OXIDE ION CHEMISTRY AND CORROSION IN MOLTEN ALKALI NITRATES AND NITRITES

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ABSTRACT

It has generally been assumed that corrosion in molten alkali nitrates proceeds by the participation of oxide ions (O²⁻) directly from the melt. Such an assumption is erroneous because oxide ions are completely converted to peroxide and superoxide ions in dry melts and to hydroxyl ions in melts exposed to water vapor. Oxide ions, however, could be stabilized by the addition of nitrite. To check whether corrosion in such melts depended on the concentration of oxide ions, experiments were carried out on zirconium and Zircaloy-2 in melts containing alkali metal nitrates, nitrite and hydroxide under different conditions. The oxide ion concentration in the melts is estimated to vary from 10⁻¹² to < 10⁻²⁰ m (m = mole kg⁻¹); too small to account for the observed kinetics and polarization data. An analysis of the corrosion data, reported in the literature, for iron and carbon steel, shows that the oxide ion concentrations existing in the nitrate melts have no relation to the observed kinetics of oxidation. The source of oxide ions has to be the reaction of nitrate, nitrite and hydroxyl ions with the anion vacancies emerging on the surface.

INTRODUCTION

Several inorganic eutectic mixtures containing alkali metal nitrates are promising candidates for thermal storage systems (1); therefore, corrosion studies in these molten salts have recently gained technological importance. In interpreting the mechanisms of corrosion in molten nitrates and nitrites it has generally been assumed that the oxide ion species, O²⁻, participates directly from the melt (2-5). Such an assumption, however, is ill-founded when the stability and hence the concentration levels of O²⁻ in these melts are considered. For example, at 573 K, the concentration of oxide ions, produced by the self-dissociation of nitrate ions, is estimated to be 2·10⁻¹² m (m = mole kg⁻¹). However, the existence of oxide ions, even at such a low concentration, is highly questionable because of their reactivity towards NO₃⁻, dissolved oxygen and water vapor in the melt. Zambonin and Jordan found that the voltammograms obtained using rotated platinum disk electrodes were similar with additions of Na₂O and Na₂O₂ to the nitrate melt (6). Their investigations revealed that oxide ions are virtually completely converted to peroxide and superoxide ions in dry...
melts and to hydroxyl ions in melts exposed to water vapor; under such conditions, the concentration of oxide ions could be \( <10^{-20} \) m (7).

The concentration of oxide ions at the self-dissociation level of \( 10^{-12} \) m could, however, be maintained by adding sufficient nitrite (one of the products of the reaction of \( O_2^- \) with \( NO_3^- \)) and having a blanket of inert gas or a vacuum over the melt. Corrosion measurements in molten alkali nitrates have been reported where no special precautions were taken to stabilize the oxide ions; yet the mechanisms proposed have assumed the participation of oxide ions directly from the melt (2,4,5). Moreover, even a concentration of \( 10^{-12} \) m is found to be too low to account for the observed kinetics of oxidation of iron and steel at 573 K in the nitrates melts. A reappraisal of the role of oxide ions in the mechanism of corrosion in molten alkali nitrates and nitrites is thus warranted. Oxidation and polarization measurements carried out on zirconium and Zircaloy-2 in melts containing alkali metal nitrates, nitrite and hydroxide are presented here; analysis of the results shows that the source of oxide ions has to be the reaction of nitrate, nitrite and hydroxyl ions with the anion vacancies emerging on the surface.

**EXPERIMENTAL**

Zirconium and Zircaloy-2 samples were cut from rolled and annealed sheets; elemental analysis data are shown in Table I. Samples were paddle-shaped and the large test sections had a surface area of \( \sim 10 \) cm². Following the mechanical polishing step, they were pickled in a bath of hydrofluoric and nitric acids. The sodium and potassium nitrates were 99.99% pure; the purity of the other salts varied from 97 to 99%. Experiments were carried out in NaN\(_3\)[41]-KNO\(_3\)[59], NaN\(_2\)[40]-NaNO\(_3\)[7]-KNO\(_3\)[31], NaNO\(_3\)[40.5]-KNO\(_3\)[58.8]-NaNO\(_2\)[0.7], NaNO\(_2\)[100], LiNO\(_3\)[100] and LiNO\(_3\)[95]-LiOH[5]; the numbers listed refer to percentages by weight. Dry argon was bubbled through the melt containing the hydroxide at all times. The other melts were generally kept open to air; however, for comparison purposes, in a number of experiments, the cell containing the melt was evacuated by connecting to a vacuum system capable of pumping down to a pressure of 1.3 mPa or argon was bubbled through the melt.

