Chemical Mechanisms and Reaction Rates for the Initiation of Hot Corrosion of IN-738

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Summary

Sodium-sulfate-induced hot corrosion of preoxidized IN-738 was studied at 975°C with special emphasis on the processes occurring during the long induction period. Thermogravimetric tests were run for predetermined periods of time, and then one set of specimens was washed with water. Chemical analysis of the wash solutions yielded information about water-soluble metal salts and residual sulfate. A second set of samples was cross sectioned dry and polished in a nonaqueous medium. Element distributions within the oxide scale were obtained from electron microprobe X-ray micrographs. Evolution of SO\(_2\) was monitored during the thermogravimetric tests. Kinetic rate studies were performed for several pertinent processes; appropriate rate constants were obtained for the following chemical reactions:

\[
\begin{align*}
\text{Cr}_2\text{O}_3 + 2 \text{Na}_2\text{SO}_4(\ell) + 3/2 \text{O}_2 & \rightarrow 2 \text{Na}_2\text{CrO}_4(\ell) + 2 \text{SO}_3(\text{g}) \\
n \text{TiO}_2 + \text{Na}_2\text{SO}_4(\ell) & \rightarrow \text{Na}_2\text{O}(\text{TiO}_2)_n + \text{SO}_3(\text{g}) \\
n \text{TiO}_2 + \text{Na}_2\text{CrO}_4(\ell) & \rightarrow \text{Na}_2\text{O}(\text{TiO}_2)_n + \text{CrO}_3(\text{g})
\end{align*}
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Introduction

Nickel-base alloys are used extensively in gas turbine engine components because of their superior mechanical properties. However, these superalloys are generally susceptible to a form of environmental attack known as hot corrosion. Hot corrosion is encountered under circumstances where Na\(_2\)SO\(_4\) is deposited from the combustion gases onto the hot-gas-path parts, especially the turbine blades and vanes. This corrosion has been a serious problem for many years in aircraft engines and also in marine engines and land-based power generating systems. It is believed that the problem will be aggravated by the anticipated use of higher operating temperatures and pressures in future gas turbine engines. Further contributions can be expected from the increased use of cheaper, "dirtier" fuels. Therefore it is desirable to obtain a clearer understanding of the chemical processes involved in the hot corrosion of these superalloys.

Recently we reported on the chemical reactions involved in the initiation of hot corrosion of the alloys B-1900 and NASA–TRW VIA (ref. 1). These are nickel-base alloys that derive their oxidation resistance from the formation of a thin, dense, continuous oxide layer composed largely of \(\alpha\)-\(\text{Al}_2\text{O}_3\). Hot corrosion was induced by coating metal samples with Na\(_2\)SO\(_4\) and oxidizing them at higher temperatures. Thermogravimetric tests were performed and SO\(_2\) evolution was monitored. Additional information about the chemical reactions occurring was obtained from chemical analysis of wash solutions and from energy dispersive X-ray analysis of the oxide scales of specimens that were corroded for predetermined periods of time. It was shown that, after an induction period, hot corrosion caused basic fluxing of the protective \(\text{Al}_2\text{O}_3\) layer by the liquid Na\(_2\)SO\(_4\) deposit. This was followed by a catastrophic rate of attack resulting from an acidic fluxing of the remaining oxide layer by a Na\(_2\)MoO\(_4\)-MoO\(_3\) molten phase that had formed underneath the oxide layer.

Unlike B-1900 and VIA, the alloy IN-738 derives its oxidation resistance from a protective layer composed largely of Cr\(_2\)O\(_3\). This superalloy is of special interest because of its present wide use, both coated and uncoated, in gas turbine engines (refs. 2 and 3). This position of prominence is due not only to its good mechanical properties, but also to its superior hot corrosion resistance.

The Na\(_2\)SO\(_4\)-induced hot corrosion of IN-738 in the temperature range 825° to 1000° C has been studied by a number of investigators using a variety of experimental techniques (refs. 3 to 13). The results have shown that either the alloy did not display hot corrosion at all under the test conditions, or the hot corrosion was preceded by a long induction period during which the corrosion rate was similar to that in simple oxidation. Most of these studies have emphasized the kinetics of the hot corrosion, usually in comparison with other alloys, or the morphology of the corrosion scale. Less effort has been devoted to the important processes that must be occurring during the long induction period. We have investigated the Na\(_2\)SO\(_4\)-induced hot corrosion of IN-738 at 975°C with special emphasis on the chemical and
physical processes occurring during the induction period, processes that lead to the initiation of catastrophic hot corrosion attack of this alloy. We have used the same techniques that were employed in our studies of B–1900 and VIA as described in reference 1. In addition, we have performed rate studies on several of the simple processes suspected of being important in the hot corrosion of IN–738. Recently we reported the effects of temperature and oxide scale thickness on the hot corrosion of IN–738 (ref. 13). Those results complement the present work, which emphasizes chemical processes.

**Experimental Procedure**

Specimens of alloy IN–738 were obtained from commercial sources and given conventional heat treatments. The composition of the alloy is presented in table I. Test samples typically measured 0.3 × 1.0 × 2.5 cm and had a 0.3-cm-diameter hangdown hole in one end. All surfaces were glass-bead blasted to give a uniform matte finish. The samples were cleaned ultrasonically in trichloroethylene, detergent, distilled water, acetone, and ethanol and then dried in an oven at 120° C.

All samples were preoxidized at 975° C in 1 atm of slowly flowing oxygen for 24 hr. Hot corrosion was induced by coating the preoxidized samples with about 3 mg cm⁻² of Na₂SO₄ followed by isothermal oxidation at 975° C. The Na₂SO₄ was applied by air brushing a saturated solution of Na₂SO₄ onto the specimen, which was heated on a hotplate to 200° C. The salt-coated specimens were oxidized in a vertical tube furnace. Oxygen flowed downward at 126 cm min⁻¹ (620 milliliters min⁻¹) in the 2.5-cm-diameter quartz furnace tube. All the experiments were performed in a horizontal furnace tube under the conditions stated above.

The specimen under test was suspended in the tube on a Pt–20Rh alloy chain. Continuous weight measurements were made with a Cahn R–100 microbalance. The recorded weight changes were corrected for flow and buoyancy effects. Drs. Reza Haque and Ajay K. Misra ran some of the hot corrosion tests.

The concentration of SO₂ in the gas flowing out of the furnace tube was measured continuously during the test with a ThermoElectron pulsed fluorescent analyzer that is specific to SO₂. The detection capability extended from 0.01 to 50 ppm. The effluent from the furnace tube was conducted into the SO₂ analyzer through stainless steel fittings and Teflon tubing.

Samples were run for predetermined periods of time and then cooled to room temperature. One set of samples was mounted and cross sectioned for morphological examination of the corrosion scale by light microscopy and electron microprobe techniques. These samples were coated with copper in an electron beam evaporator before they were mounted and were cross sectioned dry over an 8-hr period. The samples were polished in Varsol to prevent removal of water-soluble compounds. The microprobe data were obtained by Mr. Frank M. Terepka. Reaction products were identified from elemental X-ray micrographs and X-ray diffraction analyses reported previously (ref. 7). A second set of samples was washed with water to extract soluble species. Each specimen was treated for 15 min in 50 milliliters of hot water, and the resulting solutions were analyzed for metal ions by atomic absorption techniques. Residual sulfate was determined by ion chromatography. The chemical analyses were performed by Mr. Warren F. Davis and Ms. Constance S. Buchar.

**Results and Discussion**

The hot corrosion specimens used in this investigation were all preoxidized in oxygen for 24 hr at 975° C. The isothermal oxidation of IN–738 was essentially parabolic at this temperature; a typical specific weight gain curve is presented in figure 1. The 24-hr preoxidation treatment effected a weight gain of 1.7 mg cm⁻² and produced a

![Figure 1.—Typical specific weight gain as a function of time for isothermal oxidation of IN–738 at 975° C in flowing oxygen and with mol fraction of Cr₂O₃ and TiO₂ in scale.](image-url)
10-μm-thick oxide scale on the sample. Elemental X-ray micrographs of a typical oxide layer are presented in figure 2. The oxide was composed primarily of Cr₂O₃ with considerable amounts of TiO₂ associated with it. Tentacle-like internal oxides, which were essentially Al₂O₃, were observed below the Cr₂O₃ layer, extending an additional 30 μm into the substrate. In addition, an oxide of tantalum and possibly niobium lay scattered along the lower edge of the 10-μm-thick Cr₂O₃–TiO₂ layer. Titanium exhibited a marked depletion zone about 30 μm thick, and chromium showed a less marked zone of about the same thickness. Little or no nickel or molybdenum appeared in the oxide layer.

These results are in general agreement with our previous results for specimens oxidized in oxygen for 100 hr at 900° and 1000° C (ref. 14). There is one difference: the specimens oxidized for the longer time (100 hr) exhibited a definite layer of TiO₂ on top of the Cr₂O₃–TiO₂ layer. This was not observed on the present (24 hr) samples, where the TiO₂ appeared to be only intermixed with the Cr₂O₃. In situ high-temperature X-ray diffraction was performed to identify the oxides formed during isothermal oxidation. With this technique (ref. 15) the course of oxidation reactions can be followed at temperature, and the relative amounts of the oxides can be roughly calculated. The results for Cr₂O₃ and TiO₂ are presented in figure 1 as mol fractions at various times, and they show that the oxide layer formed in 24 hr was about 75-mol% Cr₂O₃ and 25-mol% TiO₂.

Thick scales formed on IN–738 during oxidation tend to spall upon cooling to room temperature, but this was not usually a problem with our samples because the oxide scale was only 10 μm thick. The preoxidation extended the length of the induction period observed during induced hot corrosion, and it produced a sample that was characterizeable and fairly stable to further oxidation, the rate after 24 hr of oxidation being about 0.04 mg cm⁻² hr⁻¹ (fig. 1). This stability made it easier to interpret the processes occurring during the initial phases of the hot corrosion.

**Thermogravimetric Results**

A typical hot corrosion curve for IN–738 is shown in figure 3(a), where the specific weight gain is plotted against time. The hot corrosion process for this alloy was characterized by a rather long induction period, that is, a period of little or no weight gain. In fact, the preoxidized specimens initially exhibited a period of slight weight loss, amounting to about 0.7 mg cm⁻² at about 10 hr. The duration of the so-called induction period is a function of the composition of the alloy, the preoxidation treatment of the specimen, the test temperature, and the amount of Na₂SO₄ applied to induce hot corrosion (ref. 7). Defining the length of the induction period is somewhat arbitrary. In our recent report on the hot corrosion of B–1900 (ref. 1) we defined it as the time when an abrupt change occurs in the slope of the corrosion curve. We will adhere to that definition herein. An examination of figure 3(a) indicates that the induction period was about 55 hr long and the corresponding specific weight gain was 5 mg cm⁻². Thus the induction period consisted of a period of small weight loss (up to 10 hr) followed by a long period of moderate weight gain (up to 55 hr).

