An Evaluation of the Stabilities of the Ternary Compounds at Low Oxygen Potentials in the Ternary System Fe-Na-O

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ABSTRACT

A clarification of the thermodynamic relationships in the ternary system Fe-Na-O at low oxygen potentials is presented. The Gibbs energy of the compound $FeNa_4O_3$ was evaluated from the enthalpy data and the phase diagram information available in literature by using the thermodynamic calculation program in the Thermo-Calc Databank System. The phase diagram of the Fe-Na-O ternary system was calculated at 853 K. An oxygen-sodium potential phase diagram of this system computed at the same temperature is also presented.

INTRODUCTION

An understanding of the thermodynamics of the ternary system Fe-Na-O is of relevance to iron-making processes in view of alkali circulation. A knowledge of the phase stabilities of the various ternary compounds in this system is extremely important in understanding the corrosion of stainless cooling tubes in nuclear reactors containing liquid sodium coolant. The FeO-Na_2O pseudo-binary section of the Fe-Na-O system worked out earlier in the present laboratory is reproduced in Fig. 1 /1/. According to this diagram, three ternary compounds exist in the FeO-Na_2O section viz. $Fe_2Na_2O_4$ ($Fe_2O_3 \bullet Na_2O$), $FeNa_2O_2$ ($FeO \bullet Na_2O$) and $FeNa_4O_3$ ($FeO \bullet 2Na_2O$). Of these, $Fe_2Na_2O_4$ which actually belongs to the Fe_2O_3-Na_2O join was shown /1/ to have extended stabilities even at lower oxygen potentials. $Fe_2Na_2O_4$ and $FeNa_4O_3$ were characterized by X-ray diffraction studies done earlier /2,3/, while the compound $FeNa_2O_2$ has so far not been structurally identified.

A study of the thermodynamics of the above compounds were done earlier /4/ in this laboratory, and from the results a phase stability diagram was drawn corresponding to 873 K, see Fig. 2. The following basic thermodynamic inconsistencies appear in this diagram:

1. The function of the partial pressures for the four-phase equilibrium, gas, $Fe_2Na_2O_4$(s), $FeNa_4O_3$(s) and $FeNa_2O_2$(s) given in Table 6 in Dai et al. /4/, viz.

$$4\log(P_{Na}) + \frac{1}{2}\log(P_{O_2}) = -\frac{59632}{T} + 43.22 \qquad (1)$$

   cannot be a function of P_{Na} and P_{O2} at constant temperature since it refers to an invariant point.

2. The partial pressure function for the three-phase equilibrium, gas, $Fe_2Na_2O_4$(s) and wüstite given in the same table /4/, viz.

$$\log(P_{O_2}) = -\frac{19385}{T} - 3.07 \qquad (2)$$

   cannot be a function of P_{O2} alone but of both P_{O2} and P_{Na}.

3. The corrosion of the stainless steel tubes with liquid sodium coolants in nuclear reactors is attributed to the formation of $FeNa_4O_3$ due to the oxygen dissolved in liquid sodium /5,6/. On the other hand, according to earlier work /4/, the standard Gibbs energies of formation of

