The Determination of the Activities in Mn-C and Mn-Si Melts by the Vapor Pressure Measurement*

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The activities of manganese in Mn-C and Mn-Si melts at 1673 K have been determined. The transportation method was applied to the vapor pressure measurement. The activities of manganese in the Mn-C melts as referred to pure liquid manganese showed the positive deviation from ideality at less than 0.17 atomic fraction of carbon and deviated negatively above this value. The activities of manganese and silicon in the Mn-Si melts showed a remarkable negative deviation from ideality. Some thermodynamic quantities at 1773 K were calculated on the assumption that the Mn-Si melts are considered to be a semi-regular solution.

(Received May 7, 1979)

I. Introduction

The demand for various kinds of ferroalloys has made a steady increase in recent years with the development of the iron and steel industry. The increase of the producibility, the rationalization of the operation, the improvement of the yield and the quality for the product are strongly demanded. However, the physical chemistry of the smelting reactions of these materials, which forms the basis of the solution of these problems, has not been clear. It is considered that this is partly due to the fact that there is very few data concerning the activities of the components of ferroalloys in the molten state at high temperature.

Commercial ferromanganese and silicomanganese can be regarded approximately as quaternary alloys of the Mn-Fe-Si-C system, regarding the activities of the various components of alloy solutions in this system with Mn as the solvent, there have been no reports as far as the author concerned. The author undertook to determine the activities of the above-mentioned alloy solutions.

Mn and its compounds are chemically extremely active at high temperature, reacting with all kinds of refractories, sample vessels

and atmospheric gases so that it is difficult to measure their activities by any method. Thus experimental errors are unavoidable in their determination. Although a few methods have been carried out, the vapor pressure measurement of Mn by the transportation method showed good results with the highest reproducibility. In this paper, the outline of this method and the activities of Mn in the Mn-C and Mn-Si alloy solutions obtained by this method are reported.

II. Experimental

A schematic diagram of the apparatus for the vapor pressure measurement used in this study is shown in Fig. 1(A). This was designed after the apparatus used by Alcock and Hooper⁽¹⁾ and Yazawa, Azakami and Kawashima⁽²⁾, but it was slightly modified for the use of the

a: Argon, b: gas purifier, c: needle valve, d: flow meter, e: inner reaction tube, f: resistance furnace, g: outer reaction tube, h: thermo-couple, i: boat holder, j: boat, k: sample, l: orifice.

* This paper was originally published in Japanese in J. Japan Inst. Metals, **41** (1977), 601.

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different materials so as to be able to withstand at high temperature experiments as Mn vapor is apt to oxidize and to erode refractory materials. As far carrier gas, commercial high-purity Ar gas was used after refining with rare gas purifier. This gas was branched into two paths, each of which was passed through a needle valve and a flow meter. Its flow rate was adjusted finely and measured. Gas flow through one path is introduced into the inner reaction tube of the furnace and it allowed to flow on the surface of the sample inserted into the end of the tube. The structure of this part is also shown in Fig. 1(B). Carrier gas saturated with the Mn vapor from the surface of the sample flows into the outer reaction tube from an orifice with 1 mm diameter installed on the upper part of the inner reaction tube. Ar gas flowing through the other path is introduced into the outer reaction tube, and then quickly washes away the Mn vapor flowing out from the orifice and discharges it out of the furnace. The inner reaction tube, the outer reaction tube, the sample boat and the thermocouple protecting tube were all made of high-purity alumina materials so that they might be able to withstand the violent erosive action due to the Mn vapor. Temperature was measured with a PR thermocouple which was inserted into the furnace in such a way that it could contact the outer surface of the end of the inner reaction tube, and its indication was thoroughly pre-adjusted so that it would be equal to the indications for the entire surface of the sample and the neighborhood of the orifice. Copper pipes wound round the outer shell of the furnace were used in order to cool the sample after measurement.

Measurement was carried out for two hours in order to attain the required accuracy. The vapor pressure of the element other than Mn are so small as compared with that of Mn. Thus a decrease in the sample weight during the measurement is considered to be only for the evaporation of Mn. The error can be disregarded. However, when the partial pressure of the oxygen of carrier gas is high, the formation of SiO having a vapor pressure which is equal to that of Mn must be considered. Therefore, attention should be paid to this

point in the measurement for the Si containing alloy solutions.

