Accelerated Oxidation (Hot Corrosion) of Alloys by Molten Salt*

By Masahiro KAWAKAMI,** Kazuhiro S. GOTO*** and Robert A. RAPP****

I. Introduction

High-temperature gaseous oxidation of transition metal and their alloys is normally protective and obeys the parabolic rate law. But the oxidation is sometimes accelerated greatly when an electrolytic deposit, (a thin layer of fused salt) covers the surface of the metal or alloy. This phenomenon is called "hot corrosion" in the broadest sense. In this paper, "hot corrosion" refers to the accelerated oxidation of metals or alloys induced by the presence of surface deposits of thin salt films.

Hot corrosion of boiler tubes made of low-carbon steel was already described as early as 1945. The serious nature of hot corrosion received more attention recently upon the attack of alloys used for land-based gas turbines, and for aircraft and ship turbine engines. Since the first scientific investigation by Simons et al., many papers have been published on the hot corrosion of superalloys. Field experiences have extensively reported the phenomenology of the morphology of corroded products, the identity of the deposits, etc. Many sorts of laboratory tests were developed to simulate the operating conditions and to screen engineering materials. As will be described later, it has proved difficult to simulate fluctuating operating conditions by laboratory tests. So, presently, some phenomenological laboratory experiments are being conducted to establish the mechanism and reveal the common features of hot corrosion. These studies have examined various alloys, various salts, various gases, and various temperatures. Generally, the proposed micromechanisms seem to be qualitative rationalizations for a given set of experimental results which were obtained under rather restricted conditions. The next stage of the investigation would seem to require a clarification of the true micromechanism in a physico-chemical sense and development of principles for understanding of future problems which will arise as various alloys find service in different operating environments. Toward this goal, it seems worthwhile if some universal conclusions can be reached about the micromechanism of hot corrosion after a review of the literature.

An excellent review paper on this topic by J. Stringer covers many important items from examples of hot corrosion in service to the micromechanisms of hot corrosion studied in laboratories. In the present paper, attention will be focused to the micromechanism. Therefore, the plan for this review will be as follows: first, phenomenological aspects will be mentioned briefly; second, several kinds of micromechanisms which have been previously proposed will be examined; a more generalized electrochemical/chemical model will be proposed, and finally some suggestions regarding future studies will be given.

II. Phenomenological Features

1. Field Experiences

When the products of combustion in gas turbines involve a combination of species containing sulfur and sodium compounds, the blades and/or vanes of the aircraft engines are severely attacked, even after a short time of 225 hr. The attack is associated with the deposition of a liquid sodium sulfate on the surface. Many reports of similar experiences are cited in the review paper by Stringer. Although the examples involve different alloys and different operating conditions, some features of the hot corrosion attack seem to be common.

Hot corrosion is associated with the formation of a corrosive, molten, electrolytic deposit on the surface of the hot component. These deposits are mainly composed of sodium sulfate and sodium chloride and other salts which lower the liquidus temperature. Sodium sulfate may, in some cases, be formed from a reaction between sodium chloride from ingested sea water aerosols in the air and sulfur dioxide or trioxide of the reaction product gases by the following reaction:

\[ 2\text{NaCl} + \left[\text{SO}_3\right] + \left[\frac{1}{2}\text{O}_2\right] = \text{Na}_2\text{SO}_4 + \text{Cl}_2 \quad \text{(1)} \]

Equilibrium calculations show that Reaction (1) should go almost completely to the right. Likewise, water vapor could supply the oxygen with the formation of HCl vapor. On the other hand, sea water contains already a significant amount of Na$_2$SO$_4$ such that the simple vaporization of the aerosol could also provide the necessary Na$_2$SO$_4$. Such a source is also consistent with calculation which indicate that the residence time and reaction rate constants are inadequate for the realization of Reaction (1) in the gas
turbine. Generally, sodium chloride is not found in the deposit. But recent papers have reported the existence of small amounts of sodium chloride in the deposits which caused severe attack. Other constituents of the deposit are calcium and magnesium sulfates. Especially, a one to one mixture of sodium and magnesium sulfate with 4 mol of hydrated water has the melting point of 621°C, compared to 884°C for anhydrous sodium sulfate. Other constituents include oxides, sulfates and vanadates of nickel and cobalt, and hematite. When carbon is found in the deposits on blades from service, it has highly enhanced hot corrosion, as does the presence of a reducing gas such as CH₄.

The temperature dependence of hot corrosion is irregular. Some blades are attacked at relatively high temperatures, but others at much lower temperatures. An appropriate temperature region for hot corrosion seems to extend from the solidus (or eutectic) temperature of a melt to the boiling temperature. Although the reaction rate depends on the composition of the alloys, salts and gases, it is generally believed that below about 600°C there is a negligible rate of attack. Attack seems virtually absent above 950°C.

The morphologies of hot corrosion products have been examined by metallographic tests. A typical morphology includes an outer layered oxide composed of NiO with some Ni₃Cr₂O₄ spinel which is rather porous and filled with the salt matrix. Under the porous outer layer, a mixture of nickel-rich metal is dispersed in a Cr₂O₃ matrix. In the metal matrix beneath this layer, particles of chromium-rich, and sometimes nickel-rich sulfides are surrounded by an alloy depleted in chromium. Because the eutectic temperature in the Ni–Ni₃S₂ system is 645°C, the formation of liquid sulfides at grain boundaries can destroy the alloy mechanical properties before surface recession would otherwise cause failure. The appearance of matrix sulfides has given rise to the name of "sulfidation" for such a kind of hot corrosion, but this name may eventually mislead one in the clarification of the micromechanism as will be shown later.

Alloy compositions for preventing hot corrosion have been discussed. Generally, more than 15% chromium is required for hot corrosion resistance in gas turbine service. Cobalt-based alloys seem to be superior to nickel-based alloys but they also have higher chromium contents. Opposing opinions have been expressed concerning molybdenum, tungsten, niobium and tantalum. To increase the hot corrosion resistance, some additives are put into the fuels; these are based on oil-soluble chromium to form stable sodium chromates. Alloys with about 5% aluminum seem to be highly vulnerable to hot corrosion and are not used without coating.

