CORROSION AND THE E-pO^{2-} DIAGRAM OF ZIRCONIUM IN $NaNO_3$-KNO_3 MELTS

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E-pO^{2-} diagrams are isothermal phase diagrams and are constructed from the potentials of the species present in various phases at equilibria; the behaviour of zirconium in $NaNO_3$—KNO_3 melts is based on the E-pO^{2-} diagram. The regions of corrosion, passivity and immunity have been determined with the help of the oxygen and nitrite tie-lines.

The corrosion data obtained for the zirconium by the weight change method seem to substantiate largely the thermodynamic predictions. The E-pO^{2-} diagram for the Zr/$NaNO_3$—KNO_3 system suggests that the metal will be inevitably corroded to form an oxide of zirconium and cathodic protection is unlikely to be effective at these temperatures under the experimental conditions.

The potential-pO^{2-} diagrams for fused oxy-salt melts are analogous to potential -pH diagrams. The E-pO^{2-} diagrams might be more useful than the aqueous analogue because the system has a greater chance of coming to equilibrium at higher temperatures. The exactness of prediction about the metal-fused salt system is therefore likely to be directly linked with the accuracy of the thermodynamic data.

This thermodynamic approach is useful in suggesting, understanding and explaining the corrosion reactions. As for the aqueous system, an equilibrium activity of cations and anions will have to be defined[1] and it is the usual practice to define it as 10^{-6} g ion/litre.

Lux[2] has defined acid-base behaviour in fused salts in terms of

$$\text{Base} = \text{Acid} + O^{2-}$$

The potential can, therefore, be expressed as a function of $pO^{2-} = -\log a\, O^{2-}$

This provides the basis for the construction of E-pO^{2-} diagrams.

The E-pO^{2-} diagram has been constructed for silver[3] in nitrate melts and for some metals in chloride melts[4]. For a carbonate melt[5], E-pO^{2-} diagrams have been drawn and the predicted behaviour has been in good agreement with the experimental results.

Oxygen electrode in nitrate melts

There is considerable disagreement with respect to oxygen electrode in nitrate melts[6–8]. However, a suitable reference scale of potential is established in the melts, by making the E° and dE°/dT equal to zero for the reference electrode[9]. NO_2, O_2/Pt, the corresponding equation being :

$$NO_2 + \tfrac{1}{2} O_2 + e^- = NO_3^-$$

The standard state for gases is 1 atm. pressure and that of nitrate ion is defined as $(a/N) = 1$, when $N = 1$ (N is the mole fraction) as occurring in the nitrate eutectic.

This enables the calculation of $E^\circ_{(Na^+/Na)}$ in fused $NaNO_3$ by setting up a cell of the type :

$$NO_2,\ O_2/NaNO_3/Na$$

The emf of the cell can be calculated from the thermodynamic data. The two half reactions can be written as follows :

$$NO_2 + \tfrac{1}{2}0_2 + e^- = NO_3^-, \quad E^\circ_1 = O \text{ (assumed)} \quad \ldots (1)$$

$$Na - e^- = Na^+, \qquad E^\circ_2 \qquad \ldots (2)$$

$$Na + NO_2 + \tfrac{1}{2} O_2 = NaNO_3 \quad E = E^\circ_2, \text{ since } E^\circ_1 = O \qquad \ldots (3)$$

From the free energy of formation of $NaNO_3$ and that of NO_2 at any particular temperature, the $E^\circ_{Na^+/Na}$ at that temperature can be calculated by referring to the assumption that the potential of the half cell NO_2, O_2/NO_3^- is zero. A similar approach has been used to evaluate the $(E^\circ_{ZrO^{2+}/Zr})$.

Standard state for the oxide ion activity

The other basic requirement for the construction of E-pO^{2-} diagram is the definition of a standard state for the oxide ion activity. Different methods[6–8] are available for introducing oxides into the melt, and the one adopted by Conte and Ingram[3] is to be made use of here. As pointed out by them, it is chiefly because

it is convenient to define the standard oxygen electrode with respect to a melt saturated with alkali metal oxide where the thermodynamic data for the solid alkali metal oxides are available. The oxygen electrode can be represented as follows :

$$O_2 + 4e^- = 2O^{2-}_{sat} \quad \ldots (4)$$

$$E = E^\circ_{O_2/O^{2-}} + \frac{2.3RT}{4F} \log p_{O^{2-}} + \frac{2.3RT}{2F} pO^{2-} \quad \ldots (5)$$

where

$$pO^{2-} = -\log \frac{a_{M_2O}}{a_{M_2O(sat)}} \quad \ldots (5a)$$

a_{M_2O} is the activity of M_2O in the solvent. The evaluation of $E^\circ_{O^2/O^{2-}}$ for the appropriate melt, however, involves the coupling of the oxygen electrode with the reference electrode to get

$$2NO_3^- = 2NO_2 + \tfrac{1}{2} O_2 + O^{2-}_{(sat)} \quad \ldots (6)$$

For the nitrate melt, therefore, $E^\circ_{O_2/^2O^{-}} = -\Delta G^\circ/2F$

where ΔG° refers to the reaction

$$2NaNO_3 = 2NO_2 + \tfrac{1}{2} O_2 + Na_2O \quad \ldots (7)$$
(liq.) (solid)

