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Dissolution Susceptibility of the Oxide Species Formed on Mild Steel During Its Oxidation in Molten $NaNO_3$-KNO_3 Eutectic Mixture

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Mild steel was oxidized in pure molten $NaNO_3$-KNO_3 eutectic mixture at temperatures of 300, 375, and 450 °C and in the presence of 0.05 molal KH_2PO_4, $K_2Cr_2O_7$, or Na_2O_2 as additives. The dissolution susceptibility of the formed oxide species was evaluated in H_2SO_4 acid solution using the potential-time and current-time measurements under the open-circuit conditions. It was found that the rate of dissolution depended on the composition of molten nitrate bath, used for oxidation of mild steel, and its temperature. This was attributed to the effect of the previous conditions of the nitrate bath on the nature and composition of the oxide species formed on the metallic surface. The more resistant to dissolution in H_2SO_4 solution were those electrodes that were oxidized in nitrate melt at 450 °C in the presence of $K_2Cr_2O_7$ or Na_2O_2 as additives.

Keywords dissolution in sulfuric acid, mild steel, $NaNO_3$-KNO_3 eutectic, oxidation

1. Introduction

Iron forms three stable oxides: wustite (FeO), magnetite (Fe_3O_4), and hematite (Fe_2O_3). FeO is a p-type conductor while hematite is an n-type conductor. Bianchi and colleagues[1] observed that there is a close relation between susceptibility to pitting corrosion and the electronic properties of the oxide film. The n-type oxides are more susceptible to pitting corrosion than the p-type.

Molten alkali salts are widely used in heat treatment baths for metals and alloys, in nuclear reactors, in fuel coolant systems, and as heat transfer or reaction media in solar electric plants. Mild steels are often used as container and tube materials for the circulation of molten fluids to heat exchangers designed to generate steam in the temperature range 250–600 °C. Hence, hot corrosion studies of mild steel in molten alkali nitrate systems at these temperatures would appear to be necessary. Corrosion studies of iron, nickel, some steels, and chromium in eutectic mixtures of $NaNO_3$-KNO_3 and $NaNO_3$-$NaNO_2$ have been reported only up to 550°C.[2-8] It has been suggested[7] that Fe_2O_3 forms the external layer in contact with the salt, whereas Fe_3O_4 is the internal layer in contact with the metal for steel exposed to molten $NaNO_3$-KNO_3 eutectic mixture at temperatures up to 450 °C.

The current work consisted of a study of the corrosion behavior of the oxide films, preformed on the mild steel in molten nitrates, in H_2SO_4 aqueous solution at 25 °C.

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2. Experimental

The $NaNO_3$-KNO_3 eutectic mixture (1:1, mol:mol; melting point 225 °C) was prepared as described previously.[9,10] Calculated amounts of the two salts (AR, Merck, Germany) were mixed together and melted at 350 °C. The last traces of water were removed by bubbling pure dry oxygen gas through the melt for a period of 2 h. Excess oxygen was then removed by bubbling pure dry nitrogen through the melt for about 30 min. The molten nitrates mixture was left to cool in a dry atmosphere, and the solidified mass was quickly crushed and kept in the closed desiccator until required. In each experiment, l00 g of the eutectic were used. These were melted at the temperature of the experiment, which was carried out in tall unlipped Pyrex glass tubes (5 cm diameter, 11 cm long). The working vessel was enveloped in a stainless steel container (7 cm diameter, 10 cm height), which was located in an electrically heated crucible-type furnace. Regulation of the temperature of the furnace was affected through a variable transformer. The temperature of the melt was measured with the help of an Ni, Ni-Cr thermocouple and temperature indicator (±2 °C). The thermocouple was separated from the melt by means of a tight-fitting Pyrex glass tube.

