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 SO2 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:

\[
\text{Cr}_2\text{O}_3 + 2 \text{Na}_2\text{SO}_4(l) + 3/2 \text{O}_2 \rightarrow 2 \text{Na}_2\text{CrO}_4(l) + 2 \text{SO}_3(g)
\]

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

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

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 Na2SO4 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 α-Al2O3. Hot corrosion was induced by coating metal samples with Na2SO4 and oxidizing them at higher temperatures. Thermogravimetric tests were performed and SO2 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 Al2O3 layer by the liquid Na2SO4 deposit. This was followed by a catastrophic rate of attack resulting from an acidic fluxing of the remaining oxide layer by a Na2MoO4–MoO3 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 Cr2O3. 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 Na2SO4-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 Na2SO4-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 \( \times \) 1.0 \( \times \) 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 Na\(_2\)SO\(_4\) followed by isothermal oxidation at 975° C. The Na\(_2\)SO\(_4\) was applied by air brushing a saturated solution of Na\(_2\)SO\(_4\) 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. 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.

<table>
<thead>
<tr>
<th>TABLE I.—COMPOSITION OF IN–738</th>
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<td>Element</td>
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<tr>
<td>Nickel</td>
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<td>Chromium</td>
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<td>Aluminum</td>
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<td>Zirconium</td>
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<td>Carbon</td>
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The concentration of SO\(_2\) 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 SO\(_2\). The detection capability extended from 0.01 to 50 ppm. The effluent from the furnace tube was conducted into the SO\(_2\) 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 with copper in an electron beam evaporator before they were mounted and were cross sectioned dry over an 8-hr period. The samples were washed 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 Cr\(_2\)O\(_3\) and TiO\(_2\) 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 spill 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. The behavior was never a typical hot corrosion attack. The hot corrosion attack occurred primarily on the bottom half and spread very slowly to the upper half of the specimen. This behavior was not 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 $\pm$0.25 ppm cm$^{-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 $\pm$10 percent in the length of their induction periods. Tests were run for 5 and 15 min, and for 2.5, 5, 10, 15, 20, 30, 40, 50, 56, 60, 73, 83, 90, and 100 hr. The results of chemical analysis are given in figure 3(c), where we have plotted as a function of time the millimols of each element found and the SO$_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 $\pm$5 percent, all quantities of the soluble species given in figure 3(c) were normalized to 0.168 mmol Na$_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 80 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 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

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

$$n \text{TiO}_2 + \text{Na}_2\text{SO}_4(l) \rightarrow \text{Na}_2\text{O(TiO}_2)_n\text{SO}_2 + \frac{1}{2} \text{O}_2$$ (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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1 Soluble 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.
SO2 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 continuous Cr2O3 layer was partly noncontinuous. Of occurrence of reaction (I) or (2) in the early part of the though the secondary electron micrograph clearly shows and the sulfate reacted and lent credence to the almost continuous the direct relationship found between the SO2 evolved the presence of chromium in the void and depicts an precluded. However, this difficulty did not detract from sodium. The chromium micrograph in figure 8 indicates the theoretical correction for the presence of SO3 was X-ray micrographs, especially those for chromium and to be quenched at the bottom of the furnace, accurate complicated the interpretation of some of the elemental thermodynamic equilibrium in our calculations: actually, these times. A large drop of Na2CrO4 was observed was obtained in two ways. The square points were denum and tungsten seemed to be present tn the alloy 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.

\[ \text{SO}_2 = \text{SO}_3 / 0.32 \text{ at } 900^\circ \text{C}. \]

The SO3/SO2 ratio in ref. 1 was mistakenly inverted during printing to SO2/SO3. It should be SO3/ \text{SO}_2 = 0.32 at 900\textdegree \text{C}. \]
Figure 7.—Secondary electron and X-ray micrographs of preoxidized IN-738 specimen corroded for 5 min at 975° C with 3 mg cm$^{-2}$ Na$_2$SO$_4$. 
Figure 8.—Secondary electron and X-ray micrographs of preoxidized IN-738 specimen corroded for 5 hr at 975° C with 3 mg cm$^{-2}$ Na$_2$SO$_4$. 
(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\(^{-2}\) Na\(_2\)SO\(_4\).

