

DEPHOSPHORIZATION OF H.C.FERROMANGANESE ALLOY WITH MAGNESIUM

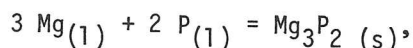
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ABSTRACT

A technology for producing low phosphorus containing ferromanganese alloys is important to the low phosphorus-high quality steel. An examination of thermodynamic information suggests that Mg would be a good dephosphorizing agent for H.C. FeMn alloy. An experiment, which consisted of adding Mg metal to H.C.FeMn melt at normal atmospheric pressure, was not successful because of premature Mg vaporization. Subsequently, experiments were carried out using a pressure vessel. An increased pressure provided a prolonged residence time of Mg in the melt. At pressure higher than about 2 atmosphere (gauge), the dephosphorization as high as 76% was obtained.

The Gibbs free energy of formation of Mg_3P_2 was calculated based on the study by Tuset and Waernes to be:



$$\Delta G_{1300^\circ\text{C}}^0 = -89,819.6 \text{ cal.}$$

This information was used to obtain the solubility of Mg and P in molten H.C.FeMn and to interpret the experimental results. It suggests that the equilibrium Mg vapor pressure may be about 2 atmosphere when the initial vessel pressure was in the range of 4 to 5 atmosphere gauge.

A plant test and analysis by a heat transfer model suggest that plunging massive Mg pieces is impractical and that Mg injection in granules or wire form may be feasible for removing phosphorus from H.C.FeMn alloy.

INTRODUCTION

Iron and steel have long been identified as prime industrial materials. However, the dominance of these metals is being challenged and, in some circumstances, eroded by other materials such as aluminum, plastics, and fine ceramics. In order for iron and steel to maintain their stature as premier materials they must possess

superior performance capabilities. A recent response to this competitive pressure has been the drive toward higher qualities, i.e., extremely clean iron and steel.

Manganese is one of the most important alloying elements in steel. It improves the rolling and forging qualities of steel while also enhancing its strength, toughness, stiffness, wear resistance, hardness and hardenability. Usually the alloying is done by addition to steel of ferromanganese alloys. However, phosphorus, often an impurity in high and medium carbon ferromanganese, tends to make steel susceptible to hot and stress corrosion cracking. Therefore, low phosphorus containing ferromanganese alloys are important to the production of high quality steels.

Generally, ferromanganese alloys are produced by carbothermic reduction of manganese ores. Most of the phosphorus in the ore passes into the smelted ferromanganese alloy. In principle, phosphorus removal can be achieved at any of the processing steps from ore preparation to treatment of the final alloy product. For example, dephosphorization of manganese ores has been attempted by leaching with a dilute acid^(1,2) and by partial reduction and vaporization of P⁽³⁻⁵⁾. Dashevskii et al. employed a selective smelting method to produce a low phosphorus containing Mn alloy⁽⁶⁾. Solid alloys have been treated with various reactive metals or salts followed by leaching⁽⁷⁻⁹⁾. However, these processes involve additional cumbersome steps which require long reaction times leading to low productivity and poor economics. In general, however, the treatment of liquid alloys in a ladle or refining vessel provides a flexibility in operation which permits the process to easily fit into existing production streams resulting in reduced investment and operating cost. Therefore, dephosphorization of liquid ferro-manganese alloys offers the potential for an effective and economic process. The present study examines the technical feasibility of a dephosphorization process treating molten high carbon ferromanganese alloy with a dephosphorizing agent.

DEPHOSPHORIZING CONDITIONS AND AGENTS

Most phosphorus removal techniques for iron and steel are carried out effectively and economically under oxidizing conditions. In such processes, phosphorus is oxidized and dissolved as a phosphate in strongly basic slags. However, these methods cannot be used to dephosphorize ferromanganese alloys because manganese tends to oxidize preferentially over phosphorus owing to its higher affinity for oxygen. Dashevskiy and Kashin⁽¹⁰⁾ arrived at the same conclusion. Recently, Wang and Shao⁽¹¹⁾ observed no phosphorus removal with Na_2CO_3 when the Mn content in ferromanganese exceeds about 20%. For ferromanganese alloys containing high Mn level, it appears reasonable to remove phosphorus under reducing conditions with appropriate dephosphorizing agents. In general, high carbon ferromanganese alloy contains about 7 wt% C, 1 % Si, and 78 % Mn. The

