

Mechanisms for the Hot Corrosion of Nickel-Base Alloys

J. A. GOEBEL, F. S. PETTIT, AND G. W. GOWARD

The Na_2SO_4 -induced accelerated oxidation of nickel-base alloys containing elements such as Cr, Al, Mo, W, and V has been studied in 1.0 atm O_2 in the temperature range of 650° to 1000°C. It has been found that the hot corrosion behavior of these alloys can usually be characterized according to one of two types of attack: 1) Na_2SO_4 -induced accelerated oxidation; 2) Na_2SO_4 -induced catastrophic oxidation. In both types of hot corrosion, accelerated oxidation occurs as a result of the formation of a liquid flux based on Na_2SO_4 which dissolves the normally protective oxide scales. Catastrophic, or self-sustaining rapid oxidation can occur in alloys which contain Mo, W, or V, because solutions of oxides of these elements with Na_2SO_4 decrease the oxide ion activity of the molten salts, producing melts which are acidic fluxes for oxide scales. The accelerated oxidation type of attack which was observed with most alloys which did not contain Mo, W, or V, was more severe than for normal oxidation, but much less severe than catastrophic oxidation. Na_2SO_4 -induced accelerated oxidation occurs because the oxide ion activity of the Na_2SO_4 increases to the point where oxide scales can partially dissolve in the basic melt. Generally, this basic fluxing results from the diffusion of sulfur from the Na_2SO_4 into the alloy. In some alloys, the formation of sulfides during basic fluxing is a sufficient condition to cause accelerated oxidation. In other alloys, changes in the oxidation mechanism occur because of depletion of the alloy surface, concomitant with basic fluxing, of those elements needed for protective oxide scales, such as aluminum and chromium.

IT is now generally accepted that the accelerated oxidation (hot corrosion) of alloys used in gas turbines is caused by the deposition of Na_2SO_4 resulting from the ingestion of salts in the engine and sulfur from the combustion of fuel. In a previous paper¹ the Na_2SO_4 -induced accelerated oxidation of pure nickel was explained in terms of a reaction between oxide ions in the Na_2SO_4 and NiO whereby a porous, nonprotective nickel oxide scale was formed. The reaction is not self-sustaining since the activity of oxide ions required for reaction with NiO is developed in the Na_2SO_4 only at the beginning of oxidation when conditions in the sulfate are favorable for the formation of nickel sulfide. The oxidation rate of nickel is therefore accelerated by a fixed amount of Na_2SO_4 only during the initial stages of oxidation.

The Na_2SO_4 -induced accelerated oxidation of numerous nickel-base alloys has been observed.²⁻⁴ The oxidation of nickel-base alloys in the presence of Na_2SO_4 is dependent on alloy composition as can be seen in Fig. 1 where the oxidation kinetics for pure nickel and two nickel-base superalloys are compared. In view of the hot corrosion mechanism proposed for pure nickel,¹ the alloying elements in the superalloys would be expected to affect the hot corrosion process by altering the oxide ion activity of the Na_2SO_4 . Bornstein and DeCrescente⁴ have suggested nickel-base superalloys containing aluminum are susceptible to accelerated oxidation since sodium aluminate formation promotes the formation of oxide ions. However, they have not shown that aluminate formation increases the oxide ion concentration in molten salts (e.g., Na_2CO_3 , Na_2SO_4).

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Manuscript submitted April 14, 1972.

Seybolt^{2,5} has proposed that accelerated oxidation of alloys in the presence of Na_2SO_4 occurs because sulfur from the sulfate enters the alloy resulting in the formation of sulfide phases and depletion in the alloy of elements necessary to develop a protective oxide scale. He proposes that the catastrophic nature of the attack lies in the rapid transport inward of liquid nickel sulfide and the simultaneous penetration of incompletely reacted liquid Na_2SO_4 which reacts with the residual alloy as penetration proceeds. Seybolt's proposal is not complete since the mechanism by which the liquid Na_2SO_4 penetrates into the alloy and causes increased oxidation has not been described.

The purpose of the present studies was to attempt to develop consistent mechanisms for the hot corrosion of nickel-base superalloys and to examine the influ-

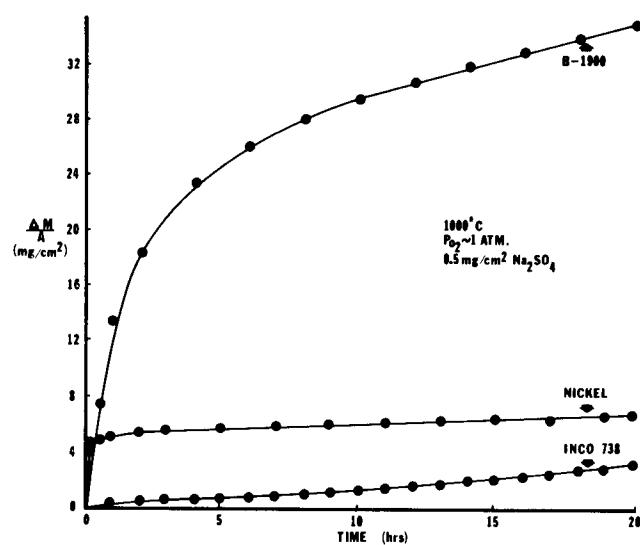


Fig. 1—Oxidation of Na_2SO_4 -coated specimens of B-1900, IN 738, and nickel at 1000°C. (Compositions of B-1900 and IN 738 are given in Table I.) The different oxidation kinetics for these materials indicate alloying elements are affecting the hot corrosion process.

ence of a few alloying elements, common to nickel-base superalloys, on these hot corrosion mechanisms.

EXPERIMENTAL

One of the problems in studying the Na_2SO_4 -induced oxidation of alloys is to devise tests which provide meaningful data with regard to the conditions actually encountered in practice. In the gas turbine industry, simulated engine testing is frequently performed by subjecting materials to flames produced by combusting fuels. The material to be tested is usually subjected not only to elevated temperatures but also high velocity gas streams. Hot corrosion testing is commonly achieved in these "burner rigs" by adding NaCl to the air ingested into the burner and by using a sulfur-containing fuel. While it may be argued whether or not burner rig tests actually simulate engine conditions, dynamic test conditions create extreme difficulty in interpreting results since it appears that equilibrium conditions may not be established and therefore the conditions to which the materials were subjected cannot be clearly defined. In view of this problem the following type of laboratory experiments have frequently been used:

- a) materials are coated with a controlled amount of Na_2SO_4 and then subjected to an oxidizing environment at elevated temperatures;
- b) materials are immersed completely or partially in crucibles containing Na_2SO_4 and the crucible is exposed to oxidizing environments;
- c) materials are periodically immersed in Na_2SO_4 and then oxidized.

Results from crucible tests are subject to criticism since, as will be shown subsequently, the Na_2SO_4 can in some cases react with the crucible. In the present studies hot corrosion tests have been performed by coating specimens with a controlled amount of Na_2SO_4 and then oxidizing these specimens under isothermal conditions. As will become apparent, by comparison of the oxidation kinetics and metallographic examination of oxidized specimens, this type of test does allow the development of hot corrosion mechanisms for the case where Na_2SO_4 is on the surfaces of alloys.

To examine the Na_2SO_4 -induced oxidation of nickel-base alloys, specimens 1 cm square by 0.1 cm thick were coated with 0.5 mg/cm² of Na_2SO_4 by spraying the specimens with a saturated aqueous solution of Na_2SO_4 . The specimens were heated on a hot plate to about 120° to 150°C prior to spraying with the Na_2SO_4 solution. The Na_2SO_4 -coated specimens were oxidized in static oxygen at 1 atm. The specimens were raised from the cold zone to the hot zone of the furnace after oxygen had been admitted into the furnace. The oxidation temperature was usually 1000°C; however, sufficient experiments were performed at other temperatures to permit an analysis of the hot corrosion process over the temperature interval 650° to 1200°C. The oxidation kinetics were obtained by determining the weight-change of the specimens as a function of time with an automatic recording vacuum microbalance. This apparatus has been described previously.⁶ The oxidation kinetics were used to compare the weight-change as a function of time of the different alloys

Table I. Composition of Alloys, Wt Pct

Alloy Designation	Ta	V	Ni	Cr	Co	Ti	Al	Mo	C	W
B-1900*	4.3	—	Bal	8.0	10.0	1.0	6.0	6.0	0.10	—
IN-738*	1.75	—	Bal	16.0	8.5	3.4	3.4	1.75	0.17	2.6
B-1900 (minus Al)	3.9	—	Bal	7.5	9.3	0.92	—	5.7	0.11	—
B-1900 (minus Ti)	4.3	—	Bal	8.0	10.0	—	6.0	6.0	0.10	—
B-1900 (minus Mo)	4.2	—	Bal	8.0	9.8	1.03	6.0	—	0.10	—
B-1900 (minus Mo-Ta)	—	—	Bal	8.0	9.8	1.04	6.0	—	0.11	—
B-1900 (minus Mo-Ta-Ti)	—	—	Bal	8.6	10.0	—	6.1	—	0.11	—
Ni-8Cr-6Al-0.1C	—	—	Bal	8.0	—	—	6.0	—	0.11	—
Ni-8Cr-6Al	—	—	Bal	8.0	—	—	6.0	—	—	—
Ni-1Al	—	—	Bal	—	—	—	1.0	—	—	—
Ni-31Al	—	—	Bal	—	—	—	31.0	—	—	—
Ni-5Cr	—	—	Bal	4.9	—	—	—	—	—	—
Ni-30Cr	—	—	Bal	28.4	—	—	—	—	—	—
Ni-30Cr-6Al	—	—	Bal	29.9	—	—	6.0	—	—	—
Ni-22Al-11Cr	—	—	Bal	10.2	—	—	21.8	—	—	—
Ni-31Al-2Mo	—	—	Bal	—	—	—	30.8	2.10	—	—
Ni-31Al-4Mo	—	—	Bal	—	—	—	31.0	3.70	—	—
Ni-32Al-2V	—	1.9	Bal	—	—	—	31.0	—	—	—
Ni-27Al-12.3W	—	—	Bal	—	—	—	27.7	—	—	12.3
Ni-8Cr-6Al-4Mo	—	—	Bal	8.1	—	—	5.8	4.10	—	—

*Nominal Composition.

tested. The oxidation kinetics were usually not analyzed for conformance to any given rate law since it is believed such an analysis would not be meaningful in view of the numerous phases and porous morphology frequently present in the oxide scale. Oxidized specimens and oxidation products were examined by conventional metallographic, microprobe, and X-ray diffraction techniques. The compositions of the alloys studied are presented in Table I. The reasons for choosing these particular compositions will become obvious in subsequent sections.

RESULTS AND DISCUSSION

The significant difference between the Na_2SO_4 -induced hot corrosion of the nickel-base superalloy B-1900 and pure nickel, which is obvious upon examination of Fig. 1, shows that certain alloying elements in the B-1900 must be influencing the hot corrosion process in a detrimental manner. To determine the elements that were responsible for the poor oxidation resistance of B-1900 in the presence of Na_2SO_4 , a series of alloys were prepared with compositions similar to B-1900 but without one or more of the major alloying elements usually present in this alloy. The oxidation kinetics obtained upon oxidizing these alloys in 1 atm O_2 without Na_2SO_4 were all similar to each other and typical results are presented in Fig. 2 for Ni-8Cr-6Al.* The results obtained upon oxidizing

*All compositions are given in wt pct.

these same alloys under the same conditions but in the presence of Na_2SO_4 are also presented in Fig. 2. It can be seen that Na_2SO_4 increases the oxidation of all of the alloys above that for normal oxidation. However, the increase in the oxidation rates caused by the Na_2SO_4 is much greater in the alloys which contained

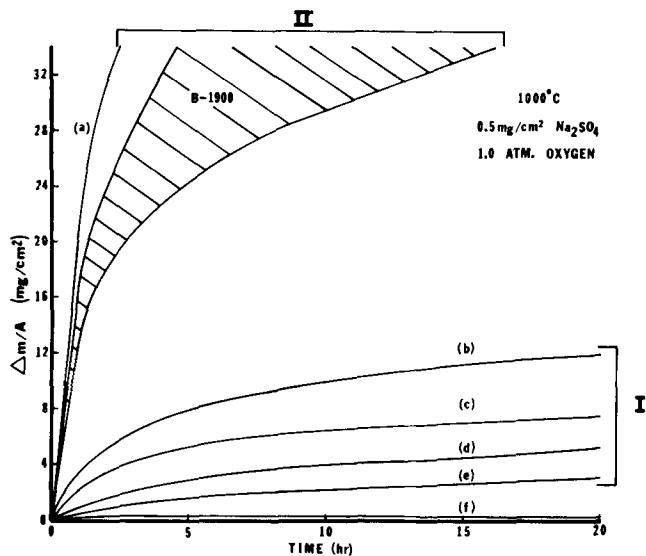


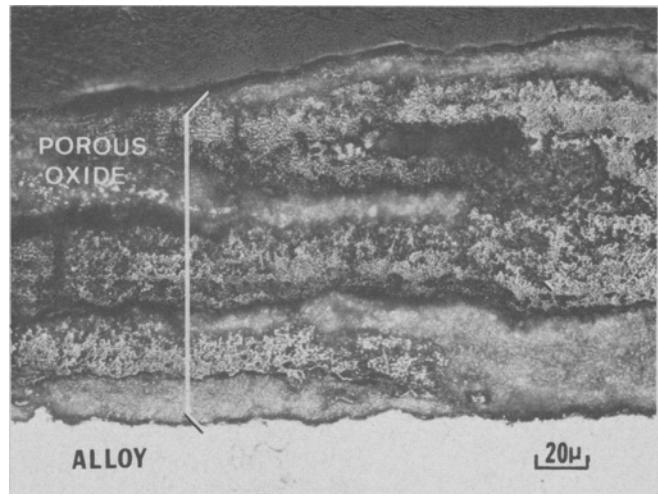
Fig. 2—Weight change vs time curves for the oxidation of nickel-base alloys coated with Na_2SO_4 and then oxidized in oxygen at 1000°C . The crosshatched area indicates the range of values obtained for the nickel-base superalloy B-1900 ($\text{Ni}-10\text{Co}-8\text{Cr}-6\text{Al}-1\text{Ti}-6\text{Mo}-4.25\text{Ta}-0.015\text{B}-0.1\text{C}-0.075\text{Zr}$). The other curves are for modified B-1900 alloys as follows: (a) B-1900 minus Al, B-1900 minus Ti; (b) B-1900 minus Mo; (c) B-1900 minus Mo and Ta; (d) Ni-8Cr-6Al-0.1C, Ni-10Co-8Cr-6Al-0.1C; (e) Ni-8Cr-6Al; (f) Ni-8Cr-6Al with no Na_2SO_4 coating. The results obtained with the Na_2SO_4 -coated specimens can be divided into two groups: I) Na_2SO_4 -induced accelerated oxidation and II) Na_2SO_4 -induced catastrophic oxidation.

molybdenum. The oxide scales which were formed on some of these alloys are compared in Fig. 3. The oxide scale which formed on B-1900, Fig. 3(a), is much thicker and much more porous than the oxide formed on Ni-8Cr-6Al, Fig. 3(b). However, the oxide layer on this latter alloy is still much thicker than the oxide that is formed during oxidation in the absence of Na_2SO_4 , Fig. 3(c).

