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Phase equilibrium studies in the Na–Fe–O system

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Abstract

In high temperature sodium–steel systems, the corrosion of structural steels by sodium is enhanced by the presence of dissolved oxygen. As iron is the major constituent in steel, the interaction between iron and sodium containing oxygen plays a decisive role in this corrosion process. A knowledge of the various phase relationships that exist in the Na–Fe–O system is essential to understand this phenomenon. In order to elucidate the equilibrium phase fields, various experiments such as in-sodium equilibrations, pseudo-isopiestic equilibrations, differential thermal analysis and solid state reactions between the oxides of iron and sodium of various compositions were carried out. On the basis of the results of these experiments an isothermal cross-section of the partial phase diagram of the Na–Fe–O system above 773 K is reported.

1. Introduction

The study of the Na–Fe–O system has evoked considerable interest on account of the role played by oxygen in the corrosion and mass transfer of structural materials by sodium in liquid-metal-cooled fast reactors [1–3]. The compound Na_4FeO_3 is known to form in liquid sodium containing dissolved oxygen [4–6]. Wu *et al.* [7] have reported the interplanar spacings of the compound Na_2FeO_2. However, Gross and Wilson [5], Tschudy *et al.* [8] and Knights and Philips [9] did not observe this compound in their experiments. Lindemer *et al.* [10] have estimated some of the thermodynamic data of various compounds reported in the Na–Fe–O system and projected a tentative phase diagram for this system. However, Lindemer *et al.* were of the view that their calculated results were not consistent with the available experimental data and have expressed the need for closed-system experiments that could permit true equilibrium in this system. In order to bridge this gap, various experiments were done to arrive systematically at the equilibrium phase relationships in this system. The details are presented in this paper.

2. Experimental details

2.1. Chemicals used

Iron(III) oxide (Fe_2O_3) from Fischer Scientific Co., USA, iron(II) oxide (FeO) from Alfa Ventron, USA, and sodium peroxide from Pfizer, India, were used in this work. The sodium oxide used in this work was prepared by the method described by Barker *et al.* [11]; sodium nitrate was heated with a large excess of sodium metal at 473 K, followed by removal of excess sodium by vacuum distillation at 623 K [12]. The sodium metal used was taken from a bath maintained at approximately 400 K, with a clean surface, in an inert atmosphere glove-box.

2.2. Handling of materials

The samples used for in-sodium equilibrations and solid state reactions were put in alumina crucibles and placed inside stainless steel reaction vessels sealed with copper gasketed knife-edge flanges at the top. In all the experiments, sample handling before and after the equilibration was carried out in an argon atmosphere glove-box.

2.3. In-sodium equilibrations

To approximately 0.2 g of Fe_2O_3 in an alumina crucible, 10 ml of liquid sodium was added, and the mixture was placed in the reaction vessel. The vessel was maintained at the desired temperature for an appropriate length of time. The products after equilibration were isolated from excess sodium by vacuum distillation and stored inside the glove-box.

2.4. Pseudo-isopiestic equilibrations

The vessel used for the pseudo-isopiestic experiments with oxides of iron and sodium vapour of known pressure is shown in Fig. 1. Approximately 15 ml of liquid sodium was put in the lower compartment of the equilibration vessel and the samples of FeO, Fe_2O_3 and $NaFeO_2$

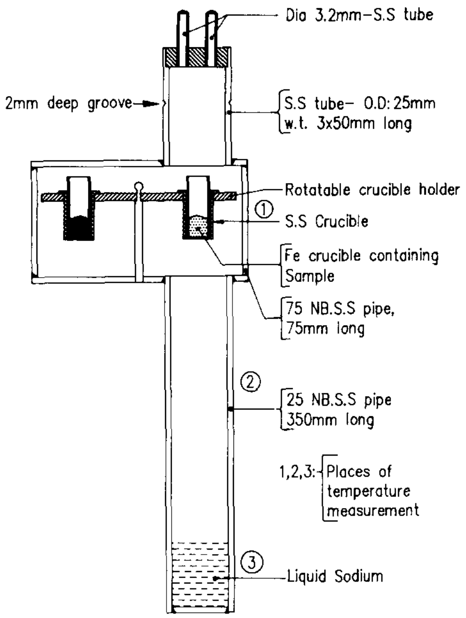

Fig. 1. Schematic diagram of the pseudo-isopiestic equilibration set-up: S.S, stainless steel.