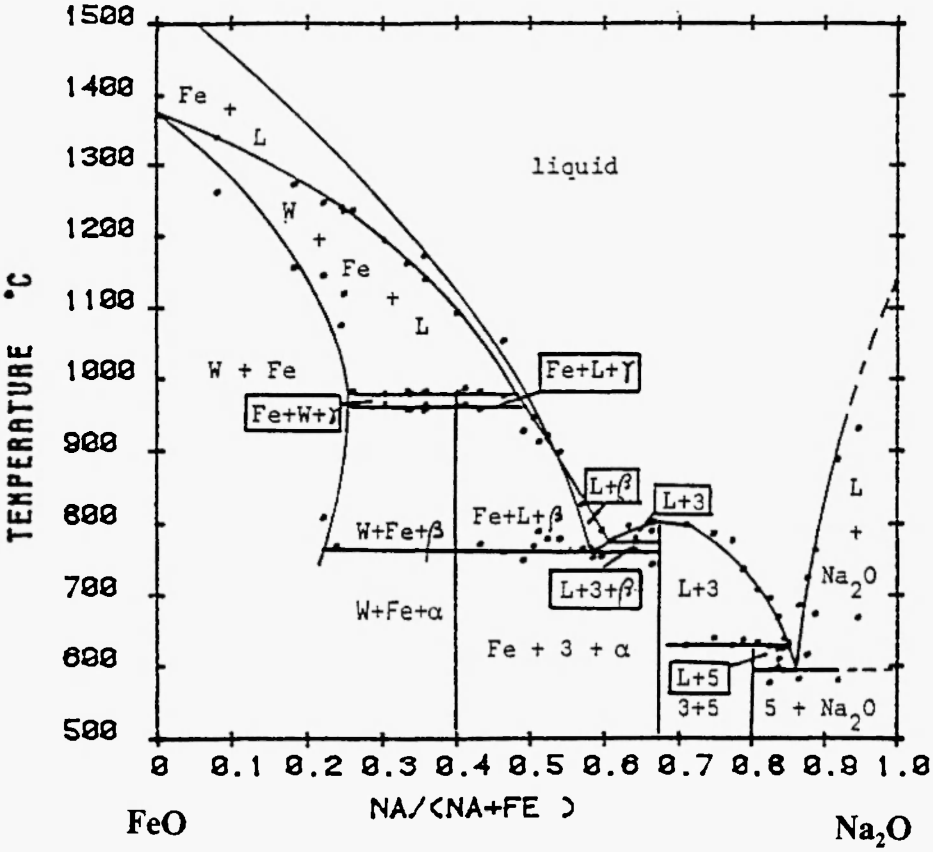

Fig. 1: The FeO-Na_2O section of the Fe-Na-O system /1/.
w: Wüstite, α: α-$Fe_2Na_2O_4$, β: β-$Fe_2Na_2O_4$, γ: γ-$Fe_2Na_2O_4$, 3: $FeNa_2O_2$, 5: $FeNa_4O_3$.

$FeNa_2O_2(s)$ and $FeNa_4O_3(s)$ from the component oxides are as follows:

$$Na_2O(s) + FeO(s) = FeNa_2O_2(s) \quad (3)$$
(Eq. 21 in Dai et al. /4/)

$$\Delta G_3° = -119106(\pm 3730) + 113.74T \quad J.mol^{-1} \quad (4)$$
(Eq. 32 in Dai et al. /4/)

$$2Na_2O(s) + FeO(s) = FeNa_4O_3(s) \quad (5)$$
(Eq. 22 in Dai et al. /4/)

$$\Delta G_5° = -147998(\pm 8210) + 164.8T \quad J.mol^{-1} \quad (6)$$
(Eq. 34 in Dai et al. /4/)

The temperature limits for Eqs. 4 and 6 are not given in Dai et al. /4/. Note that Dai et al. /4/ measured the enthalpies for reactions (3) and (5) by acid-solution calorimetry, and the uncertainties reported by these authors are given in brackets. On the other hand, these authors used an approximated Temkin approach in deriving the entropy terms in Eqs. 4 and 6, and the uncertainty limits for these terms are unknown. Combining Eqs. 4 and 6, the Gibbs energy change for the reaction

$$Na_2O(s) + FeNa_2O_2(s) = FeNa_4O_3(s) \quad (7)$$

can be expressed as

$$\Delta G_7° = -28892 + 51.06T \quad J.mol^{-1} \quad (8)$$

This indicates that $\Delta G_7°$ is zero at 566 K and $FeNa_4O_3(s)$ should spontaneously decompose to $Na_2O(s)$ and $FeNa_2O_2(s)$ above this temperature. This contradicts the stability diagram in Fig. 2. The compound $FeNa_4O_2(s)$ was synthesized and characterized structurally and was even identified