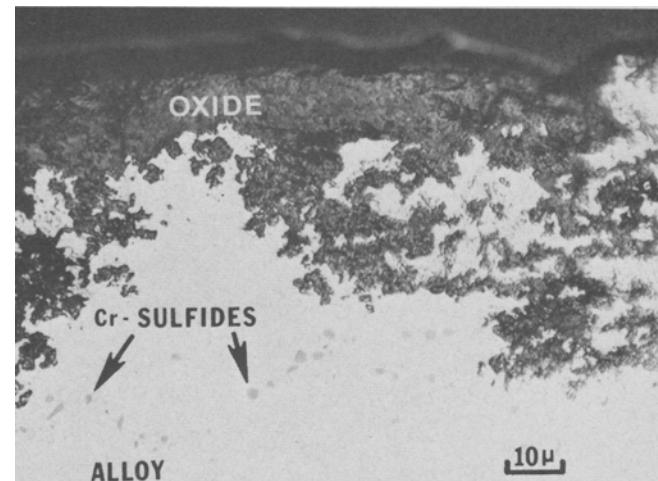
These results indicate that, due to the influence of alloying elements, there may be at least two types of Na_2SO_4 -induced accelerated oxidation of nickel-base alloys. In one case, Fig. 3(a), the morphology of the oxidation products is such that the oxidizing environment has virtually free access to the alloy surface and consequently the oxidation reaction is catastrophic (e.g., B-1900). In the other case, examination of the oxidation kinetics, Fig. 2, and the structures of oxidized alloys, Figs. 3(b) and 3(c), shows that oxidation products do inhibit the oxidation reaction but not to the extent that is prevalent during oxidation in the absence of Na_2SO_4 . In view of these differences between the two apparent hot corrosion processes, they will be differentiated by referring to one as Na_2SO_4 -induced catastrophic oxidation and to the other as Na_2SO_4 -induced accelerated oxidation.

Na_2SO_4 -Induced Accelerated Oxidation

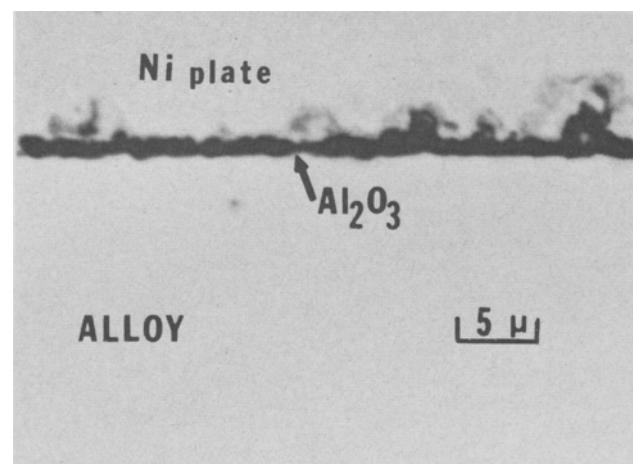
Examination of the results presented in Fig. 2 shows that all of the alloys studied, which did not contain molybdenum, undergo Na_2SO_4 -induced accelerated oxidation and therefore could be used in studies to describe this hot corrosion process. However, some of these alloys contain numerous elements in addition to



(a)



(b)



(c)

Fig. 3—Microphotographs showing the effects produced by Na_2SO_4 ($0.5 \text{ mg}/\text{cm}^2$) on the oxidation of materials in $\sim 1 \text{ atm}$ O_2 at 1000°C . (a) B-1900 after 30 min of oxidation (Na_2SO_4 -induced catastrophic oxidation); (b) Ni-8Cr-6Al, the base composition of B-1900, after 20 h of oxidation (Na_2SO_4 -induced accelerated oxidation); (c) Ni-8Cr-6Al after 20 h of oxidation without Na_2SO_4 (normal oxidation).

nickel, chromium, and aluminum (*e.g.*, Co, Ta, Ti, B, Zr, C). Even though all these alloys behave similarly in normal oxidation, since external layers of Al_2O_3 are eventually developed, it is not advisable to begin by using complex systems in studies designed to determine hot corrosion mechanisms. In the present studies, the Na_2SO_4 -induced accelerated oxidation mechanism was examined by using Ni-Al, Ni-Cr, and Ni-Cr-Al alloys. These particular systems were chosen since the principal oxides formed on nickel-base alloys are NiO , Cr_2O_3 , and Al_2O_3 . Even when using these relatively simple systems, it is necessary to consider the alloy compositions that will be most appropriate for hot corrosion studies. Ni-8Cr-6Al is not an ideal alloy to examine the influence of Na_2SO_4 on oxidation behavior, because oxidation can cause depletion of aluminum and chromium at its surface. This results in the development of Cr_2O_3 or NiO scales rather than the Al_2O_3 scale which is usually developed during normal oxidation.⁷

In the present studies the compositions of the Ni-Al, Ni-Cr, and Ni-Cr-Al alloys were chosen such that relatively small compositional changes at their surfaces should not result in the development of oxide scales substantially different from those formed during normal oxidation in the absence of Na_2SO_4 . In the following sections, results from the oxidation of Na_2SO_4 -coated Ni-Al, Ni-Cr, and Ni-Cr-Al alloys are presented and then a mechanism for Na_2SO_4 -induced accelerated oxidation is proposed.

Ni-Al Alloys

During oxidation at 1000°C in the absence of Na_2SO_4 , Ni-1Al develops an external scale of NiO beneath which a subscale of Al_2O_3 is formed, whereas only a continuous external layer of Al_2O_3 is formed on Ni-31Al.⁶ The oxidation of these two alloys with and without Na_2SO_4 is compared in Fig. 4, which shows that the amount of oxidation of both alloys is increased when Na_2SO_4 is present on the alloy surfaces.

Visual observations made with the hot stage microscope during the oxidation of Na_2SO_4 -coated Ni-31Al showed an apparently protective layer of oxide, identified as Al_2O_3 , formed on this alloy beneath the molten Na_2SO_4 . The Al_2O_3 scales formed on Ni-31Al specimens with and without Na_2SO_4 spalled from the specimen surfaces on cooling to room temperature. In both cases an aluminum-depleted region was observed on these alloys after oxidation but this region was usually thicker on the Na_2SO_4 -coated specimens consistent with the larger weight-gains obtained for these specimens as shown in Fig. 4. After 20 h of oxidation of Ni-31Al specimens coated with 0.5 mg/cm^2 Na_2SO_4 , the Al_2O_3 scales were similar to those formed on Ni-31Al without any Na_2SO_4 , but frequently, particularly at the specimen edges, small nodules of voluminous oxide were observed. When this alloy was coated with larger amounts of Na_2SO_4 , the initial oxidation kinetics and oxide structure were similar to those for a specimen with 0.5 mg/cm^2 Na_2SO_4 ; however, as shown in Fig. 5, a period of very rapid oxidation eventually occurred and large mounds of oxide were observed on the specimen surfaces. A typical structure for a specimen which has undergone this rapid breakaway-type of oxidation is presented in Fig. 6. This figure also shows

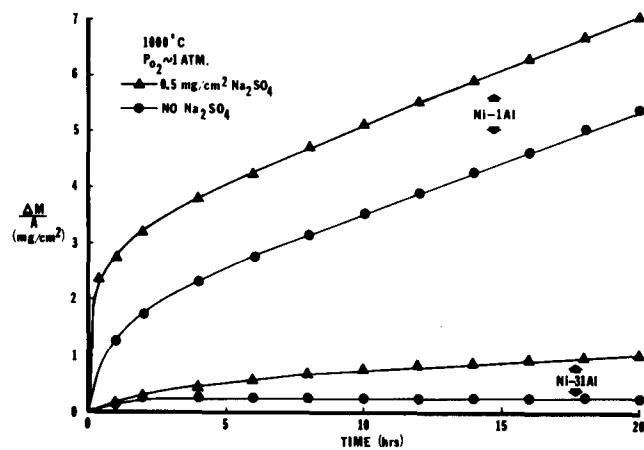


Fig. 4—Weight-change vs time curves for the oxidation of Ni-1Al and Ni-31Al with and without Na_2SO_4 in $\sim 1 \text{ atm O}_2$ at 1000°C.

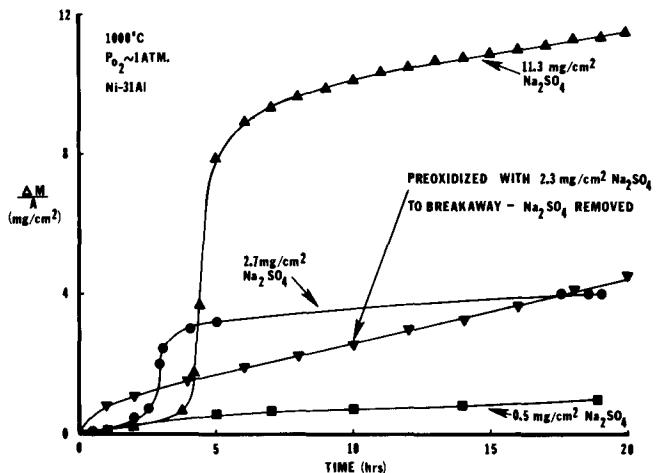
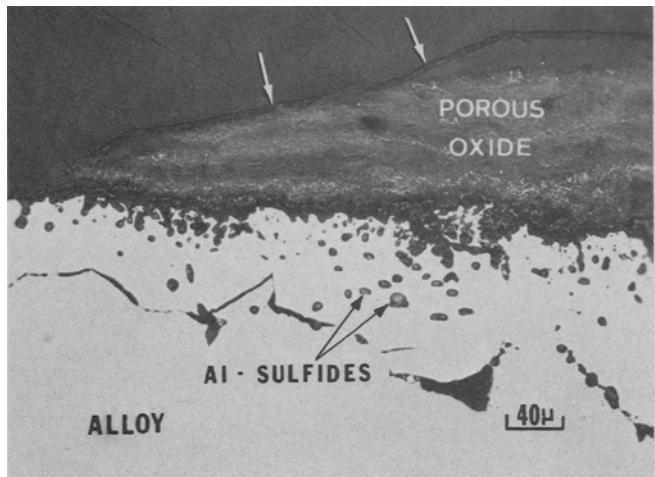


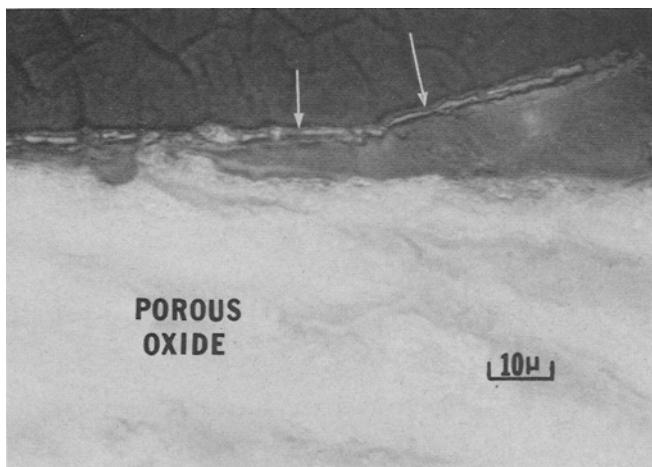
Fig. 5—Weight-change vs time curves for the oxidation in $\sim 1 \text{ atm O}_2$ at 1000°C of Ni-31Al with different amounts of Na_2SO_4 . Breakaway oxidation is obvious for specimens coated with 2.7 and 11.3 mg/cm^2 of Na_2SO_4 . Results are also presented for the oxidation of a specimen which had been previously coated with Na_2SO_4 , oxidized and the Na_2SO_4 removed. Accelerated oxidation of this specimen occurs even though the Na_2SO_4 was removed.

the outer part of the scale in which the Al_2O_3 layer that formed prior to the breakaway period of oxidation is visible. The thick, porous mounds in the oxide were found to contain NiO , NiAl_2O_4 , and Al_2O_3 whereas the oxide scale away from the mounds of oxide was Al_2O_3 . Electron-beam microprobe analyses showed that the aluminum depleted zones in the alloy beneath the mounds of oxide contained aluminum sulfide particles. In addition, aluminum sulfide was also observed in the alloy beneath the oxide scale at locations where mounds of oxide were not present.

To determine if reaction occurred between the molten Na_2SO_4 and the Al_2O_3 scale, specimens of Ni-31Al were coated with Na_2SO_4 and oxidized for different times at 1000°C in flowing oxygen at 1 atm. After oxidation the remaining Na_2SO_4 was removed from the specimen surfaces by a water leach and analyzed for aluminum. In addition, the sulfur concentration in the alloys was also determined. The oxidation kinetics of these specimens were obtained to determine if breakaway oxidation had occurred. The experimental results, which are presented in Table II, showed:



(a)



(b)

Fig. 6—Microphotographs showing structure of Na_2SO_4 -coated (2 mg/cm^2) Ni-3Al after 20 h of oxidation in $\sim 1 \text{ atm O}_2$ at 1000°C . (a) Transverse section through specimen showing porous mound of oxide with aluminum sulfides in the substrate. (b) Outer portion of mound of oxide shown in (a) (arrows) where Al_2O_3 scale that formed prior to development of the oxide mound is visible.

- a) Na_2SO_4 remains at the alloy surface for at least 8 h of oxidation;
- b) sulfur from the Na_2SO_4 does enter the alloy virtually from the beginning of the experiment; however, the amount of sulfur was greatly increased after the breakaway oxidation had been observed; and
- c) significant amounts of aluminum were detected in the leaching water which indicates reaction between the Na_2SO_4 and Al_2O_3 to form water soluble NaAlO_2 had occurred.

It was also found that when the Na_2SO_4 was washed from the specimen surface after oxidation, subsequent oxidation occurred at an accelerated rate as shown in Fig. 5.

