

CORROSION OF IRON (ARMCO) IN KCl-LiCl MELTS*

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Abstract—The corrosion of iron in molten KCl-LiCl eutectic has been studied as a function of the drying degree of the salts and temperature. Corrosion rates fall rapidly to a constant value with time and increase with temperature in the 400–800°C range, the salt moisture enhances the aggressiveness of the melt. The oxidation kinetics is governed by a para-linear law which becomes linear at high temperatures. The corrosion products in dry melts consist of α -Fe and magnetite, those produced in moist baths are formed by magnetite and ferric oxide.

The cathodic polarization curves for iron specimens show diffusion waves that fit the Heyrovsky-Ilkovic equation. The results suggest that ferric ions are the oxidizing species controlling the corrosion process.

Résumé—On a étudié la corrosion de Fe par l'eutectique KCl-LiCl fondu en fonction de la siccité du mélange et de sa température. Dans l'intervalle de 400–800°C, les vitesses de corrosion augmentent avec la température et avec le degré d'humidité des sels; avec le temps elles tombent rapidement à une valeur constante. La cinétique d'oxydation est régie par une loi quasi-linéaire qui devient linéaire aux températures élevées. Dans les mélanges secs, les produits de corrosion sont constitués de Fe α et de Fe_2O_3 ; dans les mélanges humides, de Fe_2O_3 et de Fe_3O_4 . Les courbes de polarisation cathodique de Fe présentent des ondes de diffusion vérifiant l'équation de Heyrovsky-Ilkovic. Les résultats suggèrent que les ions Fe^{3+} sont les espèces oxydantes régissant la réaction de corrosion.

Zusammenfassung—Die Korrosion von Eisen in geschmolzenem KCl-LiCl-Eutektikum wurde als Funktion des Trocknungsgrades der Salze und der Temperatur untersucht. Die Korrosionsgeschwindigkeiten fallen mit der Zeit rasch auf einen konstanten Wert ab und erhöhen sich mit der Temperatur im Bereich 400–800°C, wobei die Salzfeuchtigkeit die Aggressivität der Schmelze erhöht. Die Oxydationskinetik richtet sich nach einem paralinearen Gesetz, das bei hohen Temperaturen linear wird. Die Korrosionsprodukte in trockenen Schmelzen bestehen aus α -Fe und Magnetit, die in feuchten Bädern entstehenden werden von Magnetit und Eisen(III)-oxyd gebildet. Die kathodischen Polarisationskurven für Eisenproben zeigen Diffusionswellen, die der Heyrovsky-Ilkovic-Gleichung entsprechen. Die Ergebnisse legen die Annahme nahe, dass Eisen(III)-Ionen die Oxydationsstufe sind, die den Korrosionsverlauf bestimmt.

INTRODUCTION

THE CORROSION of iron in molten mixtures of alkali¹ and alkaline-earth chlorides² has been studied by Kochergin *et al.* who observed that the corrosion rates decreased with time and increased with higher temperature, the aggressiveness of the salts being related to the nature of the cation. Lately, electrochemical research by Tomazov³ on iron corrosion in molten NaCl and by Devyatkin⁴ on dissolution of this metal in MgCl–NaCl–KCl substantiated the electrochemical theory of corrosion in fused salts according to which the process is determined by the cathodic reduction of impurities and the oxidation of the metal, through local cells.

We try here to inform on the electrochemical study of iron corrosion in fused KCl-LiCl eutectic as a function of the dryness degree of the salts and temperature.

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EXPERIMENTAL

The experimental cell, furnace, crucible and electrodes have been described elsewhere.⁵ Merck r.g. LiCl and KCl were used to compound the eutectic melt. The importance of the drying method of the eutectic for the corrosion of iron was pointed out by the Russian authors¹⁻⁴ who included in their procedure dehydration of the salts by a HCl stream or addition of NH_4Cl to the melt. They remarked that these compounds were absorbed by the molten salts and provided subsequently high concentrations of H^+ that acted as depolarizer. Therefore, close attention was paid to the drying system applied to the salts, which, after different trials, consisted of a combination of high vacuum and temperature as it has been reported.⁵ It was lately realized that even under these conditions the melt was not completely dried but it was considered as such in the following: the experiments with dried melts were carried out under a pressure of 10^{-4} torr and those with undried, moist salts were in open atmosphere.

The weighing tests were performed with 10 Armco iron sheets of 2cm^2 area and 1 mm thickness. They were suspended from tungsten hooks sealed into Pyrex tubes and immersed in the bath. All specimens were chemically polished in a solution of H_2O_2 and oxalic acid⁶ and washed with acetone before testing. After the experiment, the foils were washed with water, dried and weighed, and an average value of the corrosion rate was calculated.