It is instructive to examine the rate of corrosion during the induction period, after the minimum in the weight gain curve (fig. 3(a)). To this end, we have plotted in figure 4 the specific weight gain, on an expanded scale, against time. The expanded scale is the same scale used in figure 1. It is evident from this plot that the specimen oxidized at a linear rate after about 15 hr, an indication that the oxide formed was not protective in the usual sense. The linear corrosion rate was 0.14 mg cm⁻² hr⁻¹, about four times the rate of normal oxidation at 24 hr (fig. 1).

The induction period was followed by a period in which the rate of corrosion accelerated rapidly until, at about 60 hr, attack became catastrophic, as shown by the region in which a rapid linear weight gain behavior is displayed. This linear attack continued until about 75 hr, at which time the rate started to decelerate slightly. However, by this time a large fraction of the specimen had been consumed and it was covered with a voluminous, porous, greenish-black oxide. A typical specimen is shown in figure 5. In figure 5(a) the specimen is shown as it appeared on the balance at the end of the 100-hr hot corrosion test. In figure 5(b) it is shown with the oxide removed so that the consumption of the alloy could be apprized. Obviously most of the attack occurred on the bottom half of the specimen. This behavior was found with all of the test specimens. The Na₂SO₄ was very fluid at 975° C and most of it "slumped" to the bottom half of the specimen. The hot corrosion attack occurred primarily on the bottom half and spread very slowly to the upper half of the specimen. This behavior was unlike the hot corrosion of B–1900 and VIA at 900° C described in reference 1, where attack usually began at one or two spots near the middle of the specimen but then spread rapidly over the entire specimen.

**Sulfur Dioxide Evolution**

The SO₂ evolved during the hot corrosion tests was monitored continuously. Results for a typical specimen are shown in figure 3(b), where the concentration of SO₂ detected in the effluent oxygen is plotted, in parts per million per unit sample area, against the test time. Some SO₂ evolved almost immediately as the sample was brought up to the test temperature. The concentration rose rapidly to about 3.4 ppm cm⁻² (25 ppm), generally within the first 5 to 10 min. Thereafter the SO₂
Figure 2.—Secondary electron and X-ray micrographs of IN-738 specimen preoxidized at 975°C for 24 hr in flowing oxygen.
concentration decreased rapidly, reaching about 0.27 ppm cm\(^{-2}\) (2 ppm) in 4 hr. It decreased more slowly after that, reaching essentially zero (i.e., <0.02 ppm) at about 20 hr. No further SO\(_2\) above this level was detected until the specimen started corroding catastrophically, at about 57.5 hr. At this time the SO\(_2\) level started to rise slowly, to about 0.014 ppm cm\(^{-2}\) (0.1 ppm) by 80 hr, and then fell back gradually to 0.02 ppm by 110 hr. Although the results for different specimens deviated somewhat from this norm, all exhibited the same qualitative behavior. The greatest variation was in the value of the original peak height, which ranged from 3 to 3.8 ppm cm\(^{-2}\) although most specimens were within ±0.25 ppm cm\(^{-2}\) of 3.4 ppm cm\(^{-2}\).

**Water-Soluble Elements**

Specimens were tested for fixed periods of time, and then water-soluble compounds were extracted for chemical analysis. The test times were normalized to a relative time scale by matching the respective individual weight gain with the curve given in figure 3(a). This procedure was necessary because individual specimens varied about ±10 percent in the length of their induction periods. Tests were run for 5 and 15 min, and for 2.5, 5, 10, 15, 20, 30, 40, 50, 56, 60, 73, 83, 90, and 100 hr. The results of chemical analysis are given in figure 3(c), where we have plotted as a function of time the millimols of each element found and the SO\(_4^{2-}\) recovered. Individual points have been eliminated for clarity and the data are presented as smoothed curves. The Na\(_2\)SO\(_4\) originally applied to the samples is given at zero time and amounted to 0.168 mmol. Because the Na\(_2\)SO\(_4\) applied to different samples varied by ±5 percent, all quantities of the soluble species given in figure 3(c) were normalized to 0.168-mmol Na\(_2\)SO\(_4\). In addition, the alloy specimens themselves were analyzed for sulfur, and these results are given as sulfides (S\(^{-2}\)) in figure 3(c).

The analytical results are different from those obtained in our recent study (ref. 1) of B-1900 and NASA-TRW VIA, alloys for which the protective scale is primarily Al\(_2\)O\(_3\). With IN-738 the amount of SO\(_4^{2-}\) recovered...
in similar studies with B-1900 and VIA (ref. 1). The soluble chromium was evidenced by the yellow chromate color found on the surfaces of cooled samples and also by the yellow color of the water-wash solutions extracted for analysis. The quantity of soluble chromium rose rapidly from the beginning of the test, maximized at around 10 hr, and then fell in a rapid, nearly linear manner until about 30 hr. After that it decreased slowly and reached very small values after about 60 hr.

Soluble molybdenum (MoO$_4$$^-$$^2$) appeared early in the hot corrosion process, after about 10 hr. It increased linearly throughout the long induction period, to more than 0.02 mmol at 55 hr. It increased more rapidly during the catastrophic corrosion of the sample (55 to 75 hr) and maximized at 0.06 mmol at 75 hr. It then decreased rapidly over the next 15 hr, back to about 0.01 mmol. Soluble tungsten (WO$_4$$^-$$^2$) was detected at about the same time as soluble molybdenum, at 10 hr. However, it increased more slowly than molybdenum and maximized earlier, namely, 0.012 mmol at 40 hr.

All extracted solutions were also analyzed for soluble aluminum, titanium, tantalum, niobium, and nickel in addition to the species discussed above. The occurrence of soluble aluminum is an important feature in the hot corrosion of B-1900 and VIA (ref. 1), but none could be detected in any of the samples from IN-738. Of these five elements, only soluble nickel was found and this at levels less than 0.01 mmol. It occurred during the period of catastrophic corrosion and decreased after 60 hr.

Sulfur was found in the 5- and 10-hr alloy specimens at a level of 0.004 mmol. The value rose to 0.01 mmol in the 20-hr specimen and remained constant at that level until after 60 hr, at which time it began decreasing, reaching zero at 100 hr.

It is informative to compare the loss of sulfate with the cumulative quantity of SO$_2$ evolved during the course of hot corrosion. If the loss of sulfate is due to reaction with (a) Edge view with oxide scale intact, the oxides in the scale, namely Cr$_2$O$_3$ and TiO$_2$, there

(b) Edge view with oxide scale removed.

Figure 5.—Typical IN-738 specimen after corrosion with 3 mg cm$^{-2}$ Na$_2$SO$_4$ for 100 hr at 975°C in slowly flowing oxygen.

dropped rapidly from zero time, to 10 percent of its original value in 12.5 hr. It continued to decrease slowly after that, to essentially zero after 25 hr. All of the applied sodium (1/2 Na$^+$) was completely recovered up to about 5 hr. After that it decreased rapidly, to about 30 percent of its original value at 30 hr. This level persisted until about 40 hr, when it began to rise slightly. It peaked at about 75 hr at 0.07 mmol, then fell sharply to about 0.02 mmol at 90 hr, and finally leveled out at a little over 0.01 mmol at longer times.

The most striking feature of the analytical results was the large quantity of soluble chromium (CrO$_4$$^-$$^2$) formed: namely, 0.11 mmol. Only 0.03 mmol was found in similar studies with B-1900 and VIA (ref. 1). The soluble chromium was evidenced by the yellow chromate color found on the surfaces of cooled samples and also by the yellow color of the water-wash solutions extracted for analysis. The quantity of soluble chromium rose rapidly from the beginning of the test, maximized at around 10 hr, and then fell in a rapid, nearly linear manner until about 30 hr. After that it decreased slowly and reached very small values after about 60 hr.

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It is informative to compare the loss of sulfate with the cumulative quantity of SO$_2$ evolved during the course of hot corrosion. If the loss of sulfate is due to reaction with the oxides in the scale, namely Cr$_2$O$_3$ and TiO$_2$, there should have been a direct proportionality between the cumulative SO$_2$ evolved and the sulfate reacted, as shown by the equations

$$\text{Cr}_2\text{O}_3 + 2\text{Na}_2\text{SO}_4(\text{l}) + \frac{1}{2} \text{O}_2 \rightarrow 2\text{Na}_2\text{CrO}_4(\text{l}) + 2\text{SO}_2 \quad (1)$$

$$n \text{TiO}_2 + \text{Na}_2\text{SO}_4(\text{l}) \rightarrow \text{Na}_2\text{O(TiO}_2)_n\text{SO}_2 + \frac{1}{2} \text{O}_2 \quad (2)$$

Cumulative values for the SO$_2$ evolved were obtained by numerically integrating the monitored concentrations over time. These values are compared with the amount of

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1Soluble molybdenum was considered to come from Na$_3$MoO$_4$ even though MoO$_3$ is slightly soluble in hot water. The assumption is probably valid because of the greater solubility of Na$_3$MoO$_4$ and, more importantly, its great thermodynamic stability.
sulfate reacted in figure 6, where all quantities are expressed in millimols. The amount of sulfate reacted was obtained in two ways. The square points were obtained from the curve of the sulfate analysis given in figure 3(c). The circular points were obtained from long-time tests in which all of the sulfate applied reacted. Using the weight of the sulfate applied was probably more accurate than using the sulfate analysis.

It was evident that a direct relationship existed between the amount of SO₂ evolved and the sulfate reacted. However, it was also evident that it was not a one-to-one relationship as one would expect for reaction (1) or (2): the millimols of SO₂ evolved were only about 0.35 of the millimols of sulfate reacted. The discrepancy arose from the fact that we did not take into account the SO₃/SO₂ thermodynamic equilibrium in our calculations: actually, both SO₃ and SO₂ were present in the effluent gas. As shown in reference 1, the SO₃/SO₂ equilibrium was characteristic not of the furnace temperature, but of some lower temperature. Because the effluent gas seemed to be quenched at the bottom of the furnace, accurate theoretical correction for the presence of SO₃ was precluded. However, this difficulty did not detract from the direct relationship found between the SO₂ evolved and the sulfate reacted and lent credence to the occurrence of reaction (1) or (2) in the early part of the hot corrosion process.

**Microprobe Analysis**

Samples were prepared for microprobe examination from specimens that had been tested for 5 min and 5, 10, 20, 30, 40, 48, 56, 62, 68, 77, and 90 hr. All of the samples were examined carefully in several different areas, although primarily in the bottom half of the specimens, where the hot corrosion occurred. For the sake of brevity only micrographs of the most pertinent areas are presented. The 5-min sample served as a point of reference for the specimens corroded for longer times and more importantly proved the efficacy of our sample preparation techniques. The secondary electron and elemental X-ray micrographs for this sample are presented in figure 7. The area displayed was just below the middle of the specimen and shows the upper part of the Na₂SO₄ deposit that had slumped onto the bottom half of the specimen. The micrographs show that the oxide layer had been little affected by the Na₂SO₄ in this short time and that the scale was essentially the same as that of the preoxidized sample shown in figure 2.