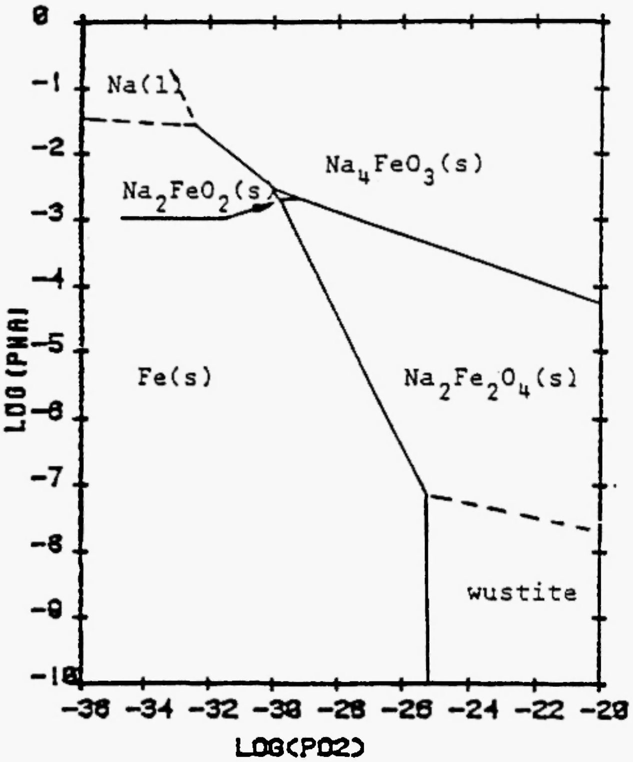

Fig. 2: Phase stability diagram of the Fe-Na-O system at 873 K /4/.

when liquid sodium containing oxygen was heated in iron containers at 873 K and above /5/. The standard Gibbs energy of formation of Na_2O has also been reasonably well established in the literature. The inconsistency of $\Delta G_7°$ may be attributed to the error associated with $\Delta G_3°$.

The present work provides an evaluation of the stabilities of the ternary compounds in the Fe-Na-O system considering all available data. Although complete data for all phases in this system are not available, a critical assessment of the existing data is presented in view of the technological importance of the phase relations at reduced oxygen partial pressures. Clearly, more thermodynamic and phase equilibrium studies are required to map the system completely.

THERMODYNAMIC CONSIDERATIONS

In the following section, a critical survey of the available thermodynamic information is made.

The Fe-O System

The Fe-O system has been extensively studied over the last decades. The various studies are not discussed here, as the thermodynamic data of this system have been well established. Recently assessed thermodynamic data /7/ was used in the present study. The information presented by this author /7/ is extensive. For the sake of brevity, the present authors chose not to reproduce this voluminous information from Sundman /7/. Since the study was aimed at the region of low oxygen potential, Fe_2O_3 was excluded in the present calculation.

Magnetite and Wüstite Phases with Dissolved Sodium

In the solid solubility region of Na in wüstite given in Fig. 1, the phase boundary curve below 1223 K is based on only two experimental points. Further, the curvature of the line indicates an abnormal bending towards the Fe-FeO-Fe_3O_4 ternary eutectoid temperature at 859 K. Hence, in the case of wüstite, the solid-state galvanic cell measurement results by Sjödén et al. /8/ in the study on FeO-$Fe_2Na_2O_4$ system were used. According to these authors, the solubility of Na in FeO in the FeO-$Fe_2Na_2O_4$ section when expressed as the cation fraction, $M_{Na}/(X_{Na} + X_{Fe})$ was 0.116 at 1074 K and 0.118 at 1159 K, respectively. No experimental data has been reported for solubility of Na in magnetite.

The Fe-Na System

No intermediate compound has been reported in this system. The solubility of liquid sodium in α-Fe is below the limit of detection /9/. On the other hand, the solubility of iron in liquid sodium was determined by Baus /10/ using a radio-chemical technique. The solubility of iron was reported to be $2.05x10^{-7}$ at% at 400 K and $3.4x10^{-7}$ at% at 500 K. In view of these very low values, the solubility of Fe in Na was considered to be negligible in the present work.

The Na-O System

The phase diagram /11/ shows that the lowest oxide in the Na-O system is Na_2O. This oxide has a CaF_2-type cubic structure below 785 K. Above this temperature, it has the hexagonal structure. It further transforms to a tetragonal modification at 843 K. The Gibbs energies of this compound as well as those of pure liquid sodium were taken from the SGTE substance database /12/ which are in turn based on JANAF /13/.

The solubility of oxygen in liquid sodium was measured by a number of workers and the results reported differ widely from each other /14,15/. For example, the solubility value at 853 K has been variously reported from 3176 ppm /14/ to 5215 ppm /15/. It was felt by the present authors that the incorporation of the highly uncertain oxygen solubilities in Na(l) at the present stage would only add to the prevailing confusion. Hence, as a first approximation, these solubilities were assumed to be negligible.