Cathodic galvanostatic and potentiostatic curves for 0.5 cm^2 iron specimens were recorded with reference to the Ag/AgCl-KCl-LiCl electrode prepared after Bockris *et al.*⁷ A graphite rod of 4 mm diameter acted as counter-electrode. The conventional galvanostatic method was applied to polarize the cell and a Wenking 6439 TR potentiostat was used for recording the potentiostatic curves.

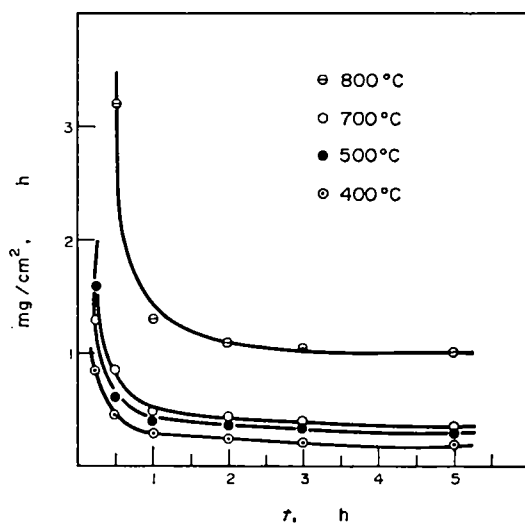


FIG. 1. Corrosion rates vs. time of iron specimens immersed in dried KCl-LiCl eutectic melts.

A Leeds and Northrup instrument recorded and controlled temperatures within $\pm 5^\circ\text{C}$ through a chromel-alumel thermocouple protected by a porcelain sheath.

RESULTS AND DISCUSSION

Weighing tests for iron specimens immersed in molten LiCl-KCl eutectic subjected to different degrees of drying have been performed for times that extend from 15 min to 12 h in the temperature range $400\text{--}800^\circ\text{C}$. Corrosion rates ($\text{mg}/\text{cm}^2\text{h}$) vs. time (h) for dried and undried melts are given in Figs. 1 and 2 respectively; it is seen that in dried melts the rate of the metal attack falls rapidly during the first hour of the test and more slowly in humid baths, attaining in both media a constant value after 5 h of specimen exposure to the liquid electrolyte. A rise in temperature increases deterioration rates in the range studied, irrespective of the water content of the melt. On the

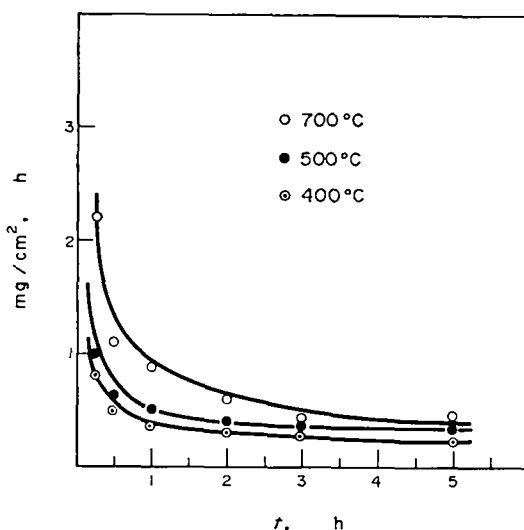


FIG. 2. Corrosion rates vs. time of iron specimens in KCl-LiCl melts not subjected to drying.

other hand, the presence of moisture in the molten eutectic causes the metal to corrode to a greater extent than in dried melts; the difference in corrosion rates is slight at 400°C but increases at higher temperatures. The oxidation rates of iron obtained in this investigation are very similar to those reported by Kochergin *et al.*¹ for the same salts system between $450\text{--}550^\circ\text{C}$.

The corrosion of iron with time in KCl-LiCl melts at 400 and 500°C obeys the parabolic rate law with two successive rate constants in the early stages of the test; as the oxidation of metal proceeds a transition from the parabolic to the linear law occurs eventually. Plots of $(\text{mg}/\text{cm}^2)^2$ against time for specimens in both melts show a linear variation that corresponds to the parabolic equation $g^2 = Kt$ (Fig. 3), where K is the rate constant. At temperatures higher than 700°C , the iron is oxidized according to the linear rate law although a short initial period is observed during which the rate decreases to the constant rate. The kinetic data suggest that the corrosion process

