THE HOT CORROSION OF METALS BY MOLTEN SALTS

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ABSTRACT

Some theoretical mechanisms for the hot corrosion attack of metals and alloys under thin fused salt films are discussed. The chemical fluxing (dissolution) of the protective oxide on a pure metal is proposed to occur wherever the gradient in the oxide solubility in the salt at the oxide/salt interface is negative, such that a re-precipitation of dissolved oxide occurs. In turn, the oxide solubility gradient is established by the nature and site of the electrochemical reduction step which always generates local basicity. The interrelation of the basicity gradient in the melt to the oxide solubility map decides the occurrence of continuing hot corrosion. In the hot corrosion of alloys, the possibility of a synergistic coupling of the dissolution for the several oxides of the components can result depending upon the specific details of the oxide solubility plots and the local basicity as established by the site of the cathodic reduction step.
Introduction

Alloys experience accelerated corrosion attack upon exposure at elevated temperatures to an oxidizing gas when a thin film of fused salt coats the surface. Corrosion problems related to the attack of metals by molten nitrates, carbonates, hydroxides, sulfates, coal ash, etc. are well known and very important to the functioning of many engineering systems. In the operation of aircraft gas turbines near and over the ocean, a fused Na$_2$SO$_4$-NaCl film from an ingested sea-salt aerosol may coat the hardware and lead to accelerated oxidation of the turbine alloys. In this corrosion environment, the oxidant gas contains the products of fuel combustion including SO$_2$ and excess O$_2$. In this paper, some novel theoretical mechanisms and criteria for the hot corrosion of metals and alloys in Na$_2$SO$_4$ are presented. These mechanistic proposals, however, should find general applicability in the analysis of other metal/salt/oxidant corrosion reactions.

A chemical mechanism(s) of hot corrosion has been previously described in terms of an acid-base dissolution of the protective oxide film (Al$_2$O$_3$ or Cr$_2$O$_3$) on a high-temperature alloy or coating. Other authors have conducted electrochemical studies of metals submerged in deep sulfate melts to establish anodic and cathodic polarization curves. However, a generalized theory which integrates the chemical and electrochemical phenomena for corrosion beneath a thin salt film has not been proposed, nor have previous experiments been properly designed to evaluate the details of a mechanism for hot corrosion. The presentation of such a generalized mechanistic theory and suggested experiments is the purpose of the present paper.

A considerable insight into the mechanism of accelerated oxidation beneath a thin fused salt film can be won from the literature on aqueous solution corrosion at ambient temperature. The geometry of hot corrosion (thin film electrolyte coating) closely resembles that for aqueous "atmospheric corrosion" where the electrochemistry and the rate-limiting step have been analyzed by Mansfeld and Kenkel. However, considerable differences with respect to ease of an electron transfer step and the rate of dissolved gas transport must be expected. Both for aqueous solutions and for fused Na$_2$SO$_4$ the thermodynamic stabilities of phases are graphically illustrated as a function of redox potential and an acid-base parameter by Pourbaix diagrams. In Figs. 1 and 2, Pourbaix-type phase stability plots are presented for the Na-Al-S-O and Na-Cr-S-O systems for those conditions where Na$_2$SO$_4$ is the stable phase in the
could be related to Na-S-O system. The ordinate of log $P_{O_2}$ could be related to an electrode potential if a proper reference electrode to indicate log $P_{O_2}$ were available. The basicity of the melt is described in terms of the thermodynamic activity of sodium oxide, $a_{Na_2O}$, relative to pure sodium oxide.

The $-\log a_{Na_2O}$ abscissa of the Pourbaix-type plot could also be considered an electrode potential, if a proper reference electrode were available to indicate log $a_{Na_2O}$. Such an electrode would be equivalent to a pH electrode in aqueous solutions. Unfortunately, the convention accepted for Pourbaix diagrams in fused salt systems plots the abscissa as $-\log a_{Na_2O}$, with high basicity at the left and low basicity at the right—opposite to the convention for aqueous solution diagrams.