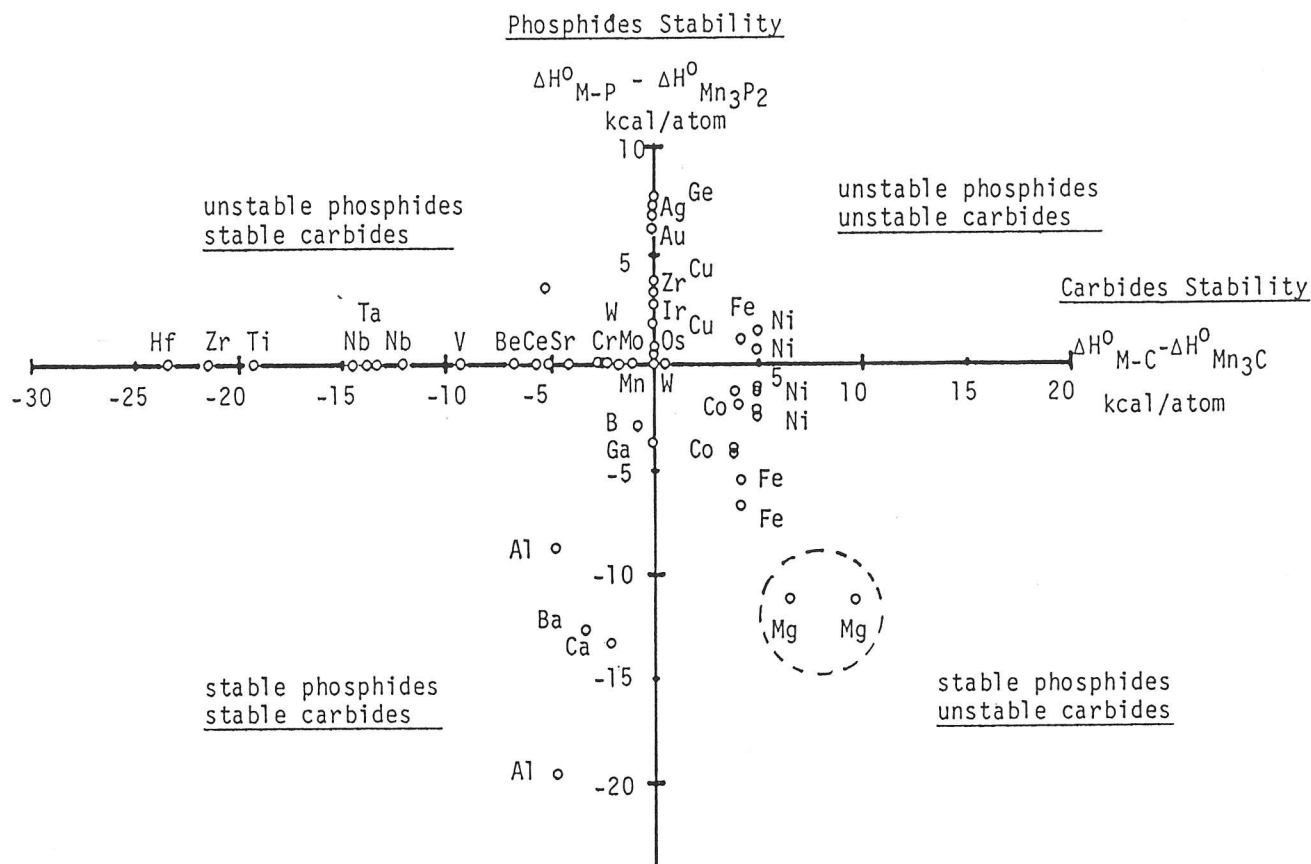


Figure 1. Relative Stabilities of Phosphides and Carbides of Various Elements against those of Mn.

relatively high C and Si contents appear to provide sufficient reducing conditions in the alloy melt for dephosphorization.

Dephosphorization agents should have a higher affinity for P than Mn to form phosphides. Also, after treatment, these constituents should not significantly alter the final alloy composition. In order to be effective under carbon saturated conditions, the agents should not form stable carbides. Candidates for such agents may be selected from thermodynamic considerations by examining the available data on the enthalpy of formation of carbides and phosphides⁽¹²⁾. It is postulated that the phosphides of elements added should be more stable than manganese phosphide and that the carbides be less stable. The relative stability is defined in this study as the difference between the enthalpy of formation of the phosphides and carbides of the potential addition agent and those of Mn. The enthalpies of formation of the compounds given by Kubaschewski and Alcock⁽¹²⁾ were adjusted to a unit of kcal/atom of mixture. If the relative stabilities are negative, the compounds of the elements are considered to be stable in relation to those of Mn. The candidate agents for dephosphorization of H.C.FeMn must show a negative value in relative stability for the phosphide and positive for carbide. In Figure 1, the relative stabilities of phosphides are plotted against those of carbides. Only magnesium stands out as a promi-

sing agent from this analysis. Al, Ba, and Ca form stable carbides as well as phosphides. Therefore, these elements can remove phosphorus effectively from low carbon but not from carbon saturated Mn alloys. Yamamura et al.⁽¹³⁾ used CaC_2 to remove phosphorus from medium carbon ferromanganese alloys, but it did not work with carbon saturated ferromanganese alloys. In the present study, therefore, Mg and Mg_2Si were selected as dephosphorizing agents for H.C.FeMn alloy melts. Also, it was subsequently found that these additions can remove other impurities such as sulfur, arsenic, antimony, tin, and nitrogen. The process was disclosed recently⁽¹⁴⁾, and the technical features are discussed below.