In the case of Ni-1Al, the increased oxidation occurred during the first 10 min of oxidation after which the Na_2SO_4 did not significantly affect the alloy oxidation rate. For example, the parabolic rate constants determined after 20 h of oxidation of Ni-1Al specimens

Table II. Sulfate, Sulfur and Aluminum Analyses of Na_2SO_4 -Coated Ni-3Al After Oxidation at 1000°C in 1 atm Oxygen*

Oxidation Time, min	Amount Na_2SO_4 , mg/cm ²		Sulfur in Alloy, $\mu\text{g}/\text{cm}^2$	Aluminum in Leach Water, mg per cm ² of Specimen Surface Area
	Initial	Final		
1	2.3	2.2	0.9	—
5	1.9	1.3	1.6	0.01
10	1.5	1.4	1.5	0.03
30	1.7	0.9	2.0	0.03
60	1.5	0.6	10.7	0.03
240	1.6	0.5	120	0.05†
480	2.5	1.2	119	0.11†

*The difference between the initial and final weights of Na_2SO_4 cannot be accounted for by the sulfur in the alloy because of vaporization of Na_2SO_4 and evolution of SO_3 as well as SO_2 .

†Breakaway oxidation kinetics were observed.

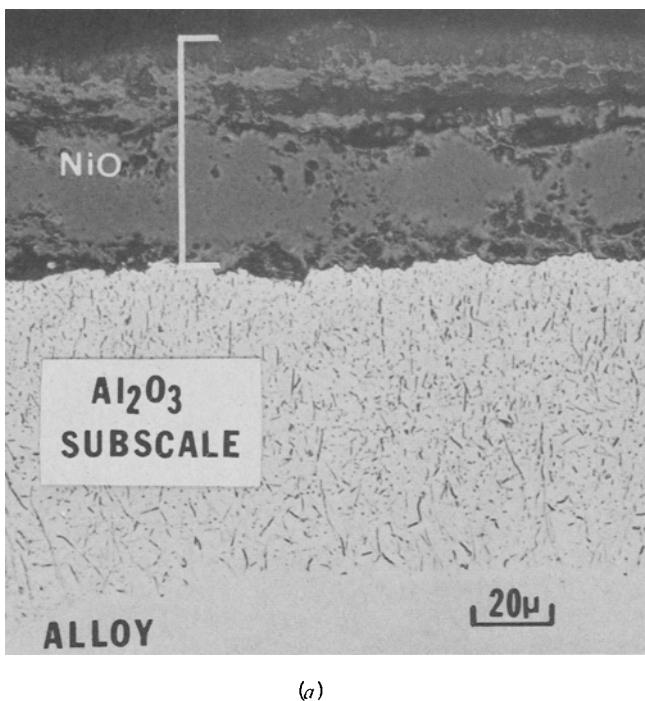
with and without Na_2SO_4 were $6.3 \cdot 10^{-10}$ and $4.6 \cdot 10^{-10}$ ($\text{g}^2/\text{cm}^4\text{-s}$), respectively. A photograph of a section through an oxidized specimen of Na_2SO_4 -coated Ni-1Al is presented in Fig. 7 which shows that a layer of NiO above a subscale of Al_2O_3 has formed. In addition, nickel sulfides were observed at the NiO -alloy interface, Fig. 7. The inner portion of the NiO scale is dense whereas the outer portion is porous. Visual observations made during the oxidation of Na_2SO_4 -coated Ni-1Al at 1000°C in air with a hot stage microscope showed the molten sulfate layer was visible for times of about 10 to 30 s after which a scale was observed to form at the Na_2SO_4 -air interface. The results obtained from the oxidation of Ni-1Al in the presence of Na_2SO_4 are virtually the same as those obtained for pure nickel under similar conditions as described in detail in a previous paper.¹

Ni-Cr Alloys

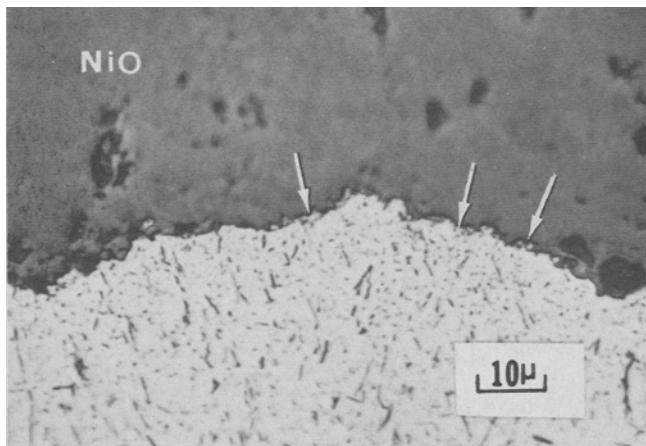
During oxidation at 1000°C in the absence of Na_2SO_4 , Ni-5Cr develops an external scale of NiO beneath which a subscale of Cr_2O_3 is formed, whereas only a continuous, external layer of Cr_2O_3 is formed on Ni-30Cr.⁸ The oxidation kinetics for these alloys with and without Na_2SO_4 are compared in Fig. 8. In contrast to the results obtained for the Ni-Al alloys, the weight-changes of Ni-Cr alloys with Na_2SO_4 are less than those for these alloys without Na_2SO_4 .

The structure of Na_2SO_4 -coated Ni-5Cr after oxidation at 1000°C , presented in a previous paper,¹ consists of an external layer of NiO above a subscale of Cr_2O_3 . In addition, chromium sulfides are observed in the alloy beneath the subscale of Cr_2O_3 . With the exception of the chromium sulfides, the structure of the oxidized, Na_2SO_4 -coated Ni-5Cr specimen is identical to the structure developed during normal oxidation. Visual examination of the oxidation of Na_2SO_4 -coated Ni-5Cr with the hot stage microscope showed that the NiO scale formed beneath the molten Na_2SO_4 layer. In addition, the Na_2SO_4 turned yellow in color and was found to contain chromium presumably as chromate ions.

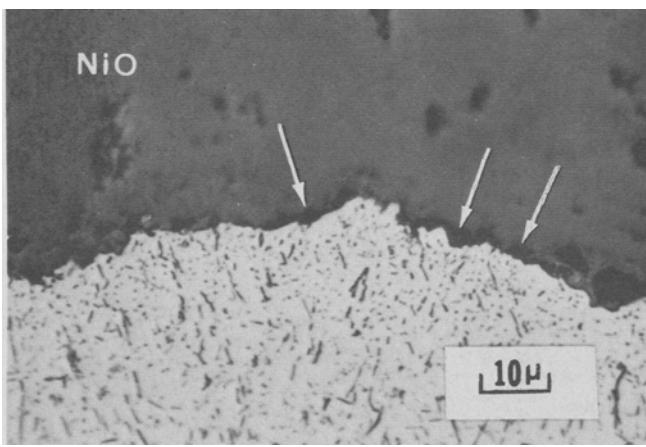
The structure of a Na_2SO_4 -coated and oxidized, Ni-30Cr specimen is presented in Fig. 9 which shows the Cr_2O_3 scale to be continuous and protective. With the exception of the chromium sulfides in the alloy beneath the Cr_2O_3 scale, this structure is identical to



(a)



(b)



(c)

Fig. 7—Microstructure of Na_2SO_4 -coated ($0.5 \text{ mg/cm}^2 \text{ Na}_2\text{SO}_4$) Ni-1Al specimen after 20 h of oxidation in $\sim 1 \text{ atm O}_2$ at 1000°C . (a) Transverse section showing NiO scale above a subscale of Al_2O_3 . The inner portion of the NiO scale is dense whereas the outer portion is porous. (b) Arrows indicate areas where nickel sulfide is present beneath the NiO scale. (c) Same as (b) but etched electrolytically with 1 pct NaNO_3 to darken nickel sulfide.

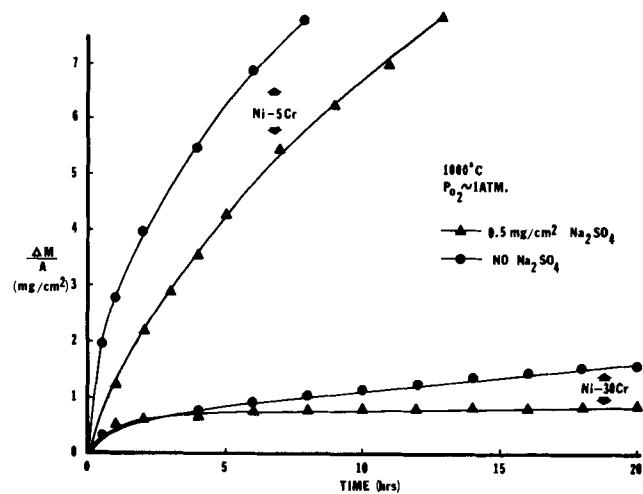


Fig. 8—Weight-change vs time curves for the oxidation of Ni-5Cr and Ni-30Cr specimens with and without Na_2SO_4 in $\sim 1 \text{ atm O}_2$ at 1000°C .

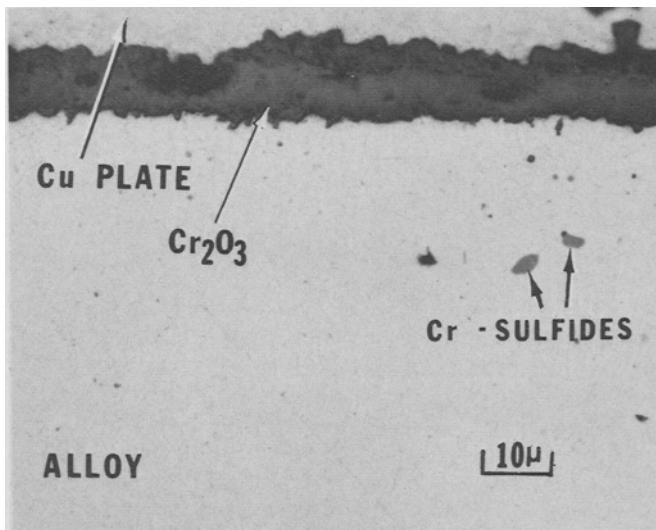
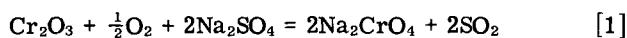


Fig. 9—Microphotograph of Na_2SO_4 -coated (0.5 mg/cm^2) Ni-30Cr after 20 h of oxidation in $\sim 1 \text{ atm O}_2$ at 1000°C . The Cr_2O_3 scale is similar to that formed on this alloy during normal oxidation in the absence of Na_2SO_4 .

that observed for this alloy in normal oxidation. To determine if reaction occurs between the molten Na_2SO_4 and the Cr_2O_3 scale, specimens of Ni-30Cr were coated with Na_2SO_4 and oxidized for different times at 1000°C in flowing oxygen. After oxidation, the amount of Na_2SO_4 remaining on the surface, the concentration of chromium in the Na_2SO_4 , and the concentration of sulfur in the alloy were determined as described previously for Ni-31Al. These results, which are presented in Table III, showed:

- Na_2SO_4 , separated from the alloy by the protective layer of Cr_2O_3 , does remain on the specimen for as long as 4 h;
- sulfur from the Na_2SO_4 does enter the alloy presumably diffusing through the Cr_2O_3 scale; and
- the Cr_2O_3 scale does react with the Na_2SO_4 .

Since the presence of chromium in the leaching water indicates that a water soluble chromate has been formed by a reaction such as the following,



a Na_2SO_4 -coated Ni-30Cr specimen was oxidized in flowing oxygen at 1000°C and the exiting gas was analyzed for SO_2^* using a procedure described previously.⁹

*Oxidation of pure sulfur at 1000°C showed that virtually all of the sulfur in the exiting gas was present as SO_2 .

The amount of SO_2 determined was 1.4 mg of SO_2 per cm^2 of specimen surface area after 24 h of oxidation whereas 0.2 mg/ cm^2 SO_2 was obtained from the decomposition of pure Na_2SO_4 on a platinum foil after 65 h at 1000°C. These results confirm that the Cr_2O_3 scale on the Ni-30Cr alloy is reacting with the Na_2SO_4 .

Ni-Cr-Al Alloys

During oxidation in the absence of Na_2SO_4 , Ni-8Cr-6Al, Ni-30Cr-6Al, and Ni-11Cr-22Al alloys all form external layers of Al_2O_3 and have virtually the same oxidation rates.⁷ Results obtained by oxidizing these alloys in the presence of Na_2SO_4 at 1000°C are compared to normal oxidation in Fig. 10. The results of the oxidation of Ni-8Cr-6Al in the absence of Na_2SO_4 are representative of normal oxidation for all three alloys.

Ni-30Cr-6Al and Ni-11Cr-22Al gained less weight during oxidation in the presence of Na_2SO_4 than was observed during oxidation in the absence of Na_2SO_4 . Examination of these two alloys after oxidation in the presence of Na_2SO_4 showed that an external layer of Al_2O_3 had formed on the alloy surfaces beneath the molten Na_2SO_4 . The microstructures of these oxidized specimens were identical to those observed in normal oxidation, Fig. 3(c), except that a few chromium sulfide particles were observed in the alloys beneath the Al_2O_3 layer. Results obtained from analyzing the Na_2SO_4 remaining on the surface of Ni-30Cr-6Al after different periods of oxidation are presented in Table III. These show:

- a) Na_2SO_4 remains on the specimen surfaces for at least 4 h;
- b) sulfur enters the alloys apparently by diffusing through the Al_2O_3 scales to form the chromium sulfide particles observed in the alloy;
- c) Cr_2O_3 , which is formed during the initial stages

Table III. Sulfate, Sulfur, Chromium and Aluminum Analyses of Na_2SO_4 -Coated Ni-30Cr and Ni-30Cr-6Al After Oxidation at 1000°C in 1 atm Oxygen*

Oxidation Time, h	Amount Na_2SO_4 , mg/ cm^2		Sulfur in Alloy, $\mu\text{g}/\text{cm}^2$	Analyses of Leach Water, mg/ cm^2 of Specimen Surface Area	
	Initial	Final		Al	Cr
Ni-30Cr					
1	2.2	1.6	16.2	—	0.16
2	2.0	1.8	21.9	—	0.22
4	2.5	0.8	24.6	—	0.11
Ni-30Cr-6Al					
1	2.1	1.9	4.6	<0.005	0.15
2	2.3	2.1	5.4	<0.005	0.14
4	2.9	2.7	6.9	<0.005	0.21

*The difference between the initial and final weights of Na_2SO_4 cannot be accounted for by the sulfur in the alloy nor the chromium in the leach water because vaporization of Na_2SO_4 and evolution of SO_3 as well as SO_2 also occur.