From Pourbaix diagrams such as Figs. 1 and 2, within the respective fields of Al$_2$O$_3$ and Cr$_2$O$_3$ stability, the solid oxides exhibit a basic and acid solubility in the Na$_2$SO$_4$ melt, which in principle, could be plotted for known values of the activity coefficients for the solute ions, according to the reactions:

- $Al_2O_3 = 2 Al^{3+} + 3 O^{2-}$ acid dissolution (la)
- $Al_2O_3 + 3 O^{2-} = 2 AlO_2^{2-}$ basic dissolution (lb)
- $Cr_2O_3 = 2 Cr^{3+} + 3 O^{2-}$ acid dissolution (lc)
- $Cr_2O_3 + 2 O^{2-} + 3/2 O_2 = 2 CrO_4^{2-}$ basic dissolution (ld)

Alternatively, lacking a prior knowledge for the solute activity coefficients, or wishing to test the validity of Eqs. (la-d), one can establish experimentally the solubility of the oxides in Na$_2$SO$_4$ as functions of $P_{O_2}$ and $a_{Na_2O}$.

Stroud and Rapp developed an electrochemical electrode to measure the sodium oxide activity in Na$_2$SO$_4$ melts equilibrated at given oxygen pressures. From Na$_2$SO$_4$ solutions equilibrated with excess $\alpha$-Al$_2$O$_3$ or Cr$_2$O$_3$, samples were taken and analyzed to establish the solubilities of these oxides as a function of $a_{Na_2O}$ at fixed $P_{O_2}$ at 1200K. Superimposed plots for Al$_2$O$_3$ solubility at $P_{O_2} = 10^{-4}$ and 1 atm are given as Fig. 3. Based on the slopes of the solubility lines, the acidic

161
dissolution reactions (1a) and (1c) were substantiated. If solid \( \text{NaAlO}_2 \) did not form on \( \text{Al}_2\text{O}_3 \) for \( \log a_{\text{Na}_2\text{O}} = -8.3 \), then Eq. (1b) is valid. The basic dissolution of \( \text{Cr}_2\text{O}_3 \) at \( P_{\text{O}_2} = 10^{-4} \) atm was consistent with Eq. (1d), but this basic solubility of \( \text{Cr}_2\text{O}_3 \) decreased with increasing \( P_{\text{O}_2} \), which cannot yet be explained. Further experiments are in progress to substantiate the values for the solubilities of \( \text{Cr}_2\text{O}_3 \) and \( \text{Al}_2\text{O}_3 \) in \( \text{Na}_2\text{SO}_4 \) at 1200K.

For the purposes of present paper, we do not need to assume that the data of Fig. 3 are exactly correct; rather we only want to admit that in general the solubility curve (s) for any given oxide must resemble those of Fig. 3, with specific slopes for the acidic and basic solutes which are decided by the stoichiometric coefficients in the dissolution reactions. Of course, the solubility curves for some oxides may be complicated by the presence of more than two important solutes. For the discussion to follow, the solutes. For the discussion to follow, the solute species of Eqs. (1a-d) and the general form of the solubility curves of Fig. 3 are accepted as correct.

An Acid-Base Fluxing Mechanism For Hot Corrosion of a Pure Metal

As a criterion for the continued (stable) hot corrosion of a pure metal, we propose that the gradient at the oxide/salt interface in the solubility of the protective oxide (as acid or basic solute species) is negative, i.e.,

\[
\frac{d[\text{oxide solubility}]}{dx} \bigg|_{x=0} < 0
\]

By this criterion, as illustrated schematically in Fig. 4, the continuous reprecipitation of the oxide in the salt film away from the oxide/salt interface is expected to permit local equilibrium between the oxide and salt throughout the salt film.