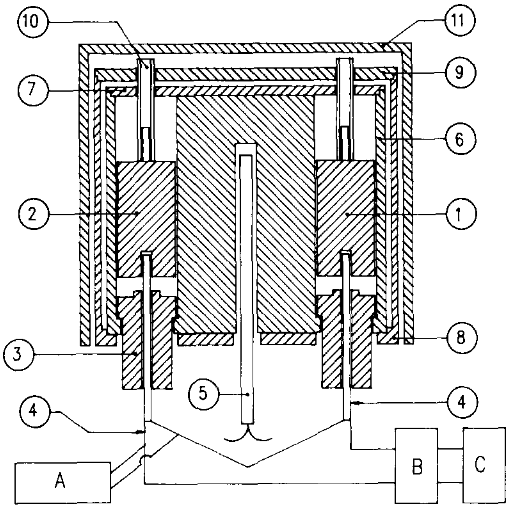

Fig. 2. Schematic diagram of the DTA set-up: A, temperature measurement (sample); B, PARC 113 pre-amplifier; 1, reference capsule; 2, sample capsule; 3, ceramic support; 4, differential thermocouple; 5, control thermocouple; 6, 7, pyrophyllite sample holder and lid; 8, 9, metallic chamber and lid; 10, quartz sample; C, recorder; 11, furnace.

were in the reaction compartment at the top. This operation was carried out in an argon atmosphere glove-box. The vessel was hermetically sealed by welding and then kept in a furnace for equilibration at the chosen temperature for approximately 340 h. This procedure was repeated with different combinations of sodium and sample temperatures. After equilibration, the products were ground well and transferred into a new equilibration vessel. The equilibration of the samples was repeated and the final products were stored in glass vials inside the glove-box.

2.5. *Differential thermal analysis experiments*

A schematic diagram of the differential thermal analysis (DTA) assembly is shown in Fig. 2. Approximately 1 g of FeO or Fe_2O_3 was put in the sample capsule through the fill tube. Around 2 cm^3 of liquid sodium was injected into the capsule. The fill tube was then crimped in at least two places, brought out of the glove-box and closed by welding. The reference capsule was made in a similar manner by filling it with only sodium.

The temperature of the sample capsule was independently measured. DTA studies were carried out at a heating rate of 4 K min^{-1}. The cooling rate varied from 3 K min^{-1} at high temperatures to 2 K min^{-1} at lower temperatures.

2.6. *Solid state reactions*

Oxides of iron and sodium in different molar ratios were mixed, pelletized and loaded into alumina crucibles kept inside the stainless steel reaction vessel. After this operation had been carried out in the glove-box, the vessel was then brought out and heated in a resistance furnace. After equilibration for 360 h, the vessel was cooled and transferred into the glove-box. The pellets were crushed, ground, repelletized and reheated, after loading into the vessel, for a further period of 360 h. The products were then stored inside the glove-box in glass vials.

2.7. *Characterization of the reaction products*

X-ray diffraction (XRD) analysis was employed to characterize the various compounds that were formed in the above experiments. Owing to the moisture-sensitive nature of these compounds, the samples were loaded and sealed in Lindemann capillaries before being taken out of the glove-box for XRD analysis.

3. Results

3.1. *In-sodium equilibrations*

The results of the in-sodium equilibrations are given in Table 1. It is found that, during the distillation of excess sodium under vacuum, the temperature did not exceed 623 K so long as some traces of liquid sodium were left in the crucible. Thereafter, the temperature of the crucible increased in an uncontrolled manner up to perhaps 973 K. The results of these experiments gave as products a mixture of iron, Na_2O and Na_4FeO_3 whereas experiments in which the distillation temperature was controlled at 623 K gave a mixture of iron and Na_2O as the products.