For these experiments, steel coupons measuring 1 cm × 3 cm^2 were cut from cold-rolled mild steel sheet having 0.1 cm thickness and the following composition: C 0.3%, Si 0.15%, Mn 0.4%, P 0.1%, and S 0.02%. These were supported in the melt by a glass hook through a small hole near the edge. Just before introduction to the melt, the coupons were abraded with emery papers of different grades and degreased with ether.

The oxidation of mild steel was carried out at temperatures of 300, 375, and 450 °C in pure nitrate melt and in the presence of 0.05 molal of KH_2PO_4, $K_2Cr_2O_7$, or Na_2O_2 as additives.

The mild steel coupons were immersed into the nitrate melt, preadjusted at the required temperature. After a definite reaction period of 4 h, the coupons were withdrawn, washed with running distilled water to remove any solidified melt, and dried. After this, the coupons were subjected to (1) visual ob-

Table 1 Appearance of Oxide Film, Formed in Different Molten Baths and at Various Temperatures

Composition of Molten Bath	Temperature (°C)	Appearance
Nitrate melt	300	Bright, pale gray
	375	Bright, brownish green
	450	Bright, greenish gray
Nitrate-KH_2PO_4	300	Dull, brownish yellow
	375	Dirty brown
	450	Dirty, dark brown
Nitrate-$K_2Cr_2O_7$	300	Bright, brownish green
	375	Bright, gray
	450	Dull, dark gray
Nitrate-Na_2O_2	300	Bright, greenish blue
	375	Bright, gray
	450	Dull, dark gray

servations to record the appearance of oxide films formed on the surface of coupons, and (2) the corrosion tests in 0.005 M H_2SO_4 solution. In the corrosion tests, the potential of the mild steel electrodes, measured against saturated calomel electrode (SCE) as a reference, was followed as a function of time until reaching steady state under the open-circuit conditions and temperature of 25 °C. Also, the current-time curves were obtained under the open-circuit conditions, where the galvanic current between the mild steel electrodes and Pt electrode was measured as a function of time.

3. Results and Discussion

The appearance of the oxide film formed on the mild steel coupons after their immersion in pure nitrate melt and in the presence of 0.05 molal of the additives for a fixed period of time of 4 h and at different temperatures is given in Table I. It is clear from this table that the appearance of the oxide film greatly depends on the composition of the bath and its temperature.

Figures 1-4 represent the potential-time curves under open-circuit conditions for the mild steel electrodes immersed in 0.005 M H_2SO_4 solution after their oxidation in pure $NaNO_3$-KNO_3 eutectic melt and in the presence of 0.05 molal of additives KH_2PO_4, $K_2Cr_2O_7$, or Na_2O_2, respectively, at temperatures of 300, 375, and 450 °C.

Inspection of the plots in these figures reveals that the general features of the curves of each figure greatly depend on the composition of the bath and its temperature. The plots of Fig. 1 indicate that in the case of the pure nitrate melt, the curves obtained for the temperatures 375 and 450 °C are identical in that each exhibits an arrest before attaining the steady state, while for the temperature of 300 °C this arrest is absent. The values of the steady-state potential attained for the three temperatures are almost near to each other.

The plots of Fig. 2 indicate that in the presence of KH_2PO_4 as an additive in the nitrate melt, the curves obtained for the temperatures 300 and 375 °C are more or less identical and differ from that obtained for the temperature 450 °C in that the latter exhibits more arrests before attaining the steady state. It is worth mentioning that the values of the steady-state potential for 300 and 375 °C are more negative than that for 450 °C.