The micrographs for the 5-hr sample, shown in figure 8, were radically different. The original, continuous Cr₂O₃-TiO₂ layer had been largely removed, as shown by islands of the alloy, with most of the active elements leached out, protruding along the surface. Only molybdenum and tungsten seemed to be present in the alloy islands along with the nickel and cobalt. The outer oxide layer was thus no longer continuous but still seemed to be composed primarily of Cr₂O₃ and TiO₂. The depletion of chromium in the alloy was becoming more pronounced. Although sulfur was not evident in these micrographs, sodium lay along the upper edge of the sample and seemed to be associated with chromium or titanium. The micrographic observations of this sample were complicated by the effects of a void that encircled most of the sample cross section between the oxide layer and the copper coating. Such voids occurred on both the 5-and 10-hr samples and also on duplicate samples taken at these times. A large drop of Na₂CrO₄ was observed visually on these specimens after hot corrosion testing, and it is believed that the void developed during polishing by removal of this Na₂CrO₄. In the microprobe examination X-rays emanating from the void complicated the interpretation of some of the elemental X-ray micrographs, especially those for chromium and sodium. The chromium micrograph in figure 8 indicates the presence of chromium in the void and depicts an almost continuous Cr₂O₃ layer on the sample even though the secondary electron micrograph clearly shows that the Cr₂O₃ layer was partly noncontinuous. Of course, the problem resulted from the poorer resolution inherent in the X-ray micrographs as compared with secondary and backscattered electron micrographs. Light micrographs were not affected by the presence of the void and show more unambiguously that the original continuous Cr₂O₃/TiO₂ layer had been removed and replaced by a discontinuous oxide. Light micrographs of the 5-hr sample and the original preoxidized sample are presented in figure 9 for comparison. The micrographs of the 10-hr sample were similar to those of the 5-hr sample and thus were omitted herein.

![Figure 6: Relationship between cumulative quantity of SO₂ evolved and quantity of sulfate reacted during hot corrosion of IN-738 at 975°C.](image-url)
Figure 7.—Secondary electron and X-ray micrographs of preoxidized IN-738 specimen corroded for 5 min at 975° C with 3 mg cm⁻² Na₂SO₄.
Figure 8.—Secondary electron and X-ray micrographs of preoxidized IN-738 specimen corroded for 5 hr at 975° C with 3 mg cm⁻² Na₂SO₄.
Figure 9.—Light micrographs of IN-738 specimens.

(a) Preoxidized for 24 hr at 975° C.
(b) Preoxidized for 24 hr and corroded for 5 hr at 975° C with 3 mg cm⁻² Na₂SO₄.

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For the 20-hr sample the micrographs (fig. 10) show that the oxide scale was reforming, having increased to 20 to 30 μm in thickness. The oxide was advancing into the region where the Al2O3 tentacles existed and was still primarily Cr2O3 and TiO2 though some NiO was now scattered throughout. Of course, the engulfed Al2O3 was also in the scale. The depletion zone for chromium was much wider and more depleted, as was that for titanium. Near the bottom of the depletion zone chromium sulfides are evident, and other sulfides, probably of chromium, were scattered throughout the upper portion of the depletion zone. Sodium was still situated along the outer edge of the sample and was probably associated with chromium and titanium. Some areas of sodium within the scale (i.e., the bright areas in the secondary electron micrograph) were associated with tantalum or niobium and were probably NaTaO3 or NaNbO3, formed from carbides that were there originally. Some of the sodium was also associated with the tantalum and niobium oxides lying along the bottom edge of the scale. No oxides of molybdenum or tungsten were evident; these components still seemed to be associated with the leached Ni–Co islands that were isolated between the Al2O3 tentacles in the growing scale: see nickel micrograph in figure 10.

The micrographs of the 30-hr sample (fig. 11) show that the oxide scale had continued to grow, being 25 to 35 μm thick. It was composed of Cr2O3, TiO2, engulfed Al2O3, and NiO. “Ghosts” of the Al2O3 tentacles appear near the bottom of the scale: the dark strings in the backscattered electron micrograph. The nickel oxide was becoming more prominent and some was concentrated along the outer edge of the oxide layer. Sodium was still distributed throughout the scale and in oxidized carbides with tantalum and niobium: one very prominent NaTaO3–NaNbO3 area was located in the upper central section of the oxide scale. Sulfur was at the bottom of the depletion zone and down along a grain boundary and was associated primarily with titanium. The most important feature on this sample was the appearance of an area of MoO3–WO3 at the bottom of the scale near the left side: the light gray area about 5μm in diameter in the backscattered electron micrograph. This was the first appearance of molybdenum and tungsten oxides.

In the 40-hr sample the oxide was about 30 to 35 μm thick although in a few spots it had grown to a thickness of 60 μm. One such area is shown in figure 12. The leached Ni–Co islands, which were isolated by the Al2O3 tentacles, seemed to have oxidized. The ghosts of the tentacles appear as the darker stringers in the backscattered electron micrograph, and they are still present in the aluminum micrograph. At the lower edge of the oxidized islands were isolated areas of MoO3–WO3. They are the bright areas in the backscattered electron micrograph, and they appear in the molybdenum and tungsten micrographs but with poorer resolution. They must have originated from the molybdenum and tungsten that were still in solution in the Ni–Co islands. The composition of the scale was similar to that of the 30-hr sample. However, all of the sodium in this area seemed to be tied up as NaTaO3/NaNbO3, and little or no sulfur was in evidence.

In the 48-hr sample a large fraction of the oxide was 60 μm thick, and as shown in figure 13, the morphology of these areas was similar to that of the thick area of the 40-hr sample. The backscattered electron micrograph shows the oxidized Ni–Co islands, lighter gray, with the ghosts of the Al2O3 tentacles still observable as darker gray tentacles. Bright areas of MoO3–WO3 lay along the bottom edge of the scale. The MoO3–WO3 areas were still discrete, but they were so numerous as to be almost continuous. Although some sodium was combined with the tantalum and niobium, some was also associated with the MoO3–WO3 areas, most probably as Na2MoO4 or Na2WO4. Sulfur was not very prevalent but occurred in a very faint concentration in the MoO3–WO3 areas. In addition to the NiO observed in the oxidized islands, some was also apparent along the outer edge of the scale.

In the 56-hr sample most of the oxide layer was similar to the area of the 48-hr sample presented in figure 13. However, in two areas the discrete MoO3–WO3 areas had obviously merged to form a large molten phase probably composed of MoO3–WO3 and Na2MoO4–Na2WO4. Micrographs of one of these areas are shown in figure 14. The light area along the bottom of the oxide scale in the backscattered electron micrograph is the molten MoO3–WO3/Na2MoO4–Na2WO4 phase. The sulfides had been engulfed by the molten phase and sulfur appeared in it. Sodium was distributed throughout the entire oxide layer and also appeared in the molten phase. The oxide scale was 80 to 90 μm thick and was composed of all of the metallic components of the alloy except molybdenum and tungsten. The striated or layered structure displayed here is characteristic of that found when acidic fluxing is occurring (ref. 1, fig. 14).

The 62-, 68-, and 77-hr samples all showed increasing occurrence of areas similar to that described for the 56-hr sample (fig. 14). One such area from the 77-hr sample is shown in figure 15. Again we see the large molten phase of MoO3–WO3/Na2MoO4–Na2WO4 lying along the underside of the oxide layer. The internal sulfides had been engulfed as the molten phase progressed across the sample under the scale. Again, the oxide was striated, or layered, and consisted of oxides of all of the metals in the alloy except molybdenum and tungsten.
Figure 10.—Secondary electron and X-ray micrographs of preoxidized IN-738 specimen corroded for 20 hr at 975° C with 3 mg cm$^{-2}$ Na$_2$SO$_4$. 
Figure 11.—Backscattered electron and X-ray micrographs of preoxidized IN-738 specimen corroded for 30 hr at 975° C with 3 mg cm\(^{-2}\) Na\(_2\)SO\(_4\).
Figure 12.—Backscattered electron and X-ray micrographs of preoxidized IN-738 specimen corroded for 40 hr at 975°C with 3 mg cm⁻² Na₂SO₄.
Figure 13.—Backscattered electron and X-ray micrographs of preoxidized IN-738 specimen corroded for 48 hr at 975°C with 3 mg cm⁻² Na₂SO₄.
Figure 14.—Backscattered electron and X-ray micrographs of preoxidized IN-738 specimen corroded for 56 hr at 975° C with 3 mg cm$^{-2}$ Na$_2$SO$_4$. 
Figure 15.—Backscattered electron and X-ray micrographs of preoxidized IN-738 specimen corroded for 77 hr at 975° C with 3 mg cm⁻² Na₂SO₄.
In the 90-hr sample the molten phase under the scale had decreased in prominence. In some areas the molten MoO3-WO3/Na2MoO4-Na2WO4 has been converted to solid NiMoO4-NiWO4.3 One such area is shown in figure 16. Here most of the thick oxide scale had peeled off the sample, leaving just the NiMoO4-NiWO4 layer. The layer exhibited a great deal of cracking within itself, which resulted from the NiMoO4 undergoing an allotropic transformation upon cooling. Some titanium, aluminum, and chromium were associated with the cracked layer, and even a little sulfur was discernible in it. Sulfur was primarily concentrated along a deep grain boundary. Sodium was no longer observed with the molybdate but had diffused deep into the alloy, where it had combined with tantalum and niobium located in internal carbides.

Rate Determinations of Pertinent Processes

To properly interpret the results presented so far, it seemed apparent that measurements of the rate of several pertinent physical and chemical processes were required. Extensive investigation of these processes was beyond the scope of this work. In addition, for the results to be applicable, we were constrained by the confines of our experimental apparatus. Nevertheless the work performed was sufficient to allow the formulation of some reasonable conclusions.

Evaporation rate of Na2SO4 and Na2CrO4.—Deposits of 3 mg cm⁻² of Na2SO4 or Na2CrO4 were air brushed onto coupons of the same size as the oxidation specimens. Gold coupons were used for Na2SO4 (ref. 16) and platinum for Na2CrO4. The weight loss was determined with the Cahn microbalance under the same experimental conditions as were used in the hot corrosion tests: namely, oxygen flow of 620 milliliters min⁻¹ and temperature of 975°C. Weight losses were monitored for periods up to 100 hr and were linear in time. After the tests the cooled coupons were washed and the resulting solutions analyzed for sodium and SO4⁻² or CrO4⁻². In all cases the analyses checked well with the measured weight losses. In addition, the pH values of the wash solutions were measured and were found to check well with the pH values of prepared solutions of the respective salts. This agreement in pH values indicated that no dissociative vaporization occurred.4 After-experiment weights of the coupons were the same as the before-experiment weights, showing that the coupons and the salts did not react. The rates of evaporation determined for the two salts are given in table II. We see that Na2CrO4 evaporated about 1.5 times more rapidly than Na2SO4.