Figure 9.—Light micrographs of IN-738 specimens.
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 5 μm 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 Na₂SO₄.
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$^{-2}$ Na$_2$SO$_4$. 
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 MoO$_3$-WO$_3$/Na$_2$MoO$_4$-Na$_2$WO$_4$ has been converted to solid NiMoO$_4$-NiWO$_4$. One such area is shown in figure 16. Here most of the thick oxide scale had peeled off the sample, leaving just the NiMoO$_4$-NiWO$_4$ layer. The layer exhibited a great deal of cracking within itself, which resulted from the NiMoO$_4$ 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 Na$_2$SO$_4$ and Na$_2$CrO$_4$.**—Deposits of 3 mg cm$^{-2}$ of Na$_2$SO$_4$ or Na$_2$CrO$_4$ were air brushed onto coupons of the same size as the oxidation specimens. Gold coupons were used for Na$_2$SO$_4$ (ref. 16) and platinum for Na$_2$CrO$_4$. 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 water washed and the resulting solutions analyzed for sodium and SO$_4^{2-}$ or CrO$_4^{2-}$. 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. 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 Na$_2$CrO$_4$ evaporated about 1.5 times more rapidly than Na$_2$SO$_4$.

**Rate of reaction of Na$_2$SO$_4$ with the pure oxides Cr$_2$O$_3$ and TiO$_2$.**—The two reactions studied can be written

$$\text{Cr}_2\text{O}_3 + 2\text{Na}_2\text{SO}_4(\ell) + 3/2\text{O}_2 \rightarrow 2\text{Na}_2\text{CrO}_4(\ell) + 2\text{SO}_3(\text{g})$$

(3)

$$n\text{TiO}_2 + \text{Na}_2\text{SO}_4(\ell) \rightarrow \text{Na}_2\text{O(TiO}_2)_n + \text{SO}_3(\text{g})$$

(4)

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 SO$_2$ detector. This change had no apparent effect on the kinetic results. The Cr$_2$O$_3$ 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 Cr$_2$O$_3$ required for reaction with the Na$_2$SO$_4$ to be applied. The TiO$_2$ sample was made by plasma spraying high-purity TiO$_2$ onto a platinum coupon and annealing at 975°C for 2 hr. Here also, the TiO$_2$ applied was more than required for reaction with Na$_2$SO$_4$.

The results for one of the Cr$_2$O$_3$ 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 SO$_2$ 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 SO$_2$ + SO$_3$ was volatilizing rapidly. Finally a slow increase occurred as some further oxidation of the chromium coupon ensued. The concentration of SO$_2$ 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 SO$_2$ evolved was proportional to the amount of SO$_4^{2-}$ reacted. As a corollary to this, it can be concluded that the amount of SO$_2$ evolving at any time was proportional to the rate of reaction of the SO$_4^{2-}$ at that time. Because the amount of SO$_2$ evolving determines its concentration in the gas phase, the concentration of SO$_2$ is then proportional to the rate of reaction of the SO$_4^{2-}$. Thus the low value for the concentration of SO$_2$ at the end of the experiment indicated that the reaction between Cr$_2$O$_3$ and Na$_2$SO$_4$ 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 SO$_4^{2-}$

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3The NiMoO$_4$-NiWO$_4$ was identified by X-ray diffraction analysis of the surface of companion specimens.