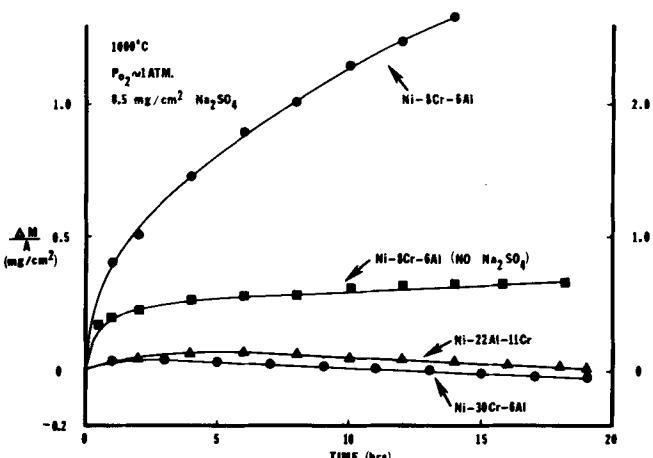


Fig. 10—Weight-change vs time curves for the oxidation of Ni-Cr-Al alloys with and without Na_2SO_4 . The results obtained for all alloys without Na_2SO_4 were approximately the same and only results obtained for Ni-8Cr-6Al are included in this figure. The results for Ni-8Cr-6Al coated with Na_2SO_4 are plotted using the right-hand ordinate whereas all the other results are plotted using the left-hand ordinate.

of oxidation prior to the formation of a continuous layer of Al_2O_3 ,^{7,10} reacts with the Na_2SO_4 ; and

d) in contrast to the observation for Ni-Al alloys, no reaction between the Al_2O_3 and Na_2SO_4 was detected.

The oxidation rate of the Ni-8Cr-6Al alloy increases in the presence of Na_2SO_4 , Fig. 10. Comparison of the oxidized structures of Ni-8Cr-6Al with and without Na_2SO_4 , presented in Figs. 3(b) and 3(c), shows a continuous Al_2O_3 scale is not formed on this alloy during oxidation in the presence of Na_2SO_4 . As mentioned previously, relatively small compositional changes in this alloy do result in the development of oxide scales other than Al_2O_3 . It appears that Na_2SO_4 has prevented the development of a continuous Al_2O_3 scale on this alloy perhaps by depleting the alloy of chromium due to chromate formation. Previous work has established that the formation of a Cr_2O_3 -rich layer is a necessary precursor for the development of an Al_2O_3 scale on this alloy.^{7,10}

Mechanism of Na_2SO_4 -Induced Accelerated Oxidation

The results obtained with the Ni-Al, Ni-Cr, and Ni-Cr-Al alloys show that Na_2SO_4 has caused increased oxidation only for the Ni-Al alloys and Ni-8Cr-6Al. To discuss the influence of Na_2SO_4 on the oxidation of alloys, it is useful to construct thermodynamic diagrams which describe the stability and composition of Na_2SO_4 and which define the conditions required for reaction between the Na_2SO_4 and the oxide scales normally formed on the alloys of interest.

In a previous paper,¹ the procedure used to develop the stability diagram presented in Fig. 11 has been described. This diagram shows the phase or phases in the Na-S-O system that are in equilibrium with gas mixtures having specified pressures of oxygen and SO_3 . In view of the following equilibria,



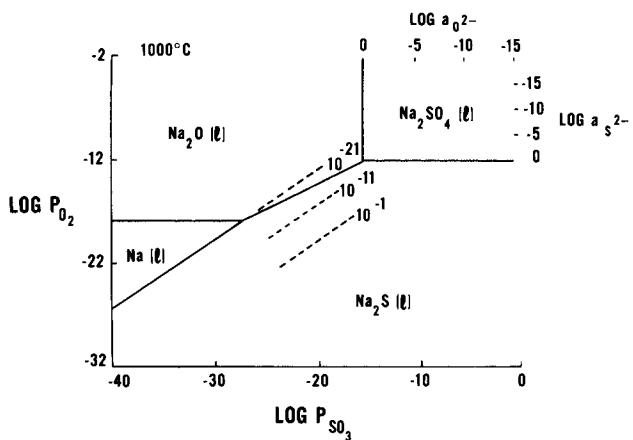


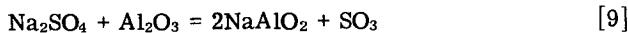
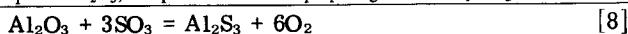
Fig. 11—Stability diagram for the Na-O-S system at 1000°C. The oxide ion and sulfide ion activity scales are for the Na_2SO_4 region of the diagram. The dashed lines are sulfur isobars (*i.e.*, p_{S_2}) and can be constructed for the entire diagram since $p_{\text{S}_2} = 10^{-20.6} p_{\text{SO}_3}^2 / p_{\text{O}_2}^3$. Thermodynamic data for the preparation of this diagram were obtained from Refs. 19, 20, and 21.

as discussed previously,¹ a number of other variables rather than P_{O_2} and P_{SO_3} could have been used. Some of the other possible variables such as the sulfur pressure, the oxide ion activity, $a_{\text{O}_2^-}$, and the sulfide ion activity, $a_{\text{S}_2^-}$, have also been included in Fig. 11. The variables P_{O_2} and P_{SO_3} have been used in the present paper since the resulting diagrams are similar to the pH diagrams developed by Pourbaix for aqueous corrosion.¹¹ The choice of SO_3 pressure as a variable necessitates writing reactions involving SO_3 to readily interpret effects produced by reactions via the diagrams. In actuality, depending on the oxygen pressure, the equilibrium pressure of SO_2 for such reactions may be significantly larger than the SO_3 pressure and therefore a variable more amenable to detection. Eq. [1] was written using SO_2 since this gas was detected in the exiting gases. However, the O_2 and SO_2 pressures for this reaction define an SO_3 pressure which could be used in an equivalent reaction. The important feature of the diagram presented in Fig. 11 is that at constant temperature, by appropriate choice of two independent variables (*e.g.*, P_{O_2} and P_{SO_3} ; $a_{\text{O}_2^-}$ and $a_{\text{S}_2^-}$), the composition of pure Na_2SO_4 is uniquely defined.

The conditions necessary for reaction between nickel and Na_2SO_4 have been discussed previously.¹ A procedure similar to that used for nickel can be used to determine the conditions necessary for reactions to occur between Na_2SO_4 and aluminum. The following reactions are used where the equilibrium pressures of SO_3 and O_2 are considered to be established by the Na_2SO_4 .



* Aluminum sulfide particles, which were found in Ni-31Al, were identified by means of the electron beam microprobe. Their composition, however, was not quantitatively determined. Since thermodynamic data is available only for the compound Al_2S_3 , this phase was used in preparing the stability diagram.



The equilibrium pressures calculated from these reactions were used to construct the diagram presented

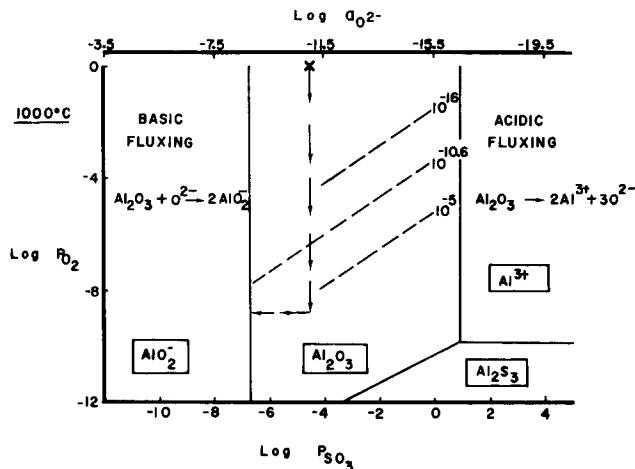


Fig. 12—Stability diagram showing the phases of aluminum that are stable in Na_2SO_4 at 1000°C. The arrows show how the composition of Na_2SO_4 can change because of removal of oxygen and sulfur. The dashed lines are sulfur isobars and the isobar of $10^{-10.6}$ is the sulfur pressure at which aluminum sulfide can be formed beneath an external Al_2O_3 scale on Ni-31Al. The diagram shows Al_2O_3 is stable in Na_2SO_4 with certain compositions and that Al_2O_3 reacts with Na_2SO_4 having either high or low oxide ion activities by what can be called basic or acidic fluxing reactions, respectively. Thermodynamic data for the preparation of this diagram were obtained from Refs. 19, 20, and 21.

in Fig. 12 which shows the phases of aluminum that are stable in Na_2SO_4 where the composition of the Na_2SO_4 is defined by the oxygen and SO_3 pressures. Since, as discussed in a previous paper, representative values of the oxygen and SO_3 pressures in the reagent grade Na_2SO_4 used in the laboratory may be taken as 1 and 3×10^{-5} atm, respectively, Fig. 12 shows that Al_2O_3 is stable in the reagent grade Na_2SO_4 at 1000°C. This was confirmed experimentally by placing Al_2O_3 single crystals in Na_2SO_4 at 1000°C for 24 h. No detectable weight-change of the Al_2O_3 was found. However, Fig. 12 also shows that there are compositions of Na_2SO_4 at which reactions with Al_2O_3 to form NaAlO_2 or $\text{Al}_2(\text{SO}_4)_3$ will occur.

It is important to emphasize that the boundaries in diagrams such as Fig. 12 are constructed by assuming that the condensed phases are at unit activity. Therefore the SO_3 and O_2 pressures at which NaAlO_2 or Al_2O_3 can coexist in Na_2SO_4 at unit activity are defined in Fig. 12. In the region where Al_2O_3 is stable in Na_2SO_4 , there is a finite activity of NaAlO_2 but it is much less than unity and a similar condition exists for Al_2O_3 in the NaAlO_2 region of the diagram. Moreover, since these types of diagram are constructed for unit activity of Na_2SO_4 , they are not valid for cases where significant solutioning occurs between the Na_2SO_4 and the phases of interest. To account for solutioning between the phases of interest and Na_2SO_4 , it is necessary to construct a three dimensional diagram. This can be done by adding an axis normal to the plane formed by the $\log P_{\text{O}_2}$ and $\log P_{\text{SO}_3}$ axes in Fig. 12 along which the activity of Na_2SO_4 varies. At present, sufficient thermodynamic data are usually not available to permit the construction of meaningful three dimensional diagrams. Although the two dimensional diagrams, *e.g.* Fig. 12, must be used with the realization that they are approximations in cases involving solutions, they do provide a very useful means to examine the conditions that can be developed

during oxidation of alloys in the presence of Na_2SO_4 .

A diagram similar to Fig. 12 cannot be constructed for chromium since sufficient thermodynamic data are not available. At 1 atm pressure of oxygen, however, the experiments with the Ni-30Cr alloy show that the reagent grade Na_2SO_4 and Cr_2O_3 react according to Eq. [1]. It therefore is apparent that this reaction will cause the composition of the Na_2SO_4 to be modified to compositions described by SO_3 pressures greater than $3 \cdot 10^{-5}$, or oxide ion activities less than 10^{-11} , Fig. 12. As the oxygen pressure is decreased below 1 atm, this same reaction should occur, but the increase in SO_3 pressure and decrease of the oxide ion activity of the Na_2SO_4 will be smaller, since examination of Eq. [1] shows the chromate- Cr_2O_3 boundary is not vertical but has a slope (*i.e.*, $d \log P_{\text{O}_2} / d \log P_{\text{SO}_3}$) of $4/3$. Finally, for sufficiently low oxygen pressures Cr_2O_3 will be stable in reagent grade Na_2SO_4 . For example, no reaction between reagent grade Na_2SO_4 and Cr_2O_3 is observed at 1000°C in an argon environment.

Fig. 12 provides the basis for formulating the mechanism of accelerated oxidation of Ni-31Al in the presence of Na_2SO_4 . Since Al_2O_3 is stable in the reagent grade Na_2SO_4 , an Al_2O_3 scale should be developed beneath the Na_2SO_4 layer as has been observed during the initial stages of oxidation of Na_2SO_4 -coated Ni-31Al. Some of the oxygen required for the formation of the Al_2O_3 scale comes from the Na_2SO_4 and a compositional gradient is developed across the molten Na_2SO_4 layer with oxygen diffusing from the gas phase through the Na_2SO_4 to the Al_2O_3 layer on the alloy surface. The development of an oxygen gradient across the Na_2SO_4 layer causes the composition of the Na_2SO_4 at the Al_2O_3 - Na_2SO_4 interface to move in the direction indicated by the vertical arrows shown in Fig. 12 which results in an increase of the sulfur activity at this interface since $a_S \equiv P_{\text{S}_2}^{1/2} = \text{constant} \times P_{\text{SO}_3}/P_{\text{O}_2}^{3/2}$. The sulfur pressure required to form aluminum sulfides in Ni-31Al in the absence of oxygen is indicated in Fig. 12. The diagram shows that for sufficiently low oxygen pressures in Na_2SO_4 , the sulfur pressure is sufficient to form aluminum sulfides in the alloy beneath the Al_2O_3 scale, providing sulfur can diffuse through the Al_2O_3 scale. The results presented in Table II show that sulfur does enter the alloy presumably by diffusing through the Al_2O_3 scale. The removal of sulfur from the Na_2SO_4 via sulfide formation in the alloy causes an additional change in the composition of the Na_2SO_4 according to the following reaction



The net effect is to increase the oxide ion concentration of the Na_2SO_4 , and, as indicated by the horizontal arrows in Fig. 12, an oxide ion activity can be reached at which the reaction



occurs. Results presented in Table II show that aluminum was found in the Na_2SO_4 ; therefore, this reaction must have occurred.

The important features of the Na_2SO_4 -induced accelerated oxidation of Ni-31Al are that aluminum sulfides are formed in the alloy and that the oxide ion-enriched Na_2SO_4 reacts with the Al_2O_3 scale. Either of these conditions could have caused the observed accelerated oxidation. Presulfidized Ni-31Al specimens containing

aluminum sulfide were found to oxidize at accelerated rates since porous, nonprotective Al_2O_3 scales are formed on aluminum sulfide.⁹ Moreover, in the present experiments accelerated oxidation of Ni-31Al was observed to continue after the Na_2SO_4 had been removed. It therefore appears that the formation of aluminum sulfide due to sulfur leaving the Na_2SO_4 and entering the alloy is a sufficient condition to cause both the accelerated and breakaway types of oxidation. The observed reaction between the oxide ion-enriched Na_2SO_4 and Al_2O_3 could also cause increased oxidation. The solubility of NaAlO_2 in Na_2SO_4 is not known but could be expected to be appreciable in Na_2SO_4 with a high oxide ion activity which would result in increased oxidation since some of the normally protective Al_2O_3 would be dissolved by the oxide ion-enriched Na_2SO_4 .