Rate of reaction of Na2SO4 with the pure oxides Cr2O3 and TiO2.—The two reactions studied can be written

\[
\begin{align*}
\text{Cr}_2\text{O}_3 + 2\text{Na}_2\text{SO}_4(l) + 3/2\text{O}_2 & \rightarrow 2\text{Na}_2\text{CrO}_4(l) + 2\text{SO}_3(g) \\
n\text{TiO}_2 + \text{Na}_2\text{SO}_4(l) & \rightarrow \text{Na}_2\text{O} (\text{TiO}_2)_n + \text{SO}_3(g)
\end{align*}
\]

The same techniques employed in the hot corrosion tests of IN-738 were used here, except that the flow rate used was 1250 milliliters min⁻¹ instead of 620 milliliters min⁻¹. The increased flow was necessitated because of a leak in the water permeation dryer of the SO2 detector. This change had no apparent effect on the kinetic results. The Cr2O3 sample was made by preoxidizing a coupon of pure chromium at 975°C. Oxidation was continued until the scale contained about three times the amount of Cr2O3 required for reaction with the Na2SO4 to be applied. The TiO2 sample was made by plasma spraying high-purity TiO2 onto a platinum coupon and annealing at 975°C for 2 hr. Here also, the TiO2 applied was more than required for reaction with Na2SO4.

The results for one of the Cr2O3 specimens, which was tested for 2.5 hr, are shown in figure 17. We have plotted as a function of time the specific weight gain and the concentration of SO2 evolved in parts per million per unit area of the specimen. The specific weight underwent a small initial increase followed by a loss during the period that the SO2 + SO3 was volatilizing rapidly. Finally a slow increase occurred as some further oxidation of the chromium coupon ensued. The concentration of SO2 evolved rose rapidly to 4.3 ppm cm⁻² and then fell at a fast, though decreasing, rate. At the end of the experiment it was only 0.2 ppm cm⁻². As shown in figure 6, the quantity of SO2 evolved was proportional to the amount of SO4⁻² reacted. As a corollary to this, it can be concluded that the amount of SO2 evolving at any time was proportional to the rate of reaction of the SO4⁻² at that time. Because the amount of SO2 evolving determines its concentration in the gas phase, the concentration of SO2 is then proportional to the rate of reaction of the SO4⁻². Thus the low value for the concentration of SO2 at the end of the experiment indicated that the reaction between Cr2O3 and Na2SO4 had been mostly completed. This conclusion was supported by the chemical analyses of the water-wash solutions, the results of which are given in the first line of table III. They show that only 0.00385 mmol of SO4⁻²

---

3The NiMoO4-NiWO4 was identified by X-ray diffraction analysis of the surface of companion specimens.

4Some SO2 was detected during the Na2SO4 evaporation: being 0.026 ppm cm⁻² (0.18 ppm) at the beginning of the test and 0.016 ppm cm⁻² (0.11 ppm) after 100 hr. This SO2 probably originated not from dissociative vaporization of Na2SO4 but from reaction between the vaporizing Na2SO4 and the hot quartz furnace tube: SiO2 + Na2SO4 → Na2SiO3 + SO3(g).
Figure 16.—Backscattered electron and X-ray micrographs of preoxidized IN-738 specimen corroded for 90 hr at 975° C with 3 mg cm$^{-2}$ Na$_2$SO$_4$. 


**Table II.—Rates of Pertinent Processes**

<table>
<thead>
<tr>
<th>System</th>
<th>Evaporation rate, mmol cm⁻² hr⁻¹</th>
<th>First-order rate constant, k₁</th>
<th>Zero-order rate constant, k₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂SO₄(l) → Na₂SO₄(g)</td>
<td>1.0 × 10⁻⁴</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Na₂CrO₄(l) → Na₂CrO₄(g)</td>
<td>1.5 × 10⁻⁴</td>
<td>1.55</td>
<td>2.6 × 10⁻²</td>
</tr>
<tr>
<td>Cr₂O₇⁺ + 2Na₂SO₄(l) + 3/2O₂ → 2Na₂CrO₄O₇⁺ + 2SO₂(g)</td>
<td>----</td>
<td>1.25 × 10⁻³</td>
<td>2.1 × 10⁻⁵</td>
</tr>
<tr>
<td>nTiO₂ + Na₂SO₄(l) → Na₂O(TiO₂)ₙ + SO₃(g)</td>
<td>----</td>
<td>5.9 × 10⁻⁴</td>
<td>9.8 × 10⁻⁶</td>
</tr>
</tbody>
</table>

Calculations of the rate of evaporation of Na₂CrO₄, based on the results given in the last section, indicated that all of the Na₂CrO₄ formed from the amount of Na₂SO₄ reacted should have evaporated in 120 hr, just the length of the test. In column 8 we see that the ratio of the total amount of SO₂ evolved to the amount of SO₄⁻² reacted was 0.355, which is close to the value obtained from the IN-738 data presented in figure 6.

We desire to calculate a rate constant for reaction (3) from the data shown in figure 17 (i.e., the concentration of SO₂ as a function of time). As stated above, the concentration of SO₂ should be proportional to the rate of reaction of SO₄⁻². Because the SO₂ concentration fell rapidly, we have assumed that the reaction was first order with respect to the concentration of SO₄⁻². Therefore the kinetics should be described by the equation

\[ \frac{dC}{dt} = k_1 C \]  

(5)

where \( k_1 \) is the first-order rate constant and \( C \) is the concentration of SO₄⁻² at time \( t \). Integration of this equation yields

\[ \log \left( \frac{C_0}{C} \right) = \frac{k_1 t}{2.303} \]  

(6)

where \( C_0 \) is the initial concentration of SO₄⁻². Equation (6) shows that a plot of \( \log C \) versus \( t \) should give a straight line, the slope of which equals \( k_1/2.303 \). It also indicates that the rate constant is independent of the concentration units used. The concentration of SO₄⁻² at any time can be obtained from the cumulative SO₂ at any time by using the relationship shown in figure 6. The procedure is as follows:

1. The cumulative SO₂ at various times is obtained by numerical integration of the concentration-of- SO₂-versus-time curve.
2. The values of the cumulative SO₂, which are in units of ppm hr, are converted to millimols SO₂ by using the definition of ppm and the flow rate of oxygen.
TABLE III.—MASS BALANCE RESULTS OF OXIDE-\(\text{Na}_2\text{SO}_4\) REACTIONS

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactant system</td>
<td>Test duration, hr</td>
<td>(\text{SO}_4^{2-}) applied, mmol</td>
<td>(\text{SO}_4^{2-}) recovered, mmol</td>
<td>(\text{SO}_4^{2-}) reacted, mmol</td>
<td>Fraction (\text{SO}_4^{2-}) reacted</td>
<td>(\text{CrO}_4^{2-}) analysis, mmol</td>
<td>(\text{SO}_2) evolved, mmol</td>
<td>Ratio of (\text{SO}_2) evolved to (\text{SO}_4^{2-}) reacted</td>
<td>Calculated (-\Delta W_{\text{SO}_2}), mg</td>
<td>Experimental (-\Delta W_{\text{SO}_2}), mg</td>
<td>Calculated (\Delta W_{\text{Na}_2\text{SO}_4}), mg</td>
<td>Experimental (\Delta W_{\text{SO}_3}), mg</td>
<td></td>
</tr>
<tr>
<td>(\text{Cr}_2\text{O}_3) on Cr</td>
<td>2.5</td>
<td>0.0665</td>
<td>0.00385</td>
<td>0.0617</td>
<td>0.94</td>
<td>0.0615</td>
<td>0.0247</td>
<td>0.40</td>
<td>(a)</td>
<td>(a)</td>
<td>(a)</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>(\text{TiO}_2) on Pt</td>
<td>120</td>
<td>0.0510</td>
<td>0</td>
<td>0.0507</td>
<td>1.0</td>
<td>0</td>
<td>0.018</td>
<td>0.355</td>
<td>13.5</td>
<td>(a)</td>
<td>14.3</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>29</td>
<td>0.169</td>
<td>0.169</td>
<td>1.0</td>
<td>(a)</td>
<td>0.057</td>
<td>0.335</td>
<td>10.5</td>
<td>(a)</td>
<td>10.1</td>
<td>(a)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Not applicable.

through the furnace. For a flow rate of 1250 milliliters min\(^{-1}\) the conversion factor is \(\text{SO}_2\)(mmol) = 3.06 \times 10^{-3} \text{SO}_2\)(ppm hr).

(3) The millimols of \(\text{SO}_2\) evolved are converted to the millimols of \(\text{SO}_4^{2-}\) reacted by using the relationship given in figure 6, namely, by multiplying by the reciprocal of the slope, 2.86.\(^5\)

(4) The residual millimols of \(\text{SO}_4^{2-}\) at any time is obtained as the difference between the millimols of \(\text{SO}_4^{2-}\) reacted and the millimols applied initially.

From the values of residual \(\text{SO}_4^{2-}\) obtained by this procedure, a plot of log \(C\) versus \(t\) was constructed for the data of figure 17. The result is shown in figure 18, where we have plotted the negative log \(\text{SO}_4^{2-}\) (residual) in units of mmol cm\(^{-2}\) against time. The data followed a straight-line relationship reasonably well for the first 2 hr, during which 95 percent of the sulfate had reacted. The first-order rate constant obtained from the slope was \(k_1 = 1.55 \text{hr}^{-1}\) and is given in table II, where we have also expressed the rate constant in reciprocal minutes. This value can be looked on as the fraction of sulfate reacting each minute, namely, 2.6 percent. It is, however, the fraction of the concentration at the beginning of each minute, which is decreasing with time.