$Na_2Fe_2O_4$

The enthalpy of the reaction

$$Na_2O(s) + Fe_2O_3(s) = Na_2Fe_2O(s) \qquad (9)$$

was estimated by Koehler et al. /16/ to be -154.6 kJ/mol from the results of calorimetric measurements. According to a later estimate by Kubaschewski /17/, $\Delta H_9°$ is -87.9 (±16.7) kJ/mol. Kelley and King /18/ estimated the entropy change for reaction (9) to be 12.97 J/mol•K. Barin and Knacke /19/ incorporated the enthalpy, heat capacity and entropy values reported in the literature /17,20/ in the estimation of the ΔG^0 for reaction (9) in the temperature range 298-1618 K, which leads to the following expression:

$$\Delta G_9° = -85973-18.755T \text{ J/mol} \qquad (10)$$

These authors did not report any error limit for the $\Delta G_9°$ values.

Dai et al. /4/ measured the standard Gibbs energy of reaction (9), $\Delta G_9°$, by means of a galvanic cell with β-Al_2O_3 as the solid electrolyte. According to these authors, $\Delta G_9°$ is represented by the equation:

$$\Delta G_9° = -86002 - 61.89\,T \text{ J/mol} \qquad (11)$$

in the temperature range 923-1023 K. The cell EMF shows a scatter corresponding to 22 $J.mol^{-1}$. A comparison of Eqs. 10 and 11 reveals that while the enthalpy terms agree with each other, there is a large discrepancy in the entropy terms. It should be noticed that for a number of reactions similar to (9) the entropy terms are comparable to that in Eq. 10. Although Eq. 11 was obtained by direct measurements, it was based on only one experimental series. In view of this, Eq. 11 was not used in the present calculation.

Shaiu et al. /21/ measured the Gibbs energies in the Fe-Na-O system by means of a galvanic cell method involving ZrO_2-CaO as well as CaF_2 solid electrolytes in the temperature range 700-1100 K. The galvanic cells used by these authors can be represented as

$$Ca, CaF_2 \,//\, CaF_2 \,//\, NaF, FeO, Fe, FeNa_2O_2 \text{ --- (I)}$$

$$FeO, Fe_2Na_2O_4, FeNa_2O_2 \,//\, ZrO_2\text{-}CaO \,//\, Cu_2O, Cu \text{ -- (II)}$$

According to Fig. 1, the various phases in the measuring electrodes are not in equilibrium with each other. Furthermore, existence of the compound $FeNa_2O_2$ is questionable. Hence, the composition of the working electrode at the experimental temperature is quite uncertain. Therefore, their results were also excluded in the calculation.

The values of the standard Gibbs energy for $Na_2Fe_2O_4$, $G^0_{Fe2Na2O4}$ relative to the enthalpy of selected reference states for the elements at 298.15 K (Stable Element Reference, SER) reported by Barin and Knacke /19/ were used in the present evaluation. These values can be expressed by the following equation in the temperature range 298-1023 K:

$$G^0_{Fe_2Na_2O_4} = -1391171.5+1167.58T-199.51T\ln(T)-0.013345T^2 \qquad (12)$$

$FeNa_2O_2$

This compound has not been structurally established so far. Its existence was briefly mentioned by Wu et al. /2/ without any X-ray evidence. Shaiu et al. /21/ incorporated a composition corresponding to this compound in their electrodes. These authors did not examine the electrodes by X-ray diffraction before or after their experiments. Dai et al. /4/ measured the enthalpy of formation of this compound from the component oxides by acid solution calorimetry. These authors "synthesized" this compound by mixing "FeO" and Na_2O and melting the mixture in sealed platinum crucibles. The Na_2O used was of synthetic grade, E Merck /1/. The sample corresponding to the composition $FeNa_2O_2$, which was molten and solidified, was used directly in the calorimetric experiments without being structurally characterized. No mention was made regarding the chemical analyses of the samples before they were used in the calorimetric experiments.

Knights and Phillips /22/ did not observe $FeNa_2O_2$ in their X-ray diffraction studies. Sridharan et al. /23/ could not succeed in their attempts to synthesize this compound. Instead, in their experiments, these authors obtained evidence for the presence of the compound $FeNa_3O_3$ ($Fe_2O_3 \cdot 3Na_2O$) with the same Na/O ratio but different Fe/Na ratio. In the absence of structural characterization for the samples used in the calorimetric studies /4/, the results of the experiments may be attributed to the heat effects produced by other phases present in the system including $FeNa_3O_3$. In a similar way, even the DTA results corresponding to the region where this phase is indicated in Fig. 1 may be attributed to the presence of other phases. Hence, according to the present authors, there is a serious case for doubting the existence of the compound $FeNa_2O_2$ as well as the corresponding portion of the phase diagram in Fig. 1.