The concentration gradient criterion of Eq. (2) may be considered as an empirical condition for dissolution and reprecipitation in the salt. However, in an isothermal system, the concentration gradient would not serve as the driving force for the transport of the soluble ionic species because no gradient in the chemical potential of the oxide would exist in a salt film in local equilibrium with the oxide throughout. In general, the diffusion flux of the oxide, \( \text{MO} \), can be expressed according to a linear law as follows:
where $\mu_j$ is the chemical potential of the component and $L_{ik}$ is the transport coefficient. When oxide is reprecipitated in the salt, $\mu_{MO}$ becomes uniform if local equilibrium is assumed. Then, in an isothermal system, the first term of the r.h.s. of Eq. (3) would be zero, as would the fourth term, while the third term should be negligible small. But the second term of the r.h.s. of Eq. (3) would not be zero so long as the basicity gradient and the cross-term $L_{12}$ were not zero.

The only other means for the transport of the soluble ionic species is local convection set up by density differences in the salt film. The Stokes sinking of the heavier oxide precipitates might in this case contribute to convective transport.

Because a reprecipitated oxide cannot form as a continuous protective layer, a voluminous, porous oxide product interspersed with salt is expected; this morphology is indeed representative of hot corrosion products. This model illustrated schematically in Fig. 4 may be considered as an empirical criterion which assumes local equilibrium at the oxide/salt interface and throughout the salt film. The occurrence of oxide reprecipitation in the salt film is common with the acid-base fluxing mechanism proposed by Goebel and Pettit, but these authors assumed that basic fluxing arose from a chemical reaction to form sulfides (sulfidation) in the metal. Indeed, the reduction of the sulfate ion to form sulfide would release oxide ions at the oxide/salt interface in excess of those required for the growth of the oxide scale, and basic fluxing should occur. Later, acid fluxing of the scale was described by Goebel et al as arising from the removal of oxide ions in the salt upon the formation of basic complexes by other metallic components in the metal, e.g., formation of $\text{MoO}_4^{2-}$ following the oxidation of Mo in the alloy.

In the present acid-base fluxing model for a pure metal, we propose that the gradient in the solubility of
the protective oxide (as given by Fig. 3, for example) in the salt film is established by the local variation of sodium oxide activity, and perhaps $P_{O_2}$, across the salt film. In turn, these conditions are established principally by the basicity necessarily generated at the site of the electrochemical reduction reaction, as well as the chemical interaction between the oxidant and the salt. As in any electrochemical process, the open-circuit half-cell potential $E_0$ for each possible reduction reaction is expressed as:

$$E_0 = E_0^\circ - \frac{RT}{nF} \ln \left( \frac{[\text{red}]}{[\text{oxid}]} \right) \quad (3)$$

for the half-cell reduction reaction

$$\text{oxidized species} + n e^{-} \rightarrow \text{reduced species}$$

where $E_0^\circ$ is the standard open-circuit half-cell potential for the reduction reaction. A tentative, standard electrochemical reduction series for Na$_2$SO$_4$ at 1200K is proposed as Table I. Quantitative values for the redox reactions of Table I have not been determined, and indeed, a standard reference electrode has not been decided. Perhaps an Au/ O$_2$-SO$_2$ (1:2) electrode, as suggested by Rahmel, would represent a suitable standard reference electrode (equivalent to standard hydrogen electrode), with the Ag/10 mole % Ag$_2$SO$_4$ : Na$_2$SO$_4$ electrode serving as the equivalent of the calomel electrode in aqueous solutions.

According to Table I, the effects of melt basicity, oxidation potential of melt, the gaseous environment, and the presence of transition metal ions are all important in deciding the predominant reduction reaction, as is also the case in aqueous solution corrosion. In a highly basic melt (perhaps, $a_{Na_2O} > 10^{-14}$) reduction reactions a and b should be favored. In a highly acid melt (perhaps $a_{Na_2O} < 10^{-15}$), reduction reaction c would be favored, at least for a salt film thin enough to support the necessary molecular $SO_2$ and $SO_3$ countertransport. As illustrated in Fig. 5a, oxygen reduction by reaction d would be favored only for reasonably neutral, thin films of Na$_2$SO$_4$, as will be discussed later. If the metal or alloy should provide dissolved transition metal ions to a highly oxidized melt, then the reactions e-g could predominate, and should introduce a very important shift in the site of the reduction reaction to the salt/gas interface, as shown in Fig. 5b.
For dilute $M^{2+}$ and $M^{3+}$ concentrations, counterdiffusion of these species would be required. But if the total concentration of the mixed valence transition metal ions were sufficiently high, then electronic exchanges between these ions ($M^{2+}_a + M^{3+} + M^{3+}_a + M^{2+}$) could introduce a more rapid transport by electronic conduction through the melt. Electronic conduction was established for $\text{SiO}_2$-$\text{CaO}$-$\text{FeO}$-$\text{Fe}_2\text{O}_3$ slags at high temperatures by Engell and Vygen.\(^\text{20}\)