From the results of the above-mentioned experiments, the apparent vapor pressure P_{Mn}^a can be obtained by use of the following expression:

$$P_{\text{Mn}}^a = \frac{22.412 W/M}{22.412 W/M + V_g} \times 101325, \text{ (Pa)} \quad (1)$$

where W is the decrease in weight of the sample during measurement (kg), M is the atomic weight of Mn and V_g is the total volume of the carrier gas introduced into the inner reaction tube during measurement (m^3).

Alcock and Hooper⁽¹⁾ from the measurement of the vapor pressure by the transportation method state as follows: when the carrier gas flow rate is low, the vapor pressure shows a high value as the result of the diffusion of volatile species, but when the carrier gas flow rate is high, on the contrary, the vapor pressure shows a low value due to the unsaturation of volatile species in out flowing gas. On the basis of these results, they propose that the value of the vapor pressure obtained by the measurement in a proper intermediate flow rate region should be considered as the saturated vapor pressure. Thus, in this study the measured value of the vapor pressure in the Ar flow rate region, which indicates the constant evaporation against flow rate was used, and regarded as the vapor pressure of Mn in the alloy solution.

The chemical composition of materials used in this experiment are shown in Table 1. As the concentration of each alloy solution, the average value between the analytical value of each element after measurement and the value before measurement as calculated on the assumption that the evaporation of Mn during the measurements should be added was adopted taking the change in concentration during the measurement into account.

III. Results and Discussion

1. Vapor pressure of pure manganese

In order to examine the accuracy of the vapor pressure by the above-mentioned method

Table 1 Chemical composition of materials used for preparing of samples (%).

	Mn	C	Si	P	S	Fe
Electrolytic manganese	99.26	0.007	0.007	0.001	0.019	0.001
Electrolytic iron	0.005	0.005	0.005	0.003	0.003	99.9
Metallic silicon	—	0.10	98.00	0.05	0.05	0.70
	Fixed carbon	Moisture	Ash	Volatile matter		
Graphite powder	99.13	0.25	0.19	0.43		

and to determine reference values for the calculation of the activities of various alloy solutions in this study, the measurement for the saturated vapor pressure of Mn was performed several times using electrolytic manganese by two sets of devices of the same design at 1623 and 1673 K. Values obtained showed comparatively good reproducibility:

$$P_{\text{Mn}} \text{ at } 1623 \text{ K} = (5.18 \pm 0.03) \times 101.325 \text{ (Pa)}$$

$$P_{\text{Mn}} \text{ at } 1673 \text{ K} = (8.93 \pm 0.02) \times 101.325 \text{ (Pa)}$$

Concerning the vapor pressure of Mn, a number of measured results have been reported hitherto. The values obtained by the present study were slightly higher than those compiled by Hultgren, Desai, Hawkins, Gleiser, Kelley and Wagman⁽³⁾, and those by Baim and Knacke⁽⁴⁾. Accordingly, the activities of Mn in various alloy melts were calculated on the basis of these numerical values.

2. Activities of Mn in Mn–C alloy melts

Table 2 shows the results of the measurement of the vapor pressure of Mn in Mn–C alloy melts with various carbon concentrations at 1673 K, and the activities (a_{Mn}) and the activity coefficient (γ_{Mn}) of Mn as referred to pure liquid Mn as the standard state. The relationships between N_{C}^2 and $\ln \gamma_{\text{Mn}}$ obtained from these figures is shown in Fig. 2. Where N_{C} is atomic fraction of carbon. It is found that each plot is nearly located on the straight lines given by the following two expressions:

$$\ln \gamma_{\text{Mn}} = 5.208 N_{\text{C}}^2, \quad (N_{\text{C}} < 0.12) \quad (2)$$

$$\ln \gamma_{\text{Mn}} = -10.714 N_{\text{C}}^2 + 0.207. \quad (N_{\text{C}} > 0.12) \quad (3)$$

As regard the phase diagram in the Mn–C system, one adopted by Hansen⁽⁵⁾ has been most widely used so far. However, this is greatly different from the result reported by

Table 2 Vapor pressure, activity, and activity coefficient of Mn in Mn–C melts at 1673 K.

