Mechanism of Corrosion of Ni Base Superalloys by Molten Na$_2$MoO$_4$ at Elevated Temperatures

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Prepared for the Fall Meeting of the Electrochemical Society Washington, D.C., October 9–14, 1983
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BY MOLTEN Na₂MoO₄ AT ELEVATED TEMPERATURES

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SUMMARY

The corrosion of nickel base superalloy, U-700, by molten Na₂MoO₄ has been studied in the temperature range 750° to 950° C. After an induction period, the rate of corrosion is linear and catastrophic corrosion is observed. The induction period is shown to be associated with the attainment of a minimum MoO₃ activity in the melt, which corresponds to the equilibrium MoO₃ activity for the reaction, 2MoO₃(γ) + Mo = 3MoO₂(s). A mechanism is proposed to describe the catastrophic nature of corrosion, which involves transport of Ni⁺⁺ through the melt resulting in formation of NiO at the melt-gas interface and basic fluxing of Cr₂O₃. The effect of the amount of Na₂MoO₄ on the corrosion kinetics has also been studied. Evaporation studies and the thermodynamic calculations for the Na₂MoO₄ - MoO₃ system have shown that the activity of MoO₃ is reduced considerably when dissolved in Na₂MoO₄, thus causing a sharp decrease in the rate of evaporation of MoO₃ from a Na₂MoO₄ - MoO₃ melt.

INTRODUCTION

Hot corrosion in aircraft combustion turbines is associated with the deposition of Na₂SO₄ on the blade and vane surfaces. The mechanism of hot corrosion of superalloys and coating systems have been studied by several investigators in the recent past (refs. 1 to 4). In general, the superalloys,
depending on the chemical composition, exhibit two different forms of corrosion; (1) accelerated corrosion, (2) catastrophic corrosion (ref. 1). The accelerated corrosion is associated with the formation of sulfides in the alloy, which increases the Na$_2$O activity of the Na$_2$SO$_4$ melt. The basic melt dissolves the protective oxides, thus causing accelerated corrosion. This form of corrosion has been observed for alloy systems containing no refractory elements, e.g., W, Mo, V.

Catastrophic corrosion has been observed in laboratory tests for alloy systems containing the refractory elements, i.e., W, Mo, and V. Goebel, Pettit and Goward (ref. 1) have postulated the acidic fluxing mechanism, in which the refractory metal oxides (MoO$_3$, WO$_3$, V$_2$O$_5$) dissolve in the Na$_2$SO$_4$ melt and thus increase the acidity of the salt melt. The acidified Na$_2$SO$_4$ melt then dissolves the other oxides like NiO, Al$_2$O$_3$, CoO, etc., thus resulting in catastrophic corrosion. Goebel and Pettit (ref. 6) have also shown that the presence of Na$_2$SO$_4$ is not essential in inducing catastrophic corrosion in the alloys containing refractory elements. In their studies, catastrophic corrosion could also be induced by Na$_2$WO$_4$. Catastrophic corrosion can also be induced by passing MoO$_3$ vapor over the Na$_2$SO$_4$ coated sample, as has been observed by Peters, et al. (ref. 5), and Goebel and Pettit (ref. 6). Bourhis and St. John (ref. 7) have shown that the catastrophic corrosion of superalloys containing Mo is due to fluxing by MoO$_3$, which is formed at the scale-metal interface. Studies in this laboratory (refs. 3 and 8) have shown that all the Na$_2$SO$_4$ was converted to Na$_2$CrO$_4$ much before the onset of catastrophic corrosion for superalloys containing Mo. The onset of catastrophic corrosion was marked by the conversion of Na$_2$CrO$_4$ to Na$_2$MoO$_4$, and frequently the scale-metal interface showed a Mo rich layer. The catastrophic corrosion was associated with the fluxing by a Na$_2$MoO$_4$ – MoO$_3$ mixture. Although it is well established that the catastrophic corrosion of superalloys containing Mo is due to the formation of Na$_2$MoO$_4$ and a Na$_2$MoO$_4$ – MoO$_3$ mixture, the mechanisms of the catastrophic corrosion are not clear. The present study is, therefore, aimed at understanding the mechanism of corrosion by Na$_2$MoO$_4$ at elevated temperatures.
EXPERIMENTAL

The alloy studied was cast U-700 (composition in weight percent = Cr 14.3, Co 15.0, Mo 4.1, Ti 3.56, Al 4.28, Ni balance). The test samples were coupons, approximately of size 23.5 by 10.8 by 2.3 mm with a hangdown hole in one end. All surfaces were glass bead blasted to give a uniform surface finish. The coupons were cleaned ultrasonically in trichloroethylene, detergent, distilled water, acetone and alcohol and then dried in an oven at 120 °C. The samples were coated with Na₂MoO₄ by air brushing a saturated solution of the salt onto the coupons which were heated on a hot plate to 200 °C. A few experiments were also conducted with a coating of either MoO₃ or a Na₂MoO₄ - MoO₃ mixture. The compound MoO₃ is not highly soluble in water. Therefore, for experiments in which a coating MoO₃ was desired, a slurry of MoO₃ in water was made and the slurry was air brushed onto the coupons. For a coating of the Na₂MoO₄ + MoO₃ mixture, the slurry of MoO₃ was first air brushed onto the coupons, and then Na₂MoO₄ was sprayed onto the MoO₃ coated sample. The corrosion experiments were performed in a vertical tube furnace. The flow of oxygen was downward at 100 cm min⁻¹. Continuous gravimetric measurements were made with a microbalance. The temperature range of interest in the present studies is 750 °C to 950 °C. The test samples, corroded for different lengths of time, were washed in hot distilled water and the solution was analyzed for various water soluble elements. The corroded samples were examined by metallography, SEM and electron probe micro analysis.

RESULTS

Kinetics. - Corrosion tests were carried out for Na₂MoO₄ coated U-700 samples under various conditions, the principal variables being the amount of Na₂MoO₄ and temperature. Figure 1 shows the schematic of the corrosion kinetics, which is valid for all the temperatures studied. The weight gain versus time curve can be characterized by four distinct stages; (1) induction period, (2) period of catastrophic corrosion, during which the weight gain versus time curve is linear, (3) period of decelerating corrosion, (4) period of parabolic oxidation, during which the rate of corrosion is nearly the same as that of oxidation in O₂ only. In subsequent figures, while presenting
aspects of the corrosion kinetics, all four stages will not be shown. The last two stages, e.g., the period of decelerating corrosion and the period of parabolic oxidation will be frequently omitted. This is done primarily to maintain clarity in presenting the graphs.

The length of the induction period is dependent on both temperature and amount of Na$_2$MoO$_4$ on the sample. At a given temperature, the length of the induction period increases with an increase in the amount of Na$_2$MoO$_4$. This is shown in figure 2. From figure 2, it is also seen that the slope of the curve during the linear period of catastrophic corrosion is almost the same for all the doses of Na$_2$MoO$_4$. This is true for all the temperatures studied. Figure 2 also shows that at the same temperature the total weight gain or the extent of corrosion at the end of the period of decelerating corrosion increases with an increase in the amount of Na$_2$MoO$_4$.

The rate of corrosion during the linear period of catastrophic corrosion (as obtained from the slope of the straight line) decreases with a decrease in temperature. This is shown in figure 3, which shows the corrosion kinetics at different temperature for a fixed amount of Na$_2$MoO$_4$. As mentioned earlier, the rate of corrosion during the linear period of catastrophic corrosion is the same irrespective of the amount of Na$_2$MoO$_4$. The temperature dependence of the length of the induction period is a strong function of the amount of Na$_2$MoO$_4$. Table I shows the length of the induction period at different temperatures as a function of the amount of Na$_2$MoO$_4$. For low doses (~1 mg/cm$^2$), the length of the induction period decreases with a decrease in temperature. At 750°C, virtually no induction period was observed for this dose of Na$_2$MoO$_4$. For intermediate doses (~2.5 mg/cm$^2$), the length of the induction period decreases with a decrease in temperature, attains a minimum at 850°C, and increases again with a decrease in temperature. For heavy doses (~4.5 mg/cm$^2$), the length of the induction period increases with decrease in temperature.

For the same amount of Na$_2$MoO$_4$, the weight gain or the extent of corrosion at the end of the period of decelerating corrosion increases with a decrease in temperature. This is shown in figure 4, which gives the corrosion kinetics at 950°C and 850°C for a dose of 0.49 mg/cm$^2$ Na$_2$MoO$_4$. 
Chemical analysis. - The U-700 coupons, corroded for different lengths of time at 950° C, were washed with hot distilled water and chemically analyzed for various elements. The solubility of various compounds of NiO, Cr₂O₃ and Al₂O₃ with MoO₃ (e.g., NiO • MoO₃, Cr₂O₃ • MoO₃, Al₂O₃ • MoO₃) in water is presumed to be low. Thus no appreciable amounts of Ni, Co, Cr, or Al were detected in the water washed solution. However, Na₂MoO₄ is soluble in water and the compound MoO₃ is fairly soluble in water. Therefore the chemical analysis showed the presence of appreciable amounts of Na and Mo in the solution. The results of the chemical analysis are shown in figure 5 for two different amounts of Na₂MoO₄. The corresponding weight gain curves are also superimposed on the plot of soluble species versus time. Figure 5(b) shows that the Mo concentration in the solution increases slowly during the induction period, and the end of the induction period is marked by a rapid increase in the Mo concentration in the solution. The concentration of Mo continues to increase during the period of catastrophic corrosion, reaches a peak, and then decreases until the end of corrosion. The time, at which the concentration of Mo starts to decrease, coincides with the beginning of the period decelerating corrosion. The Na concentration in the water washed solution decreases continuously with the progress of time.

