

CORROSION OF MILD STEEL IN MOLTEN KCl-LiCl EUTECTIC

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The attack of mild steel (0.10–0.20% C, 0.15–0.30% Si, 0.30–0.50% Mn, <0.005% S, <0.005% P) by molten-KCl-LiCl eutectic has been studied as a function of salts drying and temperature. Corrosion rates fall rapidly to a constant value with time and increase at rising temperature in the 400 to 800°C range. The oxidation kinetics proceeds through a *para*-linear law at every temperature studied. The corrosion products found in dry melts are constituted by magnetite; in humid baths, ferric oxide plus magnetite are formed. Cathodic polarization curves show the corrosion process to be controlled by diffusion of oxidizing species. Results suggest that ferric ions are the species involved, as proved by experiments with addition of ferric chloride to the melt.

Metal corrosion in molten salts has been studied to a less extent than in aqueous or gas systems, results point to the special significance that the cathodic reduction of oxyanions, thermal mass transfer and solution of corrosion products take for oxidation in this medium^{1,2}. The few data published on corrosion of chromium-nickel steels, nickel alloys and mild steel in fused alkali and alkaline-earth chlorides in the temperature range 700–850°C show a decreasing rate of metal deterioration with time and a selective attack of the specimens with removal of the less noble components^{3–5}.

This work deals with the corrosion behaviour of mild steel (0.15–0.30% Si, 0.10–0.20% C, 0.30–0.50% Mn, <0.005% P, <0.005% S) in molten KCl-LiCl eutectic at 400 to 800°C.

EXPERIMENTAL

All experiments were carried out in a Pyrex or silica tube cell of 5.5 cm bore and 40 cm length topped by a removable Pyrex manifold with vacuum pump entries and gas outlets. The top manifold was attached to the cell cap at a standard taper joint. The cap was provided with the fittings for working electrodes and thermocouple. For corrosion tests, Pyrex or quartz rods 1 cm diameter with tungsten hooks substituted for the working electrodes. An unnamed porcelain

crucible containing the eutectic salts was placed on the bottom of the cell. A conventional resistance heated tube-type furnace was used to heat the samples.

The KCl-LiCl eutectic melt was prepared from Merck r.g. chemicals without any prior treatment. Since the moisture content of the salts affects markedly the aggressiveness of the melt, a drying method was established in order to control the humidity of the eutectic bath. After several preliminary experiments, the procedure chosen for dehydration of the samples was as follows. Salts were dried under 10^{-2} Torr pressure at 200°C for two hours in a vacuum oven. A 40 g batch of the eutectic components was placed in the crucible and introduced in the cell. This was then evacuated and maintained at 400°C for two hours under a pressure 10^{-4} Torr. Next, the salt mixture was melted under nitrogen atmosphere and kept at 600°C for two hours before starting the experiment. Melts obtained by this way were considered as dried. For experiments with "humid" melts, only the vacuum oven treatment was applied to the salts.

Ten steel foils of 2 cm^2 surface and 1 mm thick were used in weighing tests. All specimens were polished chemically in a H_2O_2 and oxalic acid solution⁶ and washed with acetone prior to testing. After the experiment, the sheets were washed with water, dried and weighed. An average value of the corrosion rate was calculated. Specimens were suspended from tungsten hooks sealed into Pyrex tubes and immersed in the fused eutectic.

Cathodic galvanostatic and potentiostatic curves were obtained with a 0.5 cm^2 steel electrode against a Ag/AgCl-KCl-LiCl reference electrode prepared after Bockris and coworkers⁷. A graphite rod of 4 mm diameter was used as counter electrode. The conventional galvanostatic method was applied to polarize the cell and a Wenking 6439 TR potentiostat type for recording the potentiostatic curves.

A Leeds and Northrup recorder and controller regulated the temperatures of the furnace with a variation of $\pm 5^{\circ}\text{C}$. Temperatures were measured through a chromel-alumel thermocouple sheathed in a porcelain tube and held in contact with the melt.

RESULTS AND DISCUSSION

The corrosion of the steel specimens was studied in experiments 12 hours long between $400-800^{\circ}\text{C}$ in dried and not dried melts of KCl-LiCl eutectic. The variation of corrosion rates with time for both melts exhibits a rapid decrease of the reaction rate during the first few hours of the test reaching a constant value after about 5 hours of the specimen immersion in the bath (Figs 1 and 2). Deterioration rates appear to be scarcely affected by water traces in the molten electrolyte and are slightly higher in dried melts, a fact parallel to that observed in specimens exposed to the vapours of this eutectic⁸. Rates of attack increase with temperature in the range studied irrespective of the drying treatment of the salts. Corrosion rates reported by Stepanov and coworkers³ on mild steel corrosion in fused MgCl_2 , KCl and NaCl under equivalent experimental conditions are of the same order of magnitude as those here observed.

