OXIDATION AND HOT CORROSION OF SUPERALLOYS

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Summary

The oxidation, mixed gas corrosion and hot corrosion of nickel-, cobalt- and iron-base superalloys at temperatures above about 600C are examined. It is shown that the superalloys develop resistance to corrosion by forming either alumina or chromia scales upon their surfaces. The times for which such oxide reaction product barriers are stable upon the surfaces of superalloys is discussed by first considering how these oxide scales are formed and then how they are destroyed in use. It is shown for oxidation environments that these oxide scales are degraded primarily via cracking and spalling. When mixed gas environments are encountered, the degradation is also affected by the other reactants in the gas phase. The most severe conditions are shown to be those inducing hot corrosion attack where the oxide scales are subjected to not only mixed gas conditions but also the fluxing action of molten deposits. The behavior of nickel-, cobalt-, and iron-base superalloys are compared and the effects of the various alloying elements are discussed.

Introduction

Superalloys have been developed to be used at elevated temperatures (e.g. up to 1200°C) in corrosive environments (e.g. combustion environments). Since the superalloys must have strength at elevated temperatures, these alloys have complicated compositions containing as many as 10 to 15 different elements. Consequently the reaction of such alloys with the different environments encountered in practice can result in rather complex processes. The purpose of this paper is to describe in a general way the degradation of superalloys as may occur in commonly encountered use environments.

After briefly discussing experimental procedures, the most simple form of superalloy degradation, which is oxidation, will be considered first. Complications arising from the presence of other reactants in gases will then be considered. Finally, the effects of deposits (e.g. Na_2SO_4, NaCl) on the corrosion of superalloys, namely, hot corrosion of superalloys will be examined in detail.

Experimental Procedures

In discussing the corrosion of superalloys at elevated temperatures, namely at about 600°C and above, a variety of experimental conditions must be considered. Experience has shown that the most expedient method to determine the behavior of superalloys in the different environments encountered in practice is to use simulation tests where test procedures are used that as closely as possible reproduce the conditions that are believed to be established in the application of interest. Complete simulation is almost never obtained because the need to have a cheap test and the desire to develop alloys which are as resistant as possible to the particular degradation process of interest are not compatible. Hence, most simulation tests eventually take the form of accelerated tests having conditions substantially more severe than those existing in the particular application of interest. Simulation testing is therefore the most effective means to rank alloys and develop improved alloys for a given application but this type of testing presents very severe limitations in regards to formulating mechanisms to account for the observed degradation since the test conditions are usually poorly defined and controlled.

Testing of superalloys in tube furnaces provides a means to control conditions, such as temperature and gas composition, much more precisely than in the simulation experiments. A major shortcoming of this more controlled type of studies, however, is that the conditions almost always are not typical of the actual use conditions. The behavior of the superalloys therefore is often much different than in the application of interest.

In order to establish an understanding for the behavior of superalloys in the different environments in which they may be used, it is necessary to use data obtained from both types of testing. Ideally it is best to use initially simulation testing and then develop certain idealized laboratory tests to answer questions posed from the results of the simulation tests. In designing the laboratory tests, certain conditions can be varied systematically until the microstructural features of specimens exposed to both types of tests begin to develop some commonality.

In the present paper data will be used from a variety of tests. Since a major application for superalloys is in gas turbine engines, data and experience gained from the burner rigs use to simulate gas turbine conditions will be used (1). Results obtained from laboratory tube furnace tests will also be used extensively. These latter tests usually involved the use of small test coupons (1 cm X 1 cm X 0.1 cm) exposed to well defined temperatures

and gas compositions. When deposits were placed upon such specimens it was accomplished by using an air brush and the deposits were reapplied at prescribed time intervals. Typical experimental techniques and procedures have been presented previously (2,3). Corrosion data will be presented and discussed for a number of superalloys. The nominal compositions of the superalloys discussed in this paper are presented in Table I. This list was selected to illustrate the general behavior of the superalloys and it was not intended to provide data on a great multitude of superalloy compositions.