EXPERIMENTAL

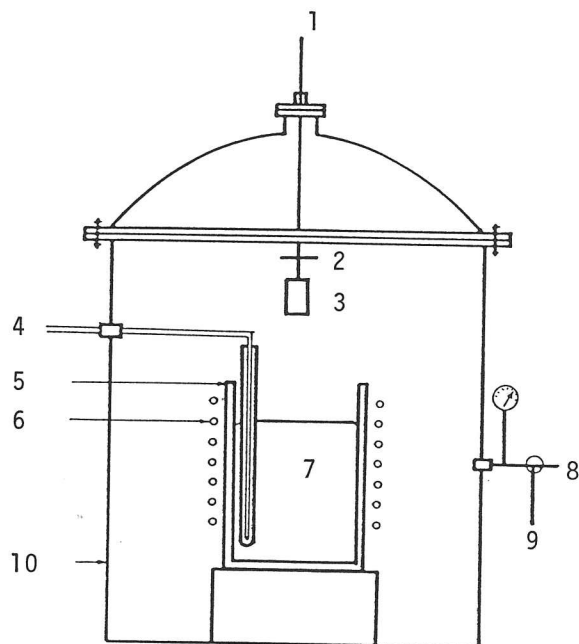
Materials

H.C.FeMn treated in these tests was a commercially available grade containing 79.5 wt% Mn, 12.5 Fe, 6.6 C, 0.61 Si, and 0.18 P. The P content of the molten alloys was increased to about 0.3 wt% by additions of FeP alloy (commercial grade, 24.4%P). Pieces of Mg metal were prepared by cutting commercial grade Mg ingot (Dow Chemical). Magnesium silicide was prepared by melting magnesium and silicon together in a graphite crucible. The composition was 60.8% Mg and 36.4 % Si. Fluxes were prepared with reagent

grade MgF_2 and CaF_2 and commercial H.C.FeMn slag.

Apparatus

The experiments involved adding pieces of magnesium metal or its silicide (Mg_2Si) to molten H.C.FeMn held at about 1300°C . A problem associated with using Mg is its low boiling point, 1090°C (15). When Mg metal or magnesium silicide were added to a H.C.FeMn melt at one atmospheric pressure, Mg vaporized immediately and burned. Consequently, no phosphorus removal was achieved during the initial attempts. This indicated that the addition of magnesium should be carried out in such manner to maximize the contact of Mg with the Mn alloy melt. The experiments in this study, therefore, were performed using a pressure vessel in order to suppress the premature vaporization of Mg.



- | | |
|--------------------------------------|------------------|
| 1 steel rod | 2 graphite foil |
| 3 Mg metal or Mg_2Si | 4 thermocouple |
| 5 graphite crucible | 6 induction coil |
| 7 H.C.FeMn melt | 8 to vacuum |
| 9 Ar gas | 10 steel shell |

Figure 2. Experimental Apparatus.

Figure 2 shows the experimental apparatus. The pressure vessel is constructed with 1.9 cm thick steel plate. It consists of a closed cylinder at one end and a matching cover. An O-ring ensures a gas tight seal between the top edge of cylinder and under side of the cover. Two sight glasses, one in the cover and the other on the cylinder wall, are provided to observe the reaction inside the vessel. An induction heating coil assembly is placed on a pedestal inside the vessel and connected to a 50 KW induction unit located outside of the vessel. A graphite crucible susceptor is located inside the induc-

tion coil. The pressure is provided by Ar gas, and is read as gauge pressure in atmospheres.

Procedure

The experimental procedure follows: 3.178kg of H.C.FeMn and FeP were added to a graphite crucible. If fluxing agents were employed, these ingredients were placed on top of the alloy. A thermocouple, Pt-10Rh/Pt, was located inside the graphite crucible to measure the melt temperature. The crucible assembly was set into the induction heating coil. The dephosphorizing agent, pieces of Mg metal or Mg_2Si , was contained in a small steel can attached to a plunging rod. The plunging rod passed through the cover via a gas tight fitting. Initially, the steel can containing the agent was located above the graphite crucible. After purging, the vessel was pressurized up to 5.1 atmospheres (gauge) with Ar gas. The furnace unit was heated slowly to melt the charge. The pressure increased slightly (about 0.2 atmosphere) during heating. The melt temperature was maintained at about 1300°C . After the temperature stabilized, the can containing the dephosphorizing agent was plunged into the H.C.FeMn melt. Some fume formation was observed after the plunge, but little increase in pressure was noted. About 15 minutes later the power was turned off, and the unit was allowed to cool under pressure.