TABLE 1. Results of in-sodium equilibrations

Reactants	Temperature (K)	Time (h)	Distillation condition	Products[a]
$Fe_2O_3(s)$ + excess Na(l)	923	50	Uncontrolled	$Na_4FeO_3(s)$ + Fe(s) + $Na_2O(s)$
$Fe_2O_3(s)$ + excess Na(l)	873	65	Uncontrolled	$Na_4FeO_3(s)$ + Fe(s) + $Na_2O(s)$
$Fe_2O_3(s)$ + $Na_2O_2(s)$ + excess Na(l)	823	187	Uncontrolled	$Na_4FeO_3(s)$ + Fe(s) + $Na_2O(s)$
$Fe_2O_3(s)$ + excess Na(l)	723	36	Uncontrolled	$Na_4FeO_3(s)$ + Fe(s) + $Na_2O(s)$
$Fe_2O_3(s)$ + excess Na(l)	723	170	Controlled	$Na_2O(s)$ + Fe(s)
$Fe_2O_3(s)$ + $Na_2O_2(s)$ + excess Na(l)	673	580	Controlled	$Na_2O(s)$ + Fe(s)
$Fe_2O_3(s)$ + excess Na(l)	623	720	Controlled	$Na_2O(s)$ + Fe(s)

[a]As analysed by XRD.

3.2. *Pseudo-isopiestic equilibrations*

The results of the pseudo-isopiestic equilibrations are shown in Table 2. The compound $Na_4FeO_3(s)$ and Fe(s) were the only products when different iron oxides were equilibrated at 923 K with sodium vapour at pressures of 1408 and 880 Pa and at 773 K with a sodium vapour pressure of 4.7 Pa.

3.3. *Differential thermal analysis*

The DTA trace for the transition observed in this work is shown in Fig. 3. Identical traces were obtained irrespective of the iron oxide that we started with. Before starting the DTA runs, the sample was heated in a furnace up to 870 K to ensure that the initial reduction of iron oxide by sodium does not complicate the DTA pattern. The thermal effect is reversible and, by repeated heating and cooling runs, the transition temperature was established as 760 ± 6 K. It can be seen from Table 3 that the transition temperatures obtained in either heating or cooling runs are reproducible, although they differ from each other by about 15 K.

3.4. *Solid state reactions*

The results of solid state reactions between oxides of iron and sodium are given in Table 4. Reactions (a) and (b) yielded a mixture of $Na_3FeO_3(s)$, Fe(s) and $NaFeO_2$ and a mixture of $NaFeO_2(s)$ and Fe(s) respectively as products whereas for reactions (c) and (d) a mixture of $Na_3FeO_3(s)$, $NaFeO_2(s)$ and Fe(s) was obtained as the products. A ternary mixture of $Na_4FeO_3(s)$, $Na_3FeO_3(s)$ and Fe(s) was obtained in reactions (e) and (f). Solid state equilibrations between Na_2O and FeO in the ratios 3:2 and 2:3 carried out in hermetically sealed capsules gave a ternary mixture of $Na_4FeO_3(s)$, $Na_3FeO_3(s)$ and Fe(s) and a ternary mixture of $Na_3FeO_3(s)$, $NaFeO_2(s)$ and Fe(s) respectively as products.

4. Discussion

The results of in-sodium equilibration experiments showed four condensed phases, namely liquid sodium (which was distilled off), iron, Na_2O and Na_4FeO_3 as products, whereas only three condensed phases are expected at equilibrium in this system. Apart from liquid sodium, if Na_4FeO_3 and iron were the products, then during distillation a part of Na_4FeO_3 could have changed to Na_2O. On the contrary, if Na_2O and iron were the products, then Na_4FeO_3 could have formed from the reaction between Na_2O and iron at high temperatures towards the end of the experiment. In order to avoid this complication, the distillation of excess sodium was done at a controlled temperature of 623 K in the subsequent experiments. The products of equilibrations in these experiments were found to be only $Na_2O(s)$ and Fe(s), in addition to sodium which was distilled off.