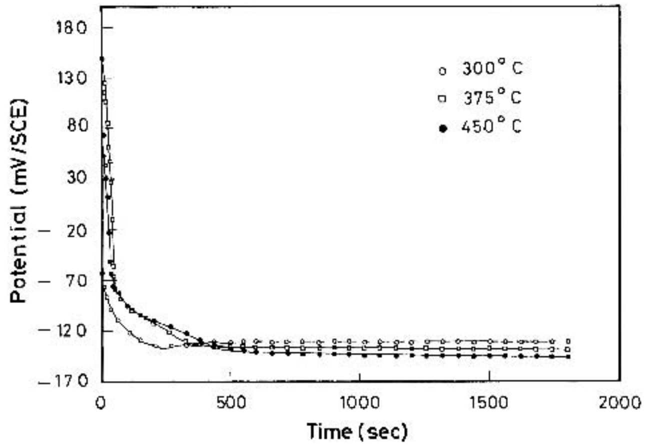

Fig. 1 Potential-time curves for mild steel electrodes in 0.005 M H_2SO_4 after immersion in pure nitrate melt at different temperatures

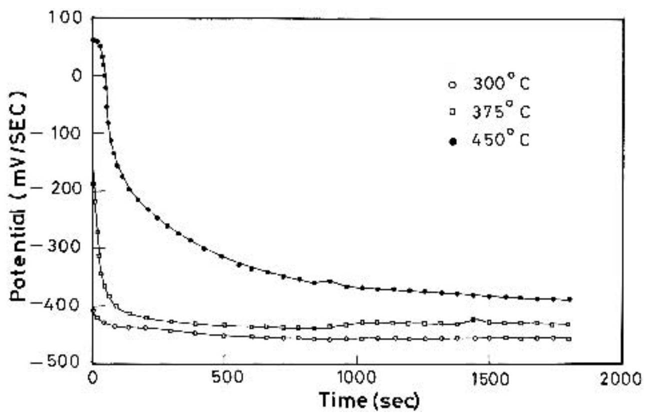

Fig. 2 Potential-time curves for mild steel electrodes in 0.005 M H_2SO_4 after immersion in nitrate melt and 0.05 molal KH_2PO_4 at different temperatures

The plots of Fig. 3 indicate that in the presence of $K_2Cr_2O_7$ as an additive in the nitrate melt, the curves obtained for the temperatures 300 and 375 °C are more or less close to each other and differ from that obtained for 450 °C: the latter contains clear arrests before attaining the steady state.

The plots of Fig. 4 indicate that in the presence of Na_2O_2 as an additive in the nitrate melt, the curves for the temperatures 300 and 375 °C are more or less identical and differ from that for 450 °C: the latter exhibits a clear arrest at the start potential of a value more positive than others.

The observed differences in the general features of the plots of Fig. 1-4 can be attributed to the variations in the composition and nature of the iron oxide species formed on the metallic surface during the preoxidation process in molten nitrate baths. It seems that the compositions of the bath and its temperature greatly affect the nature and composition of the iron oxide species formed on the metallic surface.

It has been suggested[7] that Fe_2O_3 forms the external layer in contact with the salt, whereas Fe_3O_4 is the internal layer in contact with the metal for steels exposed to a molten $NaNO_3$-KNO_3 eutectic mixture at temperatures up to 450 °C. Picard

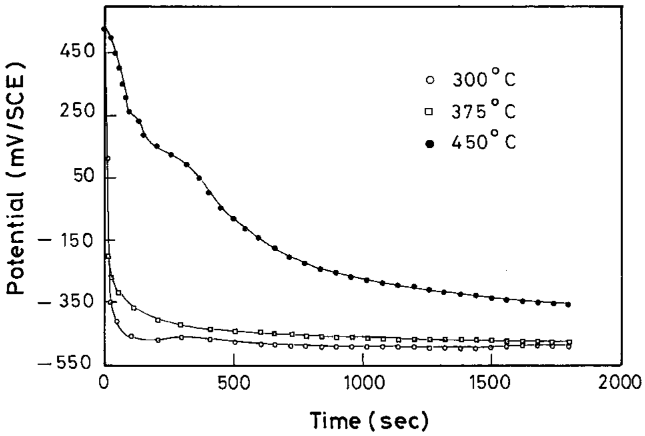

Fig. 3 Potential-time curves for mild steel electrodes in 0.005 M H_2SO_4 after immersion in nitrate melt and 0.05 molal $K_2Cr_2O_7$ at different temperatures