$FeNa_4O_3$

The data regarding the Gibbs energy of formation of $FeNa_4O_3$ is not available in the literature. The heat of formation of this compound from the component oxides was measured by Gross and Wilson /2/ and Dai et al. /4/ using acid-solution calorimetry with hydrochloric acid as the solvent. For the reaction

$$2\,Na_2O(s) + FeO(s) = FeNa_4O_3(s) \qquad (13)$$

Gross and Wilson /2/ report a $\Delta H°$ value of -104893 (±2300) J/mol while according to Dai et al. /4/ the enthalpy change for the above reaction, $\Delta H_{13}°$, is -147988 (±8210) J/mol. Notice that the heats of solution of pure Na_2O in hydrochloric acid reported in both the measurements reasonably agree with each other. For the heat of solution of pure metastable FeO, Gross and Wilson /2/ assumed the value available in the literature while Dai et al. /4/ made their own measurements. In the latter case, the experimental error is likely to be compensated. The results of Dai et al. /4/ with respect to the solution of FeO in 6N HCl are somewhat lower than similar measurements done earlier by Prasad et al. /24/. In the present work, the value of $\Delta H_{13}°$ measured by Dai et al. /4/ was accepted.

In order to evaluate the entropy of $FeNa_4O_3$ in the present work, the phase diagram information of Dai et al. /1/ at the Na-rich side in Fig. 1 was employed. A two-sublattice model for ionic solutions /25/ was applied to the liquid phase in the $FeNa_4O_3$-Na_2O section. According to this model, the liquid phase can be expressed by a formula $(Fe^{+2},Na^{+})_P(O^{-2},Va)_Q$, where P and Q represent the site number on each sublattice. Va stands for vacancies. Considering the uncertainty of the existence of $FeNa_2O_2$, the three-phase equilibrium, $FeNa_2O_2$-$FeNa_4O_3$-liquid at 904 K was not included in the calculation. Instead, this temperature was considered to coincide with the melting point for $FeNa_4O_3$. As the existence of the compound $FeNa_2O_2$ is seriously questioned in the present work, the present authors attribute the DTA points corresponding to the liquidus above 904 K to the probable presence of other ternary compounds. In this connection, it is noteworthy that Sridharan et al. /23/, in their attempts to synthesize $FeNa_2O_2$, could only arrive at the compound $FeNa_3O_3$. Hence it is re-emphasized that the DTA results produced in Fig. 1 cannot be relied upon unless corresponding structural evidence is obtained. In the present work, the entropy term in the Gibbs energy of $FeNa_4O_3$ was kept as a variable, which was optimized together with the model parameters for the liquid phase using the experimental phase diagram data. The optimization was performed on a computer using a program called PARROT /26/.

The Gibbs energy of $FeNa_4O_3$ obtained is shown in Table 1. The Gibbs energies of the other phases are

Table 1

$G°-H^{SER}$ in J/mol of formula units for the various phases

TEMP. K	Na(l) Reference [12]
298.15-3000.00:	+F6913T+2602.488-7.0146846*T
	F6913T
298.15-371.00:	+24465.1072-1352503.1*T**(-1)-708.745026*T+116.337794*T*ln(T)-.268543764*T**2+8.636822E-05*T**3
371.00-3000.00:	-10610.091+194.87787*T-37.4696446*T*ln(T)+.00957008412*T**2-1.76864653E-06*T**3

TEMP. K	Na(gas) Reference [12]
298.14- 3000.00:	+F6916T+8.31451*T*ln(9.8692327E-06*P)
	F6916T
298.15-1700.00:	+101561.541-14.3943805*T-20.786112*T*ln(T)

TEMP. K	Na_2O Reference [12]
298.15-1023	+F6953T
	F6953T
298.15-600.00:	-430663.484-209099.584*T**(-1)+146.38589*T-27.2198488*T*ln(T)-.07674502*T**2+1.6095848E-05*T**3
600.00-1023.00:	-450304.105+1147231.88*T**(-1)+485.311362*T-80.993872*T*ln(T)-.0109365576*T**2+9.42724933E-07*T**3
1023.00-1405.20:	-446703.462+489.879027*T-82.562872*T*ln(T)-.00617663*T**2