If all these reactions with higher $E^0$ exhibit a lower $E$ because of concentration polarization according to Eq. (3), then the sulfate anion itself can be reduced according to Eq. (4), although the details of these reactions have not been specifically established. The reduction of the sulfate anion is obviously favored for deep, reasonably neutral melts, especially at the start of a reaction before the transition metal ions become available. Because of the general availability of sulfate anions, reduction of the anion would certainly not be limited by a slow arrival flux to the oxide/metal interface. The reduction of the sulfate anion could lead to such high local levels of sulfur activity that the formation of metal sulfides could occur; frequently, hot corrosion is associated with simultaneous sulfidation. However, when sulfidation is viewed as the result of only one of the possible reduction reactions, hot corrosion is not necessarily tied to sulfidation.

The other half of the electrochemical hot corrosion mechanism, the oxidation half-cell reaction is the oxidation of the metal at the metal/scale interface. As revealed by the Pourbaix thermodynamic diagrams, most metals could not exist in local equilibrium in contact with $\text{Na}_2\text{SO}_4$, so generally, an intervening electronically-conducting oxide film is expected. The oxidation of the metal at the metal/oxide interface with the ensuing transport of cations plus electrons to the oxide/salt interface would equal the rate of the electrochemical reduction reaction. A time-independent rate of oxide dissolution at the oxide/salt interface with an ensuing oxide reprecipitation would lead to the maintenance of a constant steady-state oxide thickness and constant steady-state reaction kinetics as is frequently found in hot corrosion. An exactly analogous model exists for the coupling of scale growth and scale evaporation in metal/gas reactions.\(^\text{21,22}\) Then for "linear" hot corrosion kinetics at steady-state, if the interfacial reactions can be reasonably assumed to satisfy local equilibrium, the corrosion rate would be controlled by the diffusion of ca-
tions through the oxide in series with diffusion of reac-
tants and products of the electrochemical reduction reaction
through the salt film.

Let us return to an integration of the electrochemical
reduction reaction into the hot corrosion criterion of Eq.
(2) as illustrated in Fig. 4. Each electrochemical reduction
reaction of Table I introduces increased local basicity at
the reduction site. As illustrated in Fig. 5a, the reduc-
tion reaction would usually be expected to occur at the ox-
ide/salt interface, but as shown in Fig. 5b, the presence of
mixed valence transition metals could allow the reduction
step to occur at the salt/gas interface. In either case,
the site of the reduction reaction would be expected to be
the most basic local condition in the salt film.

Figure 6 illustrates a schematic oxide solubility plot
with superposition of four different sets of relative ba-
sicities at the salt/gas interface II and at the oxide/salt
interface I which would set up and support continued hot
corrosion of a pure metal according to the model outlined
here. In each case, the condition of Eq. (2) as illustra-
ed in Fig. 4 is satisfied. Of course, for some oxides, the
solubility of the oxide (Cr₂O₃, for example) also depends
upon P O₂ so that a three-dimensional diagram would be more
suitable.