The results for \(\text{TiO}_2\) were quite different from those for \(\text{Cr}_2\text{O}_3\), as shown in figure 19. The specific weight fell at a constant rate throughout the experiment except for an initial period of about 4 hr. It tailed off at 24 hr, at which time the \(\text{Na}_2\text{SO}_4\) had practically all reacted. In addition, the concentration of \(\text{SO}_2\) evolved was practically constant throughout the experiment with an average value of about 0.145 ppm cm\(^{-2}\). The observed weight loss can be correlated with the expected evolution of \(\text{SO}_3\) (and \(\text{SO}_2\)) during the experiment as indicated by reaction (4). In addition, there should be an overall weight gain of the \(\text{TiO}_2\)-Pt coupon because of the formation of \(\text{Na}_2\text{O}(\text{TiO}_2)_n\). The results presented in the last line of table III correlate well with the behavior predicted by reaction (4). The experiment was run for 29 hr, and analysis of the water-wash solution indicated that all of the \(\text{SO}_4^{2-}\) applied had reacted (columns 3, 4, and 6 of table III). The cumulative \(\text{SO}_2\) evolved (column 8) was compared with the \(\text{SO}_4^{2-}\) reacted and the proportionality constant obtained was 0.335 (column 9). The total weight loss expected from \(\text{SO}_2 + \text{SO}_3\) evolution during the actual experiment can be calculated from the \(\text{SO}_4^{2-}\) that reacted. This calculated value is given in column 10 and agrees satisfactorily with the experimental value given in column 11. In addition, the overall weight gain of the platinum coupon after the experiment, resulting from \(\text{Na}_2\text{O}(\text{TiO}_2)_n\) formation, was calculated for the amount of \(\text{SO}_4^{2-}\) that had reacted. The value, given in column 12, agrees very well with the experimental value given in column 13. After the

---

\(^5\)For the best accuracy the values of the ratio for each experiment were used (i.e., the reciprocals of the values given in column 9 of table III).
We used the first-order constant for Cr$_2$O$_3$ since this gives comparable results. The rate constant may be multiplied by the proportionality factor, 2.85. Both Cr$_2$O$_3$ and TiO$_2$ showed faster reaction rates compared to other oxides present. The rates of reaction did not become comparable until the SO$_4^{2-}$ had practically all reacted. However, as seen in reaction (4), the rate of reaction of SO$_4^{2-}$ and the rate of loss of SO$_3$ are equivalent, so that the slope of the line in figure 19 represents $k_0$ for reaction (4). The value of $k_0$ calculated from this slope is given in table II, where we have used the units mmol cm$^{-2}$ hr$^{-1}$ and also mmol cm$^{-2}$ min$^{-1}$. The rate constant can also be calculated from the concentration of SO$_2$, 0.145 ppm cm$^{-2}$, by using the procedure described previously and the proportionality constant given in table III (column 9). The same value of $k_0$ is obtained by this method.

The rate constants given in table II can be used to calculate the relative rate of Na$_2$SO$_4$ reacting with Cr$_2$O$_3$ or TiO$_2$ during the hot corrosion of IN-738. The comparison is complicated somewhat by the fact that reaction (3) follows first-order kinetics so that the rate at any given time is a function of the concentration of SO$_4^{2-}$ at that time. However, we can determine the SO$_4^{2-}$ concentration on the IN-738 at any time from the smoothed curve of SO$_4^{2-}$ recovered given in figure 3(c). It can also be obtained from the SO$_2$ evolved (fig. 3(b)) by the method described previously, namely, by calculating the cumulative SO$_2$ for the desired time and multiplying by the proportionality factor, 2.85. Both methods give comparable results.

We calculated the rates for reactions (3) and (4) at various times during the IN-738 hot corrosion process. We used the first-order constant for Cr$_2$O$_3$ given in the table II and multiplied the zero-order rate constant for TiO$_2$ by 7.5 cm$^2$, a typical area for the IN-738 specimens. The results are given in table IV.

It is obvious that the Na$_2$SO$_4$ should react much more rapidly with Cr$_2$O$_3$ than with TiO$_2$ on the IN-738 alloy. Initially the Cr$_2$O$_3$ rate was a factor of 30 times faster. When the SO$_4^{2-}$ was half gone, after 2.5 hr, the factor was still 15. After 90 percent had reacted, at around 12.5 hr, the reaction with Cr$_2$O$_3$ was still three times faster than with TiO$_2$. The rates did not become comparable until the SO$_4^{2-}$ had practically all reacted. It may therefore be concluded that most of the Na$_2$SO$_4$ applied to the IN-738 specimens should react with the Cr$_2$O$_3$ in the preoxidized scale.

Rate of reaction of Na$_2$CrO$_4$ with TiO$_2$.—Considerable Na$_2$CrO$_4$ was formed in the initial stage of hot corrosion: 0.11 mmol as shown in figure 3(c). The Na$_2$CrO$_4$ can evaporate or react with other oxides present on the preoxidized IN-738 specimens. Because TiO$_2$ is

![Figure 19. Specific weight change and concentration of SO$_2$ evolved as a function of time for plasma-sprayed TiO$_2$ corroded at 975° C in flowing oxygen with 3 mg cm$^{-2}$ Na$_2$SO$_4$. (Sample area, 5.8 cm$^2$.)](image)

### Table IV. Relative reaction rates of Na$_2$SO$_4$ with Cr$_2$O$_3$ and TiO$_2$ during hot corrosion of IN-738

<table>
<thead>
<tr>
<th>Time, hr</th>
<th>Residual SO$_4^{2-}$, mmol</th>
<th>Fraction of residual SO$_4^{2-}$</th>
<th>R(Cr$_2$O$_3$)$^b$, mmol min$^{-1}$</th>
<th>R(TiO$_2$)$^b$, mmol min$^{-1}$</th>
<th>R(Cr$_2$O$_3$)/R(TiO$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.168</td>
<td>1.0</td>
<td>4.4 x 10$^{-3}$</td>
<td>1.5 x 10$^{-4}$</td>
<td>29</td>
</tr>
<tr>
<td>0.5</td>
<td>0.135</td>
<td>0.80</td>
<td>3.5</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>0.117</td>
<td>0.70</td>
<td>3.0</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>0.092</td>
<td>0.55</td>
<td>2.4</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>0.085</td>
<td>0.50</td>
<td>2.2</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>0.054</td>
<td>0.32</td>
<td>1.5</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td>7.5</td>
<td>0.035</td>
<td>0.21</td>
<td>9.1 x 10$^{-4}$</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>0.025</td>
<td>0.15</td>
<td>6.5</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>12.5</td>
<td>0.017</td>
<td>0.10</td>
<td>4.4</td>
<td>2.9</td>
<td></td>
</tr>
</tbody>
</table>

$^b$Calculated for a specimen area of 7.5 cm$^2$. 
the most abundant oxide other than Cr₂O₃, the rate of the following reaction was studied:

\[ n \text{TiO}_2 + \text{Na}_2\text{CrO}_4(\text{l}) \rightarrow \text{Na}_2\text{O} (\text{TiO}_2)_n + \text{CrO}_3(\text{g}) \] (9)

The oxide CrO₃ is very volatile at 975°C (ref. 17) and should volatilize as fast as it is formed. However, because of boundary layer considerations some fraction may be backreflected to the hot specimen (ref. 18). These back-reflected CrO₃ molecules would be decomposed on contact with the hot specimen and result in deposition of Cr₂O₃ on the specimen. For these molecules the net reaction would be

\[ n \text{TiO}_2 + \text{Na}_2\text{CrO}_4(\text{l}) \rightarrow \text{Na}_2\text{O} (\text{TiO}_2)_n + 1/2 \text{Cr}_2\text{O}_3 + 3/4 \text{O}_2 \] (10)

The specimens used were made by plasma spraying TiO₂ onto platinum coupons as before. They were annealed in oxygen for 2 hr at 975°C before testing. The Na₂CrO₄ was air brushed onto the specimens; about 3 mg cm⁻² was applied. The reaction was followed with the same techniques used in all of this work.

Several samples were tested for as long as 14 hr. They all exhibited the same behavior: a steady decrease in specific weight similar to that exhibited in figure 19 for the reaction of TiO₂ with Na₂SO₄. The rate of decrease was constant from the beginning of the test until its termination. The rate of weight loss was calculated to be 6.6 × 10⁻² mg cm⁻² hr⁻¹. When corrected for Na₂CrO₄ evaporation, it was 4.1 × 10⁻² mg cm⁻² hr⁻¹. The constant rate of weight loss indicates that the reaction of TiO₂ with Na₂CrO₄ was of zero order like the reaction of TiO₂ with NaESO₄. However, neither the rate of weight loss nor the total weight change could be correlated with those calculated for either reaction (9) or (10), because both reactions were occurring simultaneously.

The overall rate of reaction of Na₂CrO₄ can be calculated from the results of the chromium analyses of the water-wash solutions obtained at the end of the experiments. These data gave a value for the rate constant k₀ (analogous to k₀ in eq. (8)) of 9.55 × 10⁻² mg cm⁻² hr⁻¹ for Na₂CrO₄ reacting, which is equivalent to 5.9 × 10⁻⁶ mmol cm⁻² hr⁻¹ corrected for Na₂CrO₄ evaporation. The value for the rate constant is given in table II for comparison with the rate constant for reaction (4). Using the value of 9.55 × 10⁻² mg Na₂CrO₄ cm⁻² hr⁻¹ and the experimental value of the rate of weight loss, 4.1 × 10⁻² mg cm⁻² hr⁻¹, we calculated that 60 percent of the Na₂CrO₄ reacted by reaction (9) and 40 percent by reaction (10); that is, 40 percent of the CrO₃ formed was decomposed back onto the specimen before it could escape through the boundary layer. The overall weight gain of the coupon resulting from Na₂O(TiO₂)ₙ formation also corroborated these percentages for reactions (9) and (10). As in the reaction with TiO₂ and Na₂SO₄, X-ray diffraction analysis showed the presence of Na₂Ti₂O₁₁ on the coupons after the experiment, and the water-wash solutions showed just enough soluble sodium for equivalence to that required for the unreacted Na₂CrO₄.

### Chemical Mechanisms

The diverse results obtained in the present studies of the Na₂SO₄-induced hot corrosion of IN-738 can be explained in terms of the following sequence of reactions:

1. **Induction period (0 to 55 hr)**
   - (a) Region of weight loss (0 to 10 hr)—basic fluxing by Na₂SO₄
     \[ \text{CrO}_3 + 2 \text{Na}_2\text{SO}_4(\text{l}) + 3/2 \text{O}_2 \rightarrow 2 \text{Na}_2\text{CrO}_4(\text{l}) + 2 \text{SO}_3(\text{g}) \] (3)
     \[ n \text{TiO}_2 + \text{Na}_2\text{SO}_4(\text{l}) \rightarrow \text{Na}_2\text{O} (\text{TiO}_2)_n + \text{SO}_3(\text{g}) \] (4)
     - (b) Region of slow linear oxidation (10 to 55 hr)
       \[ \text{Na}_2\text{CrO}_4(\text{l}) \rightarrow \text{Na}_2\text{CrO}_4(\text{g}) \] (11)
       \[ n \text{TiO}_2 + \text{Na}_2\text{CrO}_4(\text{l}) \rightarrow \text{Na}_2\text{O} (\text{TiO}_2)_n + \text{CrO}_3(\text{g}) \] (9)