The apparatus and the procedure followed for oxidation and polarization measurements are described in detail elsewhere (8). Vycor and stainless steel vessels were used as containers for the nitrate and nitrite melts; for the hydroxide containing melt a vessel made of Zircaloy-2 was used. Polarization data obtained in the nitrate and nitrite melts are reported here. A large area platinum wire gauze formed the counter electrode. A platinum wire fused in glass was used as a general reference electrode; its potential was frequently checked against a Ag/Ag⁺ (0.07 m in KNO\(_3\)-NaNO\(_3\)) reference electrode. The potentials are quoted relative to the silver electrode. When a sample oxidized and polarized in one melt was polarized in another melt.
sufficient time, usually half an hour, was allowed for the attainment of steady potential. Only weight gain measurements were made with some control samples. For comparison purposes polarization and voltammetric data were obtained using small area wire electrodes of platinum, iron, zirconium and Zircaloy-2. All oxidations and polarizations were carried out at 573 K.

RESULTS

Thin film (< 125 nm) growth: Two typical sets of curves showing the changes in potential with time and the kinetics of oxide growth in the initial stages are shown in Figures 1 and 2. The potentials on immersion were highly negative and they shifted in the positive direction with increasing oxidation; maximum changes occurred within the first 2 to 3 h after which they stayed nearly steady. Zirconium was always at a slightly more negative potential than Zircaloy-2. The steady potentials attained in nitrite and hydroxide containing melts (still negative) were slightly positive to those in the nitrate melts. Otherwise, in the cases of both zirconium and Zircaloy-2 the potentials attained and their variation with time was independent of the melt and the environment over the melt.

Oxide growth up to 24 h was followed by observing the changes in the interference colours developed on the sample; the colours were related to oxide thicknesses by comparison with a chart of oxide films grown anodically to various formation voltages (9). Generally two to three predominant colours, corresponding to a variation in oxide thickness of 10 to 20 nm, were revealed by the optical examination; average thickness was estimated by taking into account the extent of coverage of these colours. The thickness at the end of a 24 h oxidation was obtained from weight gain measurements. The oxidation followed a near parabolic rate law and the rate decreased from a weight gain of ~280 µg/dm²h in the first hour to ~35 µg/dm²h near the end of the 24 h period; a weight gain of 1 mg/dm²h is equivalent to an oxide thickness of 67.3 nm. A tendency towards slightly increased rates of oxidation was observed in the nitrite and hydroxide containing melts. The kinetics of oxide growth were essentially the same when the melts were exposed to air, or evacuated and covered in a blanket of argon.

Thick film (up to 1 µm) growth: The kinetics of oxidation covering a range of weight gain from 1.5 to 15 mg/dm² (oxide 100 nm to 1 µm thick) are shown in Figure 3. A slightly faster rate of oxidation is observed in the melts containing nitrite and hydroxide than in the nitrates. The rate law followed changes from a near parabolic to a cubic one with the transition occurring at a gain of 4.5 mg/dm² in the case of zirconium and at ~6.5 mg/dm² in the case of Zircaloy-2; the rate of oxidation decreases from ~40 to ~3.5 µg/dm²h during these periods of oxide growth. Bubbling argon through the melts or evacuating the cell affected the kinetics little.
Polarization measurements: Polarization curves for zirconium following oxidation, to a weight gain of 6 mg/dm², in the binary eutectic of nitrates are shown in Figure 4. These curves were traced successively in the binary nitrates, ternary nitrates-nitrite and sodium nitrite; the reverse cathodic and the forward anodic portions are shown. Oxidation current was evaluated by extrapolation of the linear anodic part and finding the intersection of the corrected cathodic curve and the extrapolated anodic curve (8). There was a good agreement between the oxidation currents obtained from polarization measurements and the oxidation rates calculated from the weight gain data (8). It is important to note here that polarization of an oxidized zirconium sample in different melts gives essentially the same oxidation current; as evidenced by the kinetics of oxidation in these melts (Figure 3(b)), this is to be expected. A set of polarization curves for Zircaloy-2 in the binary nitrates is shown in Figure 5; these were traced following oxidation of the sample in the same melt to various times. The linear portions of the anodic curves scan a shorter range of potentials than in the case of zirconium; the oxidation currents obtained from the polarization curves matched the kinetically derived oxidation rates well (8).