After opening the vessel, the inside of the steel shell was covered with a layer of white, presumably MgO , fume. The slag layer on top of the alloy was found to contain numerous metallic beads which turned out to be elemental Mg, indicating that some magnesium had condensed in the slag layer. The slag gave off an odor similar to that associated with CaC_2 . Alloy samples from the cold ingot were taken for chemical analysis.

RESULTS

Table I summarizes the mix orders and results of the experiments. The results were evaluated by examining the degree of dephosphorization, which is defined as follows:

$$\text{degree of dephos.} = (P_i - P_f) / P_i \times 100.$$

A degree of dephosphorization as high as about 76% was obtained. Examination of the data indicates that dephosphorization is affected mostly by vessel pressure. This point is illustrated in Figure 3 which shows the relationship between degree of dephosphorization and pressure in the vessel. Efficient dephosphorization higher than about 60% was achieved only with pressure greater than about 2 atmosphere gauge. No phosphorus removal was evident at pressure below this level. This may be due to the suppression of premature Mg evaporation which results in increased Mg residence time. In a low pressure range, the rate of Mg evaporation is extremely high, and the residence time for the reaction is very short. When evaporated Mg leaves the alloy melt, it cannot contribute to dephosphorization. Increased vessel pressure also increases the residual Mg content, as shown in Figure 4. High levels

Table I

Mix Order and Analysis of Treated Alloy

No.	mix order, grams					vessel press. atm.	P initial wt%	P final wt%	Mg residual wt%	degree of dephos. %
	dephos. agent		flux							
	Mg	Mg ₂ Si	MgF ₂	CaF ₂	Slag					
6		100	70			4.08	0.33	0.21	0.31	36.4
7		192	140			4.08	0.33	0.12	1.54	63.6
8		200	140			4.08	0.34	0.09	1.70	73.5
9	126		140			4.08	0.34	0.15	0.90	55.9
10		200				4.08	0.34	0.11	0.74	67.7
11		200	140			5.10	0.34	0.13	0.50	61.8
12		165	140			4.08	0.335	0.079	1.50	76.4
13	100		140			4.08	0.335	0.12	0.58	64.2
14	100					4.08	0.335	0.105	0.73	68.7
15	100		140			5.10	0.335	0.14	0.48	58.2
16		165				3.74	0.33	0.13	0.59	60.6
17	100					4.76	0.34	0.135	0.90	60.3
18	100					3.74	0.34	0.13	0.95	61.8
19	100					2.72	0.34	0.13	0.97	61.8
20	100					2.04	0.34	0.14	0.81	58.8
21	100		160			4.76	0.34	0.135	1.60	60.3
22	100		160			3.74	0.34	0.13	1.30	61.8
23	100		160			2.72	0.34	0.135	1.01	60.3
24	100		160			2.04	0.34	0.13	0.57	61.8
25	100		160			0.00	0.34	0.29	0.12	14.7
26	100				300	3.74	0.32	0.12	1.36	62.5
27	100				300	2.04	0.32	0.20	0.21	37.5
28	100				300	1.02	0.32	0.32	0.05	0.0
30	100				300	0.68	0.32	0.34	0.05	0.0
31	100			50	200	1.02	0.32	0.32	0.05	0.0
32	100			50	200	1.36	0.32	0.32	0.05	0.0

note: degree of dephosphorization = $(P_i - P_f) / P_i \times 100$.
 P_i , P_f = initial and final P contents.

Mg₂Si = 60.8% Mg, 36.36% Si.

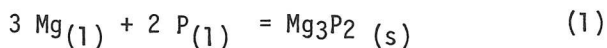
H.C. FeMn = 3178 grams.

of dephosphorization are the result of increased solubility and residence time of Mg in the alloy. The effect of a flux addition is not discernible. Those runs with and without external flux added dephosphorized similarly. Examination of the solidified ingots shows that some alloy manganese was oxidized and itself behaved as a flux. However, this study did not systematically examine the effect of fluxes and does not offer a quantitative statement as to its beneficial effects. A potential benefit of fluxes, however, will be discussed in the next section.

DISCUSSION

Standard Free Energy of Formation of Mg₃P₂

The dephosphorization reaction with Mg is expressed by the following equation (1):



The previously discussed experimental results could be interpreted according to the equation (1) if all pertinent thermodynamic data were available.

table.