Oxidation

Since superalloys contain numerous alloying elements, their reaction with oxygen can be expected to be complex. These alloys, however, have been developed to achieve resistance to oxidation by utilizing the concept of selective oxidation. Hence, the oxidation processes are not as complex as one would initially suppose. In the following sections the selective oxidation process as related to superalloys is discussed, and then the specific behavior of nickel, cobalt and iron-base superalloys is described.

Selective Oxidation

The selective oxidation approach to obtaining oxidation resistance in superalloys consists of oxidizing essentially only one element in the superalloy and relying upon this element's oxide for protection. In order for this approach to be feasible, the oxide that is formed must completely cover the surface of the alloy and it must be an oxide through which diffusion of the reactants (i.e. the element being selectively oxidized and oxygen) takes place at comparitively slow rates.

The elements which satisfy these requirements are relatively few. In particular, the only elements whose oxides are sufficiently protective, and that have affinities for oxygen sufficient for selective oxidation, are aluminum, chromium and silicon, Figure 1 and Table II. The presence of silicon in superalloys at concentrations sufficent to permit selective oxidation is not compatible with the high melting point requirement of superalloys and, hence, the selective oxidation of silicon to achieve oxidation resistance is not feasible. Nickel-, cobalt- and iron- base superalloys utilize the selective oxidation of aluminum or chromium to develop oxidation resistance and these alloys are therefore often referred to as Al_2O_3-, or Cr_2O_3- formers depending upon the oxide scale or barrier that is used to obtain resistance against oxidation degradation.

Detailed discussions of selective oxidation processes are available (4-6). It is sufficient in this paper to emphasize that the selective oxidation of elements in superalloys is always preceded by a transient stage (7,8) where other elements in the superalloys are oxidized prior to the formation of continuous barriers of either Al_2O_3 or Cr_2O_3 over the surfaces of the alloys. The selective oxidation of chromium and aluminum in Ni-Cr-Al alloys is described schematically in Figure 2.

It is necessary to emphasize that selective oxidation processes are affected by a number of factors which include alloy compositions, alloy surface conditions, gas environment, and cracking of the oxide scale. The gas composition and deposits accumulated on the superalloys surfaces can exert very significant effects and these factors will be considered in subsequent sections of this paper. Cyclic oxidation conditions whereby the oxide scales crack and spall, as well as certain phases present in superalloys, both affect the capability to selectively oxidize aluminum or

TABLE I

NOMINAL COMPOSITIONS* (W/O) OF ALLOYS DISCUSSED IN THIS PAPER

ALLOY	C	Mn	Si	Cr	Ni	Co	Mo	W	Nb	Ti	Al	B
B-1900	.1	.2	.25	8	Bal	10	6	0.1	0.1	1.0	6	.01
IN 738	.17	.2	0.3	16	Bal	8.5	1.75	2.6	0.9	3.4	3.4	.01
Mar M 200	.15	--	--	9	Bal	10	--	12.5	1.0	2.0	5.0	.015
IN 100	.18	--	--	10.0	Bal	15	3.0	--	--	4.7	5.5	.014
IN 713	.12	--	--	12.5	Bal	--	4.2	--	2.0	0.8	6.1	.012
IN 792	.21	--	--	12.7	Bal	9	2	3.9	--	4.2	3.2	.02
IN 597	.05	--	--	24.5	Bal	20.0	1.5	--	1.0	3.0	1.5	.012
IN 587	.05	--	--	28.5	Bal	20.0	--	--	0.7	2.3	1.2	.003
U 710	.07	.1	.2	18	Bal	15	3	1.5	--	5.0	2.5	.02
MM 421	.15	.2	.2	15.5	Bal	10	1.75	3.5	1.75	1.75	4.25	.015
Hast X	.15	1.0	1.0	21.8	Bal	2.5	9.0	.6	--	--	--	--
TD NiCr	0.1	--	--	21	Bal	--	--	--	--	--	--	--
Cabot Alloy 214	.04	--	--	16	Bal	--	--	--	--	--	4.5	--
Cabot Alloy 600	.08	.8	.5	21	32.5	--	--	--	--	.4	.4	--
X-40	0.5	.5	.5	25	10	Bal	--	7.5	--	--	--	--
Mar M 509	0.6	.1	.1	21.5	10	Bal	--	7.0	--	0.2	--	.01
WI 52	.45	.5	.5	21	1.0	Bal	--	11	2.0	--	--	--
Haynes 188	.08	--	--	22	22	Bal	--	14	--	--	--	--
310 SS	.08	2.0	1.5	25	21.5	--	--	--	--	--	--	--
Incoloy 800	.08	1.0	.5	16	Bal	--	--	--	--	.3	.35	--

*All compositions are given in weight percent unless stated otherwise.