Corrosion by Na₂MoO₄ - MoO₃ mixture. - The results of the chemical analysis clearly demonstrates that the end of the induction period is associated with the addition of a certain amount of MoO₃ to the Na₂MoO₄ melt. To further confirm the role of MoO₃ in inducing catastrophic corrosion, additional experiments were conducted in which a slurry of MoO₃ was airbrushed on to the sample and above this, a Na₂MoO₄ layer was applied by airbrushing. The mixture applied corresponds to Na₂MoO₄ - 23 mole percent MoO₃. For comparison, the weight gain data for Na₂MoO₄ only are also presented in figure 6. It can be seen from figure 6 that when MoO₃ is added to the Na₂MoO₄ melt, the induction period decreases considerably. These results further demonstrate that addition of MoO₃ to the Na₂MoO₄ melt is a prerequisite in inducing catastrophic corrosion in this alloy.

Scale morphology. - Figure 7 shows the top surface a sample coated with 1.5 mg/cm² of Na₂MoO₄ and corroded for 15 minutes at 950° C. This represents the initial period of corrosion. Figure 7 shows the top surface to
consist of the melt and a few NiO precipitates above the melt. Figure 8 shows a typical scale morphology, that is produced during the induction period. The outer oxide layer has spalled off at several places. The spalling tendency of the outermost scale decreases with a decrease in temperature. At 750°C, no spalling of the outmost oxide was observed during this period. Examination of outermost scale at higher magnification (fig. 8(b)) shows it to be NiO precipitates. It is believed that these NiO precipitates were formed during the initial period. The region where the outermost oxide layer had spalled from the surface consists of oxide grains and a melt in between the oxide grain (fig. 8(c)). This is indicative of melt penetration through the oxide. The cross section (fig. 8(d)) shows the scale to consist of two layers. The outermost layer is NiO, which is believed to be the precipitates formed during the initial period. The inner scale is porous and EDAX analysis shows the scale to consist of all the elements in the alloy, e.g., Ni, Co, Cr, Ti, Al. However, the scale appears to be rich in Cr and Ti. EDAX analysis also shows the presence of Na and Mo in the inner scale layer. The presence of Na and Mo in the inner scale layer further demonstrates that melt penetrates the oxide in this layer. It is presumed that melt penetration occurs along the pores in the oxide.

For samples corroded for a length of time corresponding to that of the period of catastrophic corrosion, thick porous oxide scale was produced. The thick external porous scale completely spalled off on cooling for corrosion experiments at high temperatures, e.g., 950° and 900° C. The spalling tendency decreases with a decrease in temperature, and at 750°C, the spalling was minimum. Therefore to obtain the details of the complete scale during the period of catastrophic corrosion, the cross section of the samples, corroded at 750°C, were examined. Figure 9 shows the scale morphology produced during the early stage of catastrophic corrosion. The top surface consists of NiO and shows a large number of blisters (fig. 9(a)). The cross section through the blister (fig. 9(b)) shows the blisters to be formed by lifting of the scale by a melt at localized sites, thus resulting in pitting type of corrosion. The details of the cross section and the X-ray maps for various elements are shown in figure 10. The X-ray maps of the important elements, e.g., Ni, Cr and Mo are only shown. The other elements, Na, Ti, Al are present in small amounts, and X-ray maps for these elements are not shown in order to maintain simplic-
ity and emphasize the primary constituents. Co is usually observed to be present where Ni is, and therefore not shown in the X-ray maps. The X-ray maps in figure 10 show the outermost oxide layer to be primarily NiO. Beneath this NiO layer there is a layer consisting of Cr$_2$O$_3$ + NiO. This layer also contains Al, Ti and Co. These two layers, towards the scale–gas interface, were formed during the induction period (see fig. 8(d)). These oxide layers are lifted off the alloy surface by the formation of a thick Mo rich molten layer, which is seen as a solidified melt in the S • E • Image. EDAX analysis of this solidified melt layer shows the presence of Na, suggesting that this layer is a Na$_2$MoO$_4$ – MoO$_3$ mixture. As seen from the X-ray maps, the melt layer contains Ni, which is believed to be Ni dissolved in the melt. Just above the layer of solidified melt, there are precipitates consisting primarily of NiO and small amount of Cr$_2$O$_3$. Beneath the melt, there is a layer of oxide (main constituents Cr$_2$O$_3$ + NiO) on the alloy surface. A thin Mo rich layer is seen at the top of this oxide which is believed to be MoO$_2$(s). X-ray diffraction showed the presence of MoO$_2$(s) in the corroded sample.

The scale morphology during the period of catastrophic corrosion and after a time period longer than that in figure 10 is shown in figure 11. A pitting type of corrosion morphology is evident from figure 11, and the pit is seen to consist of a Na$_2$MoO$_4$ – MoO$_3$ melt (Na not shown). Ni and Cr are also observed to be there inside the pit. A thick porous oxide layer can be seen above the pit. The porous oxide layer consists of primarily NiO, and a small amount of Cr$_2$O$_3$. The outermost part of the scale, e.g., the NiO and Cr$_2$O$_3$ layer at the scale–gas interface in figure 10, have spalled off from the surface and cannot be seen in figure 11. Examination of the scale–metal interface (fig. 11(b)) shows a thin layer of oxide (~2 µm) to be present just beneath the pit. The detailed examination of the pit (fig. 12(a)) shows it to be Na$_2$MoO$_4$ – MoO$_3$ melt (Na not shown in the X-ray maps) containing dissolved Ni. Cr inside the pit is present as discrete Cr$_2$O$_3$ precipitates dispersed through the melt (fig. 12(b)).

The pitting type of corrosion morphology is observed at all temperatures during the period of catastrophic corrosion. Figure 13 shows the typical scale morphology at 950°C during the period of catastrophic corrosion. The
features are the same as that of 750° C, e.g., a pit consisting of Na$_2$MoO$_4$-MoO$_3$ melt with dissolved Ni and discrete Cr$_2$O$_3$ precipitates and a thin oxide layer at the pit-alloy interface. However, the external porous oxide layer had spalled off while cooling.

From the thermogravimetric results it is known that at lower temperatures, 750° and 850° C, a very long time is required for the corrosion to come to an end. Therefore the cross section of a sample, corroded at 950° C, for a time period corresponding to the end of the period of decelerating corrosion will be examined. Figure 14 shows such a cross section and the X-ray maps for various elements. The pitting type of corrosion morphology is still observed. However, the pit no longer consists of a thick Na$_2$MoO$_4$ - MoO$_3$ liquid with dissolved Ni and discrete Cr$_2$O$_3$ precipitates. Now, the pit consists of only discrete NiO and Cr$_2$O$_3$ precipitates. All the MoO$_3$ or compounds of Mo appear to have disappeared from the pit. A layer of NiO + Cr$_2$O$_3$ is observed beneath the pit. The examination of the scale-metal interface at a higher magnification shows internal Al$_2$O$_3$ stringers, which were not observed in the cross section during the induction period and the period of catastrophic corrosion. These internal Al$_2$O$_3$ stringers are typical of the scale morphology for the alloy U-700, oxidized in air or O$_2$ without any salt being present.

DISCUSSION

The thermogravimetric results have shown that corrosion of U-700 beneath a Na$_2$MoO$_4$ melt involves a period of catastrophic corrosion, during which the rate of corrosion is linear and significantly higher than the rate of oxidation in O$_2$ alone. A linear rate of corrosion or accelerated corrosion is due to the development of a non-protective corrosion product layer. One of the ways by which a protective corrosion product layer cannot be developed beneath a layer of molten salt is the dissolution of the oxides in the melt. This is the conventional fluxing process, originally proposed by Bornstein and Decrescente (ref. 2) and later modified by Goebel, Pettit and Goward (ref. 1), to describe the hot corrosion of nickel base superalloys. In the fluxing process, the oxides are dissolved at the salt-oxide interface and again reprecip-
itated at the salt-gas interface. The dissolution is either basic or acid depending on the Na$_2$O activity in the melt. Rapp and Goto (ref. 9) have proposed a model in which the fluxing process requires a negative solubility gradient at the salt-oxide interface for the oxide in question.

Thermodynamic consideration. - In order to determine the corrosion mechanism, it is instructive to examine the fluxing process beneath the Na$_2$MoO$_4$ melt. For clarity the calculations will be presented only at 1200 K and for oxides of Ni and Cr. Similar to that for Na$_2$SO$_4$, the dissolution of the oxides in the Na$_2$MoO$_4$ melt is dependent on the Na$_2$O activity in the melt. The Na$_2$O activity in the Na$_2$MoO$_4$ melt is governed by the equilibrium conditions for the reaction:

\[ \text{Na}_2\text{MoO}_4(\alpha) = \text{Na}_2\text{O}(\alpha) + \text{MoO}_3(\alpha) \quad (1) \]

\[ K(1) = \frac{\alpha_{\text{Na}_2\text{O}} \cdot \alpha_{\text{MoO}_3}}{\alpha_{\text{Na}_2\text{MoO}_4}} = 3.17 \times 10^{-15} \quad (2) \]

Where $K(1)$ is the equilibrium constant for reaction (1), $\alpha_{\text{Na}_2\text{O}}$, $\alpha_{\text{MoO}_3}$ and $\alpha_{\text{Na}_2\text{MoO}_4}$ are the activity of Na$_2$O, MoO$_3$ and Na$_2$MoO$_4$ in the melt, respectively. Rapp and his coworkers (refs. 10 and 11) have determined the solubility of various oxides as a function of $\alpha_{\text{Na}_2\text{O}}$ in the Na$_2$SO$_4$ melt, and this is shown schematically in figure 15. Figure 15 exhibits a solubility minima at a certain Na$_2$O activity in the melt. For salts other than Na$_2$SO$_4$ the slopes of the acid and basic dissolution lines are expected to remain the same, although the curves might sift upward or downward depending on the thermodynamic stability of the products of dissolution of the oxides in the salt. However, the Na$_2$O activity, at which the solubility minima is obtained is expected to be the same for different salts.