Recently, after completion of our experimental work, Tuset and Waernes⁽¹⁶⁾ determined experimentally the equilibrium concentration of Mg and P at 1300°C in Fe-Mn and Fe-Mn-C(sat.) alloy melts which were equilibrated with a solid Mg₃P₂. The Mn content in the alloys was in the range of 76 to 86 wt%, and the Fe levels were 12.2 to 14.1 wt%. The free energy for equation (1) can be determined if the solution properties of Mg and P are known.

Tuset and Waernes⁽¹⁶⁾ also determined the solubility of Mg at 1300°C in a melt of Mn, Fe-Mn(81-84), Fe-C(sat.), Mn-C(sat.), and Fe-Mn(77-82)-C(sat.) under various magnesium vapor pressures. The magnesium vapor pressure was defined by a molten Mg-Sn alloy which was in equilibrium with the alloys examined at 1300°C. From their data, the activity of Mg was calculated by taking superheated pure Mg liquid at 1300°C as the reference state.

$$a_{\text{Mg}}(l) = P_{\text{Mg}} / P_{\text{Mg}}^0$$

Table II

Calculation of Free Energy of Formation of Mg_3P_2

wt % (ref.16)					mole fraction					P_{Mg} atm.	$a_{Mg}(l)$	$a_P(l)$	$\ln K$	$\Delta G^0, \text{cal.}$
Mg	P	Mn	Fe	C	Mg	P	Mn	Fe	C					
0.43	1.02	78.5	13.2	8.3	0.0073	0.0137	0.5935	0.0982	0.2873	0.46	0.1035	1.4374×10^{-5}	29.1047	-90,968.22
0.33	2.3	77.1	12.2	7.2	0.0059	0.0322	0.6076	0.0945	0.2598	1.0	0.2251	3.2145×10^{-5}	25.1641	-78,651.68
0.28	2.6	76.0	13.8	6.9	0.0050	0.0365	0.6012	0.1074	0.2499	0.72	0.1621	3.4414×10^{-5}	26.0127	-81,304.02
0.25	2.2	78.6	12.6	6.4	0.0045	0.0313	0.6298	0.0994	0.2350	1.0	0.2251	2.2679×10^{-5}	25.8618	-80,832.37
0.31	1.67	85.9	14.1	-	0.0068	0.0286	0.8305	0.1341	-	0.46	0.1035	1.0870×10^{-6}	34.2687	-107,108.56
0.48	2.2	84.9	12.4	-	0.0106	0.0382	0.8317	0.1195	-	0.73	0.1643	1.6804×10^{-6}	32.0111	-100,052.33

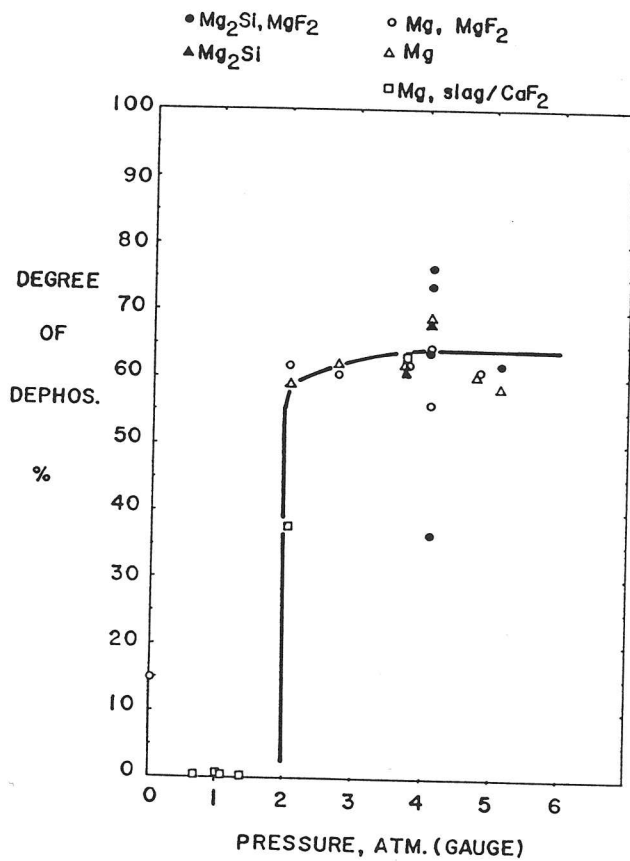


Figure 3. Degree of Dephosphorization under Various Pressures.