TEMP. K	O_2(gas) Reference [7]
	+GO2GAS+8.31451*T*ln(9.8692327E-06*P)
	GO2GAS
298.15-1000.00:	-6961.74451-76729.7484*T**(-1)-51.0057202*T-22.2710136*T*ln(T)-.0101977469*T**2+1.32369208E-06*T**3
1000.00-3300.00:	-13137.5203+525809.556*T**(-1)+25.3200332*T-33.627603*T*ln(T)-.00119159274*T**2+1.35611111E-08*T**3

TEMP. K	$Fe_2Na_2O_4$
298.15- 3000.00:	-1391171.5+1167.57665*T-199.505779*T*ln(T)-.0133451352*T**2

TEMP. K	$FeNa_4O_3$
298.15-3000:	-147988+2*F6953T+GWUSTITE+68.8496387*T
	F6953T
298.15-600.00:	-430663.484-209099.584*T**(-1)+146.38589*T-27.2198488*T*ln(T)-.07674502*T**2+1.6095848E-05*T**3
600.00-1023.00:	-450304.105+1147231.88*T**(-1)+485.311362*T-80.993872*T*ln(T)-.0109365576*T**2+9.42724933E-07*T**3
1023.00-1405.20:	-446703.462+489.879027*T-82.562872*T*ln(T)-.00617663*T**2

Table 1 (continued)

	GWUSTITE
298.15-3000.00:	-279318+252.848*T-46.12826*T*ln(T)-.0057402984*T**2

also summarized in the same table. All the standard Gibbs energy (G°) values are given relative to the enthalpy of selected reference states for the elements at 298.15 K denoted by SER (Stable Element Reference).

DISCUSSION

The equilibria of the Fe-Na-O system at 853 K and at low oxygen potentials were calculated using the Poly-3 program of the Thermo-Calc Databank System /27/. The calculated phase diagram at 853 K and at low oxygen potentials is shown in Fig. 3. It is seen that at this temperature, $FeNa_4O_3(s)$ is stable in the presence of liquid sodium and solid iron. This is in accordance with the experimental results of Barker and Wood /5/ as well as Addison et al. /6/. The relative stabilities of $Na_2O(s)$ and $FeNa_4O_3(s)$ in the presence of liquid sodium and solid iron shown in the present work were not brought out clearly in earlier thermodynamic calculations /4/.

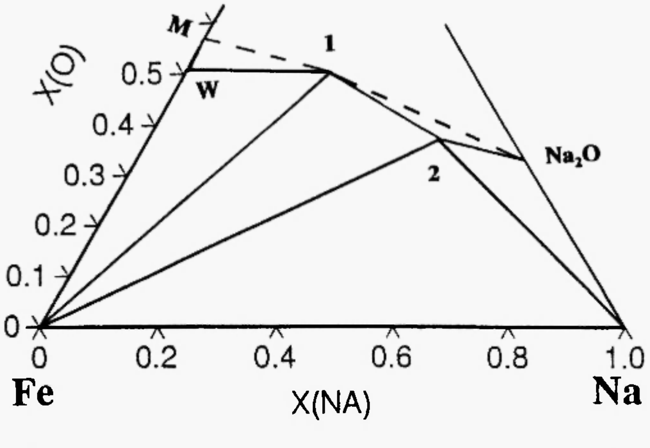

Fig. 3: The calculated phase diagram of the Fe-Na-O system at 853 K and low oxygen potentials.
1: $Fe_2Na_2O_4$, 2: $FeNa_4O_3$, W: Wüustite, M: Magnetite

Fig. 3 shows that the phase in equilibrium with α-Fe and wüstite is $Fe_2Na_2O_4$. The phases $Fe_2Na_2O_4$, $FeNa_4O_3$ and α-Fe also form a three-phase triangle. Attempts were made in the present work to include the compound $FeNa_2O_2$ in the phase diagram without success. As in the case of $FeNa_4O_3$, a calculation was done. The $\Delta H_3°$ value, -119106 J/mol, for reaction (3), was taken from the acid solution calorimetric measurement by Dai et al. /4/. The entropy terms of the Gibbs energies of both $FeNa_2O_2$ and $FeNa_4O_3$ were estimated using the phase diagram information shown in Fig. 1. In that estimation, the $FeNa_2O_2$-Na_2O section was considered. The evaluated standard Gibbs energy of formation of $FeNa_2O_2$ from FeO and Na_2O can be expressed as

$$\Delta G_3° = -119106 + 115.54\,T \text{ J/mol} \qquad (14)$$

Notice that the entropy term in Eq. 14 is unusually high for a solid-solid reaction and is comparable with the earlier estimation /4/ given in Eq. 4.

