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Corrosion of metals in molten lithium sulphate-potassium sulphate eutectic

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In conjunction with the development of a new electrochemical flue gas desulphurization process, a study is made of the corrosion of several electrode materials in molten lithium sulphate-potassium sulphate eutectic at 600° C. Measurements of the open-circuit potentials are made in air, oxygen and nitrogen to determine the existence of a stable oxide layer on the electrode surface. Voltammetric measurements are also made to determine the corrosion current densities in O_2/SO_2 mixtures at various compositions. The study shows that the valve metals studies (zirconium, tantalum and titanium) develop stable oxide layers on their surfaces which are highly corrosion-resistant. The corrosion currents decrease in the following order Ni $\sim$ Fe > CuAg > Zr.

1. Introduction

A molten-salt electrochemical cell has been proposed for the removal of sulphur oxides from the stack gases of power plants [1]. Initial experiments carried out with gold foil electrodes showed that, in principle, the process is feasible with high removal rates at reasonable current densities [2]. The mechanisms of the removal reactions were also studied on platinum and gold [3]. However, cheaper electrode materials should be developed if the process is to be economically competitive with present flue gas desulphuriztion processes. The electrolyte used in the present cell is the eutectic mixture of lithium and potassium sulphates (m.p. 535° C) with an operating temperature of 600° C. In this extremely corrosive environment the selection of suitable electrode materials is a strong challenge to cell designers. Previous work on molten salt corrosion was directed to the study of corrosion problems in boilers, gas turbines and molten-carbonate fuel cells. In the last case, the selection of suitable electrode materials received very considerable attention.

Corrosion by molten sulphates is known to be affected by the composition of the atmosphere above the melt. Rahmel [4] constructed thermodynamic diagrams to represent the stability regions of metals in molten alkali sulphates as a function of O_2 and SO_3 partial pressures. According to these diagrams, each metal exists in either the elemental form, the ionic form or the oxide and sulphide forms. These represent the stability, corrosion and immunity regions, respectively. Although these diagrams are useful in constructing electrochemical series for metals in molten salts, they do not predict the structural and kinetic features which are often important in the corrosion phenomena.

Stability against corrosion may result from the formation of a protective oxide layer which is insoluble in the molten salt. The solubility of many oxides depends on the basicity of the melt which depends on the acid-base equilibrium as determined by the concentration of the O^{2-} ion [5, 6]. In molten sulphates this depends on the equilibrium

$$SO_4^{2-} \rightleftharpoons SO_3 + O^{2-}$$

Thus, the solubility of a metal oxide, MO, in the melt is determined by the reaction

$$MO \rightleftharpoons M^{2+} + O^{2-}$$

in which the solubility product principle applies

$$K_{sp} = [M^{2+}][O^{2-}] \qquad (1)$$

A few data are available on the solubility of metal oxides in molten sulphates [7].

The kinetics of the corrosion process are manifested by the corrosion current density, which represents the balanced rates for the oxidation of the metal and the complementary reduction process. The value of log i_{corr} can be obtained by plotting log current density against overpotential ($E - E_{corr}$) and extrapolating the straight line portion of the curve to an overpotential of zero [8, 9]. Cutler [8] showed that P_{SO_3} in the gas above the melt affects the rate of corrosion because of the role of SO_3 as an oxidizing agent and also because of its effect on the solubility of the corrosion products in the melt. The kinetics of the corrosion process of pure metals were studied in molten sulphates [10].

The anodic process in corrosion is the oxidation of the metal, as long as the potential is less positive than that corresponding to the oxidation of the sulphate ion [8, 11]. The anodic oxidation of SO_4^{2-} occurs at a potential $\sim +0.9$ V against Ag/Ag^+ (1 M) with the evolution of SO_3 [12]. There is no agreement on the nature of the cathodic process but some workers suggest that the sulphate ion is reduced to sulphite, sulphur and sulphide [12, 13] at ~ -2.0 V against Ag/Ag^+ (1 M), while others suggest that SO_3 is reduced instead at -0.7 V [8, 14]. The electrochemical behaviour of SO_4^{2-} in molten ternary eutectic mixtures (Li, Na, K, Cl) was studied using cyclic voltammetry [15]. Two characteristic peaks of the electrode reaction of SO_4^{2-} were recorded at about -2.0 V in the cathodic sweep and about -0.9 V in the anodic sweep. It was assumed that the overall reaction was

$$SO_4^{2-} + 2e^- = SO_2 + 2O_2^{2-}$$

and the two peaks were caused by the cathodic adsorption and anodic desorption of SO_2. Winnick [16] studied the reaction kinetics of the electrochemical reduction of H_2S in molten sulphide at 830° C. He used a sodium and potassium sulphide mixture melting around 700° C and large exchange currents of the order of 10^{-1} A cm^{-2} were recorded. The reaction rate is dependent on square root of H_2S pressure and gives a zero-order in H_2S pressure with respect to the oxidation reaction of sulphide to elemental sulphur. The separation of H_2S from a mixture of reducing gases were also carried out [17] using a ceramic membrane with an electric field.