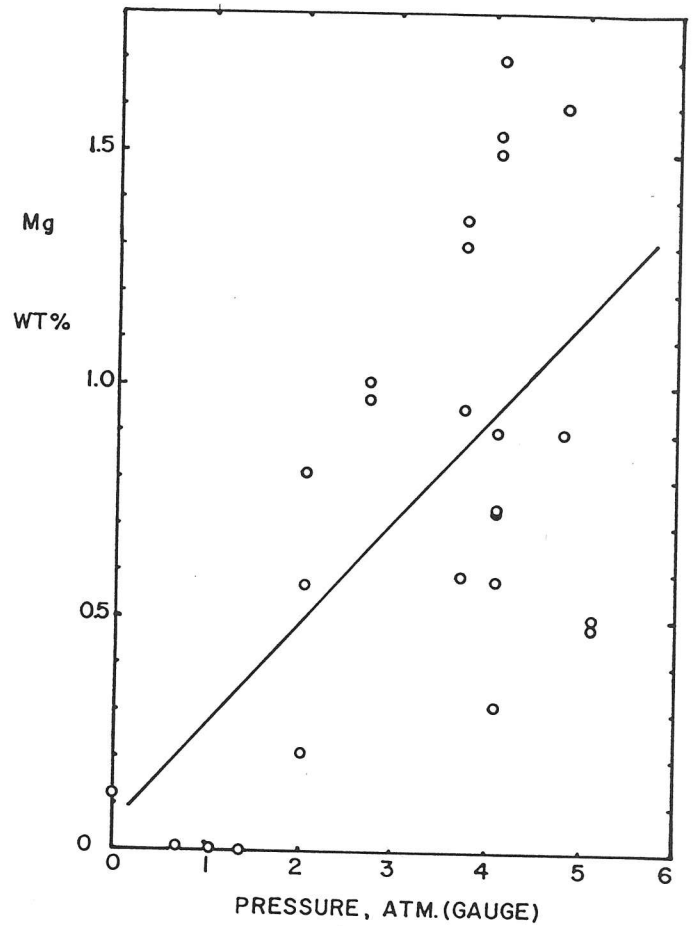


Figure 4. Relationship of Residual Mg in H.C.FeMn alloy with vessel pressure.

The pressure over a pure Mg melt was calculated from information taken from Pankratz⁽¹⁵⁾.

$$\text{Mg}(l) = \text{Mg}(g)$$

$$\begin{aligned}\Delta G^0 &= 30,250 - 22.194 T \text{ cal.} \\ &= -4,661.16 \text{ cal. at } 1300^\circ\text{C.}\end{aligned}$$

The solubility of Mg in the alloys is small. Within the terminal composition ranges examined, the activity coefficients were correlated with the Mg content. The results are listed below:

Mn-Mg system,

$$\ln \gamma_{(\text{Mg},l)} = 0.2701 + 105.1676 X_{\text{Mg}} (\pm 0.008) \quad (2)$$

Fe-Mn(81-84)-Mg,

$$\ln \gamma_{(\text{Mg},l)} = 2.6267 (\pm 0.26) \quad (3)$$

Mn-C(sat.)-Mg,

$$\ln \gamma_{(\text{Mg},l)} = 1.7466 (\pm 0.3) \quad (4)$$

Fe-Mn(77-82)-C(sat.)-Mg,

$$\ln \gamma_{(\text{Mg},l)} = 2.5724 (\pm 0.47) \quad (5)$$

Fe-C(sat.)-Mg,

$$\ln \gamma_{(\text{Mg},l)} = 2.9621 (\pm 0.32) \quad (6)$$

where X_{Mg} is a mole fraction of Mg.

With the absence of specific data, the activity of P in molten Fe-Mn-C-P alloy was estimated. The solution behavior of P in the Fe-Mn system is assumed to be similar to that in Mn. The activity coefficient of P in a dilute solution of Mn was taken from Lee⁽¹⁷⁾.

$$\begin{aligned}\ln \gamma_{\text{P}(l)} &= -10.6377 + 16.7225 X_{\text{P}} \\ &\quad - 22.3617 X_{\text{P}}^2, \text{ at } 1300^\circ\text{C.}\end{aligned}$$

where X_{P} is a mole fraction of P.