4Some SO$_2$ was detected during the Na$_2$SO$_4$ 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 SO$_2$ probably originated not from dissociative vaporization of Na$_2$SO$_4$ but from reaction between the vaporizing Na$_2$SO$_4$ and the hot quartz furnace tube: SiO$_2$ + Na$_2$SO$_4 \rightarrow$ Na$_2$SiO$_3$ + SO$_3$(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>1.55</td>
<td></td>
</tr>
<tr>
<td>Na₂CrO₄(l) → Na₂CrO₄(g)</td>
<td>1.5 × 10⁻⁴</td>
<td>2.6 × 10⁻²</td>
<td></td>
</tr>
<tr>
<td>Cr₂O₃ + 2Na₂SO₄(l) + 3/2O₂ =</td>
<td></td>
<td>1.25 × 10⁻³</td>
<td>2.1 × 10⁻⁵</td>
</tr>
<tr>
<td>2Na₂CrO₄(l) + 2SO₂(g)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>nTiO₂ + Na₂SO₄(l) →</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂O(TiO₂)ₙ + SO₃(g)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>nTiO₂ + Na₂CrO₄(l) →</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂O(TiO₂)ₙ + CrO₃(g)</td>
<td></td>
<td></td>
<td></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

\[ \frac{dC}{dt} = k₁C \]  

where \( k₁ \) is the first-order rate constant and \( C \) is the concentration of SO₄⁻² at time \( t \). Integration of this equation yields

\[ \log \left( \frac{C₀}{C} \right) = \frac{k₁t}{2.303} \]  

where \( C₀ \) 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 \( k₁/2.303 \). 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.

Figure 17.—Specific weight gain and concentration of SO₂ evolved as a function of time for preoxidized chromium specimen corroded at 975 °C in flowing oxygen with 3 mg cm⁻² Na₂SO₄. (Sample area, 2.9 cm².)

was recovered from the specimen at the end of the experiment (column 4), as compared with 0.0656 mmol applied (column 3). Thus 94 percent (column 6) of the SO₄⁻² reacted in the 2.5-hr period of the experiment. The millimols of CrO₄⁻² formed should equal the millimols of SO₄⁻² reacted (see reaction (3)), in this case 0.0617 mmol. The amount of CrO₄⁻² found by analysis was almost identical to this (column 7). In table III we have also given in column 8 the total millimols of SO₂ evolved, which was obtained by integrating under the SO₂ curve of figure 17. Comparing this with the millimols of SO₄⁻² that reacted, in column 9, shows that the ratio, 0.40, was somewhat larger than that obtained in figure 6, 0.35.

Another specimen of oxidized chromium was hot corroded for a much longer time, 120 hr, to see if chromium would corrode catastrophically. No such corrosion was observed; in fact, the specimen slowly lost weight throughout the 120 hr. The results are summarized in the second line of table III. All of the SO₄⁻² reacted (columns 4 and 6) but no CrO₄⁻² (column 7) was found in the wash solution (no Na+ was found either).
through the furnace. For a flow rate of 1250 milliliters min⁻¹ the conversion factor is SO₂ (mmol) = 3.06 × 10⁻³ SO₂(ppm hr).

(3) The millimols of SO₂ evolved are converted to the millimols of SO₄⁻² 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 SO₄⁻² at any time is obtained as the difference between the millimols of SO₄⁻² reacted and the millimols applied initially.

From the values of residual SO₄⁻² 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 SO₄⁻² (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 k₁ = 1.55 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 TiO₂ were quite different from those for Cr₂O₃, 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 Na₂SO₄ had practically all reacted. In addition, the concentration of SO₂ 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 SO₃ (and SO₂) during the experiment as indicated by reaction (4). In addition, there should be an overall weight gain of the TiO₂-Pt coupon because of the formation of Na₂O(TiO₂)₂. 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 SO₄⁻² applied had reacted (columns 3, 4, and 6 of table III). The cumulative SO₂ evolved (column 8) was compared with the SO₄⁻² reacted and the proportionality constant obtained was 0.335 (column 9). The total weight loss expected from SO₂ + SO₃ evolution during the actual experiment can be calculated from the SO₄⁻² 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 Na₂O(TiO₂)₂ formation, was calculated for the amount of SO₄⁻² that had reacted. The value, given in column 12, agrees very well with the experimental value given in column 13. After the