It is assumed in the present analysis that of all the cations, the smallest cation alone influences the acid-base behaviour of the melt. The diagram for the binary nitrate ($NaNO_3$ and KNO_3) has been calculated as for pure $NaNO_3$ melt at the required temperature.

Pourbaix criterion for immunity is involved while making use of the diagram ; i.e., a metal is considered immune if the concentration of its ions is less than 10^{-6} g ion/litre[1]. It is then possible to find out the thermodynamically stable state under the experimental conditions with the help of oxygen and nitrate ion tie-lines. The possible influence of oxide ion addition and the possibility of cathodic protection can be discussed.

Construction of E-pO^{2-} diagram for the $NaNO_3$-KNO_3 melt

The E-pO^{2-} diagram has been constructed for the $NaNO_3$-KNO_3 eutectic melt at 300° C. $E^\circ_{Na^+/Na}$ in fused sodium nitrate is given by emf of the cell

$$NO_2, O_2 \mid NaNO_3 \mid Na$$

The standard potential of zirconium is obtained by referring to a cell of the type

$$NO_2, O_2 \mid ZrO(NO_3)_2 \mid Zr$$

Therefore, the potential of a zirconium electrode in the sodium nitrate melt is given by

$$E_{ZrO^{2+}/Zr} = E^\circ_{ZrO^{2+}/Zr} + 2.3 \frac{RT}{2F} \log a_{ZrO^{2+}} \quad \ldots (8)$$

This equation helps to fix the $a_{ZrO^{2+}}$ scale in the zirconium domain of the diagram. The standard oxygen electrode has been defined with reference to a melt saturated with alkali metal oxide because the thermodynamic data are available for the solid alkali metal oxide.

The other assumption is that the acid-base properties are influenced mainly by the smallest ion present in the melt. The rate of corrosion has been measured by intermittent immersion tests[10]. At the end of corrosion, i.e., after the immersion of the test for a known length of time, the specimen is withdrawn, the surface cleaned and the change in weight measured.

Result and analysis

The thermodynamic data for the Zr/$NaNO_3$, KNO_3 system are presented in Table I. The various equilibria that are of interest in the system are presented in Table II. Equilibria (1) to (3) in Table II are plotted in Fig. 1.

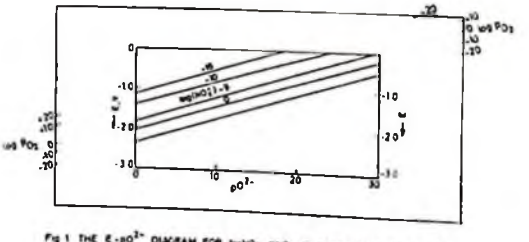


Fig 1 THE E-pO^{2-} DIAGRAM FOR $NaNO_3$-KNO_3 EUTECTIC MELT AT 600 °K

These equilibrium formulae provide information on the stability of the melt. The equilibrium (1) in Table II corresponding to the equation

$$E = -1.75 + 0.06\ pO^{2-} + 0.03 \log P_{O_2} \quad \ldots (9)$$

provides the basis for constructing the Fig. 1. For a particular value of P_{O_2}, the values of E are calculated for different pO^{2-} values. The region of stability of the nitrate melt at this temperature is, therefore, bounded by the lines corresponding to $P_{O_2} = 1$ atm

TABLE I: Free energy data as a function temperature

Formula	Standard state	$\Delta G^\circ = A + BT$(300–600°K) (cal/mole) A	B		Ref.
Na	Liquid metal	0	0		
Zr	Solid metal	0	0		
O_2	Gas, 1 atm.	0	0		
Na_2O	Solid oxide	−100,240	+34.61		11
NO_2	Gas, 1 atm.	+7990	+14.86		11
$NaNO_3$	Pure liquid	−103,910	+66.8		12,13
$NaNO_2$	Pure liquid	− 75,110	+37.0		14
		$\Delta G^\circ = A + BT \log T + CT$			
		(A)	(B)	(C)	
ZrO_2	Solid oxide	259,940	4.33	−59.12	15