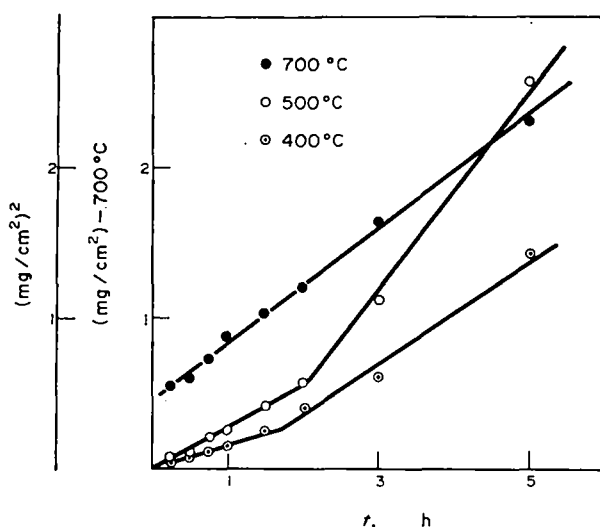


FIG. 3. Linear plots of the kinetic parabolic and linear laws for iron corrosion in undried KCl-LiCl melts.

in this medium is determined in the early stage of oxidation by the diffusion rate of the reactants through the growing layer of oxides. As the oxide growth proceeds, some kind of cracking or recrystallization of the oxide layers takes place that makes the oxide bulk porous to the reactant so that the slower process is either diffusion through a thin oxide layer or, as we will see below, the diffusion of oxidants in the melt to the metal. At higher temperatures, the mobility of the ions through the oxide layer is greater, herewith the cracking of the oxides and the constant corrosion rate would appear earlier. These suggestions are supported by the nature of the corrosion products. From the variation of the parabolic rate constants with temperature, an energy of activation of 3 and 8 kcal/mole for humid eutectics and 9 and 10 kcal/mole for dried melts was calculated. From the linear rate constants the energies for moist and dry melts are 4 and 8 kcal/mole⁻¹, respectively.

Optical micrographs of cross-sections of iron specimens after corrosion in molten KCl-LiCl at 600°C for 3 h showed an even dissolution of the metal surface similar to that obtained in aqueous solutions (Fig. 4).

The compounds produced by interaction of iron with the liquid eutectic appear to be dependent of the humidity of the bath. In every case, the products were porous flakes that scale off easily from the metal and are sparingly soluble in the melt. The moist eutectic yields at 700°C a black compound that X-ray analysis revealed to be formed of hematite and magnetite, while those obtained in dry melts at the same temperature consisted of α -Fe and magnetite. No traces of wustite were detected at any experiment at high temperature in spite of the stability of FeO at temperatures above 600°C. The equilibrium diagram of the iron-oxygen system displays phase fields of α -Fe + Fe₃O₄ in the temperature range 400–570°C and α -Fe + FeO at 570–900°C; at higher oxygen concentration, magnetite and ferric oxide are formed in the high temperature field. The absence of wustite in the corrosion products of iron



FIG. 4. Cross-section of iron specimen immersed in fused KCl-LiCl at 600°C for 3 h.

in KCl-LiCl melts indicates that either FeO is thermodynamically unstable in this environment at temperatures over 600°C and the phase $\alpha\text{-Fe} + \text{Fe}_3\text{O}_4$ is directly produced or $\alpha\text{-Fe} + \text{FeO}$ is primarily formed and FeO decomposes subsequently to $\text{Fe}_3\text{O}_4 + \text{Fe}$.

Reports on solubility of wustite and magnetite in molten KCl-LiCl⁹ disclose a sparing dissolution of the oxides at 400°C and no decomposition effect. This fact supports the hypothesis of the thermodynamical instability of FeO in the bath. On the other hand, iron corrosion in aqueous solutions of KCl¹⁰ produces hydrated FeO or $\text{Fe}(\text{OH})_2$ that is partly soluble, unstable and adsorbs oxygen easily, converting to black magnetite if the oxygen supply is scarce or to yellow-brown $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ if it is abundant. These data coincide with our results if we assume that the instability of Fe increases at high temperature in melts, being oxidized to magnetite by water traces.

From the thermodynamical view, the oxidizing power of a melt is determined by the redox potential of the reduced and oxidized species in the fused electrolyte,¹¹ in this case $E = E_0 + RT/2F \ln (\text{O})^{1/2}/(\text{O}^{=})$. On the other hand, the metal immersed in the bath assumes a potential that depends on the activity of its ions in the molten solution. In consequence, corrosion of the metal proceeds unless the equilibrium of these potentials or a passivation state of the metal is reached. In this medium, the products of iron corrosion are porous and scaly in nature, therefore no protective layer is formed and the metal may corrode to its final destruction.