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**Table III.** Mass Balance Results of Oxide-Na₂SO₄ Reactions

<table>
<thead>
<tr>
<th>Reactant system</th>
<th>Test duration, hr</th>
<th>SO₄⁻² applied, mmol</th>
<th>SO₄⁻² recovered, mmol</th>
<th>SO₄⁻² reacted, mmol</th>
<th>Fraction SO₄⁻² reacted</th>
<th>Cr₂O₃ analysis, mmol</th>
<th>SO₃ evolved, mmol</th>
<th>Ratio of SO₂ evolved to SO₄⁻² reacted</th>
<th>Calculated ΔW SO₂, mg</th>
<th>Experimental ΔW, mg</th>
<th>Calculated ΔW Na₂SO₄, mg</th>
<th>Experimental ΔW, mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr₂O₃ on Cr</td>
<td>2.5</td>
<td>0.0656</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>
</tr>
<tr>
<td>TiO₂ on Pt</td>
<td>120</td>
<td>0.0510</td>
<td>0</td>
<td>0.0070</td>
<td>1.0</td>
<td>0</td>
<td>0.18</td>
<td>0.355</td>
<td>(a)</td>
<td>(a)</td>
<td>(a)</td>
<td>(a)</td>
</tr>
<tr>
<td></td>
<td>29</td>
<td>0.169</td>
<td>0</td>
<td>0.169</td>
<td>1.0</td>
<td>(a)</td>
<td>0.255</td>
<td>13.5</td>
<td>(a)</td>
<td>(a)</td>
<td>(a)</td>
<td>(a)</td>
</tr>
</tbody>
</table>

*Not applicable.*

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⁵For 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).
experiment the platinum coupon was examined by X-ray diffraction techniques. In addition to the unreacted TiO$_2$ the compound Na$_2$Ti$_5$O$_{11}$ was identified. This is the most stable form of sodium titanate. The compound must be insoluble in water, at least with respect to our extraction technique, because no soluble sodium or titanium was detected in the wash solution from this experiment.

The kinetics of reaction (4) are also quite different from those of reaction (3). The linear weight loss and the practically constant concentration of SO$_2$ shown in figure 19 are both characteristic of a zero-order reaction: a reaction for which the rate is constant and independent of the concentration of reactants. For this type

$$- \frac{dC}{dt} = k_0$$

(7)

where $k_0$ is the zero-order rate constant and $C$ is the concentration of sulfate at time $t$. Integration yields

$$C_0 - C = k_0 t$$

(8)

where $C_0$ is the initial concentration of sulfate. Equation (8) shows that a plot of $C$ versus $t$ should give a straight line whose slope equals $k_0$. This, of course, is what we have plotted in figure 19. The ordinate is the weight loss due to SO$_3$ + SO$_2$ evolution. 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 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$_2$, mmol</th>
<th>Fraction of residual SO$_4^{2-}$</th>
<th>$R$(Cr$_2$O$_3$)$^*$, mmol min$^{-1}$</th>
<th>$R$(TiO$_2$)$^*$, mmol min$^{-1}$</th>
<th>$\frac{R$(Cr$_2$O$_3$)$^<em>}{R$(TiO$_2$)$^</em>}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.168</td>
<td>1.0</td>
<td>$4.4 \times 10^{-3}$</td>
<td>$1.5 \times 10^{-4}$</td>
<td>29</td>
</tr>
<tr>
<td>0.5</td>
<td>0.135</td>
<td>0.80</td>
<td>3.5</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>0.117</td>
<td>0.70</td>
<td>3.0</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>0.092</td>
<td>0.55</td>
<td>2.4</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>0.085</td>
<td>0.50</td>
<td>2.2</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>0.078</td>
<td>0.45</td>
<td>1.5</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>7.5</td>
<td>0.035</td>
<td>0.21</td>
<td>$9.1 \times 10^{-4}$</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>0.025</td>
<td>0.15</td>
<td>6.5</td>
<td>4.3</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>

$^*$Calculated for a specimen area of 7.5 cm$^2$. 