The corrosion was found to follow a parabolic rate law during the first hours of the test with two different rate constants and a linear law for the remaining 8 hours of the experiment. Fig. 3 shows the straight lines obtained for $(\text{mg}/\text{cm}^2)^2$ vs time in dried melts corresponding to the equation $g^2 = kt$, which confirms the parabolic behaviour. This suggests that the process is firstly controlled by the rate of diffusion

of the reactants through the growing layers of oxides, then, in the case of the linear law, as the bulk of the oxide layer has become porous or cracked because of compressional or tensional stresses it is governed by ionic diffusion through a thin film of oxide. The rate constants deduced from the parabolic equation yield an activation energy of 8 and 10 kcal/mol for the two steps of the process, respectively.

Corrosion products formed on all specimens were porous and flaky scales, non-adherent in nature and insoluble in the melt. X-ray analysis of this products revealed the scales obtained in dried baths to consist only of magnetite, whereas ferric oxide plus magnetite were the constituents of those produced in melts not subject to drying. It was surprising that no wüstite was detected in the corrosion products obtained at temperatures above 600°C where the FeO becomes stable. Delarue⁹ informs that wüstite and magnetite are slightly soluble in this eutectic and oxidize to ferric compounds by the action of chloride, while the Fe₂O₃ decomposes to magnetite and oxygen in this medium at 400°C. The latter effect was not observed in this work or by other authors¹⁰ who used bubbling oxygen to produce insoluble haematite and purify the melt from iron ions. We assume that the oxidizing power of the melt at the studied temperatures is high enough to prevent the formation of FeO or if formed it is immediately oxidized to magnetite.

The results described show that the corrosion of mild steel in fused KCl-LiCl occurs through the formation of iron oxides even though the liquid eutectic was carefully dried. The experiments were performed under nitrogen atmosphere, which along with the drying methods applied exclude any possible dissolution of air oxygen in the bath, therefore we must admit that a certain amount of absorbed water is

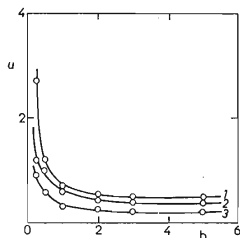


FIG. 1

Corrosion Rates $\mu(\text{mg}/\text{cm}^2 \text{ h})$ vs Time of Mild Steel Specimens Immersed in Dried KCl-LiCl Melts

1 700, 2 500, 3 400°C.

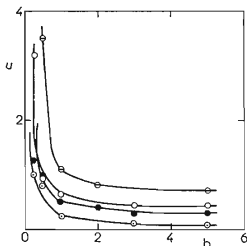


FIG. 2

Corrosion Rates $\mu(\text{mg}/\text{cm}^2 \text{ h})$ vs Time of Mild Steel Specimens in Melts not Subject to Drying

○ 800, □ 700, ● 500, ○ 400°C.

present in the melt even at high temperature. In dried salts, the moisture content is low and the oxygen concentration is not sufficient to form the higher iron oxides as it happens to be in more humid baths.

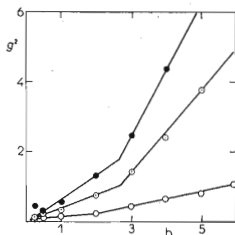
The general principles discussed by Littlewood¹ for corrosion of metals in molten salts may be applied to the problem here studied. The aggressiveness of the molten KCl–LiCl eutectic toward the steel can be defined by a redox potential which depends on the relationship of the activities of oxidized and reduced species in the melt, in this case

$$E = E_0 + (RT/2F) \ln ([O_2]^{1/2}/[O^{2-}])$$

FIG. 3

Linear Plots of the Kinetic Parabolic Law for Steel Corrosion in Dried KCl–LiCl Melts

g^2 in $mg^2 cm^4$; ● 700, ○ 500, ○ 400°C.



The metal in contact with the melt takes up a potential which is determined by the activity of its ions in solution in the fused electrolyte so that it will corrode until this potential reaches an equilibrium with the redox potential of the bath. Under conditions where passivity or equilibrium cannot be reached corrosion of metal should proceed indefinitely. The corrosion products of mild steel are, as said above, porous and non-adherent, no protection layer can be formed, consequently the corrosion of metal shall not cease.

Experimental results may be explained assuming the oxidation of the steel to be originated by the redox potential of the melt and then controlled by the film-growth of the oxide products. During the first hours of corrosion, the kinetics of the process is governed by diffusion of the reactants through the oxide layer formed on the metal and described by a parabolic law. Later, as the layer grows, stresses and porosity appear in the oxide (most probably by a selective attack and dissolution of the components of the steel), the scales split from the metal and the corrosion conforms to a linear rate law.