N_{Mn}	N_{C}	P_{Mn} (10^2 Pa)	a_{Mn}	γ_{Mn}
1.000	0	9.043	1.000	1.000
0.941	0.059	8.762	0.969	1.030
0.923	0.077	8.637	0.955	1.035
0.897	0.103	8.545	0.945	1.054
0.875	0.125	8.417	0.931	1.064
0.849	0.151	7.746	0.857	1.009
0.829	0.171	6.682	0.739	0.891
0.803	0.192	6.295	0.696	0.861
0.778	0.222	5.191	0.574	0.738
0.747	0.253	4.289	0.474	0.635
0.731	0.269	3.418	0.378	0.517

Fig. 2 Relation between N_{C}^2 and $-\ln \gamma_{\text{Mn}}$ for the Mn–C system at 1673 K.

Benz, Elliott and Chipman⁽⁶⁾. The major difference lies in stable carbide and its existing region at temperatures lower than 1400 K. For Mn_7C_3 , for example, Hansen admitted the presence of solid solution region but Benz *et al.* did not admit it at all. Concerning to the high temperature region related to this study, Hansen expressed it with many indefinite

Fig. 3 Phase diagram of the Mn-C system.

Fig. 4 Activities of Mn in Mn-C melts at 1673 K.

broken lines but Benz *et al.* did not refer to it at all. If the high temperature region shown in the diagram by Hansen and the low temperature region shown in the diagram by Benz *et al.*

are joined together according to the author's judgement, the diagram as shown in Fig. 3 was obtained. Judging from this diagram it is considered that the bending point of the straight line shown in Fig. 2 that is $N_C^2 \doteq 0.014$ ($N_C \doteq 0.12$) is the boundary between γ phase and ϵ phase. It is presumed that the difference between the atomic bondings in two different solid phases gives the effect on the thermodynamic properties of the solutions at 1673 K. Assuming the semi-regular solution defined by Chipman⁽⁷⁾, the activity curve of Mn as shown in Fig. 4 was obtained by using expressions (2) and (3).

The phase diagrams shown in Fig. 3 did not indicate the composition more than $N_C = 0.3$. In the diagram obtained by Benz *et al.* the graphite phase is present as shown in Fig. 3. However, judging from the carbon concentration measured by them, it is assumed that the formation of graphite was very small and it was undistinguishable whether it was graphite or not. Assuming that the higher Mn carbide having a solid solution region exists in the composition range when N_C is higher than 0.3, it is of no use to obtain the value of activities of carbon by the use of Gibbs-Duhem's integration. For this reason, a polished graphite piece was immersed in carbon saturated manganese solution for hours and equilibrated at 1673 and 1773 K. The interface between the graphite piece and manganese melt solidified was examined by EPMA after rapidly cooling. Changes in the concentrations of Mn and C in this part at the two temperatures are shown in Fig. 5. At 1773 K graphite layer is in direct contact with a solidified carbon saturated manganese layer while at 1673 K an intermediate layer with a thickness of about 200 μm is observed. It is presumed that a layer which was of a single phase at high temperature was separated by cooling. The preparation of the standard sample was difficult, so it was impossible to identify the intermediate layer and the further investigation is necessary. However, it can be considered that there is the possibility of the formation of higher carbide of Mn when N_C is over 0.3 at least in the case of 1673 K. Therefore, the value of the activity of carbon was not obtained by the calculation.

Fig. 5 Distribution of Mn and C in the interface between carbon saturated manganese and graphite at 1673 and 1773 K.

Table 3 Vapor pressure, activity and activity coefficient of Mn in Mn-Si melts at 1673 K.

N_{Mn}	N_{Si}	P_{Mn} (10^2 Pa)	a_{Mn}	γ_{Mn}
1.000	0	9.043	1.000	1.000
0.915	0.085	7.849	0.911	0.996
0.850	0.150	7.108	0.825	0.971
0.809	0.191	5.102	0.592	0.732
0.747	0.253	4.216	0.489	0.635
0.713	0.287	3.293	0.364	0.511
0.642	0.354	2.278	0.264	0.412
0.554	0.446	1.100	0.128	0.231
0.534	0.466	1.062	0.117	0.219
0.431	0.579	0.539	0.060	0.143
0.331	0.669	0.287	0.032	0.097

3. Activities of Mn and Si in Mn-Si alloy melts

The saturated vapor pressure of Mn at 1673 K was measured for the different Mn-Si alloy melts, and the activity of Mn was calculated from the value of saturated vapor pressure. The results are shown in Table 3. Figure 6

Fig. 6 Relation between N_{Si}^2 and $-\ln \gamma_{\text{Mn}}$ for the Mn-Si system at 1673 K.