From Gupta and Rapp's (ref. 11) measurement of the solubility of NiO in molten Na$_2$SO$_4$ as a function of $\alpha_{\text{Na}_2\text{O}}$ at 1200 K, the solubility minima lies at $\alpha_{\text{Na}_2\text{O}}$ equal to $10^{-10}$. Assuming also for the Na$_2$MoO$_4$ melt that the solubility minima lies at the same Na$_2$O activity, according to equation (2) this would correspond to $\alpha_{\text{MoO}_3}$ in the melt equal to $3.17 \times 10^{-5}$. From Stroud and Rapp's (ref. 10) measurement of the solubility of Cr$_2$O$_3$ in
molten Na$_2$SO$_4$, the solubility minima, for oxygen pressure of 1 atm, lies somewhere around Na$_2$O activity equal to $10^{-14}$. From equation (2) this would correspond to $a_{MoO_3}$ in the melt equal to 0.25. The activity of MoO$_3$ in the melt is determined by the thermodynamic properties, e.g., partial molar properties of MoO$_3$ in the Na$_2$MoO$_4$ - MoO$_3$. Appendix B gives the details of the estimation of the thermodynamic properties of the Na$_2$MoO$_4$ - MoO$_3$ system from a study of the Na$_2$MoO$_4$ - MoO$_3$ phase diagram and rate of evaporation of the Na$_2$MoO$_4$ - MoO$_3$ mixture. The acidic fluxing mechanism requires that the MoO$_3$ activity in the melt must be greater than that corresponding to the solubility minima in the solubility versus $-\log a_{Na_2O}$ plot. Thus for the acidic dissolution of NiO, the $a_{MoO_3}$ in the melt must be greater than $3.17 \times 10^{-5}$ at 1200 K, and from the MoO$_3$ activity data in appendix B, this would correspond to approximately 10 mole percent MoO$_3$ in the melt. Similarly, for the acidic dissolution of Cr$_2$O$_3$, the $a_{MoO_3}$ in the melt must be greater than 0.25 and this would correspond to approximately 80 mole percent MoO$_3$ in the melt. Thus acidic dissolution of NiO is possible with addition of small amounts of MoO$_3$ to the melt, whereas dissolution of Cr$_2$O$_3$ requires addition of large amounts of MoO$_3$ to the melt.

**Fluxing mechanism based on O$_2$ transport through melt.** - According to the acidic fluxing mechanism, as has been proposed by Goebel and Pettit (ref. 1), and by Fryburg, et al. (ref. 3), to explain the role of molybdenum in the hot corrosion process, the oxides (NiO, Cr$_2$O$_3$, Al$_2$O$_3$) dissolve at the melt-oxide interface. It has been assumed that the oxides are formed at the melt-oxide interface. The driving force for the dissolution and reprecipitation process is the concentration gradient of MoO$_3$, $(dC_{MoO_3}/dX)$, at the melt-oxide interface. The evaporation studies and the thermodynamic calculations for the Na$_2$MoO$_4$ - MoO$_3$ melt (appendixes A and B) show that the rate of evaporation of MoO$_3$ is considerably reduced when dissolved in Na$_2$MoO$_4$. The vaporization of MoO$_3$ would only be important at high concentration of MoO$_3$. Thus the concentration of MoO$_3$ in the melt would continue to rise with the progress of time, thereby reducing the magnitude of the driving force $(dC_{MoO_3}/dX)$, at the melt-oxide interface. The magnitude of the driving force is continuously reduced with the progress of time until the rate of formation of MoO$_3$ at the melt-oxide interface becomes equal to the rate of evaporation of MoO$_3$ at the melt-gas interface. After this time period, the
concentration gradient of MoO₃ across the melt remains constant and therefore, the rate of dissolution-precipitation reaction would remain constant. In terms of weight gain, this would mean an initial high rate of weight gain, the rate decreasing with time until a steady state is reached during which the rate of weight gain remains constant. The rate of weight gain during the steady state would be less than the initial rate. The experimentally observed thermogravimetric curves show just the opposite of this e.g., the rate of weight gain during the linear period of catastrophic corrosion is higher than the initial rate. In the above analysis it has been assumed that the oxides formed at the melt-alloy interface are non-protective because of the dissolution of oxides in the melt.

In the mechanism, in which acidic dissolution of oxides takes place at the melt-oxide interface with subsequent reprecipitation at a distance away from this interface, the oxides are formed at the melt-oxide interface. This requires the transport of O₂ through the melt to the salt-oxide interface, where oxidation of Mo, Ni, Cr, Al takes place. The maximum flux of O₂ through the melt is given by the expression,

\[ J = D \frac{C_o}{\delta} \tag{3} \]

where

J \hspace{1cm} \text{flux, moles/cm}^2\text{-sec} \\
D \hspace{1cm} \text{diffusion coefficient of O}_2 \text{ in the Na}_2\text{MoO}_4 \text{ melt, cm}^2/\text{sec} \\
C_o \hspace{1cm} \text{solubility of O}_2 \text{ in the melt, moles/cm}^3 \\
\delta \hspace{1cm} \text{thickness of the melt, cm}

The measurement of weight gain gives the flux of O₂ and thus, the maximum weight gain for different melt thicknesses can be calculated from equation (3). Anderson (ref. 12) has measured the solubility of O₂ in the molten Na₂SO₄, which is about 2x10⁻⁷ moles/cm³ at 900° C. The solubility of O₂ in molten salts is governed by the equilibrium criteria for the reactions (ref. 12):

\[ \text{Na}_2\text{O} + \frac{1}{2} \text{O}_2 = \text{Na}_2\text{O}_2 \]
In the present studies, the chemical analysis of the corroded samples shows that MoO$_3$ is being continuously added to the melt, thereby decreasing the Na$_2$O activity in the melt. Therefore the solubility of molecular O$_2$ in a Na$_2$MoO$_4$ - MoO$_3$ melt is expected to be lower than the measured value for the solubility in molten Na$_2$SO$_4$. However, for a conservative estimate of the maximum flux of O$_2$ through the melt, it can be assumed that the solubility of molecular O$_2$ in Na$_2$MoO$_4$ is the same as that in Na$_2$SO$_4$. Using the value of 2x10$^{-7}$ mole/cm$^3$ for the solubility of O$_2$ in molten Na$_2$MoO$_4$, and 5x10$^{-5}$ cm$^2$/sec (ref. 9) for the diffusivity of O$_2$ in molten Na$_2$MoO$_4$, the maximum weight gain for melt thicknesses of 10, 50 and 100 µm are calculated to be 1.15, 0.23 and 0.115 mg/cm$^2$/hr, respectively at 900°C. From thermogravimetric measurements, the weight gain during the linear period of catastrophic corrosion is of the order of 1.261 mg/cm$^2$/hr. The cross section of the corroded sample during the period of linear corrosion at 900°C shows the depth of the pit to be about 80 to 100 µm. Thus weight gain calculated on the basis of maximum flux of O$_2$ through the melt is much less than the observed weight gain. Clearly, then, the acidic fluxing mechanism based on the transport of O$_2$ through the melt cannot account for the rapid weight gain observed during the linear period of catastrophic corrosion. However, this mechanism may be important during the initial period of corrosion.

Fluxing mechanism based on Mo$^{4+}$/Mo$^{6+}$ Exchange reaction. - In oxides, Mo is known to exist in two different oxidation states, e.g., Mo$^{4+}$ and Mo$^{6+}$. In the oxidation of Mo, a thin layer of MoO$_2$ is usually observed in between the Mo and the external MoO$_3$ layer. In a Na$_2$MoO$_4$ - MoO$_3$ melt, two different oxidation states of Mo are also possible, i.e., dissolved MoO$_2$ and MoO$_3$. Indeed, recent electrochemical studies by Hellstorm (ref. 13) have shown that in a Na$_2$SO$_4$ - Na$_2$MoO$_4$ melt, Mo can exist in oxidation states other than Mo$^{6+}$. Rapp and Goto (ref. 9) have proposed a hot corrosion mechanism, in which the melt can be an electronic conductor, if an ion exists in two different oxidation states. The electron conduction arises due to the valence change electron transfer mechanism. A similar mechanism has also been proposed by Luthra (ref. 14) for the transport of Co through the
\( \text{Na}_2\text{SO}_4 - \text{CoSO}_4 \) melt in low temperature hot corrosion process. Assuming that Mo exists in the \( \text{Na}_2\text{MoO}_4 - \text{MoO}_3 \) melt as Mo\(^{+6}\) and Mo\(^{+4}\), (dissolved MoO\(_3\) and MoO\(_2\)), the exchange reaction in the melt can be described by the reaction:

\[
\text{MoO}_2 + \frac{1}{2} \text{O}_2 = \text{MoO}_3
\]