The results obtained from the oxidation of Na_2SO_4 -coated Ni-1Al show that the accelerated oxidation of this alloy occurs by a mechanism similar to that for pure nickel. While this mechanism has been described in detail elsewhere,¹ it is of value to discuss certain features of this mechanism in order that the accelerated oxidation mechanism for Ni-1Al can be compared to those for other alloys. Previous work¹ has shown that the reagent grade Na_2SO_4 does not react with NiO and that the sulfur activity in this Na_2SO_4 at oxygen pressures on the order of 1 atm is not sufficient to form nickel sulfide. Consequently, during the initial stages of oxidation of Na_2SO_4 -coated Ni-1Al, some NiO and Al_2O_3 are formed at the alloy- Na_2SO_4 interface. A compositional gradient is developed across the Na_2SO_4 layer which results in the establishment of decreased oxygen activities and increased sulfur activities at the alloy- Na_2SO_4 interface. Sulfur then leaves the Na_2SO_4 to form nickel sulfides in the alloy and the oxide-ion concentration of the Na_2SO_4 is increased. It has been proposed¹ that this oxide-ion rich Na_2SO_4 can apparently flux the NiO scale on the alloy surface by forming nickelate ions which decompose in the Na_2SO_4 to form discontinuous NiO particles at the Na_2SO_4 -gas interface. The alloy therefore oxidizes at an accelerated rate until the oxide-ion activity of the sulfate is no longer capable of fluxing the NiO . This condition occurs when the sulfur activity of the sulfate is not sufficient to cause nickel sulfide formation in the alloy. Since the mechanisms of accelerated oxidation of Ni-1Al and pure nickel are the same, it can be concluded that the aluminum in this particular alloy does not have a significant effect on the accelerated oxidation mechanism.

The results obtained from the oxidation of Na_2SO_4 -coated Ni-5Cr show that this alloy does not undergo accelerated oxidation. The mechanism for oxidation of this alloy in the presence of Na_2SO_4 is similar to that for Ni-1Al. During oxidation, however, the oxide ion activity of the Na_2SO_4 is not increased to values at which fluxing of the NiO scale occurs since Cr_2O_3 , formed on the alloy surface during the initial stages of oxidation, reacts with the oxide ions to form chromate. The NiO is therefore stable beneath the molten, chromate-containing Na_2SO_4 layer. An explanation for the observed decreased rate of oxidation of this alloy in the presence of Na_2SO_4 is not available. The differences in weight-changes in Fig. 8 between oxidation with and without Na_2SO_4 appear to be too large to have been caused by vaporization of Na_2SO_4 or the Na_2CrO_4 which

may have formed, or by evolution of SO_3 . The oxidation rate of this alloy is probably controlled by transport of nickel through the NiO scale. Sodium may be incorporated in the NiO during oxidation and this would decrease the cation vacancy concentration of the NiO , causing a decrease in the growth rate of the oxide. For example, Pfeiffer and Hauffe¹² have reported that the parabolic rate constants for the oxidation of nickel are decreased when Li_2O vapor is present in the oxidizing gas.

Aluminum in Ni-Al alloys may produce effects similar to chromium in Ni-5Cr since Al_2O_3 will also react with oxide ions to form aluminate ions providing the oxide ion activity is sufficiently high. It is possible that such effects were not observed for Na_2SO_4 -coated Ni-1Al because this alloy contained a small amount of aluminum. It is apparent, however, that Cr_2O_3 reduces the oxide ion activity of Na_2SO_4 to lower levels than Al_2O_3 since Cr_2O_3 was found to react with reagent grade Na_2SO_4 whereas Al_2O_3 did not.

The results obtained with the Na_2SO_4 -coated Ni-30Cr show that although accelerated oxidation of this alloy is not observed, significant amounts of chromium are observed in the Na_2SO_4 , Table III. This shows that some of the protective Cr_2O_3 scale has been converted to chromate ions in the sulfate as well as perhaps liquid Na_2CrO_4 (M.P. 822°C) if Na_2SO_4 and Na_2CrO_4 are not completely miscible at the temperature of interest. During the initial stages of oxidation of this alloy in the presence of Na_2SO_4 , Cr_2O_3 is not stable on the alloy surface because the oxide ion concentration of the Na_2SO_4 is sufficient to form chromate ions. This condition should cause the initial oxidation rate to be greater than that for normal oxidation. An increase in the oxidation rate of the sulfate-coated specimen over that for normal oxidation is not obvious in Fig. 8 probably because, as proposed by Graham and Davis¹³ as well as by Bornstein and DeCrescente,⁴ weight losses due to evolution of SO_3 and vaporization of Na_2SO_4 as well as NaCrO_4 are occurring. Since a protective layer of Cr_2O_3 does develop on this alloy beneath the Na_2SO_4 , Fig. 9, it can be concluded that the oxide ion activity of the sulfate is quickly reduced by reaction with Cr_2O_3 to values where Cr_2O_3 is stable on the alloy surface. This reduction of oxide ion activity results in an increased sulfur activity in the Na_2SO_4 and, in addition to SO_3 as well as SO_2 evolution, sulfur enters the alloy by diffusion through the Cr_2O_3 scale to form chromium sulfide, Fig. 9.

It is important to note that the fluxing reactions for NiO and Cr_2O_3 by Na_2SO_4 are similar. Both occur because oxide ions in the Na_2SO_4 react with these oxides. In the case of NiO , however, sulfur must be removed from the sulfate in order to develop the oxide ion activity required for reaction, whereas in the case of Cr_2O_3 the oxide ion activity in the reagent grade Na_2SO_4 is sufficient to cause reaction in the presence of oxygen. An important difference between these two reactions does occur, however, after the fluxing reaction. As the nickelate ions which formed during fluxing of NiO move out into the Na_2SO_4 , they decompose to NiO and oxide ions. This occurs because the oxide ion activity is sufficient for nickelate formation only in the vicinity of the alloy surface where oxide ions are produced. The Na_2SO_4 therefore becomes covered with a porous NiO scale. When chromate ions are formed and move away

from the alloy surface, however, they do not decompose since the oxide ion activity of the unmodified Na_2SO_4 is sufficient for their stability. Consequently when the oxide ion activity of the Na_2SO_4 has been reduced sufficiently to permit the formation of Cr_2O_3 , the Cr_2O_3 forms on the alloy surface as a continuous layer beneath the Na_2SO_4 .

The results obtained for the oxidation of Na_2SO_4 -coated Ni-Cr-Al alloys show that increased oxidation occurred only in Ni-8Cr-6Al where alloy depletion of chromium and aluminum is believed to have caused the development of oxide scales other than Al_2O_3 . The mechanism for oxidation in the presence of Na_2SO_4 of those alloys which did not show depletion effects is similar to that for Ni-31Al in that a protective layer of Al_2O_3 rapidly develops on these alloys beneath the Na_2SO_4 . However, the Cr_2O_3 , which is formed on these alloys during the initial stages of oxidation before the Al_2O_3 layer is continuous, reacts with oxide ions in the Na_2SO_4 and thus prevents any reaction of oxide ions with Al_2O_3 . In addition, sulfur, diffusing through the Al_2O_3 to the alloy, combines with chromium rather than aluminum, so that aluminum sulfide is not formed in the alloy. As a result of these conditions, a protective layer of Al_2O_3 is stable on these alloys and oxidation takes place much the same as in the absence of Na_2SO_4 .

The results obtained from the studies of the oxidation of Ni-Al, Ni-Cr, and Ni-Cr-Al alloys in the presence of Na_2SO_4 are not sufficient to allow the development of completely acceptable mechanisms for all of the alloys. The point to be emphasized, however, is that these results do permit the essential features of Na_2SO_4 -induced accelerated oxidation to be developed. The most essential feature is that the oxide ion activity of the Na_2SO_4 can attain sufficient magnitude for the Na_2SO_4 to become a basic flux for oxides formed on the surface of alloys and thereby cause increased oxidation. Generally, the necessary oxide ion activity required for the fluxing reaction is achieved by sulfur diffusing from the Na_2SO_4 into the alloy. Therefore, basic fluxing is not self-sustaining and stops when oxide ions are no longer developed in the Na_2SO_4 . In addition, the diffusion of sulfur into some alloys can also result in increased oxidation.⁹ Finally, the basic fluxing reactions as well as the formation of internal sulfides do cause more severe depletion of chromium and aluminum than occurs during normal oxidation. Increased oxidation can therefore occur on some alloys due to the formation of oxides with compositions different from those developed during normal oxidation.

Na_2SO_4 -Induced Catastrophic Oxidation

The results obtained with the modified B-1900 type alloys indicated that catastrophic Na_2SO_4 -induced oxidation occurred when molybdenum was present in these alloys. To confirm that molybdenum could cause Na_2SO_4 -induced catastrophic oxidation of nickel-base alloys and to determine if other elements could also produce the same effects, some Ni-Al and Ni-8Cr-6Al alloys containing either Mo, W, or V were oxidized at temperatures in the interval of interest after having been coated with Na_2SO_4 . The aluminum concentration of the Ni-Al alloys was maintained at about 30 pct because this is approximately that of aluminide coatings on nickel-base superalloys. The chromium and alu-

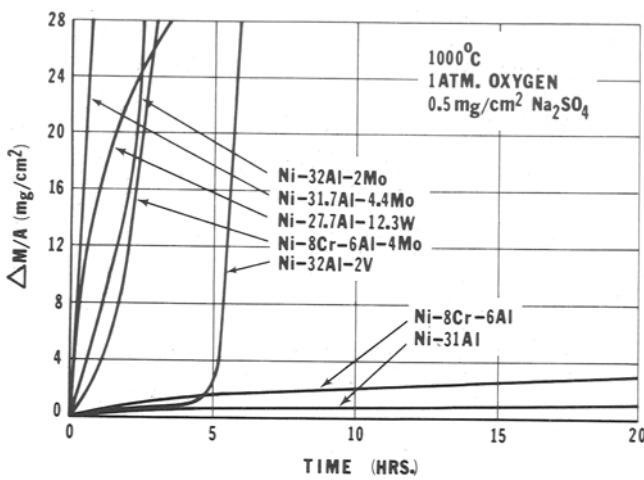


Fig. 13—Weight-change vs time curves for the oxidation of Na_2SO_4 -coated ($0.5 \text{ mg}/\text{cm}^2$) specimens of Ni-Al and Ni-Cr-Al alloys. Alloys which contain Mo, W, or V are oxidized at much faster rates than alloys with similar compositions but without these elements.

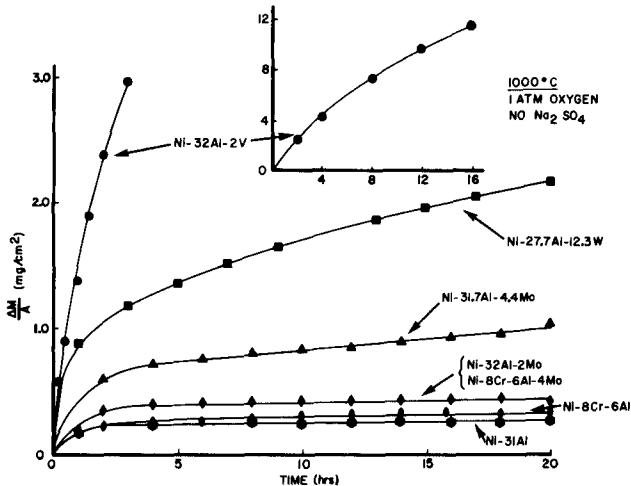
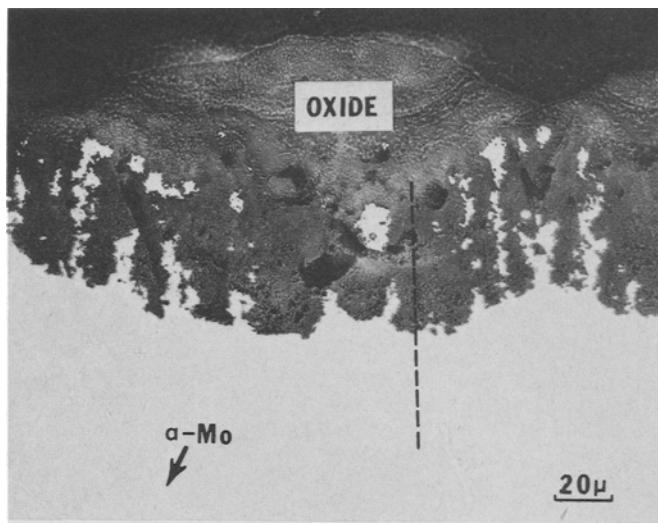


Fig. 14—Weight-change vs time curves for the oxidation of Ni-Al and Ni-Cr-Al alloys in oxygen at 1000°C. Comparison of these results to those in Fig. 13 shows the alloys are always oxidized faster when Na_2SO_4 is present except for the Ni-32Al-2V alloy which has an incubation period prior to the onset of catastrophic oxidation.

minimum concentrations of the Ni-Cr-Al alloys were maintained at about 8 and 6 pct, respectively, because these concentrations are typical of those used in many nickel-base superalloys.