2. Laboratory Tests

Several kinds of laboratory tests have been conducted, both for the development of high-temperature materials which are resistive to hot corrosion and for the investigation of the micromechanism of hot cor-

rosion. For the former purpose, a group of "burner rigs" has been devised in order to simulate at least in part the operating conditions in engines; the gas composition, pressure, velocity and temperature of the real engines. Some of these rigs are composed of a combustion chamber from a small turbine, supplying air from compressors and burning fuel in the usual way. Salt is supplied either to the fuel or to the air. Otherwise, salt can be sprayed into the combustion chamber. The hot exhaust gases are brought into the sample chamber, where several specimen coupons are placed, and in most cases, rotated in the gas stream. When thermal cycling is desired, the rig is designed so that the specimen can be brought out and in periodically. This type of test can be simplified when a small burner is used instead of the combustion chamber, and the specimens are exposed to a gas stream of atmospheric pressure. But special rigs have also been designed to conduct the experiment at pressures as high as 20 atm. The dew point of the salt differs considerably at higher pressure.

The modified Dean rig is another version of a "burner rig". The rig uses a furnace having two zones whose temperatures can be controlled independently. The specimen is placed in one zone, and a crucible containing the test salt is placed in the other, which is upstream of the specimens, the vaporized salt deposits on the surface of the specimen and may cause severe attack.

Although a burner rig can simulate the practical operating conditions more closely, it requires a long running time and a considerable cost. The simplest test to examine the material is the "crucible test" which was used in the earliest work by Simons et al. A specimen is immersed to half its length in the molten salt mixture in a ceramic crucible. The atmosphere has usually been air but it can be changed to various flowing gas mixtures. This corrosion test condition seems to be more severe than that in the normal operating condition of engines, but is considered helpful in preliminary screening of materials. Clearly the transport distance for any gas component through the salt is grossly inappropriate.

Thermogravimetric measurements, which are called as the "salt-coated test", have been conducted extensively mainly in order to clarify the micromechanism of hot corrosion. A coupon of the material is coated with a saturated salt solution, then dried, weighed, and placed in a heated furnace. Usually, the coupon weight is continuously recorded. In most cases, the weight increases as oxidation proceeds, because the vaporization rate is small compared to the oxidation rate. This test is favorable for determining the hot corrosion kinetics, because the experimental gas composition, temperature and salt loading can be controlled precisely and easily. Pretreatments of the specimen, like presulfidation or preoxidation can be studied. This test can exaggerate the effect of the possible factors affecting hot corrosion, which enables an evaluation of the individual hot corrosion test parameters. Although the mode of salt deposition onto the specimen surface does not simulate service,
and the experimental conditions are too steady, the test may give valuable information on the micro-mechanism of the hot corrosion process. From both a kinetic curve and metallographic observations of the oxidation products, the phenomenological features of hot corrosion have been rather well revealed.

A number of authors have conducted electrochemical three-electrode polarization studies of metals in alkali sulfates. These previous studies all involved relatively deep salt melts. Shores demonstrated an electrochemical testing method for the primary screening of materials. He correlated the anodic polarization current to the weight gain from the burner rig. The Ag/Ag⁺ (10 mol% Ag₂SO₄; 90 mol% Na₂SO₄) electrode was chosen as the reference electrode. Two problems are inherent in all studies. For deep (crucible) salt melts, the transport distance for reduction of an oxidant from the gas phase is grossly inappropriate. Secondly, the open-circuit voltage of Ag/Ag⁺ electrode is proportional to ln(aAg⁺/aAg), so that the two coordinates of the Pourbaix-type plot cannot be separated from each other. A new experimental arrangement recommended by Rapp and Goto involves thin-film electrochemical studies: this method should overcome the problem concerned with deep melts.

3. Results of Laboratory Testing

As the purpose of the burner rig and crucible tests is to screen or select the materials appropriate for specific engine operation, the tests establish the kinetics dependences on time, temperature, alloy composition, and amount and type of salt. Thus, the results have been generally consistent with those described previously in Section II. 1.

Thermogravimetric tests, however, revealed some new aspects of hot corrosion. Bornstein and DeCrescente studied the oxidation behavior of B-1900, U-700 and Waspaloy, with and without salt coatings. In the case of air oxidation, the oxide film on B-1900 was found to consist primarily of alumina, that on U-700, a mixture of spinels containing aluminum and chromium, that on Waspaloy, primarily of Cr₂O₃ with minor amount of TiO₂ and possibly spinel NiCr₂O₄. The oxidation of B-1900 was very much accelerated by a thin Na₂SO₄ coating. That of U-700 was also accelerated, but not so much as B-1900. But the oxidation rate of Waspaloy with Na₂SO₄ coating was quite similar to that without coating. Under these conditions, then, an alumina-rich protective film is destroyed by sodium sulfate, but a chromia-rich oxide is not. The hot corrosion of the alloys with sodium nitrate (NaN₃O₃) coating was also tested. The rates of oxidation of NaN₃O₃-coated and Na₂SO₄-coated specimens were similar to each other. In another paper, Bornstein and DeCrescente showed that sodium carbonate (Na₂CO₃) causes accelerated oxidation of B-1900, Waspaloy and Ni-Cr alloys to the same extent as Na₂SO₄. The role of sulfur in hot corrosion was examined by two series of experiments. First, a specimen was presulfidized and subsequently oxidized. Secondly a specimen was coated with Ni-Ni₃S₂ eutectic which was previously prepared and then oxidized. These experiments showed that the oxidation rate was not enhanced by the pretreatments. The authors generalized that hot corrosion was not attributable to the presence of sulfur but to Na₂O originating from sodium compounds such as Na₂SO₄, NaN₃O₃, and Na₂CO₃.

Goebel and Pettit reported accelerated oxidation of pure nickel coated with Na₂SO₄. The morphology of the oxidation product was similar to that of superalloys described previously, namely, nickel sulfide was formed beneath a porous nickel oxide layer. In another experiment, nickel was presulfidized in a H₂–H₂S gas mixture, and then oxidized in oxygen. In order to decrease the oxygen ion activity in Na₂SO₄, Cr₂O₃ was added to the salt. The Na₂SO₄-Cr₂O₃ coated nickel was oxidized. The rate was far less than that without any coating. The Na₂SO₄-Na₂O melt (high oxygen ion activity in Na₂SO₄) proved to increase the oxidation rate of pure nickel. The authors concluded that hot corrosion of pure nickel induced by Na₂SO₄ is attributable not to sulfur but to the oxygen ion activity in Na₂SO₄. A micro-mechanism for the process was proposed, which will be explained later in detail. Goebel et al. subsequently examined hot corrosion of nickel-base alloys containing chromium, aluminun, molybdenum, tungsten and vanadium. The specimens were coated with different amounts of Na₂SO₄. The alloy compositions were changed systematically in order to examine the effects of alloying elements on hot corrosion. Those alloys containing molybdenum, tungsten and vanadium exhibited catastrophic, or self-sustaining rapid oxidation. The oxidation rate was much faster than that of alloys without them. The effects of molybdenum and tungsten additions were also noticed by Reising. Nickel alloys with chromium and aluminum were attacked by Na₂SO₄ in the same manner as described by Bornstein and DeCrescente. Namely, the rate of hot corrosion was much faster than that for gaseous oxidation.