(6)

where \( a_{\text{MoO}_3} \) and \( a_{\text{MoO}_2} \) are the activity of MoO\(_3\) and MoO\(_2\) in the melt, respectively. Since the oxygen pressure at the melt-gas interface is higher than the melt-oxide interface, the concentration of Mo\(^{+6}\) species will be greater at the melt/gas interface, and the concentration of Mo\(^{+4}\) species will be greater at the melt-oxide interface. This would result in migration of Mo\(^{+6}\) inward from the melt-gas to the melt-oxide interface, and migration of Mo\(^^{+4}\) outward from the melt-oxide interface. At the melt-oxide interface, the Mo\(^{+6}\) ions are reduced to Mo\(^{+4}\) by reaction with Mo, and at the melt-gas interface, Mo\(^{+4}\) ions are oxidized to Mo\(^{+6}\). In a manner similar to that oxidation of Mo in \( \text{O}_2 \) alone (ref. 15), a thin layer of MoO\(_2\)(s) is assumed to be present at the alloy-melt interface. The oxidation of Mo beneath \( \text{Na}_2\text{MoO}_4 - \text{MoO}_3 \) melt is schematically shown in figure 16. As shown in figure 16, MoO\(_3\) is formed at the melt-gas interface. The reaction mechanism shown in figure 16 is equivalent to the following reactions:

At the melt-oxide interface:

\[
2\text{MoO}_3 + \text{Mo} \text{ (diffusing through the oxide)} = 3\text{MoO}_2
\]

(8)

At the melt-gas interface:

\[
3\text{MoO}_2 + 3/2 \text{O}_2 = 3\text{MoO}_3
\]

(9)

At the salt-oxide interface, the melt is in equilibrium with solid MoO\(_2\). Therefore, the minimum \( a_{\text{MoO}_3} \) necessary for reaction (8) to proceed in the forward direction is governed by the equilibrium conditions for the reaction:

\[
2\text{MoO}_3 + \text{Mo} = 3\text{MoO}_2(s)
\]

(10)
The activity of \( \text{MoO}_2(s) \) is unity and assuming \( a_{\text{Mo}} \) to be unity, the equilibrium \( a_{\text{MoO}_3} \) for reaction (11) at 1200 K is calculated to be \( 1.695 \times 10^{-5} \). From the thermodynamics of the \( \text{Na}_2\text{MoO}_4 - \text{MoO}_3 \) melt (appendix B), the activity value of \( 1.695 \times 10^{-5} \) corresponds to 10 mole percent \( \text{MoO}_3 \) in the melt. Thus reaction (8) will proceed in the forward direction after the \( \text{MoO}_3 \) concentration in the melt becomes equal to about 10 mole percent. As will be seen in a later section, the minimum \( a_{\text{MoO}_3} \) in the melt necessary for reaction (10) to go in the forward reaction is the basis for the existence of the induction period.

When the activity of \( \text{MoO}_3 \) in the melt becomes equal to the equilibrium \( \text{MoO}_3 \) activity for reaction (10), the \( \text{MoO}_3 \) concentration in the melt rises rapidly because of formation of \( \text{MoO}_3 \) by \( \text{Mo}^4/\text{Mo}^6 \) exchange reaction (shown in fig. 16). Now \( \text{MoO}_3 \) component of the melt becomes the principal oxidizing species. The oxidation of Ni and Cr beneath the \( \text{Na}_2\text{MoO}_4 - \text{MoO}_3 \) melt is described by the following reaction:

\[
\text{MoO}_3 (s) + \text{Ni} = \text{MoO}_2 (s) + \text{NiO (12)}
\]

\[
3\text{MoO}_3 (s) + 2\text{Cr} = \text{Cr}_2\text{O}_3 + 3\text{MoO}_2 (s) \quad (13)
\]

At 1200 K, the equilibrium \( \text{MoO}_3 \) activity in the melt for reaction (12) is calculated to be \( 3.99 \times 10^{-3} \). From the thermodynamics of the \( \text{Na}_2\text{MoO}_4 - \text{MoO}_3 \) melt (appendix B), this would correspond to approximately 50 mole percent \( \text{MoO}_3 \) in the melt. At 1200 K, the equilibrium \( \text{MoO}_3 \) activity in the melt for reaction (13) is calculated to be \( 3.89 \times 10^{-9} \). Thus formation of \( \text{Cr}_2\text{O}_3 \) requires a low \( \text{MoO}_3 \) concentration in the melt, whereas for oxidation of Ni, a considerable amount of \( \text{MoO}_3 \) must be added to the melt for reaction (12) to go in the forward reaction. At the melt-oxide interface, \( \text{MoO}_2(s) \) is in equilibrium with \( \text{MoO}_2(\ell) \), and the dissolved \( \text{MoO}_2 \) diffuses to the melt-gas interface where it is oxidized to \( \text{MoO}_3 \). Thus reactions (12) and (13) are self-sustaining.

\[
k_{10} = \frac{(a_{\text{MoO}_2(\ell)})^3}{(a_{\text{MoO}_3(\ell)})^2 \cdot a_{\text{Mo}}}
\]
At the melt-oxide interface, the acidic dissolution of oxides can take place by reactions:

\[ \text{NiO} = \text{Ni}^{++} + 0^= \]  
(14)

\[ \text{Cr}_2\text{O}_3 = 2\text{Cr}^{+++} + 3 \text{O}^= \]  
(15)

As mentioned earlier, the criteria for acidic dissolution is that the \( \bar{\text{MoO}}_3 \) at the melt-oxide interface must be greater than that corresponding to the solubility minima in the solubility versus - log\( \bar{\text{Na}_2\text{O}} \) curve. It has been shown earlier that for the acidic dissolution of \( \text{Cr}_2\text{O}_3 \) to occur, the MoO\(_3\) activity at the melt-oxide interface must be greater than 0.25. From the thermodynamics of the \( \text{Na}_2\text{MoO}_4 - \text{MoO}_3 \) melt (appendix B), this corresponds to about 75 mole percent MoO\(_3\). The MoO\(_3\) concentration in the melt is governed by two competing factors, the rate of formation of MoO\(_3\) and rate of evaporation of MoO\(_3\). The concentration of MoO\(_3\) in the melt would remain constant when the rate of formation of MoO\(_3\) became equal to the rate of evaporation. For a melt consisting of 75 mole percent MoO\(_3\), the rate of evaporation of MoO\(_3\) could be high, and it is doubtful whether the melt can attain such a high concentration of MoO\(_3\).

The chemical analysis of the corroded samples at 950° C showed the maximum MoO\(_3\) concentration to be approximately 40 mole percent. Therefore the acidic dissolution of \( \text{Cr}_2\text{O}_3 \) would not be expected at the melt-oxide interface. Instead, at the melt-oxide interface basic dissolution of \( \text{Cr}_2\text{O}_3 \) would take place by the reaction:

\[ \text{Cr}_2\text{O}_3 + \frac{3}{2} \text{O}_2 + 2\text{O}^= = 2\text{CrO}_4^= \]  
(16)

Because of the positive gradient of MoO\(_3\) at the melt-oxide interface, the gradient of oxide ion activity is negative at the melt-oxide interface. Therefore the oxide solubility gradient is negative at the melt-oxide interface and the Rapp-Goto criterion for fluxing is satisfied, thus leading to the reprecipitation of \( \text{Cr}_2\text{O}_3 \) at some distance away from the melt-oxide interface. The scale morphology in figures 11 and 12 shows \( \text{Cr}_2\text{O}_3 \) precipitates inside the melt and in the outer precipitate layer. This is believed to be due to the basic fluxing of \( \text{Cr}_2\text{O}_3 \).
At 1200 K, the activity of MoO₃ in the melt must be greater than $3.12 \times 10^{-5}$ for acidic dissolution of NiO to take place. This value of $^{\alpha}\text{MoO}_3$ in the melt corresponds to approximately 10 mole percent MoO₃ in the melt. The $^{\alpha}\text{MoO}_3$ in the melt necessary for the acidic dissolution ($3.17 \times 10^{-5}$) is of the same order of magnitude as the minimum $^{\alpha}\text{MoO}_3$ necessary at the melt-oxide interface for reaction (10) to proceed in the forward direction ($1.695 \times 10^{-5}$). Therefore, the acidic dissolution of NiO can take place at the melt-oxide interface as described by reaction (14). However, the activity gradient for MoO₃ is positive at the melt-oxide interface because of formation of MoO₃ at the melt-gas interface. Therefore the reprecipitation of the dissolved oxides would not take place. Instead the melt will be gradually saturated with Ni⁺⁺. The overall MoO₃ concentration of the melt increases with time, thus the concentration of dissolved Ni⁺⁺ would increase with time. The scale morphologies and the X-ray maps of the corroded samples (figs. 11 and 12) show dissolved Ni in the melt, suggesting the acidic dissolution of NiO. However, the scale morphology in figures 11 and 12 also show a porous NiO layer above the melt at the melt-gas interface, which cannot be explained based on acidic fluxing of NiO at the melt-oxide interface.