The oxidation kinetics obtained from oxidizing these alloys in the Na_2SO_4 test at 1000°C are presented in Fig. 13. These data show that in the presence of Na_2SO_4 , Ni-Al alloys containing Mo, W, or V and Ni-8Cr-6Al-4Mo have extremely large oxidation rates in comparison to the same base alloys without any Mo, W, or V. In addition, the Ni-32Al-2V alloy was found to undergo a period of relatively slow oxidation prior to the onset of catastrophic oxidation. The oxidation kinetics obtained upon oxidizing these alloys under the same conditions but without Na_2SO_4 are presented in Fig. 14. Comparison of the results presented in Figs. 13 and 14 shows that the weight gains of all the alloys oxidized in the presence of Na_2SO_4 except Ni-32Al-2V are always at least an order of magnitude greater than those when Na_2SO_4 is not present on the specimen sur-



(a)

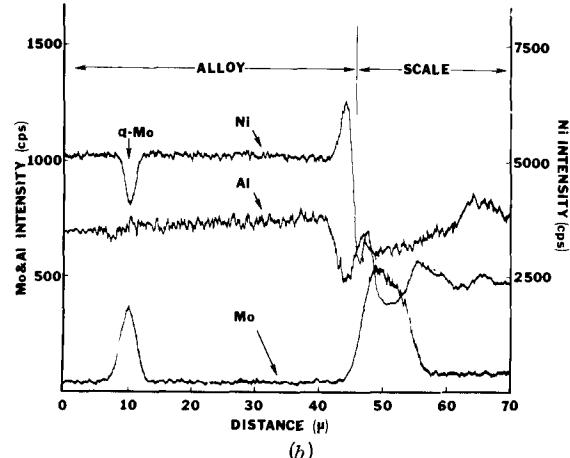


Fig. 15—(a) Microstructure of Na_2SO_4 -coated ($0.5 \text{ mg}/\text{cm}^2$) Ni-31Al-4.4Mo after 4 h of oxidation in $\sim 1 \text{ atm O}_2$ at 800°C. The oxide scale is much thicker than that formed during normal oxidation in the absence of Na_2SO_4 . (b) Results from electron beam microprobe traces across specimen as indicated in (a). Note the enrichment in molybdenum in the scale immediately adjacent to the scale/substrate interface. The absence of a significant amount of molybdenum in the outer portion of the scale may have resulted from vaporization of MoO_3 .

face. Ni-32Al-2V also oxidized much faster in the presence of Na_2SO_4 except during the incubation period prior to the onset of catastrophic oxidation where oxidation in the absence of Na_2SO_4 was greater.

To account for the Na_2SO_4 -induced catastrophic oxidation of the alloys which contained Mo, W, or V, typical oxidized specimens were examined with the light microscope, electron beam microprobe and by X-ray diffraction analyses. The oxide scales were always extremely thick and relatively porous as seen in Fig. 15(a). Although the X-ray diffraction patterns obtained from the oxide scales were complex, NiO and NiAl_2O_4 were always found. Occasionally other phases such as Al_2O_3 or $\text{Ni}(\text{Mo}, \text{W}, \text{V})\text{O}_4$ were also identified in these oxide scales. Typical results obtained with the electron beam microprobe are presented in Fig. 15(b). These results show that the Ni-31Al-4.4Mo substrate adjacent to the oxide scale has been enriched in nickel and depleted of aluminum. The small thickness of this de-

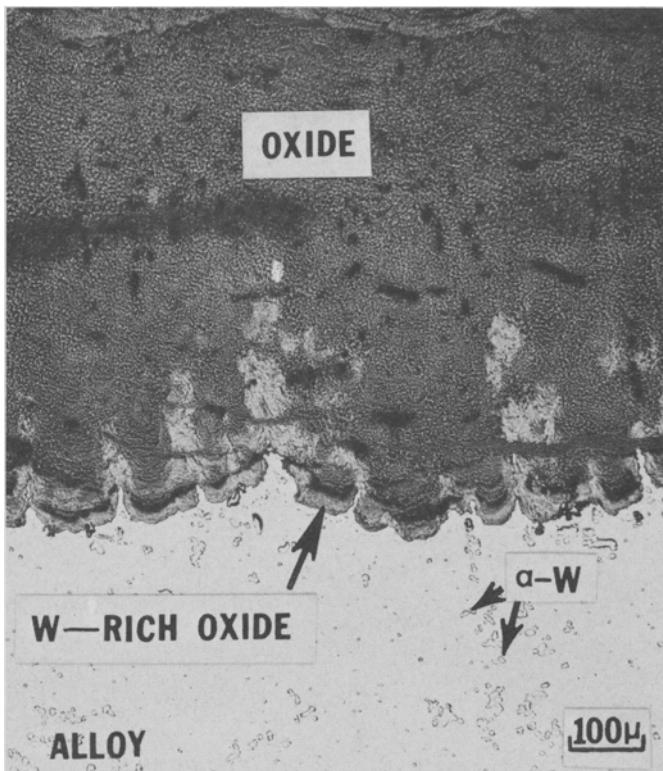
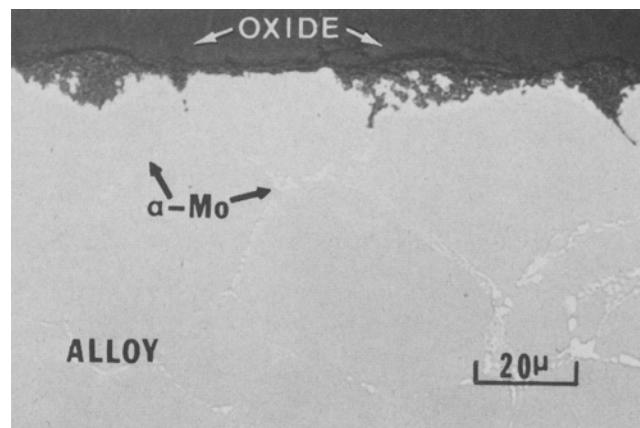


Fig. 16—Microstructure of a Ni-27.7Al-12.3W alloy which was coated with Na_2SO_4 (0.5 mg/cm^2) and oxidized 20 h in $\sim 1 \text{ atm}$ O_2 at 1000°C . The oxide scale was found to be enriched in tungsten at the scale/alloy interface.

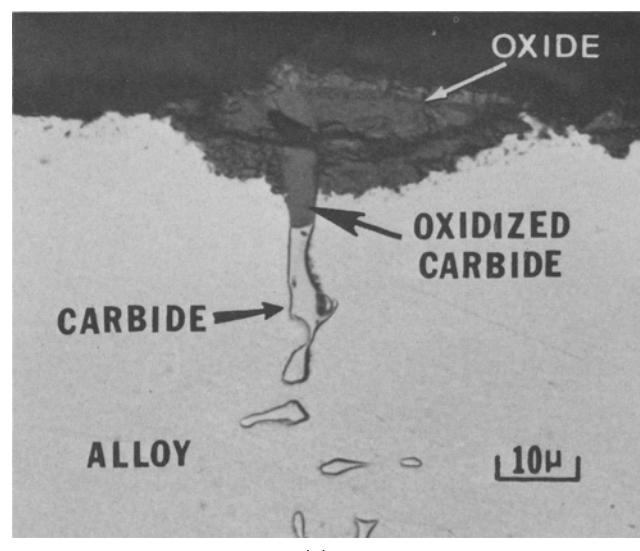
pleted zone is consistent with the rapid oxidation rate which permits only little diffusion to take place in the alloy substrate. The probe trace for molybdenum does not show any depletion nor enrichment of this element in this zone of the alloy substrate; however, it does show that molybdenum is concentrated in the oxide scale immediately adjacent to the alloy-scale interface. Similar results were obtained on alloys containing tungsten or vanadium rather than molybdenum. In some cases the enrichment of the oxide scale in Mo, W, or V caused the scale to have a different texture at the alloy-scale interface as observed in the scale formed on Ni-27.7Al-12.3W presented in Fig. 16.

The portions of the oxide scales adjacent to the alloy substrate which were enriched in Mo, W, or V were also found by electron beam microprobe analyses to contain sulfur. It is believed that the sulfur is present in the scale as Na_2SO_4 since sulfide phases were not observed metallographically and should not be thermodynamically stable in the oxide scale.¹⁴ The presence of Na_2SO_4 in the oxide at the alloy-oxide interface is consistent with visual observations of Na_2SO_4 -induced catastrophic oxidation made on the alloys containing Mo, W, or V in a hot stage microscope. Virtually at the start of oxidation the Na_2SO_4 was observed to become covered with oxide so that the Na_2SO_4 apparently remained near the alloy surface beneath the oxide scale.

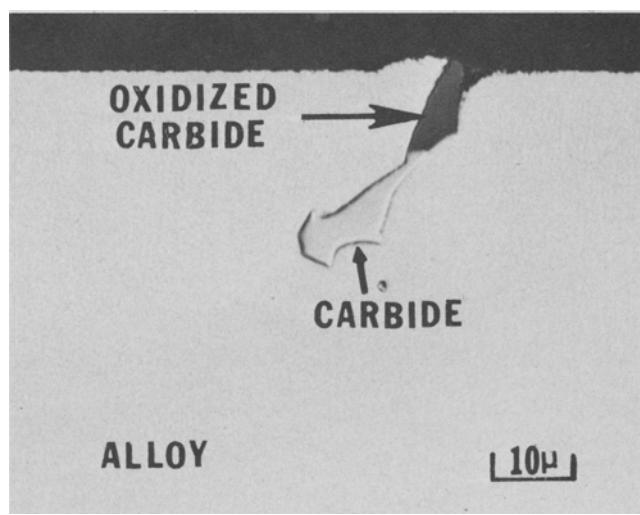
For those alloys which underwent Na_2SO_4 -induced catastrophic oxidation at 1000°C virtually from the beginning of weight-change measurements, Fig. 13, large amounts of oxides were rapidly formed all over the alloy surfaces and it was not possible to clearly



(a)

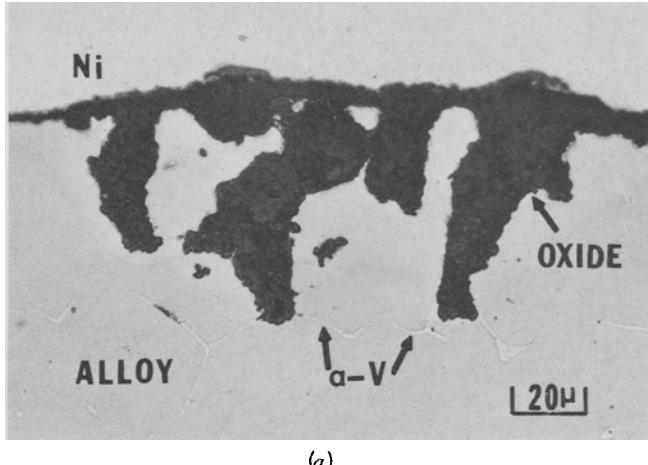


(b)

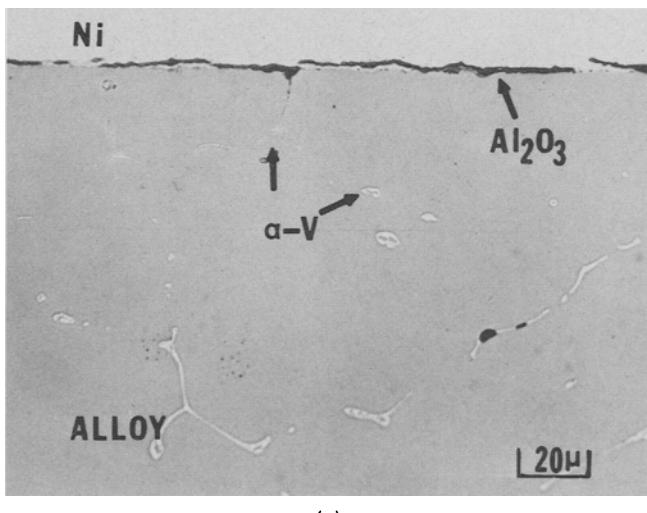


(c)

Fig. 17—Microphotograph showing preferential attack of molybdenum-rich phases in alloys. (a) Sodium sulfate coated Ni-31.7Al-4.4Mo after 3.5 h of oxidation in $\sim 1 \text{ atm}$ O_2 at 700°C . Note initiation of catastrophic oxidation of alloy at molybdenum-rich phase. (b) Sodium sulfate coated B-1900 after 20 h of oxidation in $\sim 1 \text{ atm}$ O_2 at 700°C . Note that catastrophic oxidation of alloy initiates at the molybdenum-rich carbide phase. (c) B-1900 without Na_2SO_4 after 45 h of oxidation at 700°C in $\sim 1 \text{ atm}$ O_2 . The carbide phase has been preferentially oxidized but no attack of the matrix is noticeable.



(a)



(b)

Fig. 18—Microphotographs of Ni-32Al-2V alloy after 2 h of oxidation in ~ 1 atm O_2 at 1000°C (a) without, and (b) with, a Na_2SO_4 coating. The Na_2SO_4 -coated specimen has been attacked substantially less than the uncoated specimen after 2 h of oxidation.

observe the sites of initiation of this type of attack. To observe the initiation of catastrophic oxidation on such alloys Na_2SO_4 -coated specimens were oxidized at 700°C. As shown in Figs. 17(a) and 17(b) the catastrophic attack of alloys containing molybdenum was observed to initiate at phases in these alloys which were rich in molybdenum. Preferential oxidation of the molybdenum-rich phases was also observed after oxidation in the absence of Na_2SO_4 ; however, the oxidation was confined to the molybdenum-rich phase whereas in the presence of Na_2SO_4 the alloy adjacent to the molybdenum-rich phases was also severely oxidized, as can be seen by comparing Figs. 17(b) and 17(c). Similar results were obtained with alloys which contained tungsten. It therefore appears that catastrophic oxidation initiates at the phases in these alloys which are rich in molybdenum or tungsten and then spreads laterally over the alloy surface.

Since the Ni-32Al-2V alloy exhibited an incubation period of relatively slow oxidation at 1000°C, it was possible to examine the initiation of catastrophic oxidation on this alloy at 1000°C as well as at lower temperatures. Catastrophic oxidation was found to initiate

at the vanadium-rich phase. However, the preferential oxidation of vanadium-rich phases during the incubation period prior to Na_2SO_4 -induced catastrophic oxidation was less than that which occurred in the absence of Na_2SO_4 as shown in Fig. 18. These results are consistent with the oxidation kinetics. Examination of Fig. 18(a) shows that the preferential oxidation of the vanadium-rich phase in the absence of Na_2SO_4 has resulted in increased oxidation of this alloy in areas adjacent to the vanadium-rich phase. The decreased amount of this type of oxidation in the presence of Na_2SO_4 may be due to removal of the oxides formed at the vanadium-rich phases of the alloy by reaction between the Na_2SO_4 and oxides of vanadium.

The previous results have shown that during the Na_2SO_4 -induced catastrophic oxidation of nickel-base alloys containing Mo, W, or V, thick, nonprotective oxide scales are formed with Na_2SO_4 and oxides of these elements concentrated at the scale-alloy interface. To determine the conditions developed in Na_2SO_4 due to reaction of this salt with oxides of Mo, W, or V, construction of diagrams similar to Fig. 12 could be attempted, however sufficient thermodynamic data is not available for complete construction. In addition, as will be discussed subsequently, it appears that extensive solutions of Na_2SO_4 and these oxide phases may be developed which indicates the activity of Na_2SO_4 should not be taken as unity when constructing these diagrams and therefore three-dimensional diagrams are required. In view of these conditions, the crucible experiments described in the following paragraphs were performed to determine qualitatively the conditions developed in Na_2SO_4 as a result of reaction with oxides of Mo, W, or V.