The Gibbs energy of $FeNa_2O_2$ obtained from such an estimation was incorporated in the calculation. Nevertheless, the calculated phase diagram showed the same equilibria as given in Fig. 3, thereby ruling out the possibility of the existence of $FeNa_2O_2$ at this temperature. Hence, the compound $FeNa_2O_2$ was not included in the calculation of the final phase diagram. Fig. 3 conforms with the experimental results of Sridharan et al. /23/.

It should be pointed out that the triangle connecting Na_2O, $FeNa_4O_3$ and $Fe_2Na_2O_4$, as well as the triangle connecting wüstite, magnetite and $Fe_2Na_2O_4$ in Fig. 3 are only tentative. Beside the three ternary compounds considered in the present calculation, at least four other ternary compounds at higher oxygen potentials have been reported, namely $Fe_2Na_4O_5$ /28/, $Fe_2Na_8O_7$ /29/, $Fe_5Na_3P_9$ /30/ and

$FeNa_3O_3$ /23/. All of them are located on the Fe_2O_3-Na_2O join. Since no thermodynamic data has been reported for these compounds, it was not possible to include them in the present analysis.

In order to see the stabilities of various phases at different oxygen as well as sodium partial pressures, a potential phase diagram was calculated using the Poly-3 program /27/. This diagram is presented in Fig. 4. It is seen that $FeNa_4O_3$ will form at very low oxygen partial pressures when α-Fe and liquid sodium are present, thereby explaining the corrosion reaction in nuclear reactors.

SUMMARY

An evaluation of the stabilities of the ternary compounds in the Fe-Na-O system was done in the present work considering the available thermodynamic and phase diagram information. A critical assessment of the existing data was made taking into consideration the experimental uncertainties. The existence of the ternary compound $FeNa_2O_2$ is seriously questioned. A new phase diagram at 853 K corresponding to low oxygen potentials and a phase-stability diagram for the same temperature are presented. The stability of the ternary compound $FeNa_4O_3$ in equilibrium with Fe(s) and Na(l) supports the formation of this compound during corrosion of stainless tubes by liquid Na in nuclear reactors.

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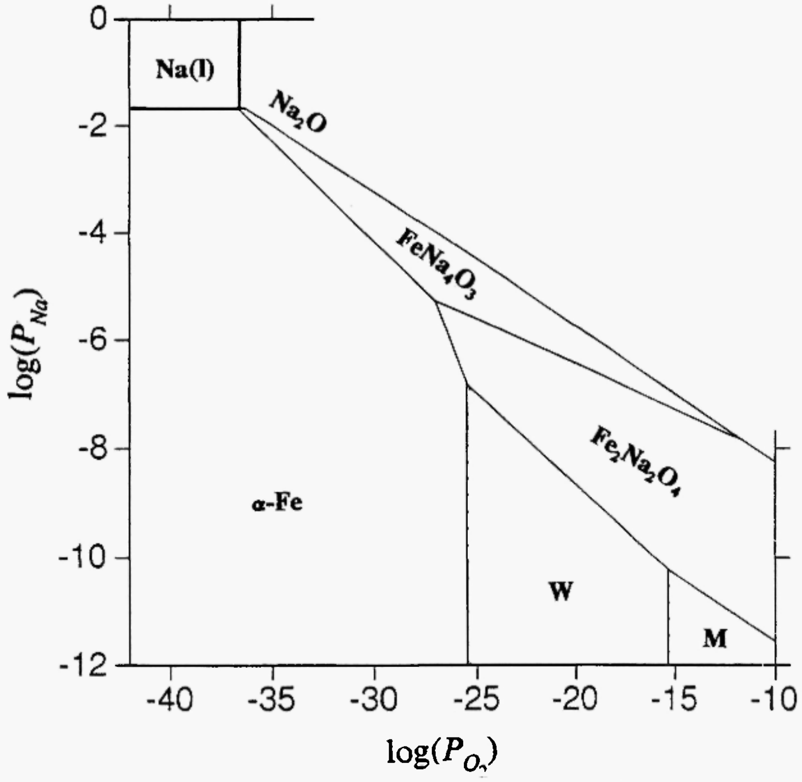

Fig. 4: The calculated oxygen-sodium potential phase diagram of the Fe-Na-O system at 853 K. W: Wüstite, M: Magnetite

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