2. **Acceleration period (55 to 60 hr)**
   \[ \text{Na}_2\text{CrO}_4(\text{l}) + \text{MoO}_3(\text{l}) \rightarrow \text{Na}_2\text{MoO}_4(\text{l}) + \text{MoO}_3(\text{g}) \] (12a)
   \[ \text{MoO}_3(\text{l}) \rightarrow \text{MoO}_3(\text{g}) \] (13)
   \[ \text{Na}_2\text{O} (\text{TiO}_2)_n + \text{MoO}_3(\text{l}) \rightarrow \text{Na}_2\text{MoO}_4(\text{l}) + \text{W} + 1/2 \text{O}_2 \] (12d)
   \[ \text{Na}_2\text{W}_2\text{O}_7(\text{l}) + 1/2 \text{Cr}_2\text{O}_3 + 3/4 \text{O}_2 \] (13)
   \[ \text{Na}_2\text{O} (\text{TiO}_2)_n + \text{MoO}_3(\text{l}) \rightarrow \text{Na}_2\text{MoO}_4(\text{l}) + \text{WO}_3 \] (15)

The results of these reactions are discussed in detail earlier in the text.
(3) Period of rapid linear oxidation (60 to 75 hr)—
acidic fluxing

\[
\begin{align*}
\text{Cr}_2\text{O}_3 + 3 \text{MoO}_3(l) &\rightarrow 2 \text{Cr}^{3+} + 3 \text{MoO}_4^{-2} \quad (17a) \\
\text{Al}_2\text{O}_3 + 3 \text{MoO}_3(l) &\rightarrow 2 \text{Al}^{3+} + 3 \text{MoO}_4^{-2} \quad (17b) \\
\text{Ni} + \text{MoO}_3(l) &\rightarrow \text{NiO} + \text{MoO}_2 \\n\text{Co} + \text{MoO}_3(l) &\rightarrow \text{CoO} + \text{MoO}_2 \\
2 \text{Cr} + 3 \text{MoO}_3(l) &\rightarrow \text{Cr}_2\text{O}_3 + 3 \text{MoO}_2 \quad (19a) \\
2 \text{Al} + 3 \text{MoO}_3(l) &\rightarrow \text{Al}_2\text{O}_3 + 3 \text{MoO}_2 \quad (19b) \\
\text{MoO}_2 + \text{1/2} \text{O}_2 &\rightarrow \text{MoO}_3(1) \quad (20) \\
\text{NiO} + \text{Na}_2\text{MoO}_4(l) &\rightarrow \text{NiMoO}_4 + \text{Na}_2\text{O} \quad (21) \\
\text{NiO} + \text{MoO}_3(l) (\text{and WO}_3) &\rightarrow \text{NiMoO}_4 (\text{and NiWO}_4) \quad (22) \\
\text{Na}_2\text{O} + \text{Ta}_2\text{O}_5(\text{and Nb}_2\text{O}_5) &\rightarrow 2\text{NaTaO}_3(\text{and NaNbO}_3) \quad (23)
\end{align*}
\]

Although these thermodiagrams have been used extensively to interpret hot corrosion behavior in terms of the chemical reactions involved, their usefulness is limited because they give no information on the rates of the reactions or the extent of reaction. Therefore the interpretation of our results is based largely on the results of the kinetic studies described in a previous section.

**Induction Period, Region of Weight Loss (0 to 10 hr)**

Immediately upon bringing the test specimens to temperature, the Na$_2$SO$_4$ melted and started reacting with the Cr$_2$O$_3$ to form Na$_2$CrO$_4$ and gaseous SO$_3$, reaction (3). An indication of the early occurrence of this reaction was found in the evolution of SO$_2$ (fig. 3(b)), in the appearance of water-soluble chromium (fig. 3(c)), and in the rapid drop in residual SO$_4^{-2}$ (fig. 3(c)). This behavior is predicted by the stability diagram for chromium (fig. 20(a)), as noted above, which shows that Cr$_2$O$_3$ was not stable in neutral Na$_2$SO$_4$ for P$_O_2$ down to $10^{-3}$ atm and that Na$_2$CrO$_4$ was the stable phase.

Our rate studies of reaction (3) discussed previously indicate that the Cr$_2$O$_3$ should react rapidly with the Na$_2$SO$_4$ until all of the Na$_2$SO$_4$ is consumed. It appears from the amount of soluble chromium found (fig. 3(c)) that 0.11 mmol of Na$_2$SO$_4$ reacted with the Cr$_2$O$_3$ in the first 10 hr of hot corrosion. This is considerably more reaction than observed with B-1900 and VIA (ref. 1) where only 0.03 mmol of soluble chromium was found. To put it in perspective, the 0.11 mmol of CrO$_4^{-2}$ found was equivalent to about two-fifths of the Cr$_2$O$_3$ on the preoxidized IN-738 sample, or since the liquid Na$_2$SO$_4$ slumped to the bottom of the specimens, it was equivalent to removal of all of the Cr$_2$O$_3$ from the bottom two-fifths of the specimen.

After an incubation period of about 5 hr the TiO$_2$ on the specimen began to react with the Na$_2$SO$_4$ and formed water-insoluble Na$_2$O(TiO$_2$)$_n$, reaction (4). This is evidenced by the drop in soluble sodium beginning at this time (fig. 3(c)). This behavior is also predicted by the stability diagram for titanium (fig. 20(b)) as noted previously. Our kinetic studies also demonstrate that reaction (4) should occur, although comparing the rate with that of reaction (3), given in table IV, indicates that most of the Na$_2$SO$_4$ should react with the Cr$_2$O$_3$.

Some clarification of the application of the rate studies of Cr$_2$O$_3$ and TiO$_2$ to the initial rate of corrosion of IN-738 is necessary. Comparing the SO$_2$ concentrations of figure 3(b) for IN-738 and figure 17 for Cr$_2$O$_3$ indicates that the reaction with the alloy continued for 20 to 25 hr but the reaction with Cr$_2$O$_3$ was effectively completed in 2.5 hr. Obviously the pure Cr$_2$O$_3$ reacted more rapidly with the Na$_2$SO$_4$ than did the mixed oxide on the IN-738 alloy, which is 75-mol% Cr$_2$O$_3$ and 25-mol% TiO$_2$. The activity of the Cr$_2$O$_3$ in the oxide.
Figure 20.—Thermodynamic phase stability diagrams at 975° C. The Cr-, Ti-, Mo-, and W-O-S diagrams are superimposed on the Na-O-S diagram. The dashed line is drawn where $\log a_{Na_2O} = \log P_{SO_3(g)}$.

Mixture on the alloy was lower than that of the pure Cr$_2$O$_3$, and this probably accounts for the difference.

Quantitative interpretation of the IN-738 kinetic data is not possible at this time. It had been hoped that the rate data for the pure oxides Cr$_2$O$_3$ and TiO$_2$ would allow calculation of the rate of reaction of these oxides on the alloy. It appears that kinetic data for known mixtures of Cr$_2$O$_3$ and TiO$_2$ are required. Nevertheless, the rate studies with the pure oxides have demonstrated that the rate of reaction of Cr$_2$O$_3$ with Na$_2$SO$_4$, reaction (3), is much faster than that of TiO$_2$ with Na$_2$SO$_4$, reaction (4), as shown in tables II and IV. In addition, these studies have disclosed the important fact that both oxides continue to react until all of the Na$_2$SO$_4$ is consumed.

Induction Period, Region of Slow Linear Oxidation (10 to 55 hr)

One result of the rapid reaction between the Cr$_2$O$_3$ and the Na$_2$SO$_4$ that occurred during the first 10 hr of corrosion was the formation of 0.11 mmol of Na$_2$CrO$_4$, as shown in figure 3(c). This large quantity of Na$_2$CrO$_4$
was liquid at 975°C and covered the surface of the specimen like the Na2SO4 did originally. Examination of
figure 3(c) shows, however, that this soluble chromium
disappeared rather rapidly between 15 and 30 hr. Concomitantly soluble sodium decreased in a similar
manner. Closer examination showed that both species
lost about 0.085 mmol between 15 and 30 hr. Because the
disappearance was nearly linear over this span of time,
we can calculate a disappearance rate, namely, \(7.7 \times 10^{-4}\)
mmol cm\(^{-2}\) hr\(^{-1}\).

The soluble sodium and chromium can be lost by two
main processes at this time: evaporation of Na2CrO4 or
reaction with TiO2, reaction (9). We have determined the
rates of these two processes, under the conditions of our
experiments, and they are given in table II. The sum of the
rates of these two processes is \(7.4 \times 10^{-4}\) mmol cm\(^{-2}\) hr\(^{-1}\), which is in good agreement with the rate of
disappearance of soluble sodium and chromium. We may
conclude therefore that the loss of Na2CrO4 depicted in
figure 3(c) can be largely accounted for by vaporization
and by reaction with TiO2: 20 percent by evaporation; 80
percent by reaction.

Another result of rapid reaction between the Cr2O3
and Na2SO4 that occurred during the first 10 hr of
corrosion was the removal of a large portion of the
protective oxide scale. Thereafter the alloy began a long,
slow reoxidation that lasted until the end of the induction
period, reactions (12). This is shown by the nearly linear
weight gain displayed in figures 3(a) and 4 for this time
period. It is also evidenced by the thickening of the oxide
layer observed in the micrographs of the 20-, 30-, 40-, 48-, and 56-hr samples given in figures 10 to 14. The
reformed oxide was not protective in the usual sense even
though the rate of oxidation was relatively slow. This is
indicated by the fact that the weight increase was nearly
linear in time rather than parabolic. The inability of the
alloy to produce a protective oxide scale at this time
probably resulted from the large depletion of chromium
from its exterior areas. The depletion of chromium resulted partly from the preoxidation treatment, as
shown in the chromium micrograph of figure 2. However,
the situation was markedly aggravated by two
additional factors: (1) reoxidation and (2) the formation
of sulfides near the bottom of the depletion zone.6 The
chromium micrographs of the 20- and 30-hr samples
(figs. 10 and 11) show a 40-μm-wide depletion zone, and
the same is true for titanium.

The most important development during this period of
reoxidation was the gradual growth of areas of
MoO3-WO3 along the lower edge of the oxide layer. Soluble molybdenum (MoO4\(^{-2}\)) and tungsten (WO4\(^{-2}\))
were first detected in the water-wash solutions after 10 hr
of corrosion, and the quantities continued to increase
slowly throughout this period. Originally the soluble
species arose from reaction between MoO3-WO3 and the
considerable quantity of Na2CrO4, reaction (13). As the
Na2CrO4 was converted to Na2O(TiO2)n by reaction (9),
the soluble molybdenum and tungsten arose from
reaction of the oxides with the Na2O(TiO2)n, reaction
(14). Some of the recovery of soluble sodium after 40 hr
is probably due to this reaction.