Recently, Kawakami et al. examined accelerated oxidation of nickel and nickel-base superalloys induced by films of NaCl–KCl melt at 700°C. The aim was to determine the effect of sodium chloride on the oxidation and to clarify the mechanism of the accelerated oxidation with a salt which does not include oxide-anion. The alloys B-1900, INCO-738 and René-80 were studied. The first is an alumina former and the latter two are chromia formers. The oxidation rate was increased for pure nickel, INCO-738 and René-80. However, B-1900 was not oxidized at an accelerated rate. The above results differ from those for Na₂SO₄, Na₂CO₃ and NaN₃O₃ coatings where chromia inhibited hot corrosion, but alumina could not. It is known that Na₂SO₄ with a small addition of NaCl can cause severe attack, and that NaCl gas can cause accelerated oxidation of a chromia-forming alloy.

As described above, some studies have been carried out on different alloys with different salts. Thus, it seems worthwhile to summarize the results in the form
of a combination of the oxide film on the alloy surface and the salts, as is shown in Table 1. An alloy with more than 5 wt% aluminum will generally form an aluminum oxide film. An alloy with more than 15 wt% chromium and less than 5 wt% aluminum will form a chromium oxide film. B-1900, IN-100, Nimonic 100 and 713C fall in the category of alumina-former. Nimonic 80A and 90, U-500, Hastelloy X, Waspaloy and INCO-738 can be the chromia-former. Nimonic 105, U-700 and René-80 seem borderline between the alumina- and chromia-formers. An NiO layer will be formed when the depletion of alloying elements like chromium and aluminum, which can combine with sulfur beneath a scale to form their sulfides.

Most papers in the literature describe the morphologies of hot corrosion products. However, these morphologies do not give much input toward the reaction mechanism. Kinetic behavior is also described in most of the papers. Generally, the oxidation curves are linear, parabolic, or have some incubation time, and so on. However, the kinetic description seems just supplemental to complete the empirical description of the attack. The morphologies and kinetic behavior of hot corrosion are described in Ref. 3), and will not be considered in detail in this paper.

III. Thermodynamics

1. Deposition of Sodium Sulfate on Alloy Surface

Since accelerated oxidation attack occurs only when Na₂SO₄ is present in condensed deposits on the alloy surface, it seems of primary importance to consider both the formation reaction and the deposition on the surface.

Sodium sulfate may be formed from sodium chloride, sulfur oxides and water by the following reactions.

\[ 2\text{NaCl} + \text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} = \text{Na}_2\text{SO}_4 + 2\text{HCl} \]  \(\text{(2)}\)

\[ 2\text{NaCl} + \text{SO}_3 + \text{H}_2\text{O} = \text{Na}_2\text{SO}_4 + 2\text{HCl} \]  \(\text{(3)}\)

DeCrescente and Bornstein\textsuperscript{25} calculated the equilibrium constants for these reactions from thermodynamic data. Since the reactions involve molar changes of gaseous species, the total pressure affects the equilibrium. However, according to their calculation, the equilibrium conversion of NaCl to Na₂SO₄ and HCl would be 75% complete at 1000°C and atmospheric pressure. For the normal operating conditions of engines, the temperature would be lower and the total pressure higher, so the complete conversion could be assumed.

Condensation of Na₂SO₄ will take place when its partial pressure is greater than its equilibrium vapor pressure. Since the partial pressure of Na₂SO₄ is a function of the initial amount of NaCl vapor in the intake gas and the total pressure, the phase stability diagram will depend on both factors. More precise calculations were made by Tschinkel\textsuperscript{61} and Bessen and Frywell.\textsuperscript{10} Elliott\textsuperscript{39} provided free energy calculations for the following reactions as a function of temperature:

\[ 2\text{Na}(v) + \text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) = \text{Na}_2\text{SO}_4(v) \]  \(\Delta G^o = -925.300 + 390.7T \text{ J/mol Na}_2\text{SO}_4 \)  \(\text{(4)}\)

\[ \text{Na}_2\text{SO}_4(v) = \text{Na}_2\text{SO}_4(l) \]  \(\Delta G^o = -297.500 + 112.17T \text{ J/mol Na}_2\text{SO}_4 \)  \(\text{(5)}\)

\[ \text{Na}_2\text{SO}_4(v) = \text{Na}_2\text{SO}_4(s) \]  \(\Delta G^o = -320.500 + 130.05T \text{ J/mol Na}_2\text{SO}_4 \)  \(\text{(6)}\)

2. Metal-Oxygen-Sulfur Diagram

Because both oxygen and sulfur participate in hot corrosion, it is useful to construct M-O-S diagrams, where the regions of stable phases are shown as a function of oxygen and sulfur potentials. These potentials can be expressed by any pair of \(P_{O_2}\) with \(P_{SO_3}\) or \(P_{SO_2}\), because the latter three partial pressures are interrelated to each other if \(P_{O_2}\) is fixed, as

\[ \frac{1}{2}\text{SO}_2 + \text{O}_2 = \text{SO}_3 \]  \(\text{(7)}\)

\[ \text{SO}_2 + \frac{1}{2}\text{O}_2 = \text{SO}_3 \]  \(\text{(8)}\)

Quets and Dresher\textsuperscript{81} constructed the diagrams for sodium and nickel choosing \(\log P_{O_2}\) and \(\log P_{SO_2}\) as coordinates. Elliott\textsuperscript{39} favored \(\log P_{O_2}\) and \(\log P_{SO_3}\). Goebel and Pettit\textsuperscript{17,18} constructed the M-O-S diagrams for sodium, nickel and aluminum, taking \(P_{O_2}\) and \(P_{SO_3}\) as coordinates. In the present paper, the choice of Goebel and Pettit will be taken, because the phase of most interest in hot corrosion is Na₂SO₄ and the stability region of Na₂SO₄ is shown in a rectangular form. Further, the components SO₃ and Na₂O are considered the acid and base components of Na₂SO₄, so that the log \(P_{O_2}\) vs. \(\log P_{SO_3}\) diagram represents an exact analogy to the Pourbaix diagrams for aqueous solution corrosion. Figure 1 is a diagram for the Na-O-S system at 1000°C. The diagram was constructed from thermodynamic data for the following reactions, assuming unit activities for condensed phases.