TABLE 2. Results of pseudo-isopiestic equilibrations. (Equilibrations generally carried out for a minimum period of 720 h)

	Sodium temperature (K)	Sodium pressure (Pa)	Equilibration temperature (K)	Products analysed by XRD
$Fe_2O_3(s)$	798	880	923	$Na_4FeO_3(s)$ + Fe(s)
FeO(s)	798	880	923	$Na_4FeO_3(s)$ + Fe(s)
$NaFeO_2(s)$	798	880	923	$Na_4FeO_3(s)$ + Fe(s)
$Fe_2O_3(s)$	823	1408	923	$Na_4FeO_3(s)$ + Fe(s)
$Fe_2O_3(s)$	598	4.7	773	$Na_4FeO_3(s)$ + Fe(s)
FeO(s)	598	4.7	773	$Na_4FeO_3(s)$ + Fe(s)

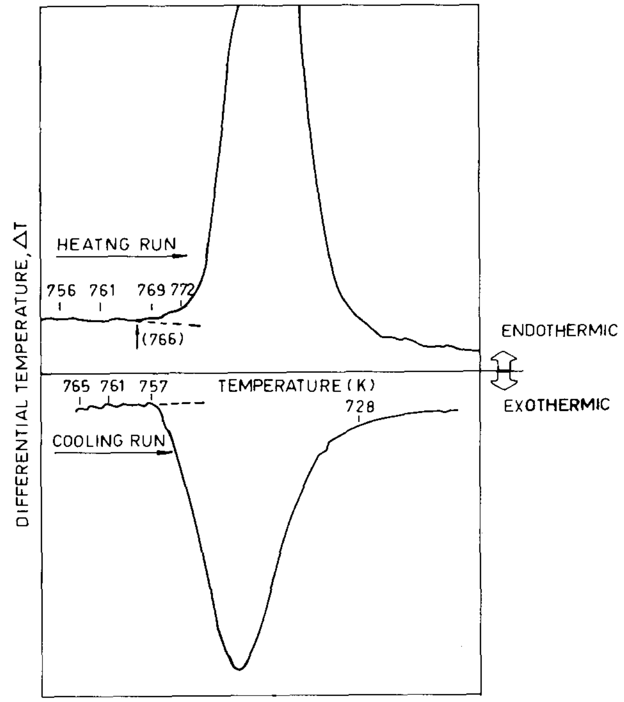

Fig. 3. The DTA trace obtained for the reversible process in the Na–Fe–O system.

TABLE 3. Differential thermal analysis of the Na–Fe–O system carried out with sodium capsules

Sample	Run	Transition temperature (K)	
		Heating	Cooling
Fe_2O_3(s) + excess Na(l)	1	765	749
Fe_2O_3(s) + excess Na(l)	2	766	757
Fe_2O_3(s) + excess Na(l)	3	766	748
Fe_2O_3(s) + excess Na(l)	4	–	752
Fe_2O_3(s) + excess Na(l)	5	764	760
FeO(s) + excess Na(l)	1	766	757

TABLE 4. Results of solid state reactions

Reaction	Reactants	Ratio	Equilibrium products observed[a] (as analysed by XRD)
(a)	Na_2O:FeO	2:1	$Na_3FeO_3 + NaFeO_2 + Fe$
(b)	Na_2O_2:Fe	1:2	$NaFeO_2 + Fe$
(c)	Na_2O_2:FeO	1:1	$Na_3FeO_3 + NaFeO_2 + Fe$
(d)	Na_2O_2:Fe	1:1	$Na_3FeO_3 + NaFeO_2 + Fe$
(e)	Na_2O_2:Fe	2:1	$Na_4FeO_3 + Na_3FeO_3 + Fe$
(f)	Na_2O:Fe	3:2	$Na_4FeO_3 + Na_3FeO_3 + Fe$
[b]	Na_2O:FeO	3:2	$Na_4FeO_3 + Na_3FeO_3 + Fe$
[b]	Na_2O:FeO	2:3	$Na_3FeO_3 + NaFeO_2 + Fe$
[b]	Na_2O:FeO	1:1	$Na_3FeO_3 + Fe$
[b]	Na_2O_2:Fe	1:1	$Na_3FeO_3 + Fe$

[a] Equilibration temperature, 923 K.
[b] Equilibration in hermetically sealed capsules.