In order to explain the formation of porous NiO at the salt-gas interface, the following mechanism is proposed. The mechanism is again based on Mo⁺⁶/Mo⁺⁴ exchange reaction and is schematically shown in figure 17. At the melt-oxide interface, Ni reacts with Mo⁺⁶, which is migrating from the melt-gas interface, to form Mo⁺⁴ and Ni⁺⁺ by the following reactions:

$$\text{Ni} = \text{Ni}^{++} + 2e$$

$$\text{Mo}^{+6} + 2e = \text{Mo}^{+4}$$

At the melt-gas interface, the Ni⁺⁺ ions are oxidized to NiO, and Mo⁺⁴ ions are oxidized to Mo⁺⁶ by the reactions:

$$\text{Mo}^{+4} = \text{Mo}^{+6} + 2e$$

$$\text{Ni}^{++} + 2e + \frac{1}{2} \text{O}_2 = \text{NiO}$$
At the melt-oxide interface, the reduction of Mo$^{6+}$ to Mo$^{4+}$ generates the O$^-$ ions, which are consumed by the reaction:

$$\text{Cr}_2\text{O}_3 + \frac{3}{2} \text{O}_2 + \text{O}^- = 2\text{CrO}_4^-$$  \hspace{1cm} \text{(21)}$$

The CrO$_4^-$ ions are reprecipitated to Cr$_2$O$_3$ by reverse of reaction (21) at some distance away from the melt-oxide interface inside the melt and at the melt-gas interface. The reverse of reaction (21) generates O$^-$ which combines with Mo$^{6+}$ to form MoO$_3$. Thus reactions (17) to (21) are self-sustaining. A steady state condition is attained when the melt is saturated with Ni$^{3+}$, after which the concentration gradient of Ni$^{3+}$ across the melt remains constant. Under steady state conditions a linear rate of weight gain is observed. The melt is saturated with Ni$^{3+}$; presumably when the NiMoO$_4$ concentration of the melt corresponds to the liquidus in the NiMoO$_4$ rich portion of the hypothetical Na$_2$MoO$_4$ - NiMoO$_4$ phase diagram, which is the maximum amount of NiMoO$_4$ that a fixed quantity of Na$_2$MoO$_4$ can dissolve. At the melt-gas interface NiO can also react with MoO$_3$ to form solid NiMoO$_4$.

Thermodynamic calculations for the oxidation of Ni beneath a Na$_2$MoO$_4$ - MoO$_3$ melt showed that the concentration of MoO$_3$ at the melt-oxide interface must be greater than approximately 50 mole percent for the oxidation of Ni to take place according to reaction (12). It is unlikely that such a high concentration of MoO$_3$ would be attained at the melt-oxide interface. However, according to the mechanism proposed in figure 17, NiO need not be formed at the melt-oxide interface. Instead, NiO is formed at the melt-gas interface by formation of Ni$^{3+}$ at the melt-alloy/oxide interface and subsequent transport to the melt-gas interface. Because of the higher diffusivity of Ni$^{3+}$ in the melt, the rate of oxidation can be substantially increased. The mechanisms proposed in figure 17 is consistent with the generalized criteria for fluxing that has been proposed by Luthra (ref. 15).

The mechanism, proposed in figure 17 also applies to corrosion beneath a melt consisting of MoO$_3$ only. This was confirmed by examining the cross section of samples coated with MoO$_3$ and oxidized at elevated temperatures. Figure 18 shows that scale morphology and the features are observed to be sim-
ilar to those observed for corrosion beneath a Na$_2$MoO$_4$ melt. The scale morphology in figure 18 also suggests that even for the melt consisting of MoO$_3$ only, acidic dissolution of Cr$_2$O$_3$ cannot take place at the melt-oxide interface. (The MoO$_3$ activity gradient is positive at the melt-oxide interface and acidic dissolution of Cr$_2$O$_3$ would not have produced the Cr$_2$O$_3$ precipitates inside the melt.)

In order for the mechanism proposed in figure 17 to be operative, the alloy must contain Cr because the O$^-$ ions (generated at the melt-oxide interface due to reduction of Mo$^{+6}$ to Mo$^{+4}$) react with Cr$_2$O$_3$ to form CrO$_4^{2-}$. The precipitation of CrO$_4^{2-}$ to Cr$_2$O$_3$ and O$^-$ takes place at the melt-gas interface. If oxidation of Mo$^{+4}$ to Mo$^{+6}$ at melt-gas interface by reaction (19) is to occur, O$^-$ needs to be supplied to maintain electrical neutrality. To confirm this, a coupon of nickel was coated with 2.62 mg/cm$^2$ of Na$_2$MoO$_4$ + 0.5 mg/cm$^2$ MoO$_3$ and oxidized at 950° C. The weight gain was only 4.08 mg/cm$^2$ at the end of 18 hr. For U-700, the weight gain for the same time period was of the order of 36 mg/cm$^2$. Brenner (ref. 16) has studied the oxidation of Fe-Mo alloys and Fe-Mo alloys containing Cr and has shown that Fe-Mo alloys containing up to 20 percent Mo were not oxidized very rapidly in air at 1000° C. However, addition of Cr to the alloy caused catastrophic oxidation. This is consistent with our mechanism and clearly shows that the alloy must contain Cr for the accelerated corrosion to occur.

Sequence of corrosion reactions. - When the alloy is oxidized beneath the Na$_2$MoO$_4$ melt, during the transient stage of oxidation, oxides of all the elements in the alloy are formed beneath the melt, the oxidants being supplied by the transport of O$_2$ through the melt. MoO$_3$ is also formed on the alloy surface, which dissolves in the Na$_2$MoO$_4$ melt at the melt-oxide interface. The activity of MoO$_3$ at the melt-oxide interface is high and therefore acidic fluxing of oxides takes place. Because of the negative gradient in the MoO$_3$ activity at the melt-oxide interface, the dissolved oxide is reprecipitated at the salt-gas interface. Discussion of fluxing process beneath the Na$_2$MoO$_4$ melt showed that this mechanism can not account for the experimentally observed weight gain and the nature of the thermogravimetric curve. Therefore this process of dissolution-reprecipitation is only of importance during the initial period of corrosion.
The results of the chemical analysis (fig. 5) show that the MoO$_3$ content of the melt increases slowly during the induction period and the end of induction period is marked by a rapid increase in the MoO$_3$ content of the melt. Consideration of the oxidation and fluxing mechanism beneath the Na$_2$MoO$_4$ melt showed that rapid oxidation of Mo takes place when Mo oxidizes according to the Mo$^{4+}$/Mo$^{6+}$ exchange reaction as shown in figure 16. For the oxidation of Mo to occur by this scheme it was also shown that the MoO$_3$ activity in the melt must attain a minimum value. The minimum $\theta$MoO$_3$ in the melt was calculated to be $1.695 \times 10^{-5}$ (10 mole percent MoO$_3$) at 1200 K. However, the mechanism by which MoO$_3$ is being added to the melt during the induction period is not clear. Shores (ref. 17), based on transport calculations through the melt, has concluded that for IN738 the oxide which developed beneath a Na$_2$SO$_4$ melt was porous and the melt could fill these pores. A similar situation is likely to exist for the oxides beneath a Na$_2$MoO$_4$ melt. This is evidenced in figure 8(c), which shows the melt penetration through the oxide. Also the EDAX analysis of the inner scale in figure 8(d) shows the presence of Na and Mo in the scale. Thus, during the induction period, it is believed that a porous nonprotective scale is formed and the melt is dispersed in the pores through out the oxide. The melt is also in contact with the alloy at the oxide-alloy interface, where oxidation of Ni and other alloying elements takes place. The oxidant is supplied by the transport of O$_2$ through the melt and therefore the rate of MoO$_3$ formation is expected to be slow because of slow transport of O$_2$ through a tortuous path of pores filled with the melt. The oxidation process continues by the transport of O$_2$ through the melt until the MoO$_3$ activity in the melt becomes equal to the equilibrium $\theta$MoO$_3$ for reaction (10). The amount of dissolved MoO$_3$ required to attain a given MoO$_3$ activity in the Na$_2$MoO$_4$ - MoO$_3$ melt increases with an increase in the amount of Na$_2$MoO$_4$. This leads to an increase in the length of the induction period with an increase in the amount of Na$_2$MoO$_4$.

At the end of the induction period, the MoO$_3$ concentration of the melt rises rapidly, and the formation of MoO$_3$ takes place according to the mechanism shown in figure 16, i.e., by Mo$^{4+}$/Mo$^{6+}$ exchange reaction. Cr$_2$O$_3$ and Al$_2$O$_3$ are formed beneath the melt by reaction with the MoO$_3$ component of the melt. The acidic dissolution of Ni and basic fluxing of Cr$_2$O$_3$ take
place as shown in figure 17. The formation of NiO takes place at the melt-gas interface. The O\textsubscript{2} required for basic dissolution of Cr\textsubscript{2}O\textsubscript{3} by reaction (21) can also be supplied by the MoO\textsubscript{3} component of the melt. The exact mode of dissolution of Al\textsubscript{2}O\textsubscript{3} is not clear. The concentration of Al in the alloy is so small that it is assumed to have no major effect on the fluxing process. The dissolution of Co is expected to take place in a manner similar to that of Ni. The thermogravimetric curves in figures 2 and 3 show a gradual transition from the end of the induction period to the beginning of the linear period of catastrophic corrosion. During this transition period, the Ni\textsuperscript{++} (also Co\textsuperscript{++}) concentration in the melt increases with time until the melt is saturated with Ni\textsuperscript{++}. The flux of Ni\textsuperscript{++} through the melt is a product of the diffusivity of Ni\textsuperscript{++} in the melt and the concentration of Ni\textsuperscript{++} in the melt. Therefore, the rate of oxidation (also the rate of weight gain) increases with time because of the increase in Ni\textsuperscript{++} concentration with time during the transition period. When the melt is saturated with Ni\textsuperscript{++}, a steady state condition is achieved and the concentration gradient of Ni\textsuperscript{++} across the melt remains constant. This results in a linear relationship between the weight gain and time.