\[ \text{Na}_2\text{SO}_4 = \text{Na}_2\text{O} + \text{SO}_3 \]  \(\text{(9)}\)

\[ \text{Na}_2\text{SO}_4 = \text{Na}_2\text{S} + 2\text{SO}_2 \]  \(\text{(10)}\)

\[ \text{Na}_2\text{S} + 2\text{O}_2 = \text{Na}_2\text{O} + \text{SO}_3 \]  \(\text{(11)}\)

\[ \text{Na}_2\text{O} = 2\text{Na} + \frac{1}{2}\text{O}_2 \]  \(\text{(12)}\)

Table 1. Combination of alloys and salts exhibiting hot corrosion.

<table>
<thead>
<tr>
<th></th>
<th>NiO former</th>
<th>Al₂O₃S form</th>
<th>Cr₂O₃ form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂SO₄</td>
<td>Accelerated oxidation</td>
<td>Accelerated oxidation</td>
<td>No acceleration</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>No acceleration</td>
<td>Accelerated oxidation</td>
<td>No acceleration</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>Accelerated oxidation</td>
<td>Accelerated oxidation</td>
<td>No acceleration</td>
</tr>
<tr>
<td>NaCl-KCl</td>
<td>Accelerated oxidation</td>
<td>No acceleration</td>
<td>Accelerated oxidation</td>
</tr>
</tbody>
</table>
Transactions ISIJ, Vol. 20, 1980

Fig. 1. Stability diagram for Na–O–S system at 1000°C. (Goebel and Pettit)(17)

Fig. 2. Stability diagram showing the phases of nickel that are stable in the Na2SO4 region of Fig. 1. (Goebel and Pettit)(17)

Na2S + 3/2O2 = 2Na + SO3 .............(13)

In the Na2SO4 region of the diagram, αO2- and αS2- are also shown, assuming the following two equilibria and unit activity of SO2- in the Na2SO4 region:

SO2- = O2- + SO3 .............(14)

SO2- = S2- + 2O2 .............(15)

Activity of oxygen ion is very important when acidic-basic fluxing mechanism is considered. If αO2- is high, basic fluxing can take place. If it is low, acidic fluxing is possible.

Figure 2 is the Ni–O–S stability diagram within the Na2SO4 region of Fig. 1. The following equilibria were assumed and thermodynamic data for them were used to construct the diagram.

Ni + 1/2O2 = NiO ..................(16)

Ni + SO3 = NiS + 3/2O2 ..........(17)

NiO + SO3 = NiS + 2O2 ..........(18)

NiO + SO3 = NiSO4 ..........(19)

NiS + 2O2 = NiSO4 .............(20)

Similarly, if the equilibrium reaction between two phases can be expressed involving either SO3 or O2, and the thermodynamic data for the reactions are available, any M–O–S equilibrium diagram can be constructed. Figure 3 is the diagram for Al–O–S by Stroud and Rapp. Figure 4 is that for Cr–O–S by Gupta and Rapp.

3. Solubility of Metal Oxide in Molten Salts

The solubilities of metal oxides in molten salts are the data of principal importance when the oxide fluxing mechanism is considered, as in the subsequent chapter. Qualitatively, water-soluble nickel and chromium salts have been found in quenched molten salts of high basicity. But no quantitative study of oxide solubility was reported until the work by Stroud and Rapp. They measured the solubilities of alumina and chromia in fused Na2SO4 at 927°C and obtained the data of Na2O activity for PO2 equal to 1 and 10^-4 atm.
IV. Proposed Micromechanisms

1. Sulfidation Model

Hot corrosion is often characterized by the appearance of sulfides in an alloy-depleted zone, and has been previously called "sulfidation." In the present paper, the sulfidation model includes all proposed mechanisms where sulfur plays a decisive role.

The first model was proposed by Simons et al., who conducted experiments on Type 310 stainless steel. The hot corrosion process was divided into two steps: Triggering and subsequent autocatalytic steps. In the former step, sodium sulfate reacts with some reducing agent to produce free sulfur, which reacts with an alloy component to form its sulfide. In contact with the metal, the sulfide can form a eutectic liquid at the service temperature. Several common metals form eutectics with their sulfides; nickel, for example, forms a binary eutectic with 21.5 wt% sulfur at 644°C, the Co–S system has a eutectic at 25 wt% sulfur at 880°C, and iron at 31 wt% sulfur at 988°C. Sulfide-forming reactions can be expressed as follows:

\[
\begin{align*}
\text{Na}_2\text{SO}_4 + 3\text{R} &= \text{Na}_2\text{O} + 3\text{RO} + \text{S} \quad \text{(21)} \\
\text{M} + \text{S} &= \text{MS} \quad \text{(22)} \\
\text{M} + \text{MS} &= \text{M} + \text{MS} (\text{eutectic}) \quad \text{(23)} \\
\end{align*}
\]

In the second step, the metal–metal sulfide eutectic is oxidized by molecular oxygen permeating through the salt film to liberate metal sulfide, which once again dissolves metal matrix in the eutectic formation, as follows:

\[
\begin{align*}
\text{M} \cdot \text{MS} + 1/2\text{O}_2 &= \text{MO} + \text{MS} \quad \text{(24)} \\
\text{M} + \text{MS} &= \text{M} + \text{MS} \quad \text{(eutectic)}
\end{align*}
\]

Thus, the reaction is self-sustaining. This model is schematically illustrated in Fig. 6. In this model, the reducing agent can be either a metallic component of the alloy or carbon (char particles) in the salt film.