Recently Winnick [18] applied an electrochemical method for the removal of hydrogen sulphide from gas mixtures and the production of sulphur. This method requires less energy than the conventional processes. Shores and Fang [19] showed that pyrosulphate might be the oxidant in molten Na_2SO_4. At potentials more negative than -2.5 V against Ag/Ag^+ (1 M), alkali metals are deposited causing cathodic corrosion of several metals through alloy formation. More recently Shores studied [20] the disolution of NiO cathodes in molten carbonate fuel cells where stable nickel complex ions can be formed. In single and mixed carbonates the slopes of the acidic and basic curves did not correspond to a single dissolution region and the observed oxygen dependence was not constant with mixtures of Ni^{2+} or NiO_2 and NiO_2^{2-} in the acidic and basic regions respectively. A review including a discussion of diffusion in high temperatures oxidation has also been contributed by Shores [21].

This paper presents a study of the behaviour of several candidate electrode materials in molten sulphates. The study consists of open-circuit potential measurements and voltammetric measurements. The variation of the potential with time and the atmosphere above the melt is used to determine the existence and the stability of the oxide layer which forms on the metal surface. Voltammetric measurements around the open-circuit potentials are used to determine the corrosion currents for each metal under O_2/SO_2 atmospheres at different SO_2 concentrations. The metals selected for this study are nickel, iron, copper, silver, zirconium, titanium and tantalum. The last three metals are representatives of the group of valve metals.

2. Experimental details

The cell assembly was contained in a vertical furnace with temperature controlled to ±5° C. The experimental cell consisted of a 500 ml 'Purox' recrystallized alumina crucible which contained two 20 ml recrystallized alumina crucibles which constituted the working and reference electrode compartments. Each small crucible was filled with 10 g of the salt mixture and as the temperature was raised to 600° C the salt melted leaving a thin layer on the inner surface forming a salt bridge with the melt in the outer crucible. Likewise, the outer crucible, which contained the counter electrode, was filled with the salt mixture up to the rim of the small crucible and when the salt melted a thin layer was left on the outer surface of the small crucibles thus completing the salt bridges. The working electrodes were swept by the different gas mixtures through a quartz tube.

Nickel, iron, copper, silver and zirconium electrodes were cut from sheets of the respective metal (99.9% purity) to form 1 cm × 1 cm squares with a connection made of the same metal. Titanium and tantalum were in the form of cylindrical rods. Each electrode was mechanically polished with 1000 emery paper then rubbed with a filter paper and finally washed with distilled water and dried. The reference electrode was prepared by anodizing a silver wire at a current density of 5 mA cm^{-2} to obtain a concentration of 0.1 M of Ag^+ ions. The measured potentials were converted to the Ag/Ag^+ (1 M) scale by subtracting the $RT/F \ln 10$ term from each reading. The counterelectrode was a gold flag (1 cm × 1 cm) dipping into the melt in the outer crucible.

The cell electrolyte was prepared by mixing Analar grade chemicals after drying for 2 h at 200° C. Air, nitrogen and oxygen were prepared from cylinder gases after drying over silica gel. O_2/SO_2 mixtures were prepared by passing oxygen gas over 5 g of $CoSO_4$ in a quartz boat which was placed at the centre of a quartz tube positioned along a horizontal furnace. The entering gas equilibriates with $CoSO_4$ according to the reaction

$$CoSO_4 \rightleftharpoons CoO + SO_2 + \tfrac{1}{2}O_2$$

Thus, by varying the temperature of the horizontal furnace the concentration of SO_2 in the gas was varied between 1.5 and 2.5%. The concentration of SO_2 was measured by titration with standard $KMnO_4$ solutions and back titration with oxalic acid. The gas flow rate was kept constant at 1 ml s^{-1}.

Potential measurements were obtained using a Hartmann & Braun digital millivoltmeter type T-2201 with an internal impedance of 10^{11} Ω. Voltammetric measurements were obtained using a Wenking potentioscan type POS 73 and a Sefram X-Y recorder type TRP. The scanning rate was kept low at 60 mV min^{-1} and the perturbation was kept small at ±100 mV with respect to the open-circuit potential. The selection of these values is consistent with the requirements of minimizing hysteresis effects between the positive and negative parts of the cycle [8]. Corrosion currents were not measured for titanium and tantalum because their configuration was different from the other metals.