According to cases A and C of Fig. 6, the basicity gra-
dient in the salt film is opposite in direction, but then
the mode of oxide dissolution is also opposite. For case B,
one would expect continued hot corrosion whenever the local
basicities at interfaces I and II straddle the minimum. In
general, one would expect that the value for the basicity
at the oxide/gas interface would be fixed approximately by
the value of P O₂ in the ambient atmosphere, unless the salt
basicity were somehow otherwise established by the detailed
mode of continuing salt deposition. If the relative basic-
ities at the interfaces I and II for cases A and C of Fig. 6
were reversed, then the hot corrosion criterion of Eq. (2)
would not be met, and one would expect the entire salt film
to saturate with the oxide consistent with the basicity at
interface I after which time accelerated hot corrosion should
stop. Nickel coated with a film of Na₂SO₄ and exposed to
air experiences transient accelerated hot corrosion.

To test this dissolution model for the hot corrosion of
a pure metal, a knowledge of the oxide solubility as a func-
tion of the P O₂ and basicity (log a Na₂O) must be known and
experimental determination of $P_{O_2}$ and basicity at both the oxide/salt and the salt/gas interfaces are required. The latter determinations have not been previously made for hot corrosion beneath thin fused salt films.

In Fig. 7, a novel experimental arrangement is introduced for electrochemical studies of the hot corrosion of metals beneath thin fused salt films. The provision of two monitoring electrodes, a ZrO$_2$-CaO oxygen sensor and a mullite-electrolyte probe with fixed $P_{SO_3}$ and $P_{O_2}$, provides the means to measure both $P_{O_2}$ and $P_{SO_3}$ (or $Na_2O$) at both the corroding metal specimen and at a submerged Au electrode. The calibration and comparison of the various electrodes in fused Na$_2$SO$_4$ at 1200K are described in detail by Watt, et al in another paper of this symposium. At this point, it should suffice to reiterate that the zirconia probe can indicate the oxygen activity at both the corroding metal surface and at the gold electrode, which should enjoy an equilibrium with the gas phase, i.e., represent the salt/gas interface. Further the Ag/Ag$_2$SO$_4$ or Pt/SO$_2$, O$_2$ electrode in a mullite electrolyte tube each respond to the ratio $Na_2O/P_{O_2}$, so that combined with the reading of the zirconia probe, the local basicity at the corroding metal and at the gas/salt interface (Au electrode) can be established. These are exactly the measurements required to test the mechanism and criterion for hot corrosion outlined here. Such measurements have been completed for several metals in several gaseous ambients and will be reported shortly.

The experimental arrangement of Fig. 7 further provides the novel possibility for anodic and cathodic polarization studies beneath a thin layer of fused salt. In such studies, either gold or the ZrO$_2$ or the mullite probe could be used as the reference electrode with the corroding metal as the working electrode, and a gold electrode as the counter electrode. Because the solubility of the oxide film on the working electrode may depend upon both $P_{O_2}$ and $Na_2O$, two probes are again required to independently track these parameters at the corroding metal (working electrode) surface. The past use of a Ag/Ag$_2$SO$_4$ electrode as the sole reference electrode in polarization studies in deep melts fixes only
the ratio $a_{Na_2O}/P_{O_2}^{1/2}$ at the oxide or metal/salt inter-
face, and this control may be inadequate to specify or
know the local solubility.

As a further use of the arrangement of Fig. 7, a freely corroding specimen can be shorted through a high-imped-
ance microammeter to an immersed gold electrode to form a
galvanic couple. As applied by Mansfeld and Kenkel\(^{15,16}\) to
study atmospheric corrosion under aqueous thin films, the
galvanic current can represent exactly the corrosion cur-
rent when transport through the electrolyte film consti-
tutes the rate limiting step. Preliminary electrochemical
thin film polarization and galvanic coupling studies have
been completed and will be reported shortly.