Wire electrodes: A typical voltammogram, traced at 20 mV/s, for platinum in the binary nitrate eutectic containing $10^{-1}$ m NaNO₂, is shown in Figure 6(a). The various peaks and their significance are interpreted as follows (10): cathodic peaks located at -1.68 and -1.9 V are due to the formation of insoluble sodium and potassium oxides on the electrode surface and their oxidation to the peroxides are associated with the corresponding anodic peaks at -1.29 and -1.56 V, respectively. Oxidation of the nitrite ion and its associated limiting current are observed at +0.3 to +0.9 V and at +1.2 V the sharp rise in current is due to the oxidation of the nitrate ion. A voltammogram obtained in the binary nitrates had similar features except that the saturation current due to nitrite ion oxidation was considerably less; in sodium nitrite the peaks due to insoluble oxide formation and its oxidation were not distinct and the rise in anodic current, due to the oxidation of the nitrite ion, occurred at 0 V. Polarization curves traced at the usually employed scan rate of 0.5 mV/s are shown in Figure 6(b); time of immersion in the melt had no effect on these curves.

Changes in the polarization curves, with time of immersion in molten binary nitrates containing $10^{-1}$ m NaNO₂, for iron, zirconium and Zircaloy-2 wire electrodes are shown in Figures 7, 8 and 9. In the case of the iron electrode, a sharp rise and fall in anodic current during the initial polarization, similar to that reported by Arvia et al. (2), was not observed. The behaviour of the wire electrodes was found to be quite similar to that of the large area samples. With increasing oxidation, the rest potentials moved in the positive direction, the oxidation currents decreased and the linear portions on the anodic curves scanned a decreasing range of potentials; thus the rest potentials and the shape of the polarization curves showed a tendency to
approach those of the platinum electrode. This tendency was most
obvious in the case of iron and decreased as Fe > Zr-2 > Zr, in the
same order as their rest potentials varied with iron staying positive
to Zircaloy-2 and zirconium.

DISCUSSION

Oxide ion chemistry: Investigations concerning the electro-
chemical nature of the oxygen electrode in molten KNO$_3$-NaNO$_3$ have
suggested the existence of the following equilibria in the melt

\[
\begin{align*}
\text{NO}_3^- & \rightleftharpoons \text{NO}_2^+ + \text{O}^{2-} \quad \ldots 1 \\
\text{O}^{2-} + \text{NO}_3^- & \rightleftharpoons \text{NO}_2^- + \text{O}_2 \text{^2-} \quad \ldots 2 \\
\text{O}_2 \text{^2-} + 2\text{NO}_3^- & \rightleftharpoons 2\text{NO}_2^- + 2\text{O}_2^- \quad \ldots 3 \\
\text{O}_2 \text{^2-} + \text{O}_2 & \rightleftharpoons 2\text{O}_2^- \quad \ldots 4 \\
\text{O}^{2-} + \text{H}_2\text{O} & \rightleftharpoons \text{2OH}^- \quad \ldots 5
\end{align*}
\]

At 500 K, the equilibrium constants for the equations 2 to 5 are 3,
6.7 x 10$^{-11}$, 3.5 x 10$^{5}$ and 10$^{18}$, respectively. Oxide ions (O$^{2-}$) are
thus rapidly converted to peroxide, superoxide and hydroxyl ions.
Therefore, an oxygen electrode in the nitrate melts is treated as one
involving a one electron transfer according to the equation

\[
\text{O}_2^- \rightleftharpoons \text{O}_2^+e \quad \ldots 6
\]