![Image of table IV](image)
the most abundant oxide other than Cr$_2$O$_3$, the rate of
the following reaction was studied:

$$n \text{TIO}_2 + \text{Na}_2\text{CrO}_4(l) \rightarrow \text{Na}_2\text{O(TIO}_2)_n + \text{CrO}_3(g) \quad (9)$$

The oxide CrO$_3$ 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 CrO$_3$ molecules would be decomposed on
contact with the hot specimen and result in deposition of
Cr$_2$O$_3$ on the specimen. For these molecules the net
reaction would be

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

The specimens used were made by plasma spraying TiO$_2$
on platinum coupons as before. They were annealed in
oxygen for 2 hr at 975° C before testing. The Na$_2$CrO$_4$
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 TiO$_2$ with Na$_2$SO$_4$. The rate of decrease
was constant from the beginning of the test until its
termination. The rate of weight loss was calculated to be
$6.6 \times 10^{-2}$ mg cm$^{-2}$ hr$^{-1}$. When corrected for Na$_2$CrO$_4$
evaporation, it was $4.1 \times 10^{-2}$ mg cm$^{-2}$ hr$^{-1}$. The
constant rate of weight loss indicates that the reaction of
TiO$_2$ with Na$_2$CrO$_4$ was of zero order like the reaction of
TiO$_2$ with Na$_2$SO$_4$. 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 Na$_2$CrO$_4$ 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 $k_0$ (analogous to $k_0$ in eq. (8)) of $9.55 \times 10^{-2}$ mg
cm$^{-2}$ hr$^{-1}$ for Na$_2$CrO$_4$ reacting, which is equivalent to
$5.9 \times 10^{-4}$ mmol cm$^{-2}$ hr$^{-1}$ corrected for Na$_2$CrO$_4$
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 $9.55 \times 10^{-2}$ mg Na$_2$CrO$_4$
cm$^{-2}$ hr$^{-1}$ and the experimental value of the rate of
weight loss, $4.1 \times 10^{-2}$ mg cm$^{-2}$ hr$^{-1}$, we calculated that
60 percent of the Na$_2$CrO$_4$ reacted by reaction (9) and 40
percent by reaction (10); that is, 40 percent of the CrO$_3$
formed was decomposed back onto the specimen before
it could escape through the boundary layer. The overall
weight gain of the coupon resulting from Na$_2$O(TIO$_2)_n$
formation also corroborated these percentages for
reactions (9) and (10). As in the reaction with TiO$_2$ and
Na$_2$SO$_4$, X-ray diffraction analysis showed the presence
of Na$_2$Ti$_2$O$_7$ on the coupons after the experiment, and
the water-wash solutions showed just enough soluble
sodium for equivalence to that required for the unreacted
Na$_2$CrO$_4$.

**Chemical Mechanisms**

The diverse results obtained in the present studies of
the Na$_2$SO$_4$-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 Na$_2$SO$_4$
     
     $$\text{Cr}_2\text{O}_3 + 2 \text{Na}_2\text{SO}_4(l) + 3/2 \text{O}_2 \rightarrow 2 \text{Na}_2\text{CrO}_4(l)$$
     
     $$+ 2 \text{SO}_3(g) \quad (3)$$

   - (b) Region of slow linear oxidation (10 to 55 hr)
     
     $$\text{Na}_2\text{CrO}_4(l) \rightarrow \text{Na}_2\text{CrO}_4(g) \quad (11)$$

     $$\text{n TiO}_2 + \text{Na}_2\text{SO}_4(l) \rightarrow \text{Na}_2\text{O(TIO}_2)_n + \text{SO}_3(g) \quad (4)$$