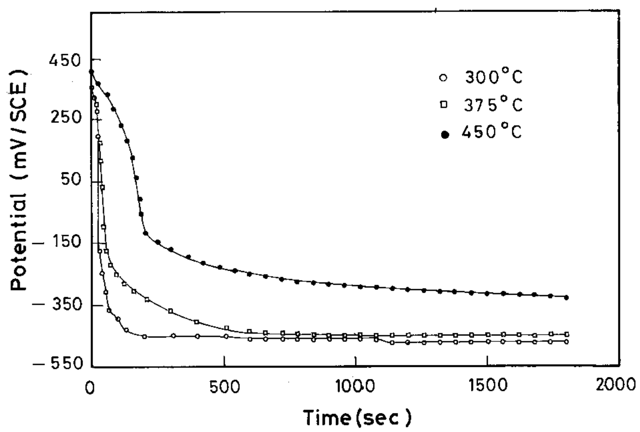

Fig. 4 Potential-time curves for mild steel electrodes in 0.005 M H_2SO_4 after immersion in nitrate melt and 0.05 molal Na_2O_2 at different temperatures

and colleagues[11] have established a relationship between iron oxide species and oxide anion content in $NaNO_3$-$NaNO_2$ melt up to 450 °C by potentiometric titration and equilibrium potential pO^{2-} diagrams. In strongly basic media, $Fe_2O_5^{4-}$ or $Na_4Fe_2O_5$ is stable in contact with the melt. In moderately basic media, the stable iron oxide species of FeO_2^- or $NaFeO_2$, and in acidic media Fe_2O_3, are formed. The formation of an innermost Fe_3O_4 up to 623 K[12-14] has already been shown by electron reflection and XRD studies. Very recently, oxide reduction studies by cyclic voltammetry technique predicted the presence of Fe_3O_4 (inner) and Fe_2O_3 (outer) up to 400 °C in $NaNO_3$-KNO_3 melt.[15] In addition, thermodynamic calculations based on potential pO^{2-} relationships suggested that the basicity of the melt increases with temperature increase,[5,7,16] which favors incorporation of sodium in the scale. The following electrochemical reactions were predicted[17] in the formation of various oxides on iron surface in the presence of oxide ions (O^{2-}).

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

However, FeO (wustite) is stable only above 570 °C. FeO decomposes into Fe_3O_4 and, apparently, Fe_2O_3 at lower temperature as:

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

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

The presence of Fe_3O_4 and Fe_2O_3 oxide layer can be proposed in the melt alone below 450 °C. In the presence of oxide and sodium ions, generally $NaFeO_2$ followed by $Na_4Fe_2O_5$ may be formed as:

$$2FeO + 5O^{2-} = Fe_2O_5^{4-} + 6e^-$$

$$Fe_2O_5^{4-} = 2FeO_2^- + O^{2-}$$

$$FeO_2^- + Na^+ = NaFO_2$$

$$Fe_2O_5^{4-} + 4Na^+ = Na_4Fe_2O_5$$

$NaFeO_2$ and $Na_4Fe_2O_5$ are highly basic in nature, and it can be suggested that in the current work, their formations may start even at 350 °C in the $NaNO_3$-KNO_3 + Na_2O_2 melt. The presence of Na_2O_2 as an additive in the nitrate melt greatly increases the basicity of the melt.[18,19]

The addition of $K_2Cr_2O_7$ to the nitrate melt decreases the basicity of the melt and increases its acidity.[18,19] In this melt the formation of multilayered oxide scales on the coupons is more favorable where the outer layer is Fe_2O_3, and the inner layer is Fe_3O_4.