3. Results and discussion

3.1. *Open-circuit potential measurements*

The variation of the potential with time was recorded for each electrode in naturally aerated melt and after injection of nitrogen and oxygen repeatedly in two cycles. The results of these experiments are shown in Fig. 1. Table 1 shows the cumulative results in a comparative way. The first column shows the initial potentials measured just after immersion of each electrode in the melt. These presumably correspond to the potentials determined by the metal phase [22]. The second column contains the standard potentials of the metal/metal ion electrodes which were calculated from the available free energy data [23] using the procedure of Ingram and Janz [24]. They have the same order of variation as the values in the first column. According to this electrochemical series silver is the most noble among the studied metals.

The variation of potential with time is another important characteristic in the corrosion process. This is indicative of the simultaneous occurrence of cathodic and anodic processes at the electrode surface. It would appear reasonable to characterize the observed potentials as mixed potentials. Normally, the potential increases as a compact oxide layer is formed on the metal surface.

In some instances, the formed metal oxides catalyze the cathodic process, causing it to proceed at a faster rate than the anodic one. This seems to be the case with copper and the valve metals studied. Steady-state is reached when no further changes in composition occur at the oxide-electrolyte interface. It seems reasonable to characterize the electrodes as metal oxide. The third column shows the steady-state potentials in naturally aerated melt; these are compared with literature values [25] in the fourth column.

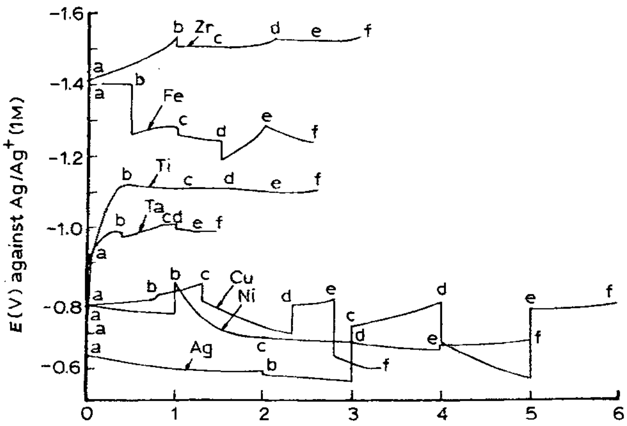

Fig. 1. Variation of the open-circuit potentials with time and upon gas cyclization in Li_2SO_4–K_2SO_4 melt at 600° C. Key: (a) start, (b) first nitrogen injection, (c) first oxygen injection, (d) second nitrogen injection, and (e) second oxygen injection.

Table 1. Open-circuit potentials in naturally aerated Li_2SO_4–K_2SO_4 melt at 600° C

Metal	E_{t+0} (*V*)	E^0_{M/M^+}* (*V*)	E_{ss} (*V*)	$E_{M/MO}$ (*literature*)† (*V*)
Zr	−1.414	–	−1.527	–
Fe(III)	−1.400	−1.26	−1.402	−1.097
Ta	−0.904	–	−0.969	–
Ni	−0.774	−1.20	−0.744	−0.788 (at 658° C)
Cu(II)	−0.770	−0.72	−0.794	−0.520 (at 714° C)
Ti	−0.744	–	−1.114	–
Ag	−0.631	−0.53	−0.558	–

* Referred to SO_3 (0.67 atm), O_2 (0.33 atm)/SO_4^{2-} electrode.
† Referred to O_2, Pt/O^{2-} electrode.

The variation of the potential on gas cycling is indicative of the surface reactivity and the stability of the oxide layer. In the case of nickel and iron cycling does not affect the steady-state potentials by more than 50 mV while the valve metals (Zr, Ti and Ta) do not show variation by more than 30 mV with titanium having the least variation. This is indicative of the development of a coherent protective oxide film on the metal surface in each case. The anodic reaction in these cases is most probably the following reaction

$$M + O^{2-} \longrightarrow MO + 2e^-$$

The gradual loss of surface reactivity and eventual independence of the potential on the nature of the gas bubbling into the melt may be ascribed to the inhibitive properties of the oxide ion probably through its specific adsorption on the bare anodic sites which leads to greater polarization of the anodic process.

On the other hand, copper shows wide variation (~ 240 mV) of the potential with gas cycling. This may be explained by the higher solubility of the oxide in molten sulphates [7] which decreases the perfection of the oxide covering layer and hence increases the surface reactivity.