Mansfeld and Kenkel\(^{15,16}\) have shown that the kinetics
of atmospheric corrosion are limited by the diffusion of
molecular oxygen through the thin aqueous surface film.
From recent measurements of the solubility\(^{24}\) and diffu-
sivity\(^{25}\) of molecular oxygen in molten Na\(_2\)SO\(_4\), a Fick's
first law calculation can be made to test the rate of ar-
rival of oxygen for the cathodic reduction reaction in
rapid hot corrosion. For a density of Na\(_2\)SO\(_4\) of 2.5gm/cm\(^3\),
a thin film of 0.5 mg/cm\(^2\) would amount to a thickness $\delta$ of
2 x 10\(^{-4}\) cm. The maximum arrival flux of molecular oxygen
from $P_{O_2} = 1$ atm is given by

$$J_{O_2} \, (\text{moles } O_2/\text{cm}^2/\text{sec}) = D_{O_2} \frac{C_{O_2}}{\delta}$$

where the solubility $C_{O_2}$ equals about 3 x 10\(^{-7}\) moles O\(_2\)/
\text{cm}\(^3\) at 1000°C and the diffusivity about 5 x 10\(^{-5}\) cm\(^2\)/sec.
Upon substitution into the preceding equation, with one
mole O\(_2\) weighing 3.2 x 10\(^4\) mg, a maximum oxygen flux of
2.4 x 10\(^{-3}\) mg/cm\(^2\) sec is calculated. This value can be
compared with the very fast rate of oxygen gain reported
in Fig. 2 of Goebel and Pettit\(^{18}\) upon the hot corrosion of
pure Ni in pure O\(_2\) under 0.5 mg/cm\(^2\) of Na\(_2\)SO\(_4\) at 1000°C.
These kinetics approximated a gravimetric rate of 1.7 x
10\(^{-2}\) mg/cm\(^2\)/sec, a factor of seven greater than the cal-
culated maximum oxygen flux. Several conclusions are
obvious: 1) in rapid hot corrosion, the arrival of oxygen may be inadequate to supply the cathodic reduction of oxygen, and 2) for hot corrosion experimentation in deep (crucible) melts, oxygen reduction cannot represent the cathodic step. Understandably, in the experiment of Goebel and Pettit, nickel sulfide was observed as a corrosion product from the reduction of the sulfate anion. Finally, the hot corrosion of metals beneath a thin fused salt film and the atmospheric corrosion of metals beneath aqueous films do not generally share the same rate limiting step (transport-limited oxygen reduction).

Finally, subsequent to the mechanism and criterion for continued hot corrosion of a pure metal proposed here, one might inquire about the behavior expected for the hot corrosion of a binary A-B solid solution alloy. Unlike some of the variable-composition, amorphous corrosion products formed in aqueous solutions, at elevated temperatures, the products usually are crystalline and frequently exhibit little mutual solubility. Thus, the adherent corrosion products in fused salt corrosion might be represented by AO and BO, each of which would exhibit solubility curves similar to those shown in Fig. 3 for Cr$_2$O$_3$ and Al$_2$O$_3$. These solubilities would depend upon $a_{\text{Na}_2\text{O}}$ and perhaps upon $P_{\text{O}_2}$. The two solubility curves would naturally exhibit some lateral and vertical displacements relative to each other. One may consider Fig. 3 as illustrative for the superposition of two solubility curves.

In highly acidic (low $a_{\text{Na}_2\text{O}}$) salts, the AO and BO oxides would each exhibit acidic dissolution which would provide oxide ions as a soluble product of each oxide. Under this condition, i.e., for interfacial values of $a_{\text{Na}_2\text{O}}$ to the right of each solubility minimum, the previously proposed criterion for a pure metal could be applied to each oxide separately. However, in an environment which would fix the $a_{\text{Na}_2\text{O}}$ value at the oxide/salt interface at a value between the two minima, the oxide with its minimum on the right would exhibit basic dissolution upon complexing with oxide ions, while the other oxide would experience acidic dissolution to release soluble oxide ions. Under this condition, the combination of an acidic and a basic dissolution, rapid synergistic attack (AO + BO → AO$_2$$^-$$^+$ + B$^{2+}$) would be expected. Obviously, a knowledge of solubility curves forms the basis
for testing and avoiding this condition. But further, the experimental assembly of Fig. 7 is required to establish the independent values of $a_{Na_2O}$ and $P_{O_2}$ at the oxide/salt interface.