654

In order for the selective oxidation process to occur, of course, the phases present in the superalloys must contain the elements to be selectively oxidized at concentrations sufficient to allow continuous scales of either Al_2O_3 or Cr_2O_3 to be developed at the alloy surface. The phases which do not contain these elements are preferentially attacked as shown in Figure 3 where carbides have been preferentially oxidized in the superalloy B-1900. Preferential attack of such phases proceeds until they have been consumed and the amount of this type of oxidation is therefore dependent upon the distribution and continuity of such phases.

Techniques are available which can be used to encourage the selective oxidation of aluminum or chromium in superalloys. For example chromium causes the selective oxidation of aluminum to occur at lower aluminum concentrations and aluminum produces a similar effect on chromium selective oxidation (6). In the case of the selective oxidation of aluminum it appears that the chromium may act as an oxygen getter which inhibits the diffusion of oxygen into alloys.

Figure 1. Temperature dependence of the parabolic rate constants for the growth various oxide barriers on metals and alloys (CoO on Co, NiO on Ni, SiO_2 on Si, Cr_2O_3 on Ni-30% Cr, α-Al_2O_3 on Ni-25% Al). The oxidizing environments for the data presented were 0.1 atm. oxygen for Ni, Ni-30Cr and Ni -25Al; 0.125 atm. oxygen for Co and 1 atm. oxygen for Si.

Other elements in superalloys can affect the selective oxidation process. Molybdenum and tungsten have been observed to enhance selective oxidation by acting as oxygen getters and to adversely affect selective oxidation by causing the diffusion of aluminum in alloys to be decreased (9). Tantalum appears to produce favorable effects on selective oxidation of aluminum but an explanation to account for this is not available. Oxide particles in superalloys also produce favorable effects on the selective formation of oxide phases at the very beginning of the scale formation process (10,11).