The effect of carbon was estimated by assuming that the interaction coefficient of C on P in Mn is the same as in Fe. This information was taken from Sigworth and Elliott⁽¹⁸⁾ and transformed to a mole fraction coordinate (X).

$$e_{\text{P}}^{\text{C}} = 0.13$$

$$\epsilon_{\text{P}}^{\text{C}} = 230 \frac{M_{\text{C}}}{M_{\text{P}}} e_{\text{P}}^{\text{C}} + \frac{M_{\text{Mn}} - M_{\text{C}}}{M_{\text{Mn}}} = 12.367$$

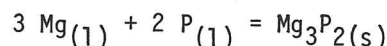
where M_{C} , M_{P} , and M_{Mn} are atomic weights of C, P, and Mn, respectively. Therefore, the activity coefficient of P in Fe-Mn-C(sat.) was estimated from the following equation (7).

$$\begin{aligned}\ln \gamma_{\text{P}(l)} &= -10.6377 + 16.7225 X_{\text{P}} \\ &\quad - 22.3617 X_{\text{P}}^2 + 12.367 X_{\text{C}} \quad (7) \\ &\quad \text{at } 1300^\circ\text{C.}\end{aligned}$$

The mutual effect of Mg and P was neglected in the present estimation. The activities of Mg and P in the Fe-Mn-Mg-P and Fe-Mn-Mg-P-C(sat.) systems were calculated from the data of Tuset and Waernes⁽¹⁶⁾ by using equations 3, 5, and 7. This information permitted an estimation of the

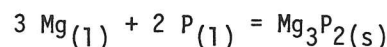
free energy for equation (1) at 1300°C as shown in Table II.

The estimated values of the free energy for equation (1) were averaged.



$$\Delta G^0 = -89,819.60 \text{ cal.} (\pm 11,700) \text{ at } 1300^\circ\text{C.} \quad (1a)$$

This value is more negative than that given by Barin and Knacke⁽¹⁹⁾.



$$\begin{aligned}\Delta G^0 &= -111,515.33 + 25.340 T \text{ cal.} \\ &= -71,655.51 \text{ cal. at } 1300^\circ\text{C.}\end{aligned} \quad (1b)$$

Solubility of Mg and P in H.C.FeMn Alloy Melt

The P content in H.C.FeMn alloy, after treatment with Mg, exhibits a relationship defined by equation (1) and can be estimated from the standard free energy of formation for Mg_3P_2 given by equation (1a). For the purpose of this study, H.C.FeMn alloy was assumed to have the following representative composition:

Mn 80 wt%, Fe 12.7 %, C 6.7, Si 0.6%.

The activity of Mg in H.C.FeMn alloy was obtained from the solution properties given by equation (5) for the Fe-Mn-C(sat.)-Mg system. The effect of P and Si was neglected.

The activity of P was calculated by using a modified form of equation (7) in order to accommodate the effect of Si. The interaction coefficient of Si on P, 0.12, was obtained from Sigworth and Elliott⁽¹⁸⁾. After transforming to a mole fraction coordinate, the resulting expression for the activity coefficient of P is given as follows:

$$\begin{aligned}\ln \gamma_{\text{P}(l)} &= -10.6377 + 16.7225 X_{\text{P}} \\ &\quad - 22.3617 X_{\text{P}}^2 + 12.367 X_{\text{C}} \\ &\quad + 25.52 X_{\text{Si}} \quad (7a)\end{aligned}$$

The effect of Mg was neglected.

The equilibrium solubility of Mg and P in H.C.FeMn alloy was calculated from equations (5) and (7a) and the standard free energy given by equation (1a) at various activities of Mg_3P_2 . The results are shown in Figure 5. The P content in the alloy varies inversely with Mg as suggested by equation (1). The experimental data of Tuset and Waernes are also shown. Barin and Knacke present a less negative value for the standard free energy formation of Mg_3P_2 (-71,655.51 cal. vs. -89,819.60). The similar relationship obtained by their value, which is also shown in Figure 5, indicates higher equilibrium contents of P and Mg than those obtained by Tuset and Waernes and this study. It appears that their value for the standard free energy, equation (1b), is in error.

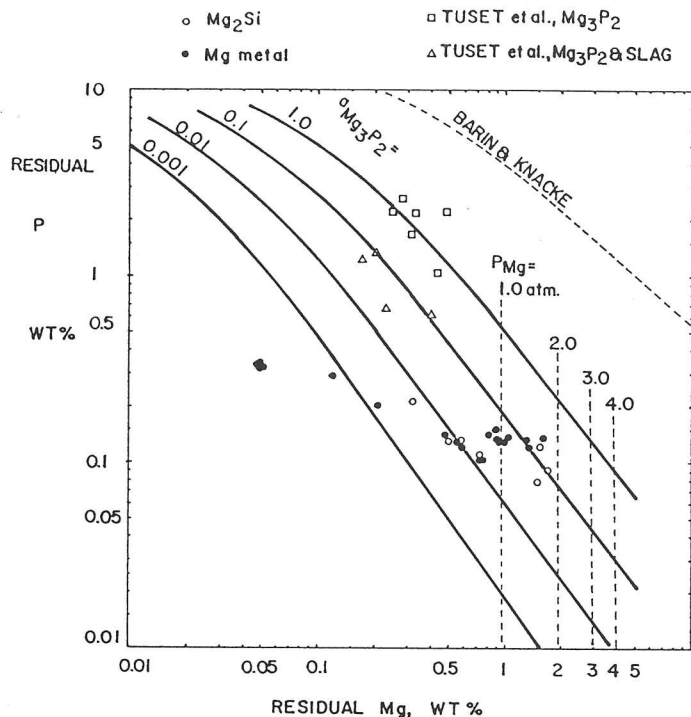


Figure 5. Relationship of Residual P and Mg in H.C.FeMn alloy.