Although this model seems to be consistent with experimental observations and field experiences, there are two fundamental postulates; the eutectic can be formed beneath a protective film and further in the metal substrates, and the eutectic would be highly reactive to oxygen. The first postulate was experimentally proved by Seybolt and Beltran. They conducted experiments on the reaction between nickel and sodium sulfate in a vacuum, finding considerable penetration by sulfur. But the validity of the second postulate seems somewhat questionable. Spengler and Viswanathan presulfidized a Ni–15Cr specimen in a 0.2% SO_2–N_2 mixture at 871°C and then oxidized...
it at the same temperature. The oxidation rate of the presulfidized specimen was faster than that for an unsulfidized one. Tedmon and Seybolt oxidized pure chromium metal and its sulfide Cr₃S₉, which is solid at the experimental temperature. The oxidation rates for these specimens were comparable. Goebel and Pettit sulfidized a Ni–Cr alloy to form a continuous external layer of “CrS” and then oxidized it. The oxidation rate was again the same as for the unsulfidized material. Bornstein and DeCrescente coated the surface of B-1900 alloy with a previously prepared Ni–Ni₃S₂ eutectic. The coated specimen was exposed at 900°C for 1000 hr in an oxygen environment. The oxidation rate was similar to that of commercial nickel without coating, and much smaller than that for Na₂SO₄-coated B-1900. The above cited experimental results seem contradictory, and several sulfidation models other than that by Simons et al. have been proposed.

Seybolt, who found that the oxidation rate of solid Cr₃S₉ was comparable to that of pure chromium, modified the first model. He proposed that if the sulfide forms a eutectic melt, it will be oxidized at an enhanced rate. But, if the sulfide is solid, like Cr₃S₉, the matrix depleted in the protective component (e.g., Cr) would be preferentially oxidized. To some extent, this model would be supported by introducing an electrochemical localized cell model to explain the preferential oxidation. The alloy-depleted zone would act as an anode, whereas the remaining matrix or carbide would serve as a cathode. For example, the chromium-depleted zone of a Ni–Cr alloy would be oxidized to release electrons in forming Ni²⁺ cations. The remaining matrix or carbides would be coated by a protective Cr₂O₃ or NiCr₂O₄ film, where reduction of gaseous oxygen could take place. Namely, at the depleted zone,

\[ \text{Ni} = \text{Ni}^{2+} + 2e^- \quad \text{(25)} \]

and on the protective film,

\[ 1/2 \text{O}_2 + 2e^- = \text{O}^{2-} \quad \text{(26)} \]

Ni²⁺ and O²⁻ would interdiffuse and precipitate as NiO depending on the solubility gradient in the molten salt. A schematic diagram of the modified model is shown in Fig. 7. The preferential oxidation of the alloy-depleted zone may not be self-sustaining, unless sodium sulfate is continuously supplied to the alloy surface.

In contrast, Bornstein and DeCrescente have discounted the importance of sulfur in hot corrosion. They conducted oxidation experiments on B-1900, U-700, Waspaloy and Ni–Cr alloys with different compositions. As already cited, the coating of B-1900 with Ni–Ni₃S₂ eutectic did not accelerate the oxidation; presulfidized B-1900 did not exhibit the accelerated oxidation. Further, a coating of NaNO₃ or Na₂CO₃ caused as much accelerated oxidation on these alloys as did a coating of Na₂SO₄. However, they noticed a difference between Na₂SO₄ and Na₂CO₃ coatings on pure nickel. Whereas Na₂SO₄ significantly increased the oxidation rate of nickel, the rate of oxidation of Na₂CO₃-coated nickel is lower than that of a salt-free specimen. Probably, Na₂CO₃ limits the availability (transport) of oxygen to the surface, and nickel carbide is not formed from the carbonate, although liquid sulfate is formed from the sulfate. However, they postulated the fluxing mechanism as will be explained in the subsequent section, whereby sulfur plays an important role in raising the oxygen ion activity. According to this model, sodium sulfate would react with nickel, forming first the oxide and then its sulfate. As a result, oxygen ions are expected to be liberated. If the salt becomes locally quite basic (high oxygen ion activity), the protective nickel oxide would be fluxed as follows:

\[ \text{SO}_4^{2-} + 3\text{Ni} = \text{NiS} + 2\text{NiO} + 1/2\text{O}_2 + \text{O}^{2-} \quad \text{(27)} \]
\[ 2\text{NiO} + 1/2\text{O}_2 + \text{O}^{2-} = 2\text{NiO}_2 \quad \text{(28)} \]

The reaction product NiO₂ is suggested to be soluble in the salt. Thus, the protective film would dissolve. On the contrary, the production of oxygen ions from carbonates by the following reaction is slow:

\[ \text{CO}_3^{2-} = \text{CO}_2 + \text{O}^{2-} \quad \text{(29)} \]

Thus, fluxing of the protective NiO film was not expected. In the sense that sulfur plays an important role, this model can be included in “sulfidation”.

2. Acid-base Fluxing Model

As already described in the preceding section, Bornstein and DeCrescente pointed out the primary importance of sodium oxide activity on the oxide/salt interface. The idea is supported and extended by Goebel and Pettit and John and Rapp as follows: in hot corrosion of pure nickel, the nickelite ion NiO₂⁻ would have a finite solubility in the fused salt; according to the reaction

\[ \text{NiO} + \text{O}^{2-} = \text{NiO}_2^- \quad \text{(30)} \]

The reaction will go to the right, and a NiO film will be dissolved, when the oxygen ion activity is high. On the contrary, if the oxygen ion activity is low, the reaction will go to the left, and the precipitation of NiO will take place. When pure nickel is coated with Na₂SO₄, the following reaction, for example, would take place at the oxide/salt interface, whereby the activity of oxygen ion may be enhanced;
SO$_4^{2-}$ + 4Ni = NiS + 3NiO + O$_2$—-(31)
Near the gas/salt interface, however, the oxygen ion activity may be low, taking into account of the following reaction where $P_{O_2}$ is quite high:

SO$_2$ + 1/2O$_2$ + O$_2^-$ = SO$_4^{2-}$ ————(32)

Combining the above two situations, NiO would be dissolved at the oxide/salt interface, and reprecipitate near the gas/salt interface to form a porous NiO and salt aggregate layer. In this mechanism, O$_2^-$ is liberated by the sulfide formation, and thus, the amount of O$_2^-$ is limited by the amount of Na$_2$SO$_4$ coated. With this model, the Na$_2$SO$_4$-induced hot corrosion of pure nickel is not self-sustaining, as is well known by the experiments. The model was supported by the following experimental results:

1. Accelerated oxidation of pure nickel takes place at the beginning of the process. Thereafter, the oxidation rate is similar to that without a coating.

2. When a coating of Na$_2$SO$_4$ is mixed with Cr$_2$O$_3$ which would consume oxygen ions to form CrO$_4^{2-}$, the accelerated oxidation is no longer observed.