It must be noted that the dissolution and reprecipitation reactions shown in figure 17 are self-sustaining because oxidation of Mo\textsuperscript{+4} at the melt-gas interface regenerates the MoO\textsubscript{3}. However, the oxidation of the Mo component of the alloy, by the mechanism shown in figure 16, generates MoO\textsubscript{3} at the melt-gas interface thus increasing the MoO\textsubscript{3} concentration in the melt. On the other hand, MoO\textsubscript{3} is lost to the atmosphere by evaporation at the salt-gas interface. Evaporation studies for Na\textsubscript{2}MoO\textsubscript{4} (appendix A) have shown that Na\textsubscript{2}MoO\textsubscript{4} is volatile, the rate of vaporization being 0.03 and 0.035 mg/cm\textsuperscript{2}/hr at 900° and 950° C, respectively. In a Na\textsubscript{2}MoO\textsubscript{4}–MoO\textsubscript{3} melt, the evaporation of Na\textsubscript{2}MoO\textsubscript{4} increases the activity of MoO\textsubscript{3} in the melt, thus resulting in an increase in the rate of evaporation of MoO\textsubscript{3}. Thus there are two competing factors, rate of evaporation of MoO\textsubscript{3} and rate of generation of MoO\textsubscript{3} (due to the oxidation of Mo) which determine the MoO\textsubscript{3} concentration in the melt at a given time. Thermodynamic calculations and evaporation studies (appendixes A and B) have shown that the rate of evaporation of MoO\textsubscript{3} is considerably reduced when dissolved in Na\textsubscript{2}MoO\textsubscript{4} melt, and the evaporation of MoO\textsubscript{3} becomes significant only at high MoO\textsubscript{3} concentra-
tions in the melt. Therefore, MoO₃ is continuously added to the melt, as seen in figure 5, until the concentration of MoO₃ becomes such that the rate of generation of MoO₃ by oxidation of Mo in the alloy becomes equal to the rate of evaporation of MoO₃. For convenience let us designate this time period as t₁. At this time, a steady state can be attained and the MoO₃ concentration of the melt would remain constant. However, Na₂MoO₄ is continuously evaporated from the melt, which effectively increases the activity of MoO₃ in the melt, thereby increasing the rate of evaporation of MoO₃. Therefore after time t₁, the MoO₃ concentration in the melt decreases with time. With a decrease in MoO₃ activity in the melt, the solubility of Ni⁺⁺ in the melt decreases, thus decreasing the concentration of Ni⁺⁺ in the melt. Some dissolved Ni⁺⁺ is precipitated as oxides because of the decrease in solubility. Also the reduction in Ni⁺⁺ concentration in the melt reduces the rate of transport of Ni⁺⁺ through the melt, thereby reducing the rate of oxidation. This is the period of decelerating corrosion, which starts at time t₁.

When all the Na₂MoO₄ is vaporized, the accelerated corrosion comes to a halt because a molten layer is no longer present. (Any MoO₃ left will evaporate quickly because of the unit activity of MoO₃.) The rate of evaporation of Na₂MoO₄ at 950° C was measured to be 0.035 mg/cm²/hr (appendix A). For a dose of 0.73 mg/cm² Na₂MoO₄, assuming unit activity, it would take 20.8 hr for all the Na₂MoO₄ to vaporize and the corrosion to stop. From the thermogravimetric data in figure 2, for a dose of 0.73 mg/cm², it takes 25 hr for the corrosion to stop at 950° C, which is longer than the time period calculated based on the evaporation of Na₂MoO₄ (20.8 hr). This discrepancy is due to the dissolution of MoO₃ in the melt, which also reduces the activity of Na₂MoO₄. Because the catastrophic corrosion stops when all the Na₂MoO₄ has evaporated, the length of the period of catastrophic corrosion is a function of the amount of Na₂MoO₄. The larger the amount of Na₂MoO₄, the longer is the length of the time period during which the material corrodes. Therefore the total weight gain at the end of the period of decelerating corrosion increases with an increase in the amount of Na₂MoO₄.
Effect of temperature. - It is seen from table I that temperature has a
major effect on the length of the induction period. As mentioned earlier, the
end of the induction period corresponds to the time at which the MoO₃ activ-
ity in the melt becomes equal to the equilibrium \( \text{MoO}_3 \) for reaction (10).
The equilibrium \( \text{MoO}_3 \) activity for reaction (10) decreases with decreasing
temperature. For example, the equilibrium \( \text{MoO}_3 \) activity for reaction (10)
was calculated to be \( 1.695 \times 10^{-5} \), \( 4.72 \times 10^{-6} \), \( 8.61 \times 10^{-7} \) at 1200, 1123, and
1023 K, respectively. The rate of oxidation of alloying elements and the rate
of transport of \( \text{O}_2 \) through the melt decrease with decreasing temperature.
Thus, there are two competing factors, thermodynamic and kinetic, which deter-
mine the length of the induction period. For low doses, and at lower tempera-
tures (750° and 850° C), the MoO₃ formed during the first few minutes may
increase the MoO₃ activity of the melt to that required for reaction (10) to
proceed. Thus at 850° and 750° C, for low doses practically no induction
period was observed. For high doses, more MoO₃ has to be added to the melt
to increase the MoO₃ activity to that of equilibrium. The MoO₃ added to
the melt during the initial period thus may not increase the activity to a
sufficiently high value to allow reaction 10 to proceed. Thus the transport
of \( \text{O}_2 \) through tortuous melt filled paths in the oxide and the rate of
oxidation at the alloy scale interface becomes rate determining. These rates
decrease with a decrease in temperature, thereby increasing the length of the
induction period with a decrease in temperature. At intermediate doses,
because of thermodynamic and kinetic factors, the length of the induction
period would be minimum at certain intermediate temper-ature, which was
observed to be the case at 850° C.

As mentioned earlier, the corrosion comes to a halt when all the
\( \text{Na}_2\text{MoO}_4 \) is vaporized. The rate evaporation of \( \text{Na}_2\text{MoO}_4 \) decreases with
temperature. Thus for the same amount of \( \text{Na}_2\text{MoO}_4 \), the length of the time
period, during which material undergoes accelerated corrosion, increases with
decreasing temperature.

SUMMARY AND CONCLUSIONS

Catastrophic corrosion of nickel base superalloys containing Mo can be
caused by formation of \( \text{Na}_2\text{MoO}_4 \). The period of catastrophic corrosion is
preceded by an induction period. It has been shown that the activity of MoO$_3$ in the melt must attain a certain minimum value before the onset of catastrophic corrosion. This is related to the equilibrium MoO$_3$ activity in the melt for the reaction $2\text{MoO}_3(s) + \text{Mo} = 2\text{MoO}_2(s)$. The length of the induction period corresponds to the time required for the attainment of equilibrium MoO$_3$ activity in the melt for the above reaction. The length of the induction period is a strong function of temperature and the amount of Na$_2$MoO$_4$. At the end of the induction period, MoO$_3$ is formed by a Mo$^{+6}$/Mo$^{+4}$ exchange reaction in the melt, in which Mo$^{+6}$ is reduced to Mo$^{+4}$ by reaction with Mo at the melt-oxide interface, and Mo$^{+4}$ is oxidized to Mo$^{+6}$ at the melt-gas interface.

During the period of catastrophic corrosion, Ni is dissolved as Ni$^{+2}$ at the melt-oxide/alloy interface by reaction with Mo$^{+6}$ thus forming Mo$^{+4}$. Simultaneously basic dissolution of Cr$_2$O$_3$ also takes place at this interface. The Ni$^{+2}$ ions are oxidized to NiO at the melt-gas interface, and CrO$_4^{2-}$ ions are converted to Cr$_2$O$_3$ and O$^-$ at a distance away from the melt-oxide interface. The dissolution-precipitation reaction is self-sustaining. The catastrophic corrosion stops when all the Na$_2$MoO$_4$ has vaporized.

The present study has shown that the rate of evaporation of MoO$_3$ is considerably reduced when dissolved in Na$_2$MoO$_4$. Thus evaporation of MoO$_3$ would not be significant in actual gas turbine situations, as has been proposed by several investigators (refs. 7 and 18). In the situation encountered in a burner rig, and probably in actual gas turbines under hot corrosion conditions, there is continuous deposition of the Na$_2$SO$_4$. The Na$_2$SO$_4$ reacts with MoO$_3$ at the melt-gas interface, and in effect acts as a sink for MoO$_3$. The mode of fluxing will then be a complex function of the rate of formation of MoO$_3$, rate of reaction between MoO$_3$ and Na$_2$SO$_4$, and the rate of deposition of Na$_2$SO$_4$. The details of the fluxing mechanism in which there is continuous deposition of Na$_2$SO$_4$ is the subject of further investigation at this laboratory.
APPENDIX A

EVAPORATION OF \( Na_2MoO_4 \), \( MoO_3 \) and \( Na_2MoO_4 - MoO_3 \) MIXTURE

To determine the rate of evaporation, the desired compound or mixture was placed in platinum crucible and the rate of evaporation was measured by measuring the weight loss in the microbalance. The flow rate of \( O_2 \) was maintained the same as that in the corrosion experiments, e.g., 100 cm min\(^{-1}\).