Cyclic oxidation conditions cause protective barriers of Al_2O_3 or Cr_2O_3 to crack and spall. The protective barriers must be reformed which causes depletion of the elements to be selectively oxidized and eventually the selective oxidation process is not possible. Often oxides other than Al_2O_3 or Cr_2O_3 begin to be formed and gradually cover larger and larger fractions of the superalloys' surfaces, Figure 4. The ability of superalloys to resist the effects of cyclic oxidation depends upon alloy compositions and as is obvious in Figure 5, the superalloy B-1900 has significantly better cyclic oxidation resistance than Mar M 200. Eventually, however, depending upon composition, temperature and exposure time, selective oxidation must stop and less protective oxides must begin to be formed. The oxidation mechanisms consequently become more complex. For such cases the oxidation resistance of the superalloys usually is no longer acceptable for elevated temperature use. An important parameter therefore is the time for which superalloys are chromia or alumina formers under certain sets of test conditions.
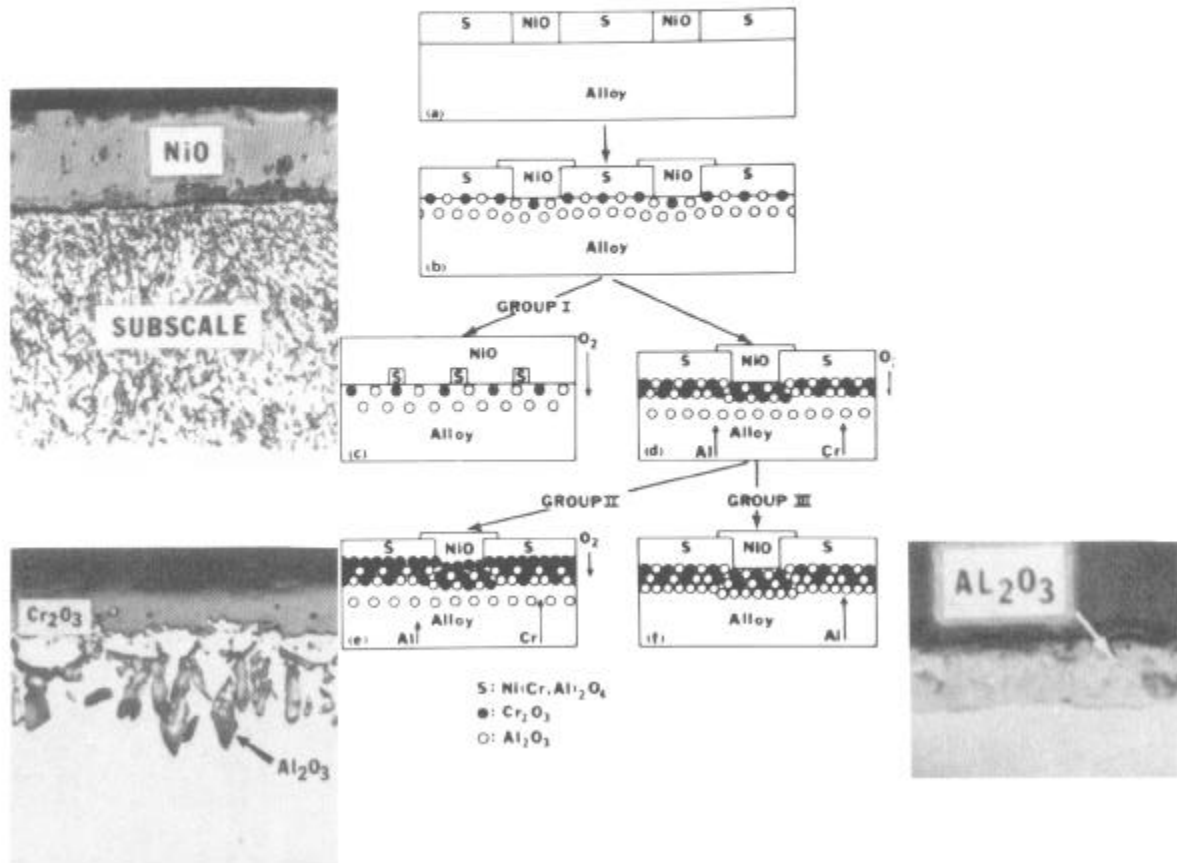
Figure 2. Schematic diagram to illustrate oxide scale development
on Ni-Cr-Al alloys as a function of time. (a) Conversion of a