The first appearance of MoO3-WO3 in the micro-
graphs of the corroded samples was in one area of the
30-hr sample (fig. 11). This sort of area increased in
number in the 40- and 48-hr samples (figs. 12 and 13),
and an almost continuous such area formed in the latter.
The micrographs of these latter two samples show how
the MoO3-WO3 areas developed. It appears that after the
reformed oxide layer reached a thickness of about 30 μm,
the underlying Ni-Co islands, which were isolated by the
Al2O3 tentacles, were leached of all active elements except molybdenum and tungsten. Further oxidation of
the specimen effect oxidized reaction of the Ni-Co islands.
The molybdenum and tungsten that were dissolved in the
islands oxidized also, but these oxides seemed to migrate
to the interface between the oxidized islands and the
alloy. Sodium was usually found to be associated with the
MoO3-WO3 areas, although the amount varied from
considerable to nearly none as in the area of the 40-hr
sample shown in figure 12. The presence of sodium
would lower the melting point of the MoO3-WO3
because of the formation of Na2MoO4-Na2WO4 and
would also reduce the effective vapor pressure, as
discussed in reference 1. Toward the latter part of this
period the soluble tungsten started to decrease, probably
by reaction (15). This resulted from the slightly greater
thermodynamic stability of Na2MoO4 as compared with
Na2WO4 (figs. 20(c) and (d)).

We see that the period from 10 hr to the end of the
induction period, 55 hr, is a time in which the alloy slowly
reoxidized to form an oxide scale about 60 μm thick. The
important characteristics of this oxide are that it is
nonprotective and, most importantly, that numerous
discrete areas of MoO3-WO3/Na2MoO4-Na2WO4 are
formed along the lower edge.

**Acceleration Period (55 to 60 hr)**

After the long period of linear weight gain the
corrosion process began to accelerate at about 55 hr (fig.
3(a)). Simultaneously, the amount of soluble molybdenum markedly increased (fig. 3(c)). This must
have resulted from an increase in the rate of formation of
Na2MoO4 by reactions (15) and (16), probably as a result
of the considerable quantity of MoO3 that had
accumulated along the oxide scale. This larger amount of
Na2MoO4 had a pronounced effect on the morphology of
the corrosion samples, because it effect melts the of the
discrete MoO3-WO3/Na2MoO4-Na2WO4 areas so that

---

6 Sulfides can undergo oxidation. The released sulfur diffuses into
the alloy and reforms additional sulfides (ref. 20).
they coalesced into a large molten phase.\textsuperscript{7} One such area is shown in the micrographs of the 56-hr sample (fig. 14). The molten oxide phase migrated across the sample, disrupting and fluxing the scale above it. In addition, it seemed to be progressing into the alloy itself. The oxide above the \(\text{MoO}_3-\text{WO}_3/\text{Na}_2\text{MoO}_4-\text{Na}_2\text{WO}_4\) was striated and layered in appearance, a typical example of acidic fluxing. However, most of the oxide layer on this sample was still similar to that for the 48-hr sample (fig. 13) with discrete areas of \(\text{MoO}_3-\text{WO}_3/\text{Na}_2\text{MoO}_4-\text{Na}_2\text{WO}_4\).

**Period of Rapid Linear Oxidation (60 to 75 hr)**

Beyond 60 hr the quantity of \(\text{Na}_2\text{MoO}_4\) increased rapidly, and more and more of the discrete oxide areas merged into large molten masses below the oxide scale. This is shown in the micrographs of the 62-, 68-, and 77-hr samples. In the 77-hr sample (fig. 15) the large molten phase of \(\text{MoO}_3-\text{WO}_3/\text{Na}_2\text{MoO}_4\) had finally become a major feature of the scale.\textsuperscript{8} This development promoted acidic fluxing of the oxide scale by reactions (17). A major breakup of large areas of the oxide scale occurred and exposed the alloy specimen to the oxidizing atmosphere. Rapid oxidation of the alloy ensued, especially nickel and cobalt, and produced a large, porous oxide scale like that shown in figure 4. The rate of oxidation was linear and amounted to nearly 3 mg cm\(^{-2}\) hr\(^{-1}\), which was about 20 times faster than the rate observed in the induction period. In addition, it appeared to us that the molten oxide phase attacked the alloy itself, possibly by reactions (18) and (19).\textsuperscript{9} Reactions like these were first suggested by Leslie and Fontana (ref. 22) and have been discussed more recently by Peters, Whittle, and Stringer (ref. 23).

The acidic fluxing was self-sustaining and accounted for the linear nature of the attack. The self-sustaining feature resulted from the cyclic operation of reactions (17)\textsuperscript{10} and their reverse reactions. After solution of the oxides in the molten \(\text{MoO}_3-\text{WO}_3/\text{Na}_2\text{MoO}_4\) phase, reactions (17), the metal cations diffused to the outer zone of the melt, where they were reoxidized by the higher oxygen potential. The cycle kept repeating as the alloy was consumed. The cyclic behavior of acidic fluxing can be explained more quantitatively by the Rapp-Goto model (ref. 25) in which attack is explained in terms of a negative solubility gradient of the corrosion product across the molten phase. The striated appearance of the oxide (fig. 15) is a result of this cyclic nature of the attack. Reactions (18) and (19) can also exhibit a cyclic behavior through reoxidation of \(\text{MoO}_2\) at the outer zone of the melt, reaction (20).

As stated previously, evolution of \(\text{SO}_2\) was observed during this period of rapid oxidation. It was first detected at about 57 hr, rose to a maximum of 0.014 ppm cm\(^{-2}\) (0.1 ppm) at 80 hr, fell off gradually, and approached zero at 115 hr. In all it amounted to around 0.005 mmol. The \(\text{SO}_2\) must have resulted from oxidation of the sulfur observed in the molten oxide phase. This conclusion is supported by the observation that the sulfur content of the test specimens dropped from 0.01 mmol for the 50-hr sample to 0.005 mmol for a 75-hr sample.

**Deceleration Period (75 hr to End)**

At just about 75 hr the corrosion rate decelerated (fig. 3(a)). The magnitude of the deceleration continued to increase with time. This resulted from the conversion of the molten \(\text{MoO}_3-\text{WO}_3/\text{Na}_2\text{MoO}_4\) to solid \(\text{NiMoO}_4-\text{NiWO}_4\) by reactions (21) and (22) and was accompanied by a rapid decrease in both soluble molybdenum and sodium (fig. 3(c)). These nickel compounds are very stable, and their formation eliminated the molten oxide phase that was causing the acidic fluxing of the alloy specimen. Figure 3(c) shows that the \(\text{Na}_2\text{MoO}_4\) was reduced to only 0.01 mmol at 90 hr. This value is below that at which the catastrophic attack began at 55 hr. As a result the rate of corrosion was reduced. An area where this transformation occurred is shown in the micrographs of the 90-hr sample (fig. 16). Here \(\text{NiMoO}_4-\text{NiWO}_4\) was found along the oxide alloy interface and no evidence of a molten phase was present. In fact, the oxide scale had cracked off at the \(\text{NiMoO}_4-\text{NiWO}_4\) phase, which itself was also full of cracks. As stated before, this resulted from an allotropic transformation that occurred upon cooling. Sodium was found deep in the alloy in the carbidic with titanium, tantalum, and niobium, reaction (23).

\textsuperscript{7}Although \(\text{MoO}_3\) melts at 800° C, \(\text{WO}_3\) melts at 1473° C. The two oxides form an eutectic melting at 770° C. However, the composition at this point is 98-mol\% \(\text{MoO}_3\) and 2-mol\% \(\text{WO}_3\) (ref. 21). Only compositions containing more than 70-mol\% \(\text{MoO}_3\) melt below 975° C, the temperature of our experiments. Because the mol percent of molybdenum and tungsten in IN-738 are 1.0 and 0.8, respectively, it is doubtful that the mixed \(\text{MoO}_3-\text{WO}_3\) areas would have a composition that would melt. The addition of \(\text{Na}_2\text{MoO}_4\) or \(\text{Na}_2\text{WO}_4\), both of which melt below 700° C (ref. 21) would undoubtedly lower the melting points of the mixed \(\text{MoO}_3-\text{WO}_3\) (ref. 21). Certainly the considerable amounts of \(\text{Na}_2\text{MoO}_4\) shown in figure 3(c) after 60 hr would lower the melting points below 975° C (ref. 21).

\textsuperscript{8}At this stage soluble tungsten had practically disappeared (fig. 3(c)) and most of the sodium was associated with molybdenum.

\textsuperscript{9}These reactions are favored thermodynamically. Calculations indicate that the standard free energies at 975° C are negative, especially in the case of \(\text{Al}\) and \(\text{Cr}\): for \(\text{Al}\), reaction (19a), \(\Delta G = -577\ \text{kJ mol}^{-1}\); for \(\text{Cr}\), reaction (19a), \(\Delta G = -1060\ \text{kJ mol}^{-1}\); for \(\text{Co}\), reaction (19b), \(\Delta G = -54\ \text{kJ mol}^{-1}\); for \(\text{Ni}\), reaction (18a), \(\Delta G = -71\ \text{kJ mol}^{-1}\).

\textsuperscript{10}These reactions are somewhat hypothetical and await substantiation from studies of the \(\text{MoO}_3-\text{WO}_3/\text{Na}_2\text{MoO}_4\) system. However, some experimental justification does exist. Bornstein et al. (ref. 24) have shown that \(\text{Al}_2\text{O}_3\) exhibits an extremely rapid rate of dissolution in molten \(\text{MoO}_3\) at 90° C.
Mass Balance

If the loss of Na₂SO₄ observed in these experiments can be ascribed to the processes that we have described, we should be able to account for the Na₂SO₄ at various times during the corrosion process by a mass balance equation. Actually, we are balancing the soluble sodium and the oxide ion, or more simply the Na₂O. The results of such calculations for various times are presented in table V. The calculations are based on the amounts of soluble species given in figure 3(c) and on the rates of evaporation of Na₂SO₄ and Na₂CrO₄ given in table II. All quantities are given in millimols and are characteristic of a specimen area of 7.35 cm².

In column 2 we give the amount of SO₄⁻² recovered, beginning at zero time with the amount originally applied. The quantity of Na₂SO₄ lost by evaporation is given in column 3. This was not continued beyond 10 hr because the Na₂SO₄ had largely reacted by this time and was mixed with a large amount of Na₂CrO₄, which lowered its activity. In column 4 we give the amount of Na₂SO₄ that reacted with Cr₂O₃, reaction (3), and formed Na₂CrO₄. The CrO₄⁻² reached a maximum at 10 hr and decreased after that because of vaporization and sequential reactions with other oxides: TiO₂, WO₃, and MoO₃. The loss due to Na₂CrO₄ evaporation is given in column 5. Values have been calculated up to 30 hr, at which time the Na₂CrO₄ was largely consumed. In column 6 we give the amount of Na₂SO₄ that reacted with TiO₂, reaction (4). It was assumed that little reaction took place during the first 5 hr because reaction (4) exhibited an incubation period in our rate studies (fig. 19) and also because the rate of the reaction on the alloy was probably less than that on the pure oxide. Because the Na₂SO₄ was largely used up after 10 hr, the reaction was not considered after that. The value given in column 6 was obtained by measuring the drop in soluble sodium at 10 hr, 0.025 mmol, and subtracting the amount of the 1/2 Na lost by evaporation of Na₂SO₄ and Na₂CrO₄ during this 10 hr, 0.007 mmol + 0.011 mmol = 0.018 mmol.