From the results of in-sodium equilibrations it could be inferred that, up to 623 K, only Na_2O and iron coexist in sodium. This is in agreement with our earlier work [13] involving measurements of oxygen concentration in liquid sodium containing iron which showed a slope change at 626 K. The oxygen concentration measured below 626 K corresponded to the saturation solubility of oxygen in sodium, indicating the presence of the phase field Na(l)–Na_2O(s)–Fe(s) up to 626 K. Pseudo-isopiestic equilibration studies indicate that Na_4FeO_3(s) is the ternary compound that coexists with Fe(s) and Na(l) at temperatures above at least 773 K.

DTA runs have recorded the presence of a reversible process at 760 ± 6 K which is corroborated by the recent in-sodium oxygen potential measurements using an e.m.f. technique reported by Bhat and Borgstedt [14]. These results, in conjunction with the pseudo-isopiestic equilibration results, indicate the existence of the phase field Na(l)–Fe(s)–Na_4FeO_3(s) above 760 K. In the temperature range 626–760 K the equilibrium phase relationships are not clear and more sensitive DTA or differential scanning calorimetry experiments are needed to obtain meaningful information in this range.

The results of solid state reactions were influenced by the existence of temperature gradients along the length of the vessel which resulted in some changes in the compositions of the samples, thus leading to a cross-over to a neighbouring phase field during the equilibration as discussed in the next paragraph. The results of these experiments were analysed to deduce the possible coexistence of various phase fields. To confirm the phase fields thus deduced, solid state equilibrations were carried out in hermetically sealed nickel capsules which ensured that no change occurred from the starting composition of the samples and that isothermal conditions were maintained during equilibration.

The results of the solid state equilibrations established the existence of the binary lines involving the pairs, Na_4FeO_3(s)–Na_3FeO_3(s), Na_4FeO_3(s)–Fe(s), Na_3FeO_3(s)–Fe(s), Na_3FeO_3(s)–$NaFeO_2$(s), $NaFeO_2$(s)–Fe(s) and the ternary phase fields bound by these lines, namely Na_4FeO_3(s)–Na_3FeO_3(s)–Fe(s) and Na_3FeO_3(s)–$NaFeO_2$(s)–Fe(s). Figure 4 shows the starting compositions and the phase fields towards which the compositions have moved at the end of equilibration periods. The results of the equilibrations carried out in hermetically sealed capsules confirmed the following ternary phase fields at 923 K: Na_4FeO_3(s)–Na_3FeO_3(s)–Fe(s); Na_3FeO_3(s)–$NaFeO_2$(s)–Fe(s).

Attempts to prepare Na_2FeO_2 by reacting either Na_2O(s) and FeO(s) in a 1:1 ratio or Na_2O_2(s) and Fe(s) in a 1:1 ratio in sealed capsules over a long period of 15 days or more did not produce Na_2FeO_2, but the products were found to be a mixture of

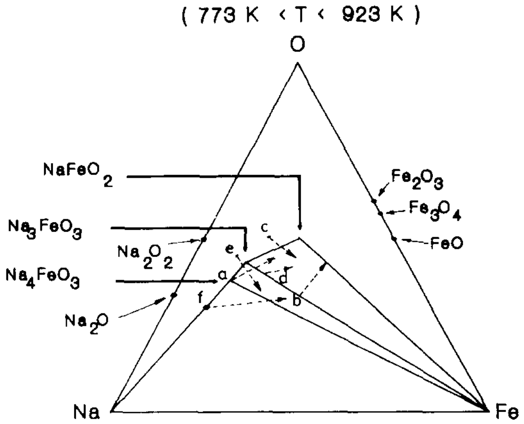

Fig. 4. Phase fields established in this work (773 K$<T<$923 K).

Na_3FeO_3(s) and Fe(s) in each case as is expected from these discussions.

From the above discussions the isothermal cross-section of the partial phase diagram of the Na–Fe–O system at 773 K$<T<$923 K was deduced and is given in Fig. 4.

5. Conclusions

Various techniques such as in-sodium equilibrations, pseudo-isopiestic equilibrations, DTA and solid state reactions were carried out to obtain information on the Na–Fe–O system. From the results of all these experiments the isothermal cross-section of a partial Na–Fe–O phase diagram was deduced and is reported. The results confirmed the existence of the Na(l)–Na_2O(s)–Fe(s) phase field up to 626 K and the Na(l)–Fe(s)–Na_4FeO_3(s) phase field above 760 K in liquid sodium.

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