The equilibrium relationship between P and Mg in H.C.FeMn alloy suggests that both are reduced as the activity of Mg_3P_2 is decreased. The relationship at activities of 0.1, 0.01, and 0.001 is shown also in Figure 5. Tuset and Waernes also determined the equilibrium relationship using $CaO-CaF_2-SiO_2$ and $CaO-CaCl_2$ based fluxes. Their results compare well with an activity of Mg_3P_2 of 0.1, as shown in Figure 5.

The vapor pressures of Mg at 1, 2, 3, and 4 atm. are also shown in Figure 5. This is to explain the effect of the vessel pressure on dephosphorization. The residual P and Mg contents determined in the present study are also shown in Figure 5. It is indicated that dephosphorization approaches the equilibrium relation at unit activity of Mg_3P_2 as the vessel pressure reaches 4 to 5 atmosphere gauge. The maximum residual Mg content is equivalent to that at an equilibrium Mg vapor pressure of about 2 atm. The difference between this and the vessel pressure is due to the premature evaporation of some of the Mg, even though this tends to decrease with increased vessel pressure.

If the product of the dephosphorization reaction, Mg_3P_2 , is dissolved in fluxes at a low activity, for example at 0.01 or less, it is feasible, in principle, to lower the P content further at a lower residual Mg content. This might be achieved at a moderate vessel pressure. The present study did not investigate the effect of fluxes systematically. However, the fluxes used in this study and by Tuset and Waernes are shown to be capable of reducing the activity to a range of 0.1. It would be desirable to develop

fluxes which dissolve magnesium phosphide at an activity of 0.01 or less.

A Plant Scale Test

The residence time of Mg can be increased by increasing the pressure. The required pressure may be effectively provided by a hydrostatic head of H.C.FeMn melt if Mg is released at a great depth.

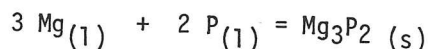
In order to test this, a Mg plunging bell was prepared by casting 20 lbs of molten Mg into a graphite crucible. This bell was plunged into 17 tons of H.C.FeMn melt contained in a ladle. During the initial 7.5 minutes, no reactivity was observed. After this time, the holder, which was one inch diameter steel bar, melted and separated from the plunging bell. Subsequently, the Mg containing bell floated to the surface of the melt and reacted with flaring and smoking but not violently. This activity continued for about 5 minutes. The next bell was plunged for only two minutes and removed from the melt and was found to be covered with a one inch thick frozen H.C.FeMn skull. Unreacted Mg was still contained inside of the bell at the time of its withdrawal from the melt.

The test shows that a frozen skull of H.C.FeMn alloy is initially formed around the bell as it is plunged. This happens because the cold mass draws heat from the immediate surroundings of the bath. Until the skull melts back, Mg can not be released. An analysis by a heat transfer model indicates that the thermal conductivity of the frozen skull of H.C.FeMn alloy is about 0.065 cal/cm-sec-K. It was judged from this experience that plunging massive Mg pieces is impractical. A subsequent heat transfer analysis suggested, however, that Mg injection in granules or wire might be practical.

CONCLUSION

Phosphorus in molten H.C.FeMn can be removed with the use of Mg and Mg_2Si under reducing conditions. Because of the low boiling point of Mg, the addition of it should be done in such manner to minimize the premature evaporation loss of Mg and to increase the residence time of it. This can be achieved by applying an external pressure or by a hydrostatic head of the alloy melt. The plunging of massive pieces of Mg is impractical, but the injection method of Mg granules or wire may be feasible.

The standard free energy of formation of Mg_3P_2 at 1300°C was estimated from the data of Tuset and Waernes⁽¹⁶⁾ as follows:



$$\Delta G^\circ = -89,819.60 \text{ cal.} (\pm 11,700) \text{ at } 1300^\circ\text{C.}$$

This information was used to estimate the solubility relationship of P and Mg in molten H.C.FeMn at various activities of magnesium

phosphide. The result suggests that a flux which dissolves magnesium phosphide at an activity of

0.01 or less will further improve the degree of dephosphorization.

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