thin alloy surface layer to oxide by rapid uptake of oxygen. The
oxide phases formed are determined by the composition of the alloy.
(b) Diffusion within the alloy results in the formation of a
Cr_2O_3 and Al_2O_3 subscale beneath the external scale. (c) For
alloys with low chromium and aluminum concentrations, the subscale
cannot become continuous and NiO in the external scale predominates.
This group of alloys could then be called NiO formers. (d) For
alloys with higher chromium and aluminum concentrations the sub-
scale becomes continuous but aluminum is still oxidized internally
(e) For alloys with smaller aluminum concentrations the con-
tinuous external scale becomes enriched in Cr_2O_3 but the aluminum
is oxidized internally. This group of alloys could be called
Cr_2O_3 - formers. (f) For alloys with larger aluminum concen-
trations the Al_2O_3 subscale zone becomes continuous beneath
the duplex oxide. This group of alloys would be called Al_2O_3 -
formers. The photomicrographs show typical microstructures
for the corresponding sketches.
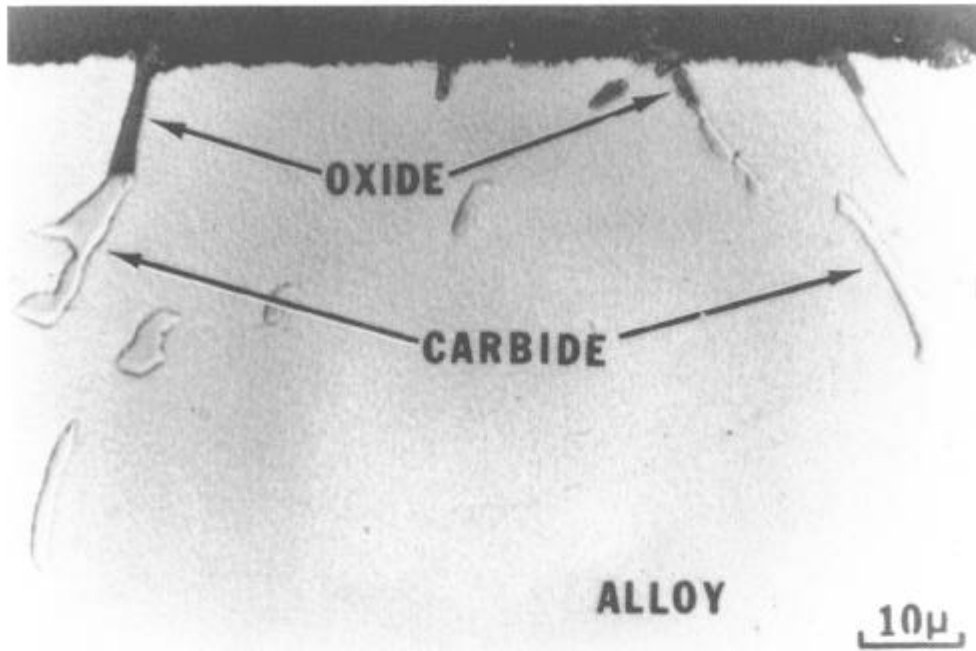
Figure 3. Preferential attack of carbide phase in nickel-base superalloy B-1900 after 45 hrs. of oxidation at 700°C in ∿ 1 atm. oxygen.
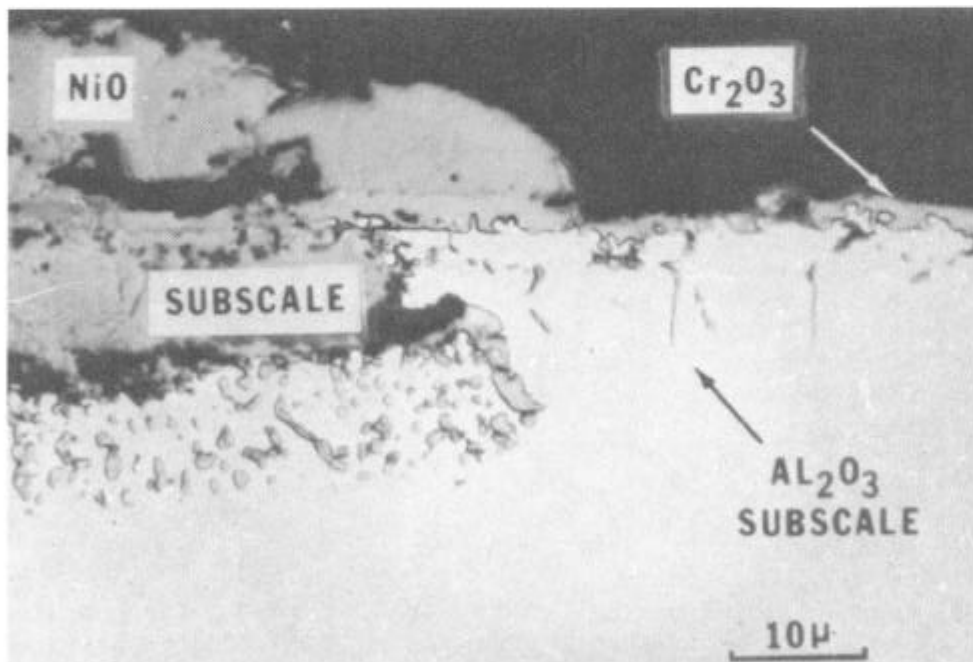