Metallographic examination of steel specimens immersed into the liquid eutectic for 3 hours at 600°C showed a uniform dissolution of the metal surface with a slight attack at the grain boundaries (Fig. 4*).

From the electrochemical view, corrosion of metals in fused salts occurs, as in aqueous solutions, through cathodic and anodic reactions. Tomašov and cowor-

* See insert facing p. 688.

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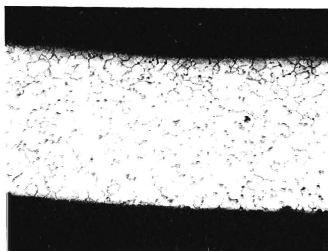


FIG. 4

Cross Section of Mild Steel Specimen Immersed in Fused
KCl-LiCl at 600°C for 3 hours.

kers¹¹ have proved that the anodic reaction for the corrosion of metals in molten chlorides is $M \rightarrow n e + M^{n+}$, while the cathodic reaction was controlled by diffusion of oxidizing species made up of impurities and oxyanions dissolved in the bath.

The cathodic depolarizers in the system here studied may come from the acknowledged traces of water (H^+) and from the steel corrosion products that dissolve into the liquid salts. The steel components Si, C and Mn oxidize in the range 400 to 800°C to form SiO_2 , CO and Mn_3O_4 , although these oxides are slightly soluble in the eutectic at 400°C⁹, their solubility and that of the iron oxide may increase at higher temperatures. We must point out that among their ions only the $Fe^{3+}-Fe^{2+}$ system has a high oxidizing potential in this solvent⁹.

The cathodic polarization curves obtained for steel electrodes in fused KCl-LiCl eutectic between 400–800°C exhibit diffusion waves (Fig. 5) with limiting current densities which are barely affected by salt moisture or the increase of temperature. The anodic curves plotted in the same figure indicate dissolution of the electrode with a slight activation polarization.

It was found that the diffusion waves are fairly well described by an equation of the Heyrovský-Ilkovič type

$$E = \text{const} + (RT/nF) \ln [(i_D - i)/i],$$

where i_D is the limiting current density and R , T , n and F have the usual meaning. This equation cannot be applied here on polarographic grounds because the electrode process is irreversible and a correction coefficient should be introduced as proposed

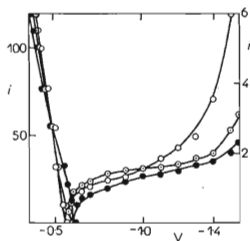


FIG. 5

Polarization Curves for Mild Steel Electrodes in KCl-LiCl Melts

i in mA/cm^2 ; \circ 600, \odot 500, \bullet 400°C; both cathodic and anodic curves are indicated.

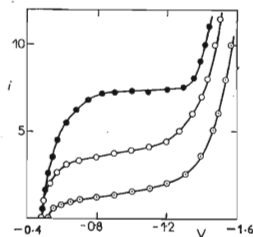


FIG. 6

Cathodic Polarization Curves for Mild Steel Electrodes in KCl-LiCl Melts with Different $FeCl_3$ mol Fractions

i in mA/cm^2 ; 600°C; \circ 0, \odot 0.001, \bullet 0.002 $FeCl_3$.

by Delimarskii¹². In any case, the n values calculated from the slopes of the logarithmic plot of the equation varied from 2.3 to 3.6, being around 3 at high temperature. The values obtained, together with the slight effect of humidity and temperature on the diffusion wave heights, suggest that the species reduced in the cathodic process are ferric ions coming from the solution of iron oxides. In fact, the cathodic polarization curves for solutions of FeCl_3 added to the eutectic at different concentrations at 600°C (Fig. 6) show the same diffusion waves with limiting currents proportional to the mole fraction of the ferric salt.

On the ground of the results reported, the corrosion of mild steel in molten KCl-LiCl appears to be initiated with the oxidation of Fe by water traces. According to the electrochemical mechanism, iron dissolves in liquid KCl-LiCl in the form of the Fe^{2+} , as it has been demonstrated by several authors^{13,14}, at the anodic site, whereas the cathodic reaction could be the reduction of H^+ or H_2O



The FeO is unstable at temperatures below 600°C and is easily oxidized by water traces or corrosive environments at higher temperatures, yielding in both cases magnetite which by further oxidation produces haematite. The solubility of iron oxides in this melt is small but sufficient to form some concentration of Fe^{3+} close to the metal. The high oxidizing potential of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ system in this medium allows the ferric ion to act as a main depolarizer in the corrosion process. In polarization experiments, the oxidation of Fe^{2+} ions might be helped by its reaction with chlorine diffused from the anode, since no separated compartments were provided for the electrodes in the cell. Delarue⁹ has proved that Fe_3O_4 is readily oxidized by chlorine dissolved in molten KCl-LiCl at 400°C.

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