ferromanganese by use of a chloride slag containing 1 %P which is a figure that corresponds to a phosphide activity of about 0.4. This requires a quantity of 100 kg slag that contains 4.5 kg of dissolved calcium as shown in Figure 9. Together with the quantity needed for the formation of the phosphide and calcium dissolved in the metal, this amounts to a total requirement of 7 - 8 kg of calcium per ton of metal treated.

CONCLUSIVE STATEMENTS

It is expected from a theoretical point of view and has been experimentally verified that phosphorus in liquid ferromanganese can be removed as phosphates, but at a carefully controlled oxygen potential and by use of $BaO-$ bearing slags, only. Water soluble barium compounds are toxic and not attractive for industrial applications, however.

The alternative is to remove the phosphorus as a phosphide either by use of magnesium or calcium.

Magnesium is effective in low carbon as well as in high carbon ferromanganese, but not as effective as expected from available thermochemical data. At 1300 °C solid magnesium phosphide forms at conditions defined by Eq[9] and data of Table I implying that a closed pressurized reaction vessel is required in order to obtain reproducible refining at low phosphorus levels, i.e. at 0.1 %P. The residual magnesium concentration in refined metal will be high, above 1 %Mg.

Calcium is effective for low carbon alloys, only, i.e. at concentrations < 1 %C at 1300 °C where solid calcium phosphide forms at conditions defined by Eq[12].

For both elements, dephosphorization is enhanced by presence of halide based fluxes provided used in quantities approaching 10 % of the metal weight. For calcium this will more than double the quantity of reagent metal required.

Phosphides of magnesium and calcium are both unstable in presence of humidity and react under formation of toxic phosphine. Thus, a process for treatment of phosphide-containing reaction products has to be included in an overall dephosphorization process for ferromanganese at reducing conditions.

ACKNOWLEDGEMENTS

The present study has been made under a contract with the Royal Norwegian Council for Scientific and Industrial Research (NTNF) and with assistance of Elkem a/s on the chemical analysis. The authors are grateful to these parties for their support, and to Mr. M. Raanes for his assistance in the experimental work.

REFERENCES

1. Y. Nakamura and S. Abe,Nippon Steei Technical Report Overseas, No. 10, 1977, pp 114 -119

2. N. Sano, "Thermodynamics of phosphate and phosphide in slag melts under strongly reducing conditions", Lecture held on the 4th of July, 1983, The University of Tokyo

3. S. Tabuchi and N. Sano, "Thermodynamics of Phosphate and Phosphide in $CaO-CaF_2$ Melts", Metallurgical Transactions B, Vol. 15B, 1984, pp351 - 356

4. O. Kubaschewski and C.B. Alcock, Metallurgical Thermochemistry, Fifth Edition, Pergamon Press Ltd., London, 1979

5. A. Tanaka, "Activities of Manganese in Mn-Fe-C, Mn-Si-C and Mn-Fe-Si-C Melts at 1673 K", Trans JIM, Vol. 21, 1980, pp 27-33

6. J. Parys, A.R. Romero, J-C. Wrampelmeyer and D. Janke, "Studies on the removal of phosphorus and sulfur from Fe-C and Fe-C-Mn melts at 1350 °C", Steel Research, Vol. 56, No. 9, 1985, pp 457-464

7. M. Maeda, S. Shiomi and N. Sano,"Dephosphorization of Fe-Mn-C molten alloys", Proceedings of the International Symposium on the Physical Chemistry of Iron and Steelmaking, The Metallurgical Society of the Canadian Institute of Metals, Toronto, Canada, 29.Aug.-2.Sept. 1982, ppV-22/V-27

8. S. Tabuchi and N. Sano,"Thermodynamics of Phosphate and Phosphide in $BaO-BaF_2$ Melts", Tetsu to Hagané, Vol. 71, No. 6, 1985, pp 687-692

9. H. Katayama, K. Harajima, M. Kawahare, H. Tsuboi, Y. Kawauchi, M. Fujita and A. Yamamoto, "Dephosphorization of high-chromium alloys and high-manganese alloys", Tetsu to Hagané, Vol. 72, No. 2, 1986, pp A41-A44

10. Y.E. Lee,"Thermodynamics of the Mn - P System", Metallurgical Transactions B, Vol. 17B, 1986, pp 777-783

11. I. Barin, O. Knacke and O. Kubaschewski,Thermochemical Properties of Inorganic Substances, Supplement, Springer-Verlag, Berlin/ Heidelberg/ New York, 1977

12. P.C. Ghosh and E.G. Hess, "On Thermodynamics of Phosphides", Science and Culture, Vol. 28, No. 8, 1962, pp 386-387

13. D.J. Min and N. Sano, "Determination of Standard Free Energy of Formation of Ca_3P_2 and Ca_2Sn at High Temperatures", Metallurgical Transactions B, Vol. 19B, No. 3, 1988, pp 433-439

14. R.A. Sharma,"Thermodynamic properties of liquid Mg+Pb and Mg+Sn Alloys by e.m.f. measurements", J.Chem.Thermodynamics, Vol.2, 1970, pp 373-389

15. F. Sommer, J-J. Lee and B. Predel,"Temperaturabhängigkeit der Mischungsenthalpien flüssiger Magnesium-Blei- und Magnesium-Zinn-Legierungen", Z.Metallkde., Vol. 71, No. 12, 1980, pp 818-821

16. T.A. Engh, H. Midtgaard, J.C. Børke and T. Rosenqvist, "Thermodynamics of the reaction between magnesium and sulphur in carbon saturated iron at 1260 °C", Scand. J. Metallurgy, Vol. 8, 1979, pp 195-198

17. E. Schürmann and H. Jacke, "Schmeltzgleichgewichte im System Fe-C-Ca", Steel Research, Vol. 58, No. 9, 1987, pp 399-405

18. F.A. Shunk, Constitution of binary alloys,Second Supplement, McGraw-Hill, Inc., USA 1969, pp 176

19. M. Köhler, H-J. Engell and D. Jancke,"Solubility of calcium in $Fe-Ca-X_i$ melts", Steel Research, Vol. 56, No. 8, 1985, pp 419-423

20. M. Ohtani, "Activities of Manganese and Carbon in Fe-C-Mn Melts", Research Inst. Tohoku Univ., Science Report No. A-9, 1957, pp 426-433

21. N. Masumitsu, K. Ito and R. J. Fruehan, "Thermodynamics of $Ca-CaF_2$ and $Ca-CaCl_2$ Systems for the Dephosphorization of steel", Metallurgical Transaction B, Vol. 19B, 1988, pp 643-648