The addition of KH_2PO_4 to the nitrate melt increases its acidity[18,19] and must favor the formation of Fe_2O_3. But, on the other hand, this additive decomposes in the melt according to the reaction:

$$KH_2PO_4 \rightarrow KPO_3 + H_2O$$

The presence of water in the melt as a result of decomposition of KH_2PO_4 greatly affects the nature of oxide species formed on the surface of coupons. It can be assumed that there is a great probability of the formation of porous nonadherent hydrated oxide species, especially at temperatures of 300 and 375 °C, while at 450 °C this probability decreases. This assumption may be confirmed from the colors of coupons recorded in Table 1.

Inspection of the potential-time curves of Fig. 1-4 reveals that the potential of the preoxidized electrodes shifts to the negative direction (active) with time until reaching its steady state. This indicates that the oxide film dissolved in H_2SO_4 solution. If we roughly take the immersion potential, E_{imm} (potential of electrode at the moment of its immersion in acid solution), as the starting potential of the preoxidized electrode, and the steady-state potential, E_s, as the end potential, the value $E_{imm} - E_s$ can be calculated. The time required for the shift of the potential from E_{imm} to E_s (time of dissolution) was recorded. The rate of dissolution of the oxide film can be roughly calculated by dividing the value of $E_{imm} - E_s$ by the time of dissolution. The obtained values of these calculations are listed in Table 2. It is clear from these results that the value of the rate of dissolution greatly depends on the composition of the bath and its temperature. Also, the values of E_{imm} and E_s depend on the composition of the bath. The more positive values

Table 2 E_{imm}, E_s, **Time, and Rate of Dissolution of Oxide Films in 0.005 M H_2SO_4 Solution After Their Formation on the Mild Steel in Pure Nitrate Melt and in the Presence of Additives at Different Temperatures**

Composition of Molten Bath	Temperature (°C)	E_{imm} (mV)	E_s (mV)	$E_{imm} - E_s$ (mV)	Time (s)	Rate of Dissolution
Pure nitrate	300	−131	−131	302	180	1.678
	375	−136	−136	304	420	0.724
	450	−140	−140	288	540	0.533
Nitrate-KH_2PO_4	300	−453	−453	82	540	0.152
	375	−430	−430	280	360	0.778
	450	−323	−323	373	540	0.69
Nitrate-$K_2Cr_2O_7$	300	−465	−465	765	120	6.375
	375	−438	−438	938	420	2.233
	450	−426	−426	957	3600	0.266
Nitrate-Na_2O_2	300	−446	−446	791	175	4.52
	375	−448	−448	1007	720	1.399
	450	−328	−328	722	1800	0.401

Table 3 i_{max}, i_{init}, $i_{max} - i_{init}$, **Time, and Rate of Dissolution of Oxide Films in 0.005 M H_2SO_4 Solution After Their Formation on the Mild Steel in Pure Nitrate Melt and in the Presence of Additives at Different Temperatures**

Composition of Molten Bath	Temperature (°C)	Temperature (K)	i_{max} (μA)	i_{init} (μA)	$i_{max} - i_{init}$ (μA)	Time (s)	Rate of Dissolution
Pure nitrate	300	573	87.4	0.5	86.9	240	0.362
	375	648	63.5	0.3	63.2	500	0.126
	450	723	74.7	1.7	73	540	0.135
Nitrate-KH_2PO_4	300	573	62.6	45.2	17.4	300	0.058
	375	648	67.1	31.4	35.7	480	0.074
	450	723	25.5	20.1	5.4	540	0.01
Nitrate-$K_2Cr_2O_7$	300	573	60.3	0.5	59.8	200	0.299
	375	648	44.5	0.9	43.6	570	0.076
	450	723	10.3	0	10.3	600	0.017
Nitrate-Na_2O_2	300	573	53.5	0.1	53.4	415	0.129
	375	648	61.9	0.1	61.8	840	0.074
	450	723	12.5	0.2	12.3	530	0.023

for E_{imm} are obtained for $K_2Cr_2O_7$ and Na_2O_2 as additives in the nitrate melt. The less positive values of E_{imm} are obtained for the pure nitrate melt, while the more negative values are obtained for KH_2PO_4 as additive.