However, data supporting a two electron transfer equilibrium

\[
\text{O}^{2-} \rightleftharpoons \frac{1}{2} \text{O}_2^+2e \quad \ldots 7
\]

have also been reported. It is recognized now that these studies were
carried out in glass containers and that the $O^{2-}$ ion might have been stabilized by the reaction (11)

$$0^{2-} + x SiO_2 \rightarrow (SiO_2)_{x}O^{2-} \ldots 8$$

The other obvious means of stabilizing $O^{2-}$ ions is to add sufficient nitrite to the melt and to avoid exposure to oxygen and water vapor. At 573 K for example, a maximum oxide ion concentration of $10^{-12}$ m can be expected in dry KN0$_3$-NaNO$_3$-NaNO$_2$ melts kept under vacuum or a blanket of inert gas. But in melts of KN0$_3$-NaNO$_3$ under all conditions and KN0$_3$-NaNO$_3$-NaNO$_2$ exposed to atmospheric conditions, the oxide ion concentration could be as low as $10^{-20}$ m, or less (7).

Mechanism of corrosion: For interpreting the corrosion of iron and steel in molten nitrates $pO_2$ (= -log[$O^{2-}$]) vs. potential diagrams, which reveal the thermodynamic stability of the various regions involved, have been constructed and used (3). The main equilibria involved are shown in Figure 10. Oxide growth is supposed to proceed by the following anodic reactions (2,4,5)

$$Fe + O^{2-} = FeO + 2e \ldots 9$$

$$3FeO + O^{2-} = Fe_3O_4 + 2e \ldots 10$$

$$2Fe_3O_4 + O^{2-} = 3Fe_2O_3 + 2e \ldots 11$$

But the discrepancy between the mechanism and the corrosion kinetics (parabolic rate law) becomes obvious when the flux of oxide ions and the rate of oxidation are compared. Assuming a diffusion coefficient of $5 \times 10^{-6}$ cm$^2$/s for oxide ions in the melt (the same as that for the diffusion of hydroxyl, peroxide and superoxide ions in nitrate melts) and the smallest possible barrier layer thickness of 0.2 nm (the size of a mean hole radius in molten salts) at an electrode surface the flux of oxide ions arriving at 573 K can be calculated as $2.8 \mu g/dm^2h$ for an oxide ion concentration of $10^{-12}$ m. For samples oxidizing in nitrate melts (5) and melts exposed to atmospheric conditions (2,4), the flux of oxide ions reaching the surface would be $< 2.8 \times 10^{-8} \mu g/dm^2h$. From the weight gain/loss data reported (4,5) the average rate of oxidation decreases from 500-800 $\mu g/dm^2h$ in the initial 10 h period to 200 $\mu g/dm^2h$ in the subsequent 100 h; the rates are $\sim 10^{10}$ times the estimated flux of oxide ions.
The main regions established by the $pO_2^-$ vs. potential diagram are correct; but at the experimental conditions the stability of the oxide phases is determined by the rest potential and the concentration of oxide ions in the melt. For example in reference (2), specific mention is not made of the reference electrode used but a Ag/Ag$^+$ electrode is implied by referring to a previous publication. Then assuming an oxide ion concentration of $10^{-12}$ m in the melt, as suggested by the authors, the passivation potential on immersion of -0.25 V and the Ag/Ag$^+$ reference zero would be located at -2.1 and -1.85 V on the diagram; these are marked as 'a' in Figure 10. Then the rest potentials reported in reference (4) and measured in the present study would be those marked as 'b' and 'c' in the figure. It can readily be seen that at these potentials, even assuming an oxide ion concentration of $10^{-12}$ m in the melt, the iron and steel are to remain immune to oxidation; a conclusion contrary to the results obtained. A more realistic approach is that the oxide ion concentration in these melts is somewhere within the range of $10^{-20}$ to $10^{-12}$ m. Then the observed immersion potential of -0.8 V and a final rest potential of -0.4 V (attained following hours of oxidation) would fix the Ag/Ag$^+$ reference zero at $\sim$ -0.8 V, as shown by the dotted line, in the $pO_2^-$ vs. E diagram.