3. On the contrary, Na$_2$SO$_4$ containing a high oxygen ion concentration greatly accelerates the oxidation.

4. Visual examination by hot-stage microscope revealed that the NiO product was formed in the Na$_2$SO$_4$ salt, but not on the nickel surface.

5. The total weight gain of the specimen increased as the thickness of the Na$_2$SO$_4$ coating was increased.

The model for accelerated oxidation of pure nickel is shown schematically in a generalized form in Fig. 8.

When pure nickel is coated with Na$_4$CO$_3$, the activity of the oxygen ion would be determined by the reaction:

CO$_3^{2-}$ = CO$_2$ + O$_2^-$ ————(29)
Because of the lower absolute stabilities of carbonates compared to those of sulfates, the equilibrium state for Reaction (29) is farther to the right than that for SO$_4^{2-}$. But if $P_{O_2}$ in the gas phase is high, the oxygen ion activity at the gas/salt interface can be lower than that at the oxide/salt interface. John and Rapp oxidized Na$_2$CO$_3$-coated nickel in a pure CO$_2$ atmosphere. At the beginning of the process, the situation analogous to that in Fig. 8 was set up. Thus, accelerated oxidation of pure nickel took place.

In the case of alumina-former alloys, similarly, alumina is considered to dissolve into the salt as an aluminate ion by the following reaction:

Al$_2$O$_3$ + O$_2^-$ = 2AlO$_2$ ————(33)
In the molten Na$_2$SO$_4$ under 1 atm of oxygen, the oxygen ion activity may not be sufficient for the above reaction to go to the right. However, at the alloy/oxide interface, aluminum in the alloy would react with sulfide ions passing through the Al$_2$O$_3$ scale so that the total reaction increases the oxygen ion activity at the oxide/salt interface, which may lead to basic fluxing of Al$_2$O$_3$:

2/3Al + SO$_4^{2-}$ = O$_2$ + 1/3Al$_2$S$_3$ + 3/2O$_2$ ————(34)
Consequently, the increase in oxygen ion activity at the oxide/salt interface can lead to the negative solubility gradient as shown in Fig. 8. Hence, alumina is dissolved at the alloy/salt interface, and precipitates near the gas/salt interface to form a porous layer. Although the above mechanism is similar to that for a NiO-former, the behavior of nickel and aluminum sulfides differ from each other. Although the oxidation rate of nickel sulfide is comparable to that of pure nickel, that of aluminum sulfide is very fast, with the formation of a porous alumina layer on the surface. Therefore, in the case of alloys containing sufficient aluminum to form both oxide and sulfide, not only the aluminum oxide, but also the oxidation of the sulfide seems important.

In the case of chromia-former alloys, on the contrary, the oxygen ion activity may be sufficiently high to form chromate ions at the chromia/Na$_2$SO$_4$ interface, according to the reaction:

Cr$_2$O$_3$ + 2O$_2^-$ + 3/2O$_2$ = 2CrO$_4^{2-}$ ————(35)
When the oxygen ion is consumed by the above reaction itself, dissolution of chromia should stop, and hence, a protective chromia film would be formed at the alloy/salt interface.

This type of fluxing to form nickelite, aluminate and chromate ions is called “basic fluxing”. The accelerated oxidation in Na$_2$SO$_4$ by basic fluxing is not self-sustaining, since the decomposition of Na$_2$SO$_4$ is inevitable in the mechanism, and the amount of Na$_2$SO$_4$ is limited, i.e., at least when the oxidant gas is pure oxygen. As a necessary component of the Goebel and Pettit basic fluxing mechanism, formation
of sulfide at the highly reduced metal/salt interface is supposed to shift the salt locally basic to support fluxing.

As described in the preceding chapter, oxidation of salt-coated alloys containing molybdenum, tungsten and vanadium is even faster than the accelerated oxidation considered above. This mechanism should be different. Alumina can also be fluxed according to the following reaction:

\[ \text{Al}_2\text{O}_3 = 2\text{Al}^{3+} + 3\text{O}^{2-} \]  \hspace{1cm} (36)

provided that the oxygen ion activity is low enough in the salt. Goebel et al.\(^{18}\) examined the interaction of Na\(_2\)SO\(_4\) with MoO\(_3\), WO\(_3\), V\(_2\)O\(_5\) and Cr\(_2\)O\(_3\) by an electrochemical method. According to them, these oxides react with the oxygen ion in the salt to form basic complex anions, as follows:

\[ \text{MoO}_3 + \text{O}^{2-} = \text{MoO}_3^{2-} \]  \hspace{1cm} (37)

\[ \text{WO}_3 + \text{O}^{2-} = \text{WO}_3^{2-} \]  \hspace{1cm} (38)

\[ \text{V}_2\text{O}_5 + \text{O}^{2-} = 2\text{VO}_5^{-} \]  \hspace{1cm} (39)

\[ \text{Cr}_2\text{O}_3 + 3/2\text{O}^{2-} + 2\text{O}^{2-} = 2\text{CrO}_4^{2-} \]  \hspace{1cm} (35)

Although the above equilibria could not be estimated quantitatively, crucible tests revealed that alumina was fluxed by Na\(_2\)SO\(_4\) containing MoO\(_3\), WO\(_3\) and V\(_2\)O\(_5\). Thus, these oxides can suppress the oxygen ion activity to the values low enough to flux alumina. On the contrary, Cr\(_2\)O\(_3\) in the Na\(_2\)SO\(_4\) could not set up Al\(_2\)O\(_3\) fluxing. From these experimental results, the "acidic fluxing" mechanism was proposed as follows.

At the initial stage of oxidation, aluminum and nickel would be oxidized, whereas molybdenum, tungsten and vanadium would also be oxidized at their zones of enrichment in the alloy. Their liquid oxides would then be dissolved into the salt by Reactions (37) to (39). From these reactions, the oxygen ion activity would eventually be lowered enough for acidic fluxing of alumina and NiO at the salt/ alloy interface. The ions Al\(^{3+}\), MoO\(_3^{2-}\) and SO\(_4^{2-}\) would diffuse through the salt to the salt/gas interface, where MoO\(_3\) and SO\(_4\) would evaporate, resulting in a higher local oxygen ion activity there. Thus, Reaction (36) would run to the left, and porous, nonprotective alumina would precipitate. It is important to emphasize that this type of accelerated oxidation is self-sustaining, because MoO\(_3\) is continually formed from the alloy as the oxidation proceeds. A schematic diagram of acidic fluxing is shown in Fig. 9.