   - 2 Cr + 3/2 O$_2$ → Cr$_2$O$_3$

   - Ti + O$_2$ → TiO$_2$

   - Ni + 1/2 O$_2$ → NiO

   - Mo + 3/2 O$_2$ → MoO$_3$

   - W + 3/2 O$_2$ → WO$_3$

   - Na$_2$CrO$_4(l)$ + MoO$_3(l)$ (and WO$_3$) → Na$_2$MoO$_4(l)$ (and
     
     $$\text{Na}_2\text{WO}_4(l)) + 1/2 \text{Cr}_2\text{O}_3 + 3/4 \text{O}_2 \quad (13)$$

     $$\text{Na}_2\text{O(TIO}_2)_n + \text{MoO}_3(l)$ (and WO$_3$)$ → \text{Na}_2\text{MoO}_4(l)$

     (and Na$_2$WO$_4(l)) + n \text{TiO}_2 \quad (14)$$


   (2) **Acceleration period (55 to 60 hr)**

   - Na$_2$O(TIO$_2)_n + MoO$_3(l)$ → Na$_2$MoO$_4(l)$ + n TiO$_2$

(3) Period of rapid linear oxidation (60 to 75 hr)—
acidic fluxing

\[
\begin{align*}
\text{Cr}_2\text{O}_3 + 3 \text{MoO}_3(\text{l}) &\rightarrow 2 \text{Cr}^{+3} + 3 \text{MoOO}_4^{-2} \quad (17\text{a}) \\
\text{Al}_2\text{O}_3 + 3 \text{MoO}_3(\text{l}) &\rightarrow 2 \text{Al}^{+3} + 3 \text{MoOO}_4^{-2} \quad (17\text{b}) \\
\text{Ni} + \text{MoO}_3(\text{l}) &\rightarrow \text{NiO} + \text{MoO}_2 \quad (18\text{a}) \\
\text{Co} + \text{MoO}_3(\text{l}) &\rightarrow \text{CoO} + \text{MoO}_2 \quad (18\text{b}) \\
2 \text{Cr} + 3 \text{MoO}_3(\text{l}) &\rightarrow \text{Cr}_2\text{O}_3 + 3 \text{MoO}_2 \quad (19\text{a}) \\
2 \text{Al} + 3 \text{MoO}_3(\text{l}) &\rightarrow \text{Al}_2\text{O}_3 + 3 \text{MoO}_2 \quad (19\text{b}) \\
\text{MoO}_2 + 1/2 \text{O}_2 &\rightarrow \text{MoO}_3(\text{l}) \quad (20) \\
\end{align*}
\]

(4) Deceleration period (75 hr to end)

\[
\begin{align*}
\text{NiO} + \text{Na}_2\text{MoO}_4(\text{l}) &\rightarrow \text{NiMoO}_4 + \text{Na}_2\text{O} \quad (21) \\
\text{NiO} + \text{MoO}_3(\text{l}) \text{ (and WO}_3\text{) } &\rightarrow \text{NiMoO}_4 \text{ (and NiWO}_4\text{)} \quad (22) \\
\text{Na}_2\text{O} + \text{Ta}_2\text{O}_5\text{ (and Nb}_2\text{O}_3\text{) } &\rightarrow 2\text{NaTaO}_3\text{ (and NaNbO}_3\text{)(23)} \\
\end{align*}
\]

These different periods are defined in figure 3(a).