The diagram in Fig. 12 can be used to determine experiments which should provide meaningful results concerning the effects produced by reaction between Na_2SO_4 and various oxide phases. Examination of Fig. 12 shows that the addition of an oxide to Na_2SO_4 at constant oxygen pressure may produce one of three possible effects:

- 1) If the oxide ion activity of the Na_2SO_4 is such that the oxide phase is stable, then the oxide phase will not react with the Na_2SO_4 and the composition of the Na_2SO_4 will remain virtually unchanged (*e.g.*, Al_2O_3 added to reagent grade Na_2SO_4).

- 2) If the oxide ion activity of the Na_2SO_4 is such that the following reaction can occur,



then the oxide phase (MO) will take oxide ions from the Na_2SO_4 making the flux less basic and the oxide ion activity of the Na_2SO_4 will be decreased (*e.g.*, Al_2O_3 added to Na_2SO_4 with an oxide ion activity of 10^{-7} at 1000°C). Furthermore, in view of Eq. [4] the SO_3 pressure of the sulfate will be increased by this reaction.

- 3) Finally, if the oxide ion activity of the Na_2SO_4 is such that



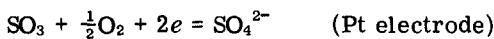
then the oxide phase will donate oxide ions to the Na_2SO_4 making the flux more basic, the oxide ion activity of the Na_2SO_4 will be increased, and the SO_3 pressure will be decreased (*e.g.*, Al_2O_3 added to Na_2SO_4 with an oxide ion activity of 10^{-19}).

In view of these considerations, reactions between oxide phases and Na_2SO_4 can be examined by comparing the oxide ion activity of Na_2SO_4 before and after addition of an oxide as well as by comparing the amount of SO_3 evolution in these two cases.

In the present studies, the oxide ion activities of the Na_2SO_4 before and after addition of oxides were compared by determining the potentials of the following cell in flowing oxygen:

Ag	10 mole pct Ag_2SO_4	mullite	eutectic salt mixture	Pt
Argon	90 mole pct eutectic salt mixture			$P_{\text{O}_2} = 1 \text{ atm}$

This cell was constructed as described by Brown, Bornstein, and DeCrescente.¹⁵ The electrolyte was a eutectic mixture of 78 mole pct Li_2SO_4 , 13.5 mole pct K_2SO_4 , and 8.5 mole pct Na_2SO_4 rather than pure Na_2SO_4 in order that the measurements could be made at 727°C to prolong the life of the cell. The reference electrode contained 10 mole pct Ag_2SO_4 and 90 mole pct eutectic mixture. The half-cell reactions can be written as



however, these reactions can be reversed depending on the oxide ion activity differences between the reference electrode and the oxide-modified eutectic mixtures. The expression for the change of the potential of this cell upon addition of an oxide to the eutectic mixture is

$$\begin{aligned} E_{\left(\substack{\text{pure} \\ \text{eutectic}}\right)} - E_{\left(\substack{\text{oxide-} \\ \text{modified}}\right)} &= \Delta E \\ &= \frac{RT}{2F} \ln \frac{[P_{\text{SO}_3}] \text{oxide-modified eutectic}}{[P_{\text{SO}_3}] \text{pure eutectic mixture}} \\ &= \frac{RT}{2F} \ln \frac{[a_{\text{O}^{2-}}] \text{pure eutectic mixture}}{[a_{\text{O}^{2-}}] \text{oxide-modified eutectic}} \end{aligned} \quad [14]$$

Eq. [14] shows the potential change will be positive if the oxide which is added decreases the oxide ion activity of the salt whereas it will be negative if the oxide increases the oxide ion activity of the salt. The results presented in Table IV show MoO_3 , WO_3 , and Cr_2O_3 decreased the oxide ion activity of the eutectic mixture whereas Na_2O increased it. Measurements were not made for the addition of V_2O_5 to Na_2SO_4 but Bornstein and coworkers¹⁶ have shown that V_2O_5 also decreases the oxide ion activity of Na_2SO_4 . Measurements were made using Na_2O to obtain results for an oxide which would obviously donate oxide ions to the Na_2SO_4 . Measurements were made with Cr_2O_3 since this oxide is frequently formed during the oxidation of nickel-base superalloys. Experiments were also performed with the other principal oxides formed on nickel-base alloys, namely NiO and Al_2O_3 . These two oxides did not react with reagent grade Na_2SO_4 .

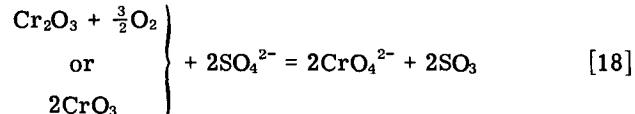
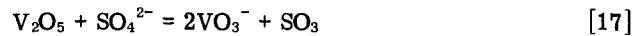
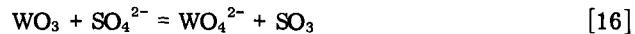
To compare the SO_3 evolution from Na_2SO_4 with and without oxide additions, Na_2SO_4 in Al_2O_3 crucibles was heated at 1000°C in flowing argon and the effluent gas was analyzed for SO_2 . The results from these experiments, which are presented in Table IV, show the SO_2

Table IV. Results from Crucible Experiments on Reactions Between Oxides and Na_2SO_4

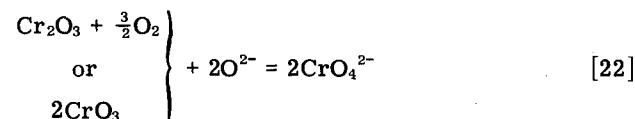
Oxide Added	Cell Potential Relative to Pure Na_2SO_4 in Flowing O_2 , 727°C	Na_2SO_4 in Al_2O_3 Crucible			Precipitate Formed in Melt Containing 50 mole Pct Na_2CrO_4 in Na_2SO_4 , Air, 1000°C	
		1000°C				
		SO_2 Evolution Over First 10 Minutes in Flowing Argon, mg	Wt. Loss Crucible After 2 Hrs in Static Air, mg	Wt. Pct Al in Melt After 2 Hrs in Air		
None	—	0.6	0.0	0.001	None	
MoO_3	Positive	>15	6.3	0.12	Cr_2O_3	
WO_3	Positive	10.5	6.2	0.15	Cr_2O_3	
V_2O_5	—	7.5	4.6	0.06	Cr_2O_3	
Cr_2O_3	Positive	1.4	0.0	<0.002	—	
Na_2O	Negative	—	33.9	0.23	—	

evolution from Na_2SO_4 is increased upon addition of MoO_3 , WO_3 , V_2O_5 , or Cr_2O_3 .

The results obtained from the comparison of cell potentials as well as the measurements of SO_2 evolution show the following reactions take place between the oxides of interest and Na_2SO_4 .



In view of the equilibrium which exists between oxide ions, SO_3 and SO_4^{2-} as described in Eq. [4], these reactions could also be written as,



which shows more explicitly that these oxides reduce ion activity of the Na_2SO_4 . In view of these conditions, the question arises as to whether the reaction of MoO_3 , WO_3 , V_2O_5 , and Cr_2O_3 can reduce the oxide ion activity of Na_2SO_4 to values where protective oxides such as Al_2O_3 and NiO are no longer stable. It is not possible to calculate with confidence the appropriate oxide ion activities for such cases, even when values for the standard free energy of formation of the pure phases are available, since solutions of sulfate ions and molybdate ions or sulfate ions and vanadate ions, and so forth, are formed. For example, the SO_3 pressure established by the equilibrium given by Eq. [15] cannot be calculated since the activities of SO_4^{2-} and MoO_4^{2-} ions cannot be taken as unity. In addition, even if the SO_3 pressure were determined experimentally, the oxide ion activity could not be calculated by using Eq. [3] since the sulfate ion activity cannot be taken as unity.

To determine qualitatively if reactions between the oxides of MoO_3 , V_2O_5 , WO_3 , and Cr_2O_3 could decrease

the oxide ion activity of Na_2SO_4 to levels where Al_2O_3 would dissolve, mixtures of Na_2SO_4 and 10 wt pct of the oxides were heated in Al_2O_3 crucibles for 2 h in air at 1000°C. The results from these experiments are presented in Table IV. It can be seen that the crucibles containing Na_2SO_4 and MoO_3 , V_2O_5 , or WO_3 additions all lost weight. In addition, aluminum was detected in each molten salt mixture after the experiment. These results indicate that reaction of MoO_3 , V_2O_5 , or WO_3 with Na_2SO_4 decreases the oxide ion activity of Na_2SO_4 to levels where the following reaction can occur in the acid flux



It is also to be noted that the Al_2O_3 crucible with Na_2SO_4 and Cr_2O_3 did not lose weight. This shows that even though Cr_2O_3 decreases the oxide ion activity of Na_2SO_4 , the decrease is not sufficient to permit reaction [23] to take place. Finally, the results obtained from the Na_2O addition to Na_2SO_4 also show a reaction has occurred between the molten salt and the Al_2O_3 crucible. However, since this oxide addition increased the oxide ion activity of the Na_2SO_4 , the weight loss occurred because of the reaction described by Eq. [11] rather than that described by Eq. [23]. The results obtained by the Na_2O addition and those obtained by additions of MoO_3 , V_2O_5 , or WO_3 show that Al_2O_3 can react either with an oxide ion-rich Na_2SO_4 (basic salt) or an oxide ion-deficient Na_2SO_4 (acidic salt) as indicated in Fig. 12.

To examine the influence of the oxide-modified Na_2SO_4 on Cr_2O_3 , mixtures of 50 mole pct Na_2CrO_4 in Na_2SO_4 were prepared in platinum crucibles to which additions of 10 wt pct MoO_3 , V_2O_5 , or WO_3 were made. After the crucibles were heated 2 h in air at 1000°C, a precipitate of Cr_2O_3 was observed as indicated in Table IV. In addition, SO_3 was evolved during the experiment. These results indicate that MoO_3 , V_2O_5 , and WO_3 take oxide ions from the chromate ions as well as sulfate ions and Cr_2O_3 is formed. It appears that in these particular experiments the activities of MoO_3 , V_2O_5 , or WO_3 were not sufficient to remove oxide ions from Cr_2O_3 ; however, similar experiments did cause reaction with Al_2O_3 . It therefore appears that Cr_2O_3 is stable at a lower oxide ion activity than Al_2O_3 , but in view of results obtained by Brenner¹⁷ who found Fe-Cr-Mo alloys were catastrophically oxidized in the absence of Na_2SO_4 due to reaction between molten MoO_3 and Cr_2O_3 as well as iron oxide, it appears that there is some activity of MoO_3 and probably V_2O_5 and WO_3 above which reaction with Cr_2O_3 does occur.

The reaction of NiO with oxide-modified Na_2SO_4 was only examined for the case where 10 wt pct MoO_3 was added to the Na_2SO_4 . The MoO_3 - Na_2SO_4 melt was held in a platinum crucible and a single crystal of NiO was added to the melt. The NiO tablet lost 26 mg/cm² of weight after 2 h at 1000°C in air. In addition, nickel was detected in the molten salt after the experiment. These results show that NiO also reacts with low oxide ion activity Na_2SO_4 . This result complements the knowledge that NiO is fluxed to form NiO_2^- ions at high oxide ion activities.¹

The results obtained from the crucible experiments indicate that MoO_3 -, V_2O_5 -, or WO_3 -modified Na_2SO_4 are efficient fluxes for dissolution of NiO and Al_2O_3 and probably Cr_2O_3 scales on alloys. A lower oxide ion

activity may be required for fluxing of Cr_2O_3 than either Al_2O_3 or NiO . Fluxing of Al_2O_3 , NiO , or Cr_2O_3 appears to occur by reaction between the oxide and the modified Na_2SO_4 whereby a product which is soluble in the Na_2SO_4 is formed. It is also possible, however, that the reaction product itself is a liquid but that its solubility in the modified Na_2SO_4 is not significant; in this case, the liquid product should not afford any protection to the alloy substrate. It is important to note that most of the phases that may form by reaction between Al_2O_3 , NiO , or Cr_2O_3 and MoO_3 -, V_2O_5 -, or WO_3 -modified

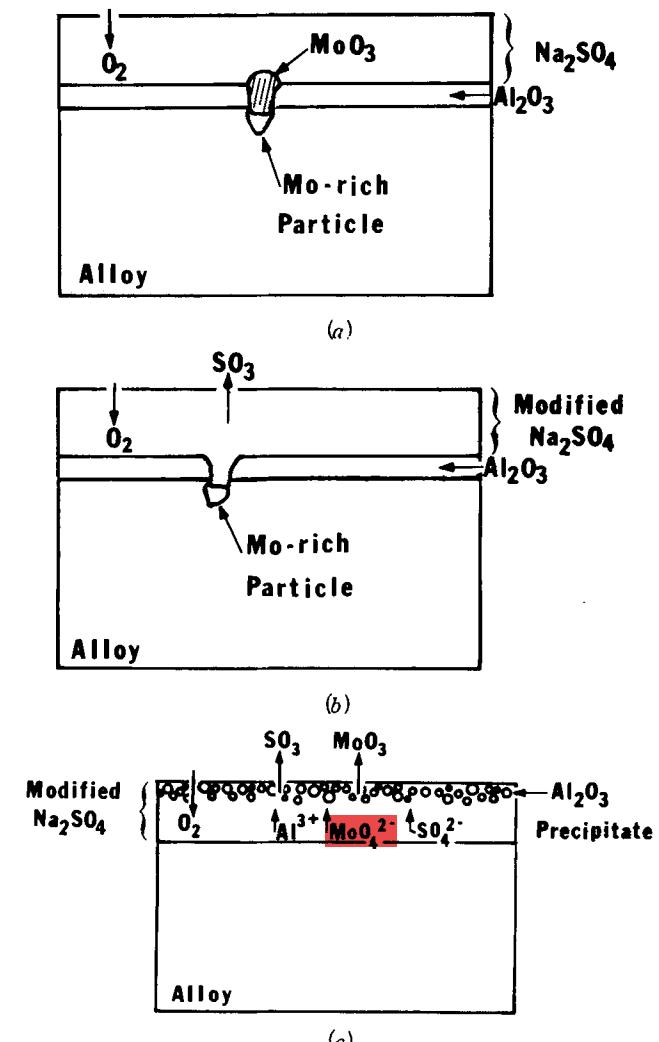


Fig. 19—Model for the Na_2SO_4 -induced catastrophic oxidation of a Ni-31Al-Mo alloy. (a) Oxygen moves from the gas through the Na_2SO_4 to the alloy surface where oxide phases similar to those formed during normal oxidation are developed. (b) MoO_3 formed by the oxidation of molybdenum-rich phases, as well as MoO_3 formed during the transient period of oxidation prior to the development of a continuous Al_2O_3 scale, reacts with the Na_2SO_4 which decreases the oxide ion activity of Na_2SO_4 and produces acidic conditions. (c) The acidic condition of the Na_2SO_4 causes the protective Al_2O_3 scale to be destroyed since the Al_2O_3 scale donates oxide ions to the modified Na_2SO_4 (i.e., $\text{Al}_2\text{O}_3 \rightarrow 2\text{Al}^{3+} + 3\text{O}^{2-}$). However, vaporization of MoO_3 causes the Al_2O_3 to precipitate as a porous network at the Na_2SO_4 /gas interface. (d) Rapid oxidation ensues and aluminum is preferentially removed from the alloy and the alloy/scale interface becomes irregular. (e) The nickel-rich islands developed because of preferential oxidation of aluminum are converted to NiO . The rapid oxidation is self-sustaining because MoO_3 is continually added to the Na_2SO_4 by oxidation of molybdenum in the alloy.