The main sequential reaction that decreased CrO₄⁻² was that with TiO₂, reaction (9), which became important at about 15 hr. The amount of CrO₄⁻² reacting (column 7) was obtained from the drop in the 1/2 Na from time zero by subtracting the 1/2 Na lost by evaporation of Na₂SO₄ (column 3) and Na₂CrO₄ (column 5) and by reaction (4) (column 6). Soluble tungsten (WO₄⁻²) is given in column 8; it was formed from WO₃ in sequential reactions with Na₂CrO₄ (10 to 40 hr), reaction (13), and with Na₂O(TiO₂)ₙ (30 to 45 hr), reaction (14). After 45 hr it was lost by reaction with MoO₃, reaction (15). Soluble molybdenum (MoO₄⁻²) is given in column 9; it was formed in sequential reactions with Na₂CrO₄ (10 to 40 hr), reaction (13), and with Na₂O(TiO₂)ₙ (30 to 75 hr), reaction (16); and finally with Na₂WO₄ (45 to 75 hr), reaction (15). Beyond 75 hr, soluble molybdenum was lost by another sequential reaction with NiO, reaction (21). Concomitantly soluble sodium was lost by reaction (23). The last column, 10, gives the sums of columns 2 to 9 inclusive and should always equal 0.168 mmol, the amount of Na₂SO₄ applied. Although the sums for the different times chosen (except zero time) check fairly well within themselves, their average value is 0.158 mmol, 0.01 mmol less than the amount applied. This discrepancy is not too disturbing if we consider the complexity of the system, the many processes involved, and the inaccuracies inherent in some of the chemical analyses. Actually both Na₂SO₄ and Na₂CrO₄ crept up the platinum hangdown that supported the samples. Corrections for this problem were made, but the accuracy was limited. In addition, in our water-wash procedure the

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<th>Loss by Na₂CrO₄</th>
<th>Reaction (4), mmol -1/2 Na</th>
<th>Reaction (9), mmol -1/2 Na</th>
<th>Reactions (13) and (14), mmol WO₄⁻²</th>
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TABLE V.—SODIUM SULFATE MASS BALANCE
The self-consistency displayed by the totals at different times (column 10) is taken as support for the validity of the corrosion mechanism that has been enumerated here and as an indication that no major processes have been overlooked. Some have been included but not discussed, for instance, the formation of the chromium and titanium sulfides observed in the micrographs of the 20-and 30-hr samples. As shown in figure 3(c), sulfur was present even in the 5- and 10-hr samples and increased to 0.01 mmol in the 20- to 50-hr samples. Although this sulfide formation leads to degradation of the alloy, it is thought to be of secondary importance in the overall mechanism. However, it does contribute to the depletion of chromium and the resulting inability of the alloy to form a protective oxide scale during the induction period. Finally, the formation of NaTaO₃ and NaNbO₃, also present in the micrographs of the 20- and 30-hr samples, has not been discussed. This is an important reaction in some alloys, as discussed previously (ref. 26), because NaTaO₃ seems to act as a sink for Na₂O and thus inhibits the formation of Na₂MoO₄. However, it has not been effective in this case because of the low concentration, 0.6 mol%, of tantalum and niobium in IN–738.

**Conclusions**

We have shown that hot corrosion of IN–738 was initiated by basic fluxing of the protective Cr₂O₃–TiO₂ scale and that the fluxing reaction continued as long as Na₂SO₄ was available. Reoxidation of the alloy could not produce a protective scale because chromium was depleted from the exterior surfaces. A long, slow, but linear, oxidation ensued during which MoO₃–WO₃ built up along the oxide-alloy interface. Gradually, MoO₃ reacted with Na₂CrO₄ and Na₂O(TiO₂)ₙ to form Na₂MoO₄, which lowered the melting point of the MoO₃–WO₃ areas. Large areas of the molten phase MoO₃–WO₃/Na₂MoO₄ were formed, and these areas effected acidic fluxing of the oxide scale and resulted in catastrophic attack of the alloy. Eventually, the attack slowed down as Na₂MoO₄ and MoO₃–WO₃ were converted to their corresponding nickel salts. However, the alloy specimen was largely destroyed by this time.

The Na₂SO₄ had two main effects in this mechanism of hot corrosion: (1) it removed the protective Cr₂O₃–TiO₂ scale; and (2) it supplied sodium that eventually formed Na₂MoO₄, which caused the MoO₃–WO₃ area to melt. Therefore any method of removing the scale should cause hot corrosion if sodium is available; in contrast, if sodium is extracted after scale removal, no hot corrosion should occur. With reference to the first effect, Bourhis and St. John found in Na₂SO₄-induced hot corrosion tests at 900 °C that alloys forming a protective Cr₂O₃ layer are not susceptible to accelerated attack. However, if the oxide scale is removed by abrasion, heavy corrosion occurs. We performed tests in which the preoxidation scale was removed by water quenching. The specimen was then coated with 2 mg cm⁻² of Na₂CrO₄ to supply a source of sodium and to simulate our normal tests. The specimen was oxidized at 975 °C and catastrophic hot corrosion occurred in 60 hr, a time not much different from our normal induction period. With reference to the second effect, a normal hot corrosion test was stopped after 10 hr. By this time the protective oxide scale had been largely fluxed. The specimen was cooled and water washed; this removed the Na₂CrO₄ that had formed and any Na₂SO₄ that had not reacted. The oxidation was then restarted and continued for times out to 200 hr. Although a long period of reoxidation ensued, no catastrophic hot corrosion occurred.

The corrosion mechanism postulated herein includes several new ideas and new processes. We have demonstrated that Na₂SO₄ fluxed the Cr₂O₃–TiO₂ scale until all of the Na₂SO₄ was consumed. Generally, it has been believed that reaction (3) resulted in the Na₂SO₄ becoming so “acidic” that the Cr₂O₃ became stable in the Na₂SO₄ and reaction ceased (ref. 27). We have shown that Na₂CrO₄ reacted with TiO₂ to form Na₂O(TiO₂)ₙ and that both of these compounds reacted with MoO₃–WO₃ to form the low-melting Na₂MoO₄ and Na₂WO₄. We have further shown that acidic fluxing was caused by a molten MoO₃–WO₃ oxide phase containing Na₂MoO₄, instead of a molten Na₂SO₄ phase “acidified” by dissolved MoO₃–WO₃ (ref. 28). In addition, we have suggested that the molten MoO₃–WO₃/Na₂MoO₄ phase can attack the components of the alloy itself by a form of basic fluxing involving MoO₃ and MoO₂.

Two methods of preventing hot corrosion of these alloys that form principally Cr₂O₃ protective scales are suggested by this research: increase the chromium content of the alloy, and replace the molybdenum and possibly the tungsten with tantalum or niobium. This latter suggestion has been made previously in references 1 and 26. It appears that in IN–738, in which there is such a small amount of molybdenum to begin with (1.0 mol%), catastrophic corrosion would be eliminated by this replacement.

The application of the corrosion mechanism postulated herein to the problem of hot corrosion of IN–738 in gas turbine engines is complicated by the widely different environmental conditions encountered in service. Although the mechanism is based on laboratory results, we feel that the same processes are involved in practice. However, the relative importance of the various processes may be quite different. Certainly the rate of evaporation of Na₂CrO₄ will be considerably higher in the high-velocity flow environment of a gas turbine. As
compared with our tests, this should decrease the formation of Na$_2$MoO$_4$ and lengthen the induction period for catastrophic corrosion. However, the repeated engine cycling and attendant spallation would accelerate chromium depletion and probably shorten the induction period. The most significant and probably the overriding factor is that in an operating gas turbine the Na$_2$SO$_4$ in being deposited more or less continuously. If the salt level is high, as in a marine environment, the Na$_2$SO$_4$ will probably effect catastrophic hot corrosion. But if the salt level is low, as in a power generating turbine, the high rate of vaporization of Na$_2$CrO$_4$ and MoO$_3$ may prevent catastrophic hot corrosion entirely. A quantitative evaluation of these many complex processes is not possible at this time.

It is necessary to stress the importance of using kinetic data in interpreting hot corrosion processes. To the present time interpretation has been based on thermochemical Pourbaix diagrams. Such diagrams have been invaluable, but, as stated previously, their usefulness is limited because they give no information on the rate of the reactions or the extent of reaction. In addition, the environment in a gas turbine is hardly an equilibrium system. Even if the SO$_3$ pressure is maintained at some constant value, SO$_3$ is only one of the products being evolved in the reaction between Na$_2$SO$_4$ and Cr$_2$O$_3$. The Na$_2$CrO$_4$ also evaporates, as we have shown, at a measurable rate of 1.5 x 10$^{-4}$ mmol cm$^{-2}$ hr$^{-1}$. In the high-velocity environment of a gas turbine this rate would be increased markedly.

Unfortunately there is little kinetic data available for reactions of the type involved in hot corrosion. Although we have studied three such reactions, reactions (3), (4) and (9), our investigation was limited. The need for more extensive information of this type is imperative to the proper interpretation of hot corrosion phenomena.

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References


11Gas turbine combustion gases contain SO$_3$ at partial pressures between 10$^{-6}$ and 10$^{-4}$ atm depending on the fuel sulfur content. The SO$_3$ evolved in our tests were equivalent to a partial pressure of 5 x 10$^{-5}$ to 5 x 10$^{-6}$ during the course of reaction (3).
Sodium-sulfate-induced hot corrosion of preoxidized IN-738 was studied at 975°C with special emphasis placed on the processes occurring during the long induction period. Thermogravimetric tests were run for predetermined periods of time, and then one set of specimens was washed with water. Chemical analysis of the wash solutions yielded information about water-soluble metal salts and residual sulfate. A second set of samples was cross sectioned dry and polished in a nonaqueous medium. Element distributions within the oxide scale were obtained from electron microprobe X-ray micrographs. Evolution of SO3 was monitored throughout the thermogravimetric tests. Kinetic rate studies were performed for several pertinent processes; appropriate rate constants were obtained from the following chemical reactions:

\[
\begin{align*}
\text{Cr}_2\text{O}_3 + 2 \text{Na}_2\text{SO}_4(1) + 3/2 \text{O}_2 & \rightarrow 2 \text{Na}_2\text{CrO}_4(1) + 2 \text{SO}_3(g) \\
n \text{TiO}_2 + \text{Na}_2\text{SO}_4(1) & \rightarrow \text{Na}_2\text{O(TiO}_2)_n + \text{SO}_3(g) \\
n \text{TiO}_2 + \text{Na}_2\text{CrO}_4(1) & \rightarrow \text{Na}_2\text{O(TiO}_2)_n + \text{CrO}_3(g)
\end{align*}
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16. Key Words (Suggested by Author(s))

Alloy; Analysis; Corrosion; Oxidation

18. Distribution Statement

Unclassified - unlimited
STAR Category 26