FACTORS GOVENRING THE CORROSION OF METALS IN FUSED SALTS*

By : Y. V. P, Ramachandra Row,
Central Electrochemical Research Institute, Karaikudi-

Abstract

The factors which govern the corrosion of metals, like gases stability of the melt, Redox potentials, free energy of the formation and passivity are discussed in this paper.

The corrosion of metals in fused salts is more complicated than the corrosion of metals in aqueous solutions. The external factors, like water vapour, H_2, and other gases, which can be in equilibrium with melt, are quite important. The solubility of metal in melt is important when the metal dissolves in nonoxidisable atmosphere. When the solubility is greater the corrosion shall also be greater. Secondly a metal can be oxidised when it can reduce the substances present as impurities. In this respect the the Redox Potential (Redox) of melt, which is dependent on the impurities and the dissolved metallic ions, plays a large role.

Stability of Melt :

Let us now consider the stability of the melt. Stability of the melt can be predicted from the dissociation constant. If one considers the following reaction

$$MCl_2 = M + Cl_2 \uparrow$$

the melt can be dissociated into metal and chlorine. The dissociation constant can be given by

$$K_d = \frac{{}^aM \ {}^aCl_2}{{}^aMCl_2}$$

when $aMCl_2 = 1$ we have

$$K_d = {}^aM \ {}^aCl_2 - 1$$

From the constant it can be concluded that lesser the quantities of a_m and a_{cl2} the more stable is melt. Otherwise it can be stated that the corrosion of metal in the melt is more governed by stability of the melt. If the metal corrodes more, the stability of the melt is less (i.e. the dissociation of melt is higher) and therefore the dissociation constant is higher. On the other hand if the stability of the melt is higher (i.e. the dissociation of melt is less) the corrosion is lesser.

Redox Potential :

The redox potential of the melt is an important factor in the corrosion of metals. Considering the individual reactions

$$\tfrac{1}{2} Cl_2 + e = Cl^-$$
$$M^{++} + 2e = M$$

in the case of melt dissociating into above components (M^{++} and cl^-) and their equilibrium with the gas and the metal, the potentials can be given by

$$eCl_2/Cl^- = O + \frac{RT}{F} \ln \frac{{}^{\frac{1}{2}}Cl_2}{aCl^-}$$

$$^eM/M^{++} = {}^{e^\circ}M/M^{++} + \frac{RT}{2F} \ln \frac{{}^aM^{++}}{{}^aM}$$

when the equilibrium sets in we have

$$^eCl_2/Cl^- = {}^eM^{++} = {}^eRedox$$

The potential at equilibrium is known as redox potential of melt. The equilibrium can be shifted by either varying the pressure of the gas or the metal content in the melt. The corrosion of the metal can take place until the redox potential is obtained. If the potential of the metal is below the redox potential of melt, the metal dissolves until the redox potential is reached.

Free Energy of Formation :

One more factor governing the corrosion of metal in fused salts is the free energy of the formation. The free energy of the reaction

$$MCl_2 = M + Cl_2$$

is given by

$$\Delta G^\circ = -RT \ln K_e$$

Ke is the equilibrium constant. In this respect Kd is for dissociation,which is given by equation(I)

$$K_d = aM \ aC_{l2}$$

we have

$$\ln K_d = \ln aM + \ln aC_{l2}$$

---

*This paper was presented at 9th Seminar on Electrochemistry, Karaikudi-3.

ΔG° is dependent on $\ln K_d$ and therefore on K_d. The higher the stability of the melt the lesser will be $\ln K_d$ and therefore the free energy of reaction is more negative. In this respect the corrosion will be less. If the stability of the melt is low, $\ln K_d$ is more and therefore the free energy of the formation is less negative; Now the corrosion is more.

Passivity :

The onset of passivity of metal in high temperature melts is very difficult. Some of the oxides or the corrosion products, which render the metal passive, may dissolve into the melt. The retardation of corrossion is dependent more on thermodynamic equilibrium. To predict some of the results on thermodynamic considerations sufficient data is not available on activity co-efficient.

Acknowledgement :

The author thanks Dr. K. S. G. Doss and Dr. H. V. K. Udupa, Scientist--in--Charge for their encouragements.

The Mettur Chemical & Industrial Corporation Limited

METTUR DAM R. S., SALEM DIST.

Manufacturers of

Caustic Soda, Commercial & Rayon-grade (in lye, solid and flake forms), Stable Bleaching Powder (commercial), Hydrochloric Acid (commercial), Liquid Chlorine, Sulphate of Alumina, Calcium Chloride (Commercial & Anhydrous), Ferric Chloride, Potassium Chlorate, Methyl Chloride, Methylene Dichloride, Chloroform, Carbon Tetrachloride (Refrigerent grade).

MANAGING AGENTS :

Seshasayee Brothers (Private) Ltd.