In the present study, the rate of oxidation of zirconium and Zircaloy-2 decreased gradually from 300 to 30 $\mu$g/dm$^2$h during the thin film growth and then to 3 $\mu$g/dm$^2$h during the thick film growth period. The kinetics followed a near parabolic rate law initially and then a cubic rate law; therefore surface reactions, e.g., arrival of oxide ion species to the surface from the melt, are not controlling the rate of oxidation. The oxidation rates and the kinetic behaviour were independent not only of the composition of the melts but also of the environment over them. The oxide ion concentration would have varied from $10^{-12}$ m in the specific cases of nitrate-nitrite melts kept under vacuum or argon to $< 10^{-20}$ m in all the melts generally kept exposed to atmospheric air; too low to account for the observed oxidation rates. In melts exposed to air the concentration of dissolved oxygen is estimated to be $10^{-5}$ m and of peroxide and superoxide ions to be $\sim 10^{-7}$ m (7); such levels are high enough for these species to participate in the oxidation process. However, the concentrations of these species in the melt under a vacuum or an argon atmosphere would still be extremely small. Therefore, a general mechanism operating under a variety of conditions in these melts could be the reaction of nitrate and/or nitrite ions with the anion vacancies emerging on the surface

$$\square^{++} + NO_3^-/NO_2^- \rightarrow \square + NO_2^+/NO^+$$

Zirconium dissolving in the oxide at the metal-oxide interface creates the oxygen ion vacancies; oxide growth is controlled by the diffusion of oxygen ions which is shown to be occurring along oxide crystallite
boundaries (12). The cathodic half of the reaction at localized conducting sites might then be

\[ \text{NO}_2^+ + e \rightarrow \text{NO} \quad \ldots 13 \]

and/or

\[ \text{O}_2 + e \rightarrow \text{O}_2^- \quad \ldots 14 \]

to complete the oxidation process. In the case of iron and steel, corrosion proceeds by the diffusion of cations in the magnetite layer and oxygen ions in the hematite layer. At the hematite-salt interface, the reaction would be the same as equation 12 and at the magnetite-salt interface the reaction would be the oxidation of Fe\(^{2+}\) ions

\[ 3\text{Fe}^{2+} + 4\text{NO}_3^- + \text{Fe}_3\text{O}_4 + 4\text{NO}_2^+ + 2e \quad \ldots 15 \]

Polarization measurements: The voltammograms and polarization curves obtained for platinum in the nitrate and nitrate-nitrite melts indicate that although reduction and oxidation of the nitrate and nitrite ions occurs at potentials highly cathodic and anodic to the rest potential, considerable current flows under steady state polarization conditions (cf. Figure 6(b)). The possible reactions contributing to the current flow are the anodic reaction 6 and the cathodic reactions 13 and 14. When zirconium or iron is corroding in these melts ionic and electronic transports are occurring through the growing oxide film; ion current is associated with the diffusing species in the oxide and the reactions 12 and 15 at the oxide-salt interface and the electron current is associated with reactions 13 and 14 at the oxide-salt interface. On immersion in the melts iron, zirconium and Zircaloy-2 attain highly negative potentials with respect to platinum indicating that the thin oxide films existing on their surfaces are resistive to electron transport. As a result the reactions 13 and 14 and the reaction 6 occur at potentials more cathodic and anodic, respectively, than on platinum. Anodic polarization curves thus reveal a linear portion of gradually increasing current, that is characteristic of ion transport occurring through the growing oxide film, prior to the sharp increases in current due to reaction 6. When the polarizations are carried out immediately after immersing an unoxidized metal/alloy in the melt, these linear anodic portions would include contributions due to the high field anodic oxide growth. However, contributions to the oxide growth by the applied field during polarizations decrease rapidly with increase in oxide thickness and then the linear anodic portions represent mainly the variation of the ion current with the applied potential.
In the case of iron the absence of an anodic peak in the prepassivation region, during the initial polarization, would imply that a passive film was already existing on the surface or was formed during the time elapsed between immersion and polarization. The linear anodic portion distinctly evident in the initial polarization curve represents the growth of the passive magnetite layer. With increasing oxidation the changes observed in the rest potential and polarization curves indicate that this magnetite film, resistive to electron flow, is converted into a duplex film of magnetite and hematite having a good electronic conductivity. The behaviour of the oxidized iron electrode thus becomes similar to that of platinum.