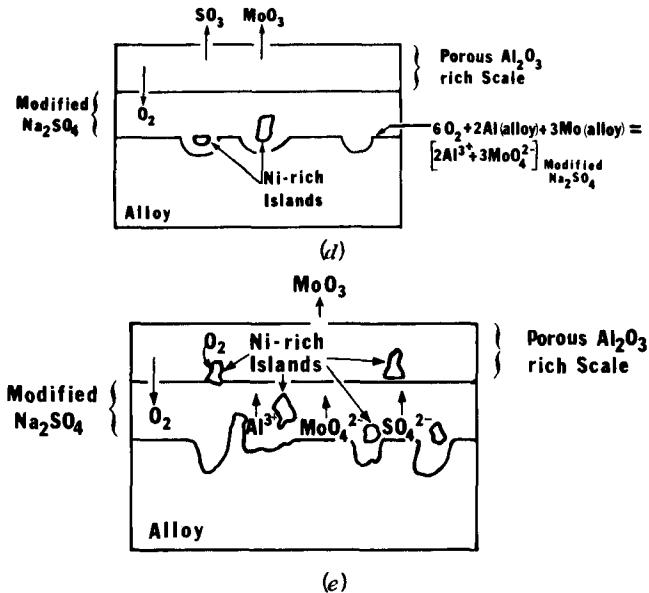


Fig. 19—Continued.

Na_2SO_4 (which is equivalent to saying the Na_2SO_4 has a low oxide ion activity) have low melting points. For example, AlVO_4 and CrVO_4 melt at 695°C and 810°C ,¹⁸ respectively. Similar conditions exist for NiO but the melting points of the phases do increase with the NiO content. For example, $\text{Ni}_3(\text{VO}_4)_2$ or $3\text{NiO} \cdot \text{V}_2\text{O}_5$ melts at 1200°C , whereas $\text{Ni}_2\text{V}_2\text{O}_7$ or $2\text{NiO} \cdot \text{V}_2\text{O}_5$ melts at 875°C .¹⁸

Considering all the results that have been obtained for Na_2SO_4 -induced catastrophic oxidation, the following model can be constructed for this type of oxidation. For simplicity, a Ni-31Al-Mo alloy will be discussed but the basic features of the model are believed to be generally applicable to the Na_2SO_4 -induced catastrophic oxidation of all nickel-base alloys and to the catastrophic oxidation which occurs from external application of Na_2SO_4 - V_2O_5 mixtures, as observed, for example, on alloys used in environments resulting from combustion of impure fuels. During the initial stages of oxidation of a Na_2SO_4 -coated Ni-Al-Mo alloy, conditions are similar to those described previously for Na_2SO_4 -induced accelerated oxidation. As shown in Fig. 19(a), oxygen moves from the gas through the Na_2SO_4 to the alloy surface where oxide phases similar to those formed during normal oxidation are developed. For the alloys under consideration, this can be taken to be the eventual formation of a continuous layer of Al_2O_3 that develops after a transient period of oxidation during which NiO and MoO_3 also are initially formed. In addition, predominantly MoO_3 is formed at the molybdenum-rich particles. Any MoO_3 that has been formed reacts with the Na_2SO_4 to decrease the oxide ion activity of the Na_2SO_4 . The reaction of MoO_3 with the Na_2SO_4 prevents the basic fluxing reaction from occurring. This effect is similar to that described previously for reaction between Cr_2O_3 and Na_2SO_4 . However, the present results show MoO_3 can decrease the oxide ion activity of Na_2SO_4 to levels where acidic fluxing of Al_2O_3 or NiO occur; Cr_2O_3 in Na_2SO_4 cannot cause such an effect. As shown in Fig. 19(b), the acidic fluxing initiates at molybdenum-rich particles in the alloy since the activity of MoO_3 in the

Na_2SO_4 is largest in these areas. However, the activity of MoO_3 throughout the Na_2SO_4 layer gradually increases, and eventually the oxide ion activity becomes sufficiently low that the acidic Na_2SO_4 layer can react with the protective Al_2O_3 scale on all areas of the alloy.

As shown in Fig. 19(c), reaction between the Al_2O_3 scale and the modified Na_2SO_4 results in the formation of Al^{3+} , MoO_4^{2-} , and SO_4^{2-} ions which diffuse through the Na_2SO_4 to the Na_2SO_4 -gas interface where SO_3 and MoO_3 vapor are evolved and Al_2O_3 is precipitated to form a porous scale upon the molten Na_2SO_4 . (MoO_3 crystals were deposited in the cold zone of the furnace after the oxidation of Na_2SO_4 -coated Ni-32Al-4Mo at 1000°C in a stream of oxygen.) Since the alloy is no longer covered with a protective scale, rapid oxidation ensues. Once the protective scale is no longer stable on the alloy surface, oxygen can react with aluminum and molybdenum in the alloy to form a reaction product which is nonprotective in the molten modified (acidic) Na_2SO_4 . As a result of this condition, aluminum is preferentially removed from the alloy, its surface becomes irregular, and nickel-rich stringers or islands are developed as shown in Fig. 19(d). Nickel also may oxidize and react with the Na_2SO_4 at the alloy surface along with the aluminum and molybdenum, but the development of structures such as that shown in Fig. 15 indicates that a large amount of the nickel is incorporated into the molten Na_2SO_4 as stringers. As oxidation continues, the nickel-rich stringers become incorporated into the porous Al_2O_3 layer, which grows inward by precipitation from the modified Na_2SO_4 . Eventually these nickel-rich stringers are converted to NiO as shown in Fig. 19(e). It is important to emphasize that this type of accelerated oxidation is self-sustaining since MoO_3 is continually formed in the Na_2SO_4 adjacent to the alloy surface.

The mechanisms of Na_2SO_4 -induced catastrophic oxidation of Ni-8Cr-6Al-4Mo, Ni-27.7Al-12.8W, Ni-32Al-2V, as well as B-1900 are believed to be essentially the same as that described for Ni-31Al-Mo alloys. The major differences are probably only in the process by which MoO_3 , WO_3 , or V_2O_5 are initially introduced into the Na_2SO_4 due to the formation of these oxides during the transient period of oxidation or from the preferential oxidation of phases in the alloy that are rich in Mo, W, or V. The results from the present studies are not sufficient to permit a meaningful description of the effects of Mo, W, or V on the initiation of catastrophic oxidation in single and even multiphase alloys. Mo, W, or V-rich phases in alloys would be expected and usually do result in the rapid onset of catastrophic oxidation. However, for some alloys even when Mo, W, or V-rich phases are present, it appears that relatively long periods of time are required to develop an acidity in the Na_2SO_4 sufficient to flux the protective oxide scale and therefore incubation periods prior to catastrophic oxidation can occur as observed in the present studies for Ni-32Al-2V. This alloy is believed to oxidize more slowly when coated with Na_2SO_4 because the increased oxidation that occurs in the absence of Na_2SO_4 in areas where the vanadium-rich phase is exposed to the surface does not take place since the vanadium oxides that are formed in these areas dissolve in the Na_2SO_4 . In the absence of Na_2SO_4 , Ni-32Al-2V suffered localized

catastrophic oxidation. There are a number of examples in the literature¹⁷ of catastrophic oxidation of alloys in the absence of Na_2SO_4 . In all cases it appears that the alloys contain sufficient amounts of elements such as molybdenum or vanadium to permit the development of a nonprotective liquid reaction product. Most oxidation resistant alloys contain small amounts of these types of elements and consequently the oxides of these elements are formed only during the initial stages of oxidation, after which protective layers of Al_2O_3 or Cr_2O_3 are developed beneath these oxides. Since oxides such as MoO_3 and V_2O_5 have high vapor pressures and are present in small amounts, they are soon removed from the surface of the protective oxide layer and have little influence on the oxidation behavior of the alloy. When Na_2SO_4 is present on the surface of the alloy, however, oxides such as MoO_3 or V_2O_5 are lost more slowly to the vapor and are retained longer, especially in the product zone near the alloy/scale interface, in the Na_2SO_4 . Moreover, even though the formation of these oxides may be localized, reaction with the Na_2SO_4 establishes a uniform activity of the oxides over the whole alloy surface. Consequently, alloys with small amounts of Mo, V, or W are susceptible to catastrophic oxidation in the presence of Na_2SO_4 .

To confirm that MoO_3 could produce catastrophic oxidation of Ni-8Cr-6Al and Ni-32Al in the presence of Na_2SO_4 , these alloys were coated with Na_2SO_4 and heated in flowing oxygen at 1000°C. A platinum crucible with MoO_3 was placed up-stream from the specimens at a temperature of 960°C. Catastrophic oxidation of both specimens occurred. Since the MoO_3 container was at a lower temperature than the specimens, MoO_3 could not condense on the specimens in the absence of Na_2SO_4 . The MoO_3 in the gas reacted with the Na_2SO_4 on the specimens to form an acid flux.

Influence of Temperature

Both Na_2SO_4 -induced accelerated oxidation and Na_2SO_4 -induced catastrophic oxidation require a liquid phase to be present on the surfaces of alloys. These two types of attack are not confined to temperatures above the melting point of Na_2SO_4 (883°C) since reaction between solid oxide phases developed on the surface of an alloy and solid Na_2SO_4 can result in the formation of liquid phases. This condition is especially prevalent in the case of Na_2SO_4 -induced catastrophic oxidation, as shown in Figs. 17(a) and 17(b), since phases with relatively low melting points are common in $\text{Na}_2\text{SO}_4\text{-V}_2\text{O}_5$,¹⁸ $\text{Na}_2\text{SO}_4\text{-MoO}_3$, and $\text{Na}_2\text{SO}_4\text{-WO}_3$ systems. For example, initial melting was observed by differential thermal analysis measurements* of a 10

*DuPont Model 900 Differential Thermal Analyzer.

mole pct $\text{MoO}_3\text{-Na}_2\text{SO}_4$ mixture at about 565°C. The formation of a liquid phase has also been observed by hot stage microscopy during the Na_2SO_4 -induced accelerated oxidation of pure nickel at 800°C. Sufficient experiments have not been performed in the present studies to determine the temperatures below which liquid phases are no longer developed on alloys containing Mo, W, or V. However, providing liquid phases are developed, it is believed that the models proposed in this paper are applicable to describe the oxidation processes.

SUMMARY AND CONCLUDING REMARKS

The hot corrosion of nickel-base alloys, which is observed in the presence of Na_2SO_4 , has been found to occur by two different mechanisms. In both mechanisms, the formation of a liquid flux based on Na_2SO_4 dissolves the normally protective oxide scales. The main difference between these two types of hot corrosion lies in the oxide ion concentration of the melts which flux the protective scales. Melts which cause catastrophic oxidation are deficient in oxide ions and can be described as acidic, whereas the melts responsible for the less-severe accelerated oxidation contain an excess of oxide ions and are basic. Oxides of alloy elements such as Mo, W, and V have been found to produce acidic Na_2SO_4 melts which are efficient fluxes for Al_2O_3 and NiO . The oxidation process is catastrophic or self-sustaining since, once initiated, elements in the alloy insure the continued presence of the acidic flux. The basic fluxes which cause accelerated oxidation are usually developed due to removal of sulfur from the Na_2SO_4 by the alloy. The accelerated oxidation is not self-sustaining since sulfur removal from the Na_2SO_4 by the alloy eventually ceases unless continued deposition of Na_2SO_4 occurs. However, permanent effects can be produced by a limited amount of Na_2SO_4 since the introduction of sulfur into some alloys or depletion of elements in others, both of which occur during basic fluxing, can result in increased rates of oxidation. Chromium is effective in retarding accelerated oxidation because Cr_2O_3 establishes an oxide ion activity in Na_2SO_4 which is not sufficient to cause basic fluxing but is still not low enough to cause acidic fluxing. In addition, chromium also inhibits adverse effects produced by sulfur in some alloys by forming chromium sulfide and thereby preventing the formation of other deleterious sulfide phases such as aluminum sulfide or liquid nickel sulfide.

Other investigators have obtained results from hot corrosion studies which have not always appeared to be in agreement. It is believed that the results from the present studies can be used to begin to resolve such apparently contradictory results. For example, under certain test conditions on a given alloy, sulfur movement into the alloy could be the primary cause of increased oxidation. In other cases involving different alloys and test conditions, alloy depletion, basic fluxing, or acidic fluxing may be prevalent. In addition, the influence of different elements on the hot corrosion process will depend on the particular mechanism of accelerated oxidation that is operative. For the case where movement of sulfur into the alloy has caused increased oxidation, molybdenum may produce beneficial effects similar to chromium by combining with the sulfur, whereas in other systems where the molybdenum is introduced into the Na_2SO_4 in sufficient amounts catastrophic oxidation will occur. Continued studies on the hot corrosion of alloys is required. It is necessary to examine the initial stages of Na_2SO_4 -induced catastrophic oxidation in more detail and determine how elements such as chromium or titanium apparently prevent this type of oxidation. In addition, studies to examine the effects of tantalum and cobalt on hot corrosion should in general be fruitful. Finally, studies whereby results obtained from burner rig tests and laboratory tests are compared should permit defini-

tion of the conditions that are prevalent in the former type of tests.

ACKNOWLEDGMENTS

The authors are indebted to C. E. Londin and V. Nevins for their technical assistance, and to A. R. Geary for his assistance in metallographic preparation and interpretation.

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