The rate of evaporation of \( Na_2MoO_4 \), \( MoO_3 \) and \( Na_2MoO_4 - MoO_3 \) mixtures are shown in table II. It can be seen that \( MoO_3 \) is highly volatile, the rate of evaporation increasing with temperature. It is interesting to note that the rate of evaporation of \( MoO_3 \) is drastically reduced when dissolved in \( Na_2MoO_4 \). For example, for a \( Na_2MoO_4 - 13 \) mole percent \( MoO_3 \) mixture, assuming ideal solution, \( a_{Na_2MoO_4} = 0.87 \) and \( a_{MoO_3} = 0.13 \). Thus under ideal solution conditions, 22.04 mg of \( MoO_3 \) and 0.253 mg of \( Na_2MoO_4 \) would vaporize in 1 hr. However, the total amount evaporating is 0.25 mg in 1 hr, which is much less than that which would have evaporated under ideal solution conditions.

The disadvantage of measuring the rate of evaporation from a crucible containing the salt is that the surface area is unknown, therefore, the rates cannot be directly related to the corrosion measurements. No measurement of the rate of evaporation of \( MoO_3 \) could be carried out on a Pt coupon of known surface area because of the high volatility of \( MoO_3 \). For example at 900° C, all the \( MoO_3 \), that could be applied to a Pt coupon, evaporated within the first 2-3 minutes of the start of the experiment. The rate of evaporation of \( Na_2MoO_4 \) from a sample of known surface area could be carried out by airbrushing \( Na_2MoO_4 \) on to Pt coupons, and measuring the weight loss from the \( Na_2MoO_4 \) coated coupons. Such measurements gave vaporization rate of 0.035 mg/cm\(^2\)/hr at 950° C and 0.03 mg/cm\(^2\)/hr at 900° C.
APPENDIX B

THERMODYNAMICS OF THE Na$_2$MoO$_4$ - MoO$_3$ SYSTEM

There is no experimental data on the thermodynamic properties of Na$_2$MoO$_4$ - MoO$_3$ melts. However, the thermodynamic properties can be estimated from the relevant binary phase diagram. The estimation of thermodynamic properties from the phase diagram has been extensively used for molten salts and slag systems (ref. 19). The Na$_2$MoO$_4$ - MoO$_3$ phase diagram is taken from reference 20 and shown in figure 19. The phase diagram does not show the existence of any solid solution between Na$_2$MoO$_4$ - MoO$_3$. The solid-liquid equilibrium can be described by the reaction:

$$s + x$$

(B-1)

$$\Delta G^0 = \frac{\Delta H^0_{\text{fusion}} (T_m - T)}{T_m} = -RT \ln a_x$$

(B-2)

where $\Delta G^0$ = Gibbs free energy change for reaction (B-1), $\Delta H^0_{\text{fusion}}$ = heat of fusion of the solid at the melting point. $T_m$ = melting point, $T$ = temperature along the liquidus line and $a_x$ is the activity of the component in the liquid in reference to the pure liquid as the standard state. The data calculated along the liquidus can be extrapolated to other temperatures by assuming that at a fixed composition, the partial heat of solution is independent of temperature (ref. 21).

Then,

$$RT \ln v_x = RT \ln v_T$$

(B-3)

$$a_T = x_x \cdot v_T$$

(B-4)

Where $T_x$ and $v_x$ are the liquidus temperatures and activity coefficient at the liquidus, respectively, $T$ and $v_T$ are the temperatures and activity co-efficients at the chosen temperature $T$, $a_T$ is the activity at a temperature $T$ for a composition corresponding to the liquidus composition, $X_x$ is the liquidus composition at temperature $T_x$. 25
From Barin and Knacke's (ref. 22) test, the melting point and heat of fusion for MoO$_3$ are 1068 K and 11,507 kcal/mole, respectively. Using these data, the activity of MoO$_3$ at the liquidus in the MoO$_3$ rich portion of the phase diagram can be calculated from equation (B-2). The calculated values of $a_{\text{MoO}_3}$ at the liquidus composition for different temperatures is shown in table III. The activity of MoO$_3$ at other temperatures for compositions corresponding to the liquidus can be calculated from equation (B-3). From the MoO$_3$ rich side of the binary Na$_2$MoO$_4$ - MoO$_3$ phase diagram, the activity of MoO$_3$ can be determined only in the composition range 0.77 < $\chi_{\text{MoO}_3}$ < 1, where $\chi_{\text{MoO}_3}$ is the mole fraction of MoO$_3$ in the melt.

For composition ranges other than 0.77 < $\chi_{\text{MoO}_3}$ < 1, the MoO$_3$ activity in the melt can be estimated from the vaporization rate of Na$_2$MoO$_4$ - MoO$_3$ mixture (given in appendix A) and a study of the Na$_2$MoO$_4$ rich portion of the binary Na$_2$MoO$_4$ - MoO$_3$ phase diagram, which is described as follows. Let $P_{\text{Na}_2\text{MoO}_4}$ and $P_{\text{MoO}_3}$ be the equilibrium vapor pressure of Na$_2$MoO$_4$ and MoO$_3$, respectively, at unit activity. The rate of evaporation of Na$_2$MoO$_4$ and MoO$_3$ at unit activity can be expressed as:

$$K^\circ_{\text{Na}_2\text{MoO}_4} = h \left[ P_{\text{Na}_2\text{MoO}_4}^\circ - P_{\text{Na}_2\text{MoO}_4} \right]$$ (B-5)

$$K^\circ_{\text{MoO}_3} = h \left[ P_{\text{MoO}_3}^\circ - P_{\text{MoO}_3} \right]$$ (B-6)

Where $K^\circ_{\text{Na}_2\text{MoO}_4}$ and $K^\circ_{\text{MoO}_3}$ are the rate of evaporation of Na$_2$MoO$_4$ and MoO$_3$, respectively, $h$ is the mass transfer coefficient, $P_{\text{Na}_2\text{MoO}_4}^\circ$ (ambient) and $P_{\text{MoO}_3}^\circ$ (ambient) are the partial pressure of Na$_2$MoO$_4$ and MoO$_3$ in the ambient, respectively. For the flow conditions used in the present experiments, $P_{\text{Na}_2\text{MoO}_4}$ (ambient) and $P_{\text{MoO}_3}$ (ambient) are assumed to be zero. Because all the evaporation studies were conducted under the same experimental conditions, i.e., same flow rate and specimen geometry, the mass transfer coefficient is assumed to be constant for all the experiments. In a Na$_2$MoO$_4$ - MoO$_3$ mixture, the equilibrium vapor pressure of Na$_2$MoO$_4$ and MoO$_3$ can be expressed as:

$$P_{\text{Na}_2\text{MoO}_4} = a_{\text{Na}_2\text{MoO}_4} \cdot P_{\text{Na}_2\text{MoO}_4}^\circ$$ (B-7)

$$P_{\text{MoO}_3} = a_{\text{MoO}_3} \cdot P_{\text{MoO}_3}^\circ$$ (B-8)
Where \( P_{Na_2MoO_4} \) and \( P_{MoO_3} \) are the equilibrium vapor pressure of Na\(_2\)MoO\(_4\) and MoO\(_3\), respectively in the Na\(_2\)MoO\(_4\) - MoO\(_3\) mixture, \( a_{Na_2MoO_4} \) and \( a_{MoO_3} \) are the activity of Na\(_2\)MoO\(_4\) and MoO\(_3\) in the melt, respectively. The rate of evaporation of the Na\(_2\)MoO\(_4\) - MoO\(_3\) mixture can be expressed as:

\[
K^*_{Na_2MoO_4 - MoO_3} = a_{Na_2MoO_4} \cdot K^*_{Na_2MoO_4} + a_{MoO_3} \cdot K^*_{MoO_3}
\] (B-9)

Thus, if \( K^*_{Na_2MoO_4 - MoO_3}, a_{Na_2MoO_4}, K^*_{Na_2MoO_4} \) and \( K^*_{MoO_3} \) are known, \( a_{MoO_3} \) at a given composition can be calculated from equation (B-9).

From appendix A, at 900° C, \( K^*_{Na_2MoO_4}, K^*_{MoO_3}, K^*_{Na_2MoO_4 - MoO_3} \) (\( \chi_{MoO_3} = 0.13 \)) were measured to be 0.291 mg/hr, 169.56 mg/hr and 0.245 mg/hr, respectively. From the Na\(_2\)MoO\(_4\) rich side of the phase diagram, \( \chi_{MoO_3} = 0.13 \) corresponds to liquidus temperature of 610° C. From Barin and Knacke's (B-4) text, the melting point and heat of fusion for Na\(_2\)MoO\(_4\) are 962 K and 5.12 kcal/mole, respectively. Using this data, the activity of Na\(_2\)MoO\(_4\) in the melt at 610° C at the liquidus composition (\( \chi_{MoO_3} = 0.13 \)) was calculated to be 0.786. From the activity data at 610° C, the activity of Na\(_2\)MoO\(_4\) at 900° C for a melt consisting of Na\(_2\)MoO\(_4\) - MoO\(_3\) (\( \chi_{MoO_3} = 0.13 \)) was calculated to be 0.806. Substitution of this value of \( a_{Na_2MoO_4} \) and the vaporization data for Na\(_2\)MoO\(_4\), MoO\(_3\), Na\(_2\)MoO\(_4\) - MoO\(_3\) (\( \chi_{MoO_3} = 0.13 \)) in equation (B-9) gives the value of \( a_{MoO_3} \) (\( \chi_{MoO_3} = 0.13 \)) at 900° C to be 6.16x10\(^{-5}\).