The electrochemical approach to corrosion of metals in molten salts leads to interpretation of the process by the same mechanism as in aqueous solutions, i.e. through local cells. The metal goes into the melt from anodic sites of the lattice, specially at the grain boundaries of the crystal,^{3,4} and the depolarizers are reduced at cathodic sites. Thus, in fused NaCl-KCl mixtures at 700°C, iron goes into solution as ferric ions¹² and the impurities of the solution, SiO_2 from the Pyrex electrolytic cell, CO_2 , CO, O_2 , H_2O etc., may act as depolarizers.

The formation of oxides in dried KCl-LiCl melts proves that H_2O , HO^- or oxygen ions remain in the solution. As reported above, iron corrosion increases with the water content, which has been shown to be absorbed in accordance with the polarizing power of the cation of the molten salt, being maximum for Li^+ .¹⁻³ Thus, some moisture or OH^- ions have been detected even at higher temperature.⁹

The cathodic depolarizers in this system may proceed from the water traces (H^+) or from dissolution of iron compounds. Owing to the nature of the oxides, the corrosion should proceed ceaselessly and be determined by diffusion of oxidizing species to cathodic sites. The diffusion rates increase with temperature and so does the corrosion. Initially, the oxidant concentration being relatively high near the metal, the limiting diffusion current is not reached and the process will be determined by the material transport or ionic mobility of the reactants through the oxide layer. After a while, the concentration of depolarizer decreases and the process is determined by the limiting diffusion current of the reducible ions, as it is implied by the value of the activation energy obtained from the linear kinetic law which is of the same order of magnitude as that of the diffusion process. At higher temperature, reaction and diffusion rates increase and the limiting current is attained earlier, therewith the processes governed by the parabolic law is short-lived and goes experimentally unnoticed, only the linear dependence of the metal weight-loss with time remaining.

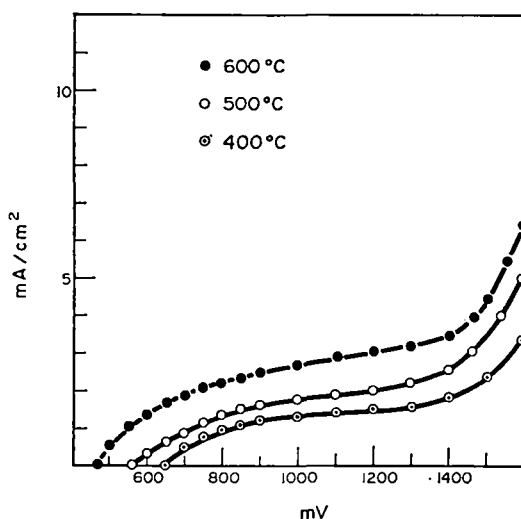


FIG. 5. Cathodic polarization curves for iron electrodes in dried KCl-LiCl melts at different temperatures.

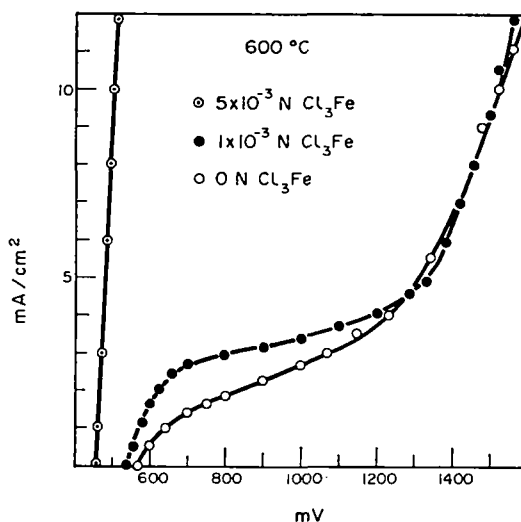


FIG. 6. Cathodic polarization curves for iron electrodes in KCl-LiCl melts with different FeCl_3 mole fractions.

The polarization curves recorded for Fe cathodes in humid and dried fused electrolytes at 400–600°C (Fig. 5) show diffusion waves the limiting current of which increases with temperature. They appear to be barely affected by the moisture content of the liquid eutectic, as only the alkali ion deposition is depolarized by water traces. The anodic polarization showed a direct dissolution of the metal into the melt, in which the polarization curve fits the Tafel plot if a transfer of two electrons is provided for the process, as it was already demonstrated by other authors.^{13,14} The cathodic diffusion

waves are fairly described by the Heyrovsky-Ilkovic equation $E = cte + RT/nF \ln(i_D - i)/i$ where i_D is the limiting c.d. and R , T , n and F have the usual meaning, the n value being near to 3, which suggested the diffusion of ferric ions. In fact, addition of FeCl_3 to the melt yielded similar cathodic waves (Fig. 6) described by the same type of equation in agreement with the results for Fe^{3+} reduction in molten NaCl-CaCl_2 mixture.¹⁵