The initial corrosion reactions, which are oxide fluxing reactions, have generally been discussed with reference to thermodynamic stability diagrams of the type first constructed by Pourbaix. We have constructed such diagrams for the Cr-O-S and Ti-O-S systems, superimposed on a diagram for the Na-O-S system, all for a temperature of 975°C (figs. 20(a) and (b)). Similar diagrams for the Mo-O-S and W-O-S systems are also presented in figures 20(c) and (d). The diagrams were constructed by using the FACT computer program (ref. 19). The diagrams show the phases that are in equilibrium with gas mixtures having specified pressures of O2 and SO3. As discussed in reference 1, the choice of variables is arbitrary, but precedent has dictated the preference. As a result, to more readily interpret our results with the aid of the diagrams, we have written our reactions involving SO3 even though species such as SO2, S2, S2O7−2, etc., may be involved. The dashed vertical line in the diagrams is the boundary where the log aNa2O = log PSO2 in Na2SO4 and is representative of “neutral” Na2SO4 at 975°C. C.

Examining the thermograms given in figure 20 shows that the oxides of all four of the elements considered should be converted to the appropriate sodium salts in neutral Na2SO4 under 1 atm of oxygen. In addition, the most stable sodium salts under high SO3 pressure (or low oxide ion activities) were Na2MoO4 and Na2WO4, with the former being slightly more stable than the latter.

Although these thermograms 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 Na2SO4 melted and started reacting with the Cr2O3 to form Na2CrO4 and gaseous SO3, reaction (3). An indication of the early occurrence of this reaction was found in the evolution of SO2 (fig. 3(b)), in the appearance of water-soluble chromium (fig. 3(c)), and in the rapid drop in residual SO4−2 (fig. 3(c)). This behavior is predicted by the stability diagram for chromium (fig. 20(a)), as noted above, which shows that Cr2O3 was not stable in neutral Na2SO4 for P02 down to 10−3 atm and that Na2CrO4 was the stable phase.

Our rate studies of reaction (3) discussed previously indicate that the Cr2O3 should react rapidly with the Na2SO4 until all of the Na2SO4 is consumed. It appears from the amount of soluble chromium found (fig. 3(c)) that 0.11 mmol of Na2SO4 reacted with the Cr2O3 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 CrO4−2 found was equivalent to about two-fifths of the Cr2O3 on the preoxidized IN-738 sample, or since the liquid Na2SO4 slumped to the bottom of the specimens, it was equivalent to removal of all of the Cr2O3 from the bottom two-fifths of the specimen.

After an incubation period of about 5 hr the TiO2 on the specimen began to react with the Na2SO4 and formed water-insoluble Na2O(TiO2)4, 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 Na2SO4 should react with the Cr2O3.

Some clarification of the application of the rate studies of Cr2O3 and TiO2 to the initial rate of corrosion of IN-738 is necessary. Comparing the SO2 concentrations of figure 3(b) for IN-738 and figure 17 for Cr2O3 indicates that the reaction with the alloy continued for 20 to 25 hr but the reaction with Cr2O3 was effectively completed in 2.5 hr. Obviously the pure Cr2O3 reacted more rapidly with the Na2SO4 than did the mixed oxide on the IN-738 alloy, which is 75-mol% Cr2O3 and 25-mol% TiO2. The activity of the Cr2O3 in the oxide
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.

In any event, the first 10 hr of IN-738 corrosion was a period in which the Na$_2$SO$_4$ was mostly consumed by reaction with the protective oxide scale on the alloy, although some sulfide formation can take place. The Cr$_2$O$_3$-TiO$_2$ scale was largely removed from the bottom half of the specimen by this basic fluxing as shown in the micrographs of the 5-hr sample (fig. 8). The weight loss observed during this period resulted from the evolution of considerable amounts of SO$_3$ + SO$_2$ from the sample during the reactions. Of course, the magnitude of the weight loss and the time at which the minimum in the weight change curve occurred (fig. 3(a)) are functions of the amount of Na$_2$SO$_4$ applied and, indirectly, of the thickness of the original oxide scale (ref. 13).