When the electrochemical probes indicate that the oxide/salt interface lies to the left (is more basic) than either of the minima of the solubility curves, then each oxide should exhibit basic dissolution without rapid synergistic attack. The previously suggested criterion would then be individually applied for each product oxide.

In conclusion, we suggest here that accelerated hot corrosion corresponds to a rapid dissolution and reprecipitation of an oxide film, a process supported by a negative gradient in the solubility of the oxide across the salt film. The local values for oxide solubility should be established by an increased basicity necessarily introduced at the site of the electrochemical reduction reaction. A novel experimental arrangement is proposed to test these ideas by independent measurements of $a_{Na_2O}$ and $P_{O_2}$ locally in thin fused salt films. A model is suggested for the occurrence of rapid synergistic hot corrosion of a binary alloy.

Acknowledgments

For financial support of this research through grant DMR 75-17204 and U.S.-Japan coop grant INT 77-17720, the authors express their appreciation to the National Science Foundation. For valuable discussions, and for the testing of the experiments described here, the authors express their appreciation to W.P. Stroud, G.W. Watt, R.E. Andresen, and R.C. John.
Table I. Tentative (Qualitative) Standard Electrochemical Reduction Series for Na$_2$S0$_4$ at 1200K

| Reaction                                                                 | Symbol |
|--------------------------------------------------------------------------|--------|
| $O_2^-$ (superoxide) + 1e $\rightarrow$ $O_2^2-$ (peroxide)              | a      |
| $O_2^2-$ (peroxide) + 2e $\rightarrow$ $2O^2-$ (oxide ions)              | b      |
| $SO_3$ (g) + 2e $\rightarrow$ $SO_2$ (g) + $O^2-$                        | c      |
| $1/2 O_2$ (g) + 2e $\rightarrow$ $O^2-$                                  | d      |
| $Fe^{3+}$ + e $\rightarrow$ $Fe^{2+}$                                    | e      |
| $Co^{3+}$ + e $\rightarrow$ $Co^{2+}$                                    | f      |
| $Ni^{3+}$ + e $\rightarrow$ $Ni^{2+}$                                    | g      |
| $SO_4^{2-}$ + 2e $\rightarrow$ $SO_3^{2-}$ + $O^2-$                     | h      |
| $SO_3^{2-}$ + 2e $\rightarrow$ $SO_2^{2-}$ + $O^2-$                     | i      |
| $SO_2^{2-}$ + 2e $\rightarrow$ S + $2O^2-$                              | j      |
| S + 2e $\rightarrow$ $S^{2-}$                                           | k      |
| $Ni^{2+}$ + 2e $\rightarrow$ Ni                                         | l      |
| $Co^{2+}$ + 2e $\rightarrow$ Co                                         | m      |
| $Fe^{2+}$ + 2e $\rightarrow$ Fe                                         | n      |
| $Cr^{3+}$ + 3e $\rightarrow$ Cr                                         | o      |
| $Al^{3+}$ + 3e $\rightarrow$ Al                                         | p      |
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Fig. 1 Thermodynamic Phase Stabilities in the Na-Al-S-O System at 1200K

Fig. 2 Thermodynamic Phase Stabilities in the Na-Cr-S-O System at 1200K
Fig. 3 Solubilities of Al₂O₃ and Cr₂O₃ in Molten Na₂SO₄ at 1200K

Fig. 4 Reprecipitation of Porous MO Oxide Supported by Solubility Gradient in Fused Salt Film
Fig. 5 Cathodic Reduction of Molecular Oxygen
(a.) for a high permeability of O$_2$ in thin salt film
(b.) for high concentrations and diffusivities of W$^{2+}$ and W$^{3+}$
or else for electronic conduction in the salt film.

Fig. 6 Cases of Continuous Hot Corrosion of a Pure Metal
(I is the oxide/salt interface, and II is the salt/gas interface)
Fig. 7 Schematic Diagram of Cell Assembly to Measure Na$_2$O Activity and P$_2$O$_5$ both at the Metal/Salt Interface and in the Fused Salt During Hot Corrosion