The behaviour of silver is different from the other metals and this may be explained by the fact that a stable oxide film does not form as Ag_2O decomposes at temperatures above 400° C [23]. It is also possible that the slow diffusion of Ag^+ ions from the reference electrode compartment to the working electrode compartment [10] retards the anodic process which takes place on the metal surface

$$Ag \longrightarrow Ag^+ + e^-$$

and may thus cause the abnormal behaviour of the potential on gas cycling.

Visual inspection of the metal samples after these experiments showed that silver is the only metal which retains its metallic appearance. Apart from this titanium is the only other metal which had an electrically conductive surface after experiments. This results from the fact that the lower oxides of titanium are electrically conducting.

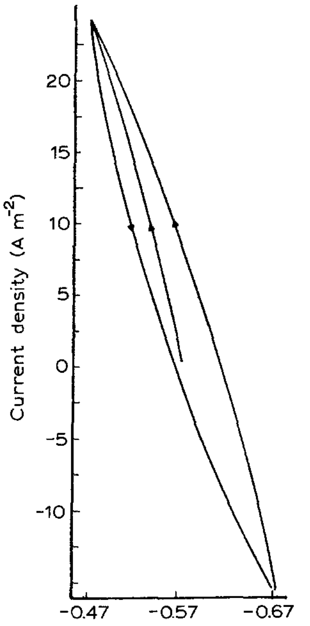

Fig. 2. Cyclic voltammogram around the open-circuit potential for nickel in Li_2SO_4-K_2SO_4 melt swept by O_2/SO_2 mixture (2.1% SO_2) at 600° C.

3.2. *Corrosion current densities*

Figure 2 shows the cyclic voltammogram obtained for nickel at SO_2 concentration of 2.1%. Figure 3 shows a plot of E against ln I from which the corrosion current density is obtained. Similar plots were made to obtain the corrosion current densities for each metal at different SO_2 concentrations. The results are summarized in Table 2.

From these results it is obvious that, generally, the corrosion current densities increase slightly with SO_2 concentration in the experimental range. The role of SO_2 in the corrosion process is complicated and cannot be separated from the effect of SO_3. Corrosion currents also decrease in the following order: Ni ~ Fe > Cu > Ag > Zr. It appears also that both the nobility of the metal (in terms of $E^0_{M,M+}$) and the formation of a coherent oxide layer on the metal surface affect the rate of metal corrosion in molten sulphates. Zirconium and possibly other members of the valve metals group show high resistance towards corrosion in molten sulphates because of the apparent stability of the oxide layer.

Table 2. Corrosion current densities in Li_2SO_4-K_2SO_4 melt swept by O_2/SO_2 mixtures at 600° C

Metal	*SO_2 concentration (%)*	*Corrosion current density ($A\,m^{-2}$)*
Ni	1.6	9.1
	2.1	7.9
	2.6	7.4
Fe	1.5	6.2
	2.0	6.7
	2.5	8.7
Cu	1.6	3.8
	2.0	4.5
	2.6	5.5
Ag	1.5	1.6
	1.8	1.9
	2.4	2.3
Zr	3.3	1.3
	3.7	1.4

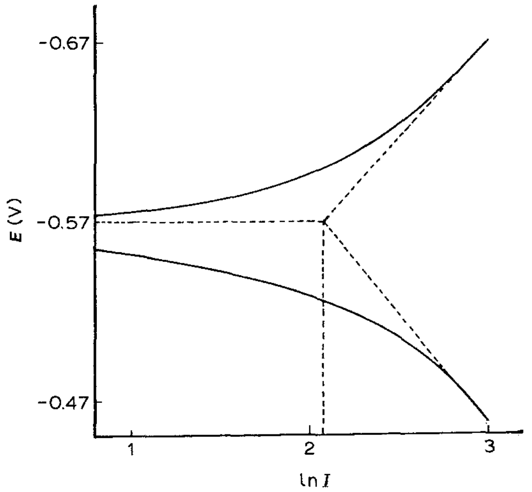

Fig. 3. E against ln I for nickel in Li_2SO_4-K_2SO_4 melt swept by O_2/SO_2 mixture (2.1% SO_2) at 600° C. (I in A m^{-2}).

4. Conclusions

This study has shown that valve metals have a high tendency to passivation in molten sulphates. Titanium seems to exhibit the least variation in potential upon gas cycling. Combined with the fact that the lower oxides of titanium have a high electrical conductivity, it seems that this is the most suitable electrode material for the proposed process. Silver is also suitable, probably as a cathode material, since silver is known to be the best catalyst for oxygen reduction (and possibly the SO_2 removal reaction) in molten salts. Zirconium and tantalum may be suitable electrode materials if the conductivity of the oxide layers formed on their surfaces can be increased by doping of these metals in suitable reagents [26].

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