As already described, NaHSO\(_4\) can dissolve NiO in a detectable amount.\(^{24}\) Since exhaust gas contains significant amounts of water, there should be a chance to form some NaHSO\(_4\) in the salt. Above 500°C, however, HSO\(_4^{-}\) ion is likely to decompose by the following reactions:\(^{41}\)

\[ 2\text{HSO}_4^{-} = \text{S}_2\text{O}_7^{2-} + \text{H}_2\text{O} \]  \hspace{1cm} (40)

\[ \text{S}_2\text{O}_7^{2-} = \text{SO}_4^{2-} + \text{SO}_3 \]  \hspace{1cm} (41)

But, if \( P_{\text{SO}_3} \) would be kept at a high level near the oxide/salt interface, the HSO\(_4^{-}\) ion would be stable there. Thus, fluxing of NiO would take place. Dissolved NiO would precipitate near the gas/salt interface, if \( P_{\text{SO}_3} \) is relatively low. According to Reaction (14), high \( P_{\text{SO}_3} \) is equivalent to low \( a_{\text{O}_2} \). Therefore, this model can also be called "acidic fluxing".

One criterion for scale fluxing is that a negative gradient in the solubility of the protective oxide is developed as a result of a gradient in \( a_{\text{O}_2} \) (or \( P_{\text{O}_2} \)) in the salt phase. This criterion was illustrated schematically recently by Rapp and Goto\(^{25}\) in Fig. 10 in terms of an oxide solubility diagram. In the figure, dashed lines show the positions of respective interfaces: I, the oxide/salt interface and II, the gas/salt interface. The right-hand case C illustrates acidic fluxing, and on the left, basic fluxing, case A, is illustrated. Whenever the interfacial activities would straddle the minimum solubility, case B, oxide precipitation and hot corrosion should be favored. In each of these cases, a negative gradient in the solubility of protective oxide is achieved at the oxide/salt interface.
3. Pseudo-scale Model

Reising opposed the fluxing model described in the preceding section. According to this model, which is denoted as "pseudo-scale model", a salt coating can be considered as a kind of scale, through which both oxygen molecules and cations can migrate. In the cases of high-temperature oxidation of metals and alloys by gases (i.e., no molten salt present), dominant one-way diffusion of the cations toward the scale/air interface causes a dense, adherent metal surface is coated with molten salt, the following reaction would take place at the metal/salt interface:

\[
\text{Ni} + 1/2\text{O}_2 \rightarrow \text{NiO} \quad \text{(42)}
\]

The nickel ions formed would diffuse toward the gas/salt interface by virtue of the concentration gradient established. Therefore, two-way diffusion, i.e., Ni\(^{2+}\) cations out and oxygen molecules in through the salt takes place as in Fig. 11, and thus, a porous oxide scale is formed. Figure 11 shows that the nickel ions are thermodynamically unstable as they approach the gas/salt interface, where they form a porous oxide structure by Reaction (43).

\[
\text{Ni}^{2+} + \text{O}^2^- \rightarrow \text{NiO} \quad \text{(43)}
\]

When sufficient porous nickel oxide scale has been produced as shown in Fig. 11, the accelerated oxidation ceases. Then, a non-porous film begins to form as shown in Fig. 11 (D).

Reising examined the effects of alloying elements like molybdenum, tungsten and chromium on Na\(_2\)SO\(_4\) hot corrosion. Alloys with more than 20% chromium developed a protective chromium sesquisulfide layer, and thus, do not exhibit accelerated oxidation.

Although the model of Cutler and Grant\(^{43}\) incorporates a consideration of the cathodic reduction of a gaseous oxidant, namely SO\(_3\) to SO\(_2\) and O\(^2-\) at the oxide/salt interface, their suggested mechanism can also be called the "pseudo-scale model". Cutler and Grant attribute hot corrosion to the gradual increase in the formation of a metal sulfide beneath an imperfectly protective oxide layer contacting the salt. Then the steady-state corrosion process is caused by balanced fluxes of sulfur and oxygen through the salt film (as SO\(_4\)) in series with a transport of sulfur and oxygen (atoms or ions?) through the oxysulfide scale. The ratio of sulfur to oxygen fluxes through the scale is supposed to equal the ratio of MS to MO activities at the scale/salt interface. To support their theory, Cutler and Grant\(^{43}\) compared the relative amounts of sulfide to oxide formed experimentally to those calculated from diffusion flux equations.

4. Formation of Volatile Products

Oxidation of chromia-forming alloys is accelerated, either when a gaseous environment or a salt coat contains some amount of sodium chloride.\(^7\) After exposure to sodium chloride, the alloy surface is generally covered with blistered and cracked layers. Davin et al.\(^{9}\) attribute this blistering to the formation of volatile metallic chlorides, like NiCl\(_2\), in locally reducing conditions. When these chlorides are exposed to oxidizing conditions, they transform to oxides, releasing Cl\(_2\) or HCl gas, as shown schematically in Fig. 12. Jones\(^7\) gave the similar explanation. Hurst et al.\(^{91}\) postulated an alternative mechanism. Gaseous NaCl is suggested to reach the alloy surface below the oxide scale; NaCl(g) is likely to penetrate through microcracks in the oxide and form volatile chromium oxychlorides, for example, Cr\(_2\)O\(_3\)Cl\(_2\)(g) which may cause scale lifting and cracking. Once the protective oxide film is broken, fresh salt with high oxygen potential and high sodium chloride concentration can make direct contact with the metal surface, as schematically shown in Fig. 13. However, Fryburg et al.\(^{44}\)

![Fig. 11. Pseudo-scale mechanism proposed by Reising.\(^{21}\)](image)

![Fig. 12. Schematic diagram for a model of volatile product formation. (Davin et al.\(^{9}\))](image)

![Fig. 13. Schematic diagram for an alternate model of volatile product formation. (Hurst et al.\(^{91}\))](image)
Thay detected no chromium chlorides or oxychlorides oppose this model. They examined volatile products in hot corrosion of superalloys exposed to O₂ containing NaCl gas by high-pressure mass spectrometry. They detected no chromium chlorides or oxychlorides in the vapor phase.

5. Local Cell Model

The idea that some electrochemical process takes place in accelerated oxidation induced by a molten salt is very old and quite logical. Simons et al. already examined the effect of an applied electrical potential.