In order to confirm the absence of Fe^{2+} in the solution, a previous anodic polarization of the iron electrode at 5 mA/cm^2 was applied for different periods of time. The cathodic curves obtained subsequently exhibited a second wave, the height of which increased with the anodic polarization time whereas the first wave remained almost unaffected except for longer anodizations (Fig. 7). Both waves fit the Heyrovsky-Ilkovic equation, the second wave rendering $n = 2$. The second wave was also verified by addition of FeCl_2 to the melt and recording cathodic potentiostatic curves for every concentration. These results agree with the data reported on polarographic reduction of Fe^{2+} in fused solutions of alkali chlorides mixtures.^{15,16}

The presence of ferric ions might be due to oxidation of Fe^{2+} by the chlorine evolved at the anode since no separation of the electrode compartments was provided, but this is not sufficient to explain the initial quantity of ferric ions.

As it is known,¹³ the dissolution potential of Fe to Fe^{2+} is more negative than that for Fe/Fe^{3+} , hence during chemical corrosion iron must go into solutions as Fe^{2+} at the anodic site of the local cell while the cathodic reaction will be the reduction of O_2 , H_2O or H^+ , the final product of the process being FeO . As this oxide is unstable in oxidizing media or at temperatures lower than 600°C , oxidation must proceed to Fe_3O_4 and then to Fe_2O_3 in accordance with the oxidizing agent concentration. The ferric oxide is sparingly soluble in this medium but sufficient so as to give a small concentration of Fe^{3+} which acts on the iron metal as depolarizer. At higher

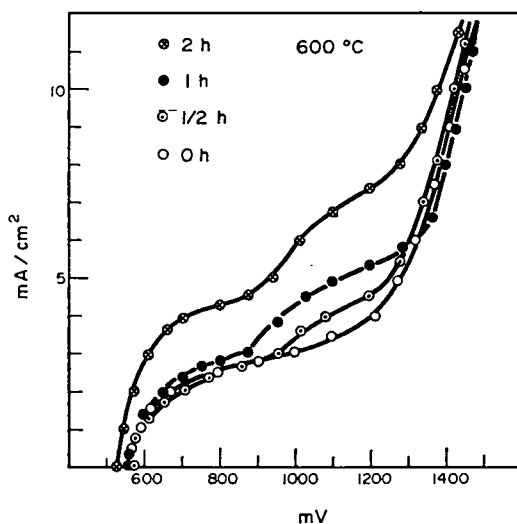


FIG. 7. Cathodic galvanostatic curves for iron electrodes in KCl-LiCl melts with previous anodic polarization of the metal at 5 mA/cm^2 during different periods of time.

temperature, the ferric ion concentration increases with the solubility of the oxide and is detected by cathodic polarization curves. The plot of $\log i_D$ vs. $1/T$ produces a linear relationship which corresponds to an energy of activation of about 4 kcal/mole, which is of the same order of magnitude as that reported for metal ions in several fused alkali chlorides¹⁷ and similar to that obtained from the linear kinetic equation. Higher energies of activation have been reported for Fe^{3+} (12.7 kcal/mole) in $\text{AlCl}-\text{NaCl}$ at 200–300°C¹⁸ and for Fe^{2+} in $\text{NaCl}-\text{KCl}$ ¹⁹ at 790–910°C (9.81 kcal/mole) and in $\text{NaCl}-\text{CaCl}_2$ ¹⁵ at 550–750°C (7.79 kcal/mole).

The application of cathodic potentials to iron specimens lowered their corrosion rates in the $\text{KCl}-\text{LiCl}$ eutectic to a greater extent the higher the negative value of the potential. Thus, at 500°C and 0.550 V (a value slightly more negative than the rest potential of iron in the melt, Fig. 5), the weight-loss of the specimen with time follows the parabolic law during the first hour of the experiment and then the linear law with values very similar to those reported above for the chemical corrosion but shorter times. At 0.650 and 1 V, potentials corresponding to the limiting diffusion current, the corrosion rates decreased from 1.6 and 1 mg/cm² h, respectively, to a constant 0.1 mg/cm² h with different times (1 and $\frac{1}{2}$ h, respectively), obeying a mixed parabolic law. No attack of the metal was observed when the iron specimen was subjected to the cathodic potential 1.4 V during 3 h in the melt. We hope to study the corrosion diagram of the $\text{Fe}-\text{KCl}-\text{LiCl}$ system in order to understand more completely the phenomena here described.

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