From appendix A, the rate of evaporation of a Na\(_2\)MoO\(_4\) - MoO\(_3\) mixture (\( \chi_{MoO_3} = 0.54 \)) is 0.75 mg/hr at 900° C. A liquid of this composition is not in equilibrium with solid Na\(_2\)MoO\(_4\). Thus the activity of Na\(_2\)MoO\(_4\) at this composition can not be obtained from a study of the Na\(_2\)MoO\(_4\) rich portion of the binary phase diagram. For this liquid mixture (\( \chi_{MoO_3} = 0.54 \)), assuming that the activity of Na\(_2\)MoO\(_4\) is the same as the mole fraction (\( a_{Na_2MoO_4} = 0.46 \)), and using the vaporization data for Na\(_2\)MoO\(_4\), MoO\(_3\), and Na\(_2\)MoO\(_4\) - MoO\(_3\) (\( \chi_{MoO_3} = 0.56 \)), the \( a_{MoO_3} \) was calculated to be 3.63x10\(^{-3}\). On the other hand by assuming that all the vaporization was due to the evaporation of MoO\(_3\) only, the \( a_{MoO_3} \) was calculated to be 4.42x10\(^{-3}\). The two calculated values have the same order of magnitude, which is due to the rate of evaporation of MoO\(_3\) being
much greater than the rate of evaporation of Na₂MoO₄ at this composition. The actual value for \( \alpha_{\text{MoO}_3} \) will lie somewhere in between these two values, and a value of \( \alpha_{\text{MoO}_3} \) equal to approximately \( 4 \times 10^{-3} \) will not be unreasonable.

Table IV shows the \( \alpha_{\text{MoO}_3} \) values at 900° C for a range of composition. In the composition range \( 0.77 < x_{\text{MoO}_3} < 1 \), the \( \alpha_{\text{MoO}_3} \) was obtained by extrapolating the data from table III to 900° C by using equations (B-3) and (B-4). For other compositions, the activity values were obtained from the evaporation studies for the Na₂MoO₄ - MoO₃ mixture. Table V shows the \( \alpha_{\text{MoO}_3} \) values at 1200 K, which were obtained from table IV. From tables IV and V, it can be seen that the activity of MoO₃ is considerably reduced for low concentrations of MoO₃ in the melt.
REFERENCES


TABLE I. - LENGTH OF INDUCTION PERIOD
AT DIFFERENT TEMPERATURES

<table>
<thead>
<tr>
<th>Amount of Na$_2$MoO$_4$, mg/cm$^2$</th>
<th>Temperature, °C</th>
<th>Length of the induction period, hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>950</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>No induction period</td>
</tr>
<tr>
<td>2.5</td>
<td>950</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>27</td>
</tr>
<tr>
<td>4.5</td>
<td>900</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>140</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>160</td>
</tr>
</tbody>
</table>
### TABLE II. - RATE OF EVAPORATION OF Na$_2$MoO$_4$, MoO$_3$ AND Na$_2$MoO$_4$ - MoO$_3$ MIXTURE

<table>
<thead>
<tr>
<th>Compound or mixture</th>
<th>Temperature, °C</th>
<th>Weight loss in 1 hr, mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO$_3$</td>
<td>950</td>
<td>584</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>169.56</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>77.5</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>15</td>
</tr>
<tr>
<td>Na$_2$MoO$_4$</td>
<td>900</td>
<td>.291</td>
</tr>
<tr>
<td>Na$_2$MoO$_4$ - MoO$<em>3$ ($X</em>{MoO_3} = 0.13$)</td>
<td>900</td>
<td>.245</td>
</tr>
<tr>
<td>Na$_2$MoO$_4$ - MoO$<em>3$ ($X</em>{MoO_3} = 0.54$)</td>
<td>900</td>
<td>.75</td>
</tr>
<tr>
<td>Na$_2$MoO$_4$ - MoO$<em>3$ ($X</em>{MoO_3} = 0.8$)</td>
<td>900</td>
<td>15.32</td>
</tr>
</tbody>
</table>

### TABLE III. - ACTIVITY OF MoO$_3$ AT THE LIQUIDUS COMPOSITION IN THE MoO$_3$ RICH SIDE OF THE BINARY Na$_2$MoO$_4$ - MoO$_3$ PHASE DIAGRAM

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Mole fraction of MoO$<em>3$, $X</em>{MoO_3}$</th>
<th>Activity of MoO$<em>3$, $\alpha</em>{MoO_3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>0.9</td>
<td>0.587</td>
</tr>
<tr>
<td>600</td>
<td>.8</td>
<td>.295</td>
</tr>
<tr>
<td>537</td>
<td>.77</td>
<td>.176</td>
</tr>
</tbody>
</table>
### TABLE IV. - ACTIVITY OF MoO$_3$ IN THE Na$_2$MoO$_4$ – MoO$_3$ MELT AT 900°C

<table>
<thead>
<tr>
<th>Mole fraction of MoO$<em>3$, $X</em>{MoO_3}$</th>
<th>Activity of MoO$<em>3$, $a</em>{MoO_3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.13</td>
<td>6.16x10$^{-5}$</td>
</tr>
<tr>
<td>.54</td>
<td>4x10$^{-3}$</td>
</tr>
<tr>
<td>.77</td>
<td>0.277</td>
</tr>
<tr>
<td>.8</td>
<td>0.380</td>
</tr>
<tr>
<td>.9</td>
<td>0.631</td>
</tr>
</tbody>
</table>

### TABLE V. - ACTIVITY OF MoO$_3$ IN THE Na$_2$MoO$_4$ – MoO$_3$ MELT AT 1200 K

<table>
<thead>
<tr>
<th>Mole fraction of MoO$<em>3$, $X</em>{MoO_3}$</th>
<th>Activity of MoO$<em>3$, $a</em>{MoO_3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.13</td>
<td>7.3x10$^{-5}$</td>
</tr>
<tr>
<td>.54</td>
<td>4.46x10$^{-3}$</td>
</tr>
<tr>
<td>.77</td>
<td>0.283</td>
</tr>
<tr>
<td>.8</td>
<td>0.386</td>
</tr>
<tr>
<td>.9</td>
<td>0.636</td>
</tr>
</tbody>
</table>
Figure 1. - Schematics of the corrosion kinetics.

Figure 2. - Corrosion kinetics at 950°C as a function of the amount of Na₂MoO₄.
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Figure 5. - Analysis of water soluble elements for the corroded sample at 950° C.

Figure 6. - Corrosion kinetics with a deposit of Na₂MoO₄ - MoO₃.
Figure 7. - Scale morphology during the initial period for U-700, coated with 1.5 mg/cm$^2$ Na$_2$MoO$_4$ and oxidized in 1 atm O$_2$ for 15 minutes at 950$^\circ$ C.
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Figure 10. - S.E. image and X-ray maps for the cross-section shown in figure 9.
Figure 11. - Scale morphology during advanced stage of catastrophic corrosion, sample coated with 0.985 mg/cm$^2$ Na$_2$MoO$_4$ and oxidized in 1 atm O$_2$ for 173 hrs at 750$^0$ C.
(b) Details of the scale-metal interface.

Figure 11. - Concluded.
(a) S.E. Image and X-ray maps.

Figure 12. - Details of the pit in figure 11.
(b) Pit at a higher magnification showing Cr$_2$O$_3$ precipitates.

Figure 12. - Concluded.
Figure 13. - Scale morphology during the period of catastrophic corrosion for a sample coated with 1.4 mg/cm² Na₂MoO₄ and oxidized in 1 atm O₂ for 40 hrs at 950°C.
Figure 14. - Scale morphology at the end of the period of catastrophic corrosion for a sample coated with 1.45 mg/cm² Na₂MoO₄ and oxidized in 1 atm O₂ for 70 hrs at 950°C.
Figure 15. - Schematics of the plot of the solubility of oxides versus $-\log a \text{Na}_2\text{O}$.

Figure 16. - Schematics of the mechanism of oxidation of Mo beneath the Na$_2$MoO$_4$ - MoO$_3$ melt.
Figure 17. - Schematics of the mechanism of corrosion during the period of catastrophic corrosion.
Figure 18. - S. E. image and X-ray maps for U-700, coated with 0.8 mg/cm² MoO₃ and oxidized on 1 atm O₂ for 15 hrs at 800°C.
Figure 19. Na$_2$MoO$_4$ - MoO$_3$ phase diagram.
**Abstract**

The corrosion of nickel base superalloy, U-700, by molten Na$_2$MoO$_4$ has been studied in the temperature range 750$^\circ$C to 950$^\circ$C. After an induction period, the rate of corrosion is linear and catastrophic corrosion is observed. The induction period is shown to be associated with the attainment of a minimum MoO$_3$ activity in the melt, which corresponds to the equilibrium MoO$_3$ activity for the reaction, 2MoO$_3$(l) + Mo = 3MoO$_2$(s). A mechanism is proposed to describe the catastrophic nature of corrosion, which involves transport of Ni$^{++}$ through the melt resulting in formation of NiO at the melt-gas interface and basic fluxing of Cr$_2$O$_3$. The effect of the amount of Na$_2$MoO$_4$ on the corrosion kinetics has also been studied. Evaporation studies and the thermodynamic calculations for the Na$_2$MoO$_4$ - MoO$_3$ system have shown that the activity of MoO$_3$ is reduced considerably when dissolved in Na$_2$MoO$_4$, thus causing a sharp decrease in the rate of evaporation of MoO$_3$ from a Na$_2$MoO$_4$ - MoO$_3$ melt.

**Key Words** (Suggested by Author(s))

Nickel alloys; Corrosion; Sodium sulfate; Sodium molybdate

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