TABLE II. Equilibrium formulae for different reactions

No.	Description of the reaction	Reaction	Equilibrium formulae
1	Oxygen reference electrode (Pt)	$O_2 + 4e^- = 2(O^{2-})$	$E = -1.75 + 0.06pO^{2-} + 0.03 \log p_{O_2}$
2	Nitrite formation in the melt	$NO_3^- = NO_2^- + \frac{1}{2}O_2$	$\log (NO_2^-) = -4.85 - \frac{1}{2} \log p_{O_2}$
3	Alkali metal liberation	$Na^+ + e^- = Na$	$E^\circ_{Na^+/Na} = -3.5V$
4	Zirconium electrode	$ZrO^{2+} + 2e^- = Zr + \frac{1}{2}O_2$	$E_{ZrO^{2+}/Zr} = 10.68 + 0.06 \log a_{ZrO^{2+}}$
5	Stability of ZrO_2	$ZrO_2 = Zr + O_2$	$\log P_{O_2} = -84.37$
6	Solubility of ZrO_2	$ZrO_2 = ZrO^{2+} + O^{2-}$	$\log a_{ZrO^{2+}} = 32 + pO^{2-}$

and unit activity of nitrite ions. Equilibria (4) to (6) presented in Table II refer to the zirconium electrode and the stability and solubility of ZrO_2. The paucity of thermodynamic information on zirconium salts renders a detailed analysis impossible. The ΔG or ΔH values of $Zr(NO_3)_4$ were not available, nor were those corresponding to $Ti(NO_3)_4$. However, the enthalpy of formation of $ZrO(NO_3)_2$ is available, but not its variation with temperature. With the available information, the thermodynamic diagram for the Zr/nitrate system is calculated and presented in Fig. 2. A simplified diagram is alone presented without including all the oxygen and nitrite tie-lines as it is employed only to predict the general corrosion behaviour. The Pourbaix criterion[1] of immunity is assumed to be true for fused salts as well.

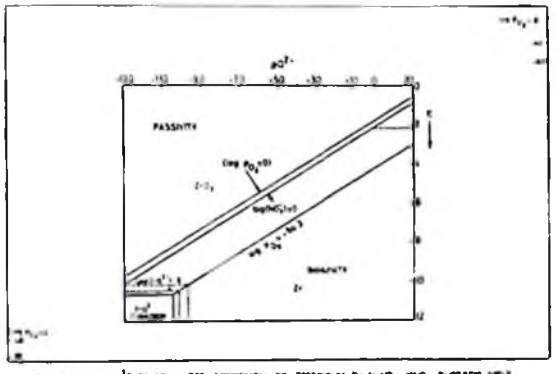


Fig. 2 The E-pO^{2-} diagram for corrosion of zirconium in $NaNO_3$-KNO_3 eutectic melt at 300°C

At a temperature of 300°C, the zirconium specimens have invariably gained in weight (+24.32 mg/cm²/day) and the corrosion rates have not been

influenced either by cathodic protection (+31.20) or by the addition of nitrite (+29.32) (Table III). In the corrosion experiments in pure nitrate melts a decrease in weight of the metal is observed initially However, there is an eventual weight gain which remains nearly constant. The corrosion rate cited above refers to the nearly constant value region (Table III).

TABLE III. Weight change of zirconium in $NaNO_3$–KNO_3 eutectic melts

Test No.	Temp. °C	Cell atm.	Condition of the experiment	Weight change mg/cm²/day
1	300	air	—	+24.30
2	300	air	Cathodic at—1.4V (vs Ag/Ag^+ 0.1M)	+31.20
3	300	air	with added nitrite	+29 32
4	300	N_2	—	+27.26
5	400	air	—	+54.60
6	400	air	added nitrite	+47.54
7	400	N_2	—	+44.72
8	500	air	—	+ 8.46
9	500	air	added nitrite	+10.72
10	500	N_2	—	+ 9.20

An inert atmosphere was maintained which also did not show any tendency towards decreased corrosion rates (+27.26). The same seems to be the pattern of behaviour of the metal in the melt at 400°C also; the corrosion rate varies from +55 to +45 mg/cm²/day.

At 500°C, there is a considerable reduction in the rate of weight gain (+10 mg/cm²/day) when compared with the values at 400°C (about +50) and at 300°C (about +30). The decrease in the weight gain at 500°C is probably due to changes in the nature of scale which, in the present case, prevent the continued oxidation and further build-up of the scale.

It, therefore, implies that zirconium will be oxidised to ZrO_2 under the experimental conditions. It can also be seen that cathodic protection will not be useful. The reductive dissolution of the oxide of zirconium is impracticable as a high concentration of oxide ions is necessary. The thermodynamic predictions, are, thus largely borne out.

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