**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, 7.7×10⁻⁴ 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 7.4×10⁻⁴ 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 vaporization; 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 evident 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. 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 micrographs 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 effected oxidation 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 effected melting of the discrete MoO₃-WO₃/Na₂MoO₄-Na₂WO₄ areas so that
they coalesced into a large molten phase. 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 MoO$_3$–WO$_3$/Na$_2$MoO$_4$–Na$_2$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 MoO$_3$–WO$_3$/Na$_2$MoO$_4$–WO$_4$.

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

Beyond 60 hr the quantity of Na$_2$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 MoO$_3$–WO$_3$/Na$_2$MoO$_4$ had finally become a major feature of the scale. 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). 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) and their reverse reactions. After solution of the oxides in the molten MoO$_3$–WO$_3$/Na$_2$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 MoO$_2$ at the outer zone of the melt, reaction (20).

As stated previously, evolution of 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 SO$_2$ must have resulted from oxidation of 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 MoO$_3$–WO$_3$/Na$_2$MoO$_4$ to solid NiMoO$_4$–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 Na$_2$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 NiMoO$_4$–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 NiMoO$_4$–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 carbides with titanium, tantalum, and niobium, reaction (23).

---

7 Although MoO$_3$ melts at 800° C, 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% MoO$_3$ and 2 mol% WO$_3$ (ref. 21). Only compositions containing more than 70 mol% MoO$_3$ melt below 975° C, the temperature of our experiments. Because the mol percents of molybdenum and tungsten in IN–738 are 1.0 and 0.8, respectively, it is doubtful that the mixed MoO$_3$–WO$_3$ areas would have a composition that would melt. The addition of Na$_2$MoO$_4$ or Na$_2$WO$_4$, both of which melt below 700° C (ref. 21) would undoubtedly lower the melting points of the mixed MoO$_3$–WO$_3$ (ref. 21). Certainly the considerable amounts of Na$_2$MoO$_4$ shown in figure 3(c) after 60 hr would lower the melting points below 75° C (ref. 21).

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

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

10 These reactions are somewhat hypothetical and await substantiation from studies of the MoO$_3$–WO$_3$/Na$_2$MoO$_4$ system. However, some experimental justification does exist. Bornstein et al. (ref. 24) have shown that Al$_2$O$_3$ exhibits an extremely rapid rate of dissolution in molten MoO$_3$ at 900° 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>Reaction (4), mmol - 1/2 Na</th>
<th>Reaction (9), mmol - 1/2 Na</th>
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oxide was not removed or abraded, so that small quantities of some deep-lying compounds may not have been dissolved.

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 Na₂MoO₄ 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 Na₂SO₄ in being deposited more or less continuously. If the salt level is high, as in a marine environment, the Na₂SO₄ 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 Na₂CrO₄ and MoO₃ 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 SO₃ pressure is maintained at some constant value, SO₃ is only one of the products being evolved in the reaction between Na₂SO₄ and Cr₂O₃. The Na₂CrO₄ also evaporates, as we have shown, at a measurable rate of 1.5 × 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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11Gas turbine combustion gases contain SO₃ at partial pressures between 10⁻⁶ and 10⁻⁴ atm depending on the fuel sulfur content. The SO₃ evolved in our tests were equivalent to a partial pressure of 5 × 10⁻⁵ to 5 × 10⁻⁶ during the course of reaction (3).

References

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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 SO$_3$ was monitored throughout the thermogravimetric tests. Kinetic rate studies were performed for several pertinent processes; appropriate rate constants were obtained fro the following chemical reactions:

\[
\begin{align*}
Cr_2O_3 + 2 Na_2SO_4(1) + 3/2 O_2 & \rightarrow 2 Na_2CrO_4(1) + 2 SO_3(g) \\
n TiO_2 + Na_2SO_4(1) & \rightarrow Na_2O(TiO_2)_n + SO_3(g) \\
n TiO_2 + Na_2CrO_4(1) & \rightarrow Na_2O(TiO_2)_n + CrO_3(g)
\end{align*}
\]