Fig. 7 Phase diagram of the Mn-Si system.

shows the relationships between N_{Si}^2 and $\ln \gamma_{\text{Mn}}$ calculated from these values in Mn-Si alloy melts at 1673 K. It is found from this figure that each point is located on the two straight lines which cross with each other when $N_{\text{Si}}^2 \div 0.18$ ($N_{\text{Si}} \div 0.42$).

Figure 7 shows the phase diagram of Mn-Si system adopted by Hansen⁽⁸⁾. Later, in 1973, the new phase diagram of this system was published in the Metals Handbook⁽⁹⁾, but this phase diagram does not cover all concentration regions of this system and there is no significant differences in the high temperature region between the two diagrams. In this paper, therefore, Hansen's phase diagram was used for the present discussion.

According to Hansen's diagram, $N_{\text{Si}} \div 0.42$ is close to that of the compound Mn_5Si_3 having its melting point at 1558 K. It is impossible to determine only from this fact that it is the

Fig. 8 Activities of Mn and Si in Mn-Si melts at 1673 K.

semiregular solution, but activity of silicon and some thermodynamic values were calculated on the assumption of the semiregular solution.

The two straight lines at 1673 K in Fig. 6 can be given by the following expressions:

$$\ln \gamma_{\text{Mn}} = -7.06 N_{\text{Si}}^2, \quad (N_{\text{Si}} < 0.42) \quad (4)$$

$$\ln \gamma_{\text{Mn}} = -4.05 N_{\text{Si}}^2 - 0.52. \quad (N_{\text{Si}} > 0.42) \quad (5)$$

Calculating the value of the activity of Mn from these two expressions and plotting it against the N_{Si} , the activity curve of Mn was obtained as shown in Fig. 8. Each points along this line are based on the actual measurement and there is little difference between each measuring points and the calculated curve.

The values of activities of Si can be obtained from the values of the activities of Mn shown in Fig. 8 by Gibbs-Duhem's integration. However, this solution cuts the primary crystallization line of Si at 1673 K when $N_{\text{Si}} = 0.92$ as shown in the phase diagram (Fig. 7), and therefore solid and liquid coexist when N_{Si} exceeds 0.92. Therefore, the activities of Si by the above calculation were obtained with respect to the solid silicon as the standard state. Figure 8 shows the results from the conversion of the value of $a_{\text{Si(solid)}}$ to $a_{\text{Si(liquid)}}$ by use of the melting point (1683 K) and heat of fusion (50.626 kJ/mol) adopted by Kubaschewski, Evans and Alcock⁽¹⁰⁾.

Fig. 9 Some thermodynamic quantities of Mn-Si melts at 1773 K.

The results shown in Fig. 8 were converted to the values at 1773 K at which the solution is of liquid phase in all concentration regions on the assumption of the semi-regular solution, and from the results the value of partial molar free energy of mixing $\Delta \bar{G}_{\text{Mn}}^{\text{M}}$, $\Delta \bar{G}_{\text{Si}}^{\text{M}}$, integral molar free energy of mixing ΔG^{M} , partial molar heat of mixing $\Delta \bar{H}_{\text{Mn}}^{\text{M}}$, $\Delta \bar{H}_{\text{Si}}^{\text{M}}$ and integral molar heat of mixing ΔH^{M} in the Mn-Si alloy melts were calculated. These results are shown in Fig. 9.

IV. Summary

The transportation method was used in order to determine the activity of Mn in Mn-C and Mn-Si melts at 1673 K. The results of this study can be summarized as follows:

(1) The saturated vapor pressure of the electrolytic manganese was measured using Ar gas as carrier gas. Consequently the measured value of vapor pressure was found to be in agreement with the previously reported value.

(2) Activities of Mn in Mn-C alloy melts with the concentration ranging from 0 to 0.269 atomic fraction of C, which is carbon saturated composition, were obtained as the results of the vapor pressure measurement.

It was found from the results that the activities of the melts in this system deviated positively at lower carbon concentrations than 0.17 atomic fraction of C, and negatively at higher carbon concentrations than 0.17 atomic fraction of C.

(3) Activities of Mn in Mn-Si melts were obtained by the same method. Activities of Si with respect to liquid silicon as the standard state were determined from the calculation assuming the semi-regular solution. It was observed that the activities of Mn and Si in this system deviated remarkably negative in all concentration ranges. Further, the integral and partial molar heat of mixing and the free energy of mixing at 1773 K were calculated.

The author wishes to express his sincere thanks to those who advised and cooperated me throughout this study.

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