It was mentioned above that the nature and composition of oxide species formed on the surface of electrodes greatly depend on the composition of the bath; that is, its basicity (acidity). These conditions of bath reflect their effect on the values of E_{imm} recorded for the different preoxidized electrodes.

The values of E_s for the pure nitrate melt differ from those obtained in the case of the presence of different additives: the latter values are more negative than the former ones by about 200–300 mV. This may be attributed to the fact that the inner layer of Fe_3O_4 formed on the electrode surface in the pure nitrate melt is stable and insoluble in the present acid solution of low concentration.

Taking into consideration the more positive values of E_{imm} and the low rate of dissolution, the preoxidized electrodes in the nitrate melt containing $K_2Cr_2O_7$ or Na_2O_2 as additives and at 450 °C are more resistant to dissolution in the acid. On the other hand, if we take into consideration the values of E_s and the rate of dissolution, the preoxidized electrodes in pure nitrate melt are more resistant to dissolution where the rates of dissolution are more or less low and E_s more positive.

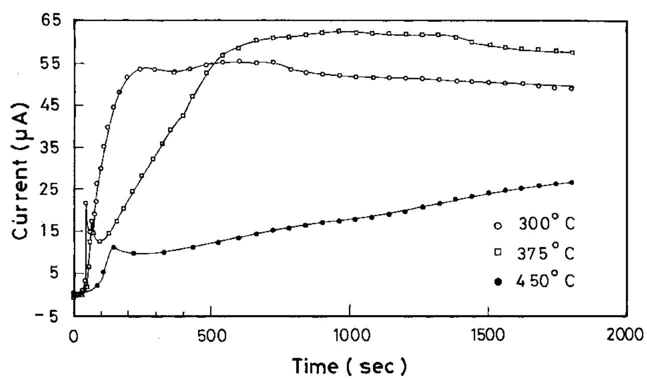

Fig. 5 Current-time curves for mild steel electrodes in 0.005 M H_2SO_4 after immersion in nitrate melt and 0.05 molal KH_2PO_4 at different temperatures

Figure 5 represents the current-time curves under open-circuit conditions for the mild steel electrodes immersed in 0.005 M H_2SO_4 solution after their oxidation in nitrate melt containing 0.05 molal Na_2O_2 as additive. Similar curves are obtained for the pure nitrate melt and in the presence of $K_2Cr_2O_7$ or KH_2PO_4 as additives.

The plots of Fig. 5 and similar ones indicate that the galvanic current increases with time, reaching steady state. The mode and rate of the increasing current depend to a great extent on the previous conditions of the oxidation process in molten nitrate baths. This gives an indication about the dissolution of the oxide species film in H_2SO_4 solution.

If we recorded the initial current, i_{init} (current at the moment of immersion of the electrodes in the acid solution), and the maximum current, i_{max}, the value of $i_{max} - i_{init}$ can be calculated. The time required for reaching the current from i_{init} to i_{max} was also recorded. The rate of dissolution can be roughly calculated by dividing the value of $i_{max} - i_{init}$ by time of dissolution. The calculated values are listed in Table 3.

The results of Table 3 indicate that the values of i_{init} and rate of dissolution greatly depend on the previous conditions of the oxidation process, such as the composition of the molten nitrate bath and its temperature. Taking into account the value of i_{init} and rate of dissolution for the different electrodes, it is found that those preoxidized at 450 °C in nitrate melt containing 0.05 molal $K_2Cr_2O_7$ or Na_2O_2 as additives are more resistant to dissolution in H_2SO_4 solution. The values of i_{init} and rate of dissolution for these electrodes are very low.

From the results of Table 3, it is noteworthy that the values of i_{init} for KH_2PO_4 are high. This indicates that the oxide species films formed in the presence of KH_2PO_4 are less protective. These situations indicate that the results of Table 3 are in agreement with those recorded in Table 2.

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