The pertinent electrochemical process may involve not only oxidation of the metal and reduction of an oxidant but also the subsequent fluxing of the oxide scale. The recently proposed mechanism of hot corrosion by Rapp and Goto for a pure metal is illustrated in Fig. 14. The electrochemical reaction can be divided into two half-reactions. At the metal/salt interface, anodic half-reaction takes place:

\[ M = M^{3+} + 2e \]  

A variety of cathodic half-reactions are possible, and these might occur at either the oxide/salt interface as in Fig. 14 (a) or under exceptional circumstances at the gas/salt interface (Fig. 14 (b)). In Fig. 14 (a), oxygen or SO₂ molecules permeate through the salt to the oxide/salt interface, where the reduction process generates a locally basic condition;

\[ \frac{1}{2}O_2 + 2e = O^{2-} \]  
\[ SO_2 + 2e = O^{2-} + SO_2 \]

The alternate possibility is shown in Fig. 14 (b) if a transition metal impurity should exist with sufficiently high concentration in the salt. At the oxide/salt interface, the following reaction could occur:

\[ Me^{2+} \text{(oxide)} + Me^{3+} \text{(melt)} = 2Me^{3+} \text{(melt)} \]  
\[ + h \text{(oxide)} \]

Either multivalent transition cations would diffuse through the salt to the gas/salt interface, or else for sufficient Me content, electronic hopping may occur in the salt to move the electrochemical reduction reaction to the gas/salt interface.

\[ 2Me^{3+} + \left\{ \frac{1}{2}O_2 \right\} = 2Me^{3+} + \left\{ O^{2-} + SO_2 \right\} \]

Subsequently, trivalent transition cations would diffuse in the opposite direction. Reaction (47) would move the side of high local basicity to the gas/salt interface. As a special case, the corrod ing metal could also serve as the alloyvalent cation.

Rapp and Goto suppose that the electrochemical reduction reaction generates high local basicity at the cathode, which is important in setting up a gradient for the solubility of the protective oxide, as illustrated in Fig. 10. The criterion for continuing hot corrosion

\[ \frac{d}{dx} \text{(solubility)} < 0 \]

should lead to a reprecipitation of dissolved oxide within the salt film, as shown in Fig. 8. The thinning in the protective oxide to produce nonprotective reprecipitated oxide particles in the salt leads to accelerated metal recession and consumption of the protective component. For an alloy, depletion of the protective component in this way should lead to the formation of stable sulfides or oxides of poorly protective components, such that a liquid phase or a fast growing solid will lead to rupture and destruction of the protective film. This model integrates the electrochemical and oxide/salt chemistry, but experimental verification is not yet complete.

V. Critique of Models and Suggested Experiments

Generally, the acidic-basic fluxing model is most acceptable for an oxyanion salt such as sulfate, nitrate, or carbonate. Although hot corrosion of pure nickel by a Na₂SO₄ deposit seems to be qualitatively explained by the model, sulfide formation plays an important role to disrupt the protective NiO film. When alumina-forming alloys are corroded by Na₂SO₄, the sulfidation mechanism cannot be neglected, because oxidation of aluminum sulfide has been proved very fast. The Reising pseudo-scale model does not explain why Reactions (42) and (43) go to the right at the metal/salt and gas/salt interfaces, respectively. At first glance, NaCl-KCl induced hot corrosion would not seem to fit the acidic-basic fluxing mechanism, because oxyhalide ions would not be stable at high temperature. However, the salt must exhibit a definite oxygen solubility and a definite oxygen ion

![Fig. 14.](image-url)
activity in the presence of oxygen, which is indeed the oxidant reduced by the corrosion reactions. The effect of NaCl addition to salt deposits and that of NaCl vapor on gaseous scaling are still open to question, although the formation of volatile products seems likely to explain some observations.

Although each model has been summarized above qualitatively, satisfactory quantitative verification has not been given for any model. Therefore, the next step would require the formulation of rate equations for the models. A most important, but uncertain, part of the reaction mechanism is the nature and site of the cathodic reduction for different conditions of salt thickness and gas and salt compositions. Solubility data for O₂ and SO₂ in Na₂SO₄ by Andersen and diffusivity data for O₂ in the same salt by John and Shores show that neither O₂ nor SO₂ diffusion in Na₂SO₄ is sufficiently rapid to support rapid hot corrosion. In agreement with Cutler and Grant, SO₄ reduction seems to be required. Further determinations of oxide solubilities as functions of salt basicity and oxygen ion activity are required.

Electrochemical corrosion studies and polarization studies involving only thin salt films, as suggested by Rapp and Goto are required to establish the gradients in salt chemistry and the associated gradients in oxide solubility in thin salt films. The magnitude of the electrochemical corrosion current at the corrosion potential for thin film corrosion should provide the corrosion rate. But the relative contributions to rate control by diffusion in the scale, a charge transfer reaction at the cathode, a dissolution reaction at the scale/salt interface, and ionic and molecular diffusion in the salt have not been sorted out.

Formulaion of diffusion flux for a soluble ionic product, such as Ni²⁺ is not so simple, because the flux is a linear function of the gradient in the electrochemical potential of the ionic species itself, as well as that for each other ionic species. Then for the acidic dissolution of NiO, according to Goto et al.:  

$$rate = A(j_{Ni^{2+}})$$  

$$j_{Ni^{2+}} = -L_{11} \frac{d\gamma_{Ni^{2+}}}{dx} - L_{12} \frac{d\gamma_{Na^+}}{dx} - L_{13} \frac{d\gamma{S^{2-}}}{dx} - L_{14} \frac{d\gamma{O^2-}}{dx} \ldots (51)$$

where A is the total area, γ is the electrochemical potential, and 1, 2, 3, 4, denote Ni²⁺, Na⁺, S²⁻, O²⁻, respectively, and L₁ is the transport coefficient. Although the rate equation is set up as described above, quantitative estimation of such equations is not possible at present. Future determination of the transport coefficients L₁ in the salt can be done by measuring electrical conductivity, internal transfer number, tracer diffusivities, and interdiffusivities in the molten salt.

Acknowledgements

This paper has resulted from a cooperative Japan–USA research effort on Hot Corrosion of Metals funded by the U.S. National Science Foundation grant INT 77-17720 and by Japan Society for the Promotion of Science.

REFERENCES


34) Y. Kaneko and K. S. Goto: to be published.


46) R. C. John and D. A. Shores: unpublished research.