In the cases of zirconium and Zircaloy-2 electron conduction is localized at impurity (iron) and intermetallic sites which exist as second-phase precipitates in the metal and alloy (8). A thin film of zirconia existing on these precipitates leads to highly negative immersion potentials initially. Migration of iron through this thin zirconia layer and formation of iron oxides lead to increased electron transport at these sites and to changes in the rest potentials towards the positive direction. However, the electronic conductivity of these oxide films does not increase to the levels attained by the oxide films on iron and steel. Thus the potentials of oxidized zirconium and Zircaloy-2 stay negative to platinum and iron and the anodic polarization curves reveal linear portions even after hundreds of hours of oxidation. The observation that the oxidation currents derived from these linear anodic portions agree with the oxidation rates obtained from the kinetic data confirms that these anodic linear portions represent the variation of the ion current through the growing oxide with the applied potential.

CONCLUSIONS

The concentration of oxide ions ($O_2^-$) in molten alkali nitrates and nitrites is too low to account for the observed rates of corrosion or iron, steel, zirconium and Zircaloy-2. Oxide ions for oxide growth are provided by the reaction of nitrate/nitrite ions with emerging anion vacancies or cations at the oxide-salt interface. Analysis of the polarization curves obtained on corroding samples yields oxidation currents which agree with the kinetically derived oxidation rates. The higher the resistance of the growing oxide to electron transport, the more negative are the rest potentials and the more distinct are the anodic linear portions representing ion transport through the growing oxide films.

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TABLE I
INGOT ANALYSIS

| Material      | Sn  | Fe  | Cr  | Ni  | Amount |
|---------------|-----|-----|-----|-----|--------|
| Zirconium     | < 10| 80  | 20  | < 10| ppm    |
| Zircaloy-2    | 1.46| 0.13| 0.08| 0.05| wt%    |
Fig. 1 Variation of rest potential with time of oxidation in KNO₃-NaNO₃-NaNO₂ (0.1 m) at 573 K; a - zirconium, b - Zircaloy-2 and c - iron.

Fig. 2 Interference colored oxide film growth at 573 K; o - Zircaloy-2 in NaNO₂, ▽ - zirconium and □ - Zircaloy-2 in NaNO₃-KNO₃-NaNO₂.
Fig. 3 Kinetics of oxidation at 573 K:
(a) Zircaloy-2 in • - binary nitrates,
△ - ternary nitrates-nitrite, □ - sodium nitrite, ● - LiNO₃ and ▼ - LiNO₃-LiOH;
(b) zirconium in • - binary nitrates
△ - ternary nitrates-nitrite and
□ - sodium nitrite.

Fig. 4 Polarization curves for zirconium at 573 K (weight
gain 6 mg/dm²): a₁ - binary nitrates, a₂ - ternary nitrates-
nitrite and a₃ - sodium nitrite.

Fig. 5 Oxidation and polarization of Zircaloy-2 at 573 K
in NaNO₃-KNO₃; after b₁ - 20, b₂ - 165 and b₃ - 330 h of
oxidation.
Fig. 6  Platinum wire electrode, 0.06 cm$^2$ in area, in KNO$_3$-NaNO$_3$-NaNO$_2$ (0.1 m) at 573 K; a - voltammogram at a scan rate of 20 mV/s and b - polarization traced at 0.5 mV/s.

Fig. 7  Polarization curves for an iron wire electrode (0.1 cm$^2$ in area) obtained at 573 K in NaNO$_3$-KNO$_3$-NaNO$_2$ (0.1 m) after immersion and 24 h oxidation in the same melt; curves for platinum under same conditions are shown by dashed lines.
Fig. 8 Curves similar to those in Fig. 7 obtained for a zirconium wire electrode, 0.3 cm² in area.

Fig. 9 Curves similar to those in Figs. 7 and 8 obtained for a Zircaloy-2 wire electrode, 0.47 cm² in area.
Fig. 10 Potential vs. pH diagram for iron in NaNO₃ at 600 K; Ag/Ag⁺ reference zero is likely to be located at "d" rather than at "a" (cf. discussion section).

Fig. 11 Schematic diagram of polarization curves resulting from electron transfer reactions at the oxide-salt interfaces and ion transport through the growing oxide films.