Figure 4. Nonuniform oxidation morphology developed on Ni-10Cr-1Al after 20 hrs. of oxidation in 0.1 atm. of oxygen at 1000°C. This type of oxide scale morphology frequently develops on alloys during cyclic oxidation testing as less protective oxides become stable.

TABLE II

Standard Free Energies of Formation at 1000K of
Some Oxides Whose Metallic Elements Are
Often Present in Superalloys

Element	$\Delta G°$ (k joule/g atom oxygen)	
Hf	459.6	(HfO_2)
Al	453.7	(Al_2O_3)
Zr	451.8	(ZrO_2)
Ti	381.7	(TiO_2)
Si	348.9	(SiO_2)
Ta	321.0	(Ta_2O_5)
Mn	311.9	(MnO)
Nb	308.4	(Nb_2O_5)
Cr	291.7	(Cr_2O_3)
Mo	303.7	(MoO_2)
W	200.6	(WO_2)
Fe	198.9	(FeO)
Co	163.2	(CoO)
Ni	150.3	(NiO)

Nickel Base Superalloys

The nickel base superalloys may contain both chromium and aluminum at concentration levels sufficient to permit the selective oxidation of either aluminum or chromium. Hence, nickel base superalloys may be either alumina- or chromia formers. In Figure 6 an oxide map for the Ni-Cr-Al system is presented upon which the compositions of a number of superalloys have been indicated (12). It can be seen that some of the superalloys occupy the alumina region of the map whereas other of the superalloys are in the Cr_2O_3 region. Those alloys which are in the alumina region (e.g. B-1900) generally have better oxidation resistance than the chromia formers (e.g. IN 738) since diffusion through alumina scales is generally slower than through chromia. Furthermore, chromia scales cannot be used to develop oxidation resistance at temperatures above about 1000°C since the formation of gaseous oxides of chromium begin to become significant. The formation of volatile products can become a problem for Cr_2O_3 scales at temperatures below 1000°C as the gas velocity is increased. Significant amounts of CrO_3 has been observed at 870°C in burner rigs with gas velocities on the order of 300 m/s.

In the diagram presented in Figure 6, the indicated oxide scales can be expected to be formed on the superalloys during isothermal oxidation. Under cyclic oxidation conditions depletion of chromium and aluminum will result in movement from the Al_2O_3 region into the Cr_2O_3 region and eventually into the NiO region of this diagram. Some alloys move toward the NiO region of this diagram much more rapidly than others. For example the data presented in Figure 5 shows that the alloy B-1900 remains in the alumina region for much longer times than Mar M 200. Of course, as is evident in Figure 5, the application of aluminide coatings to both superalloys makes them remain in the alumina region even longer times than obtained for the uncoated alloys.
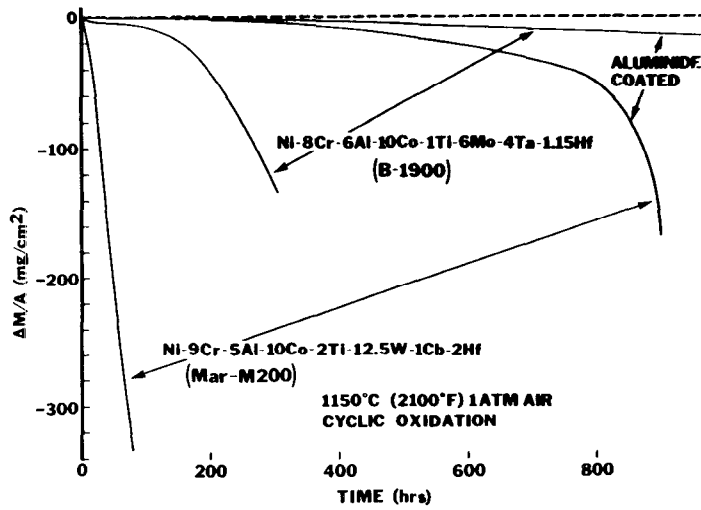
Figure 5. Weight change versus time data for the cyclic oxidation
of two nickel-base superalloys and these two alloys coated using
a diffusion aluminizing treatment. The degradation of these alloys
consists of two stages. An initial stage of less severe attack
(not evident on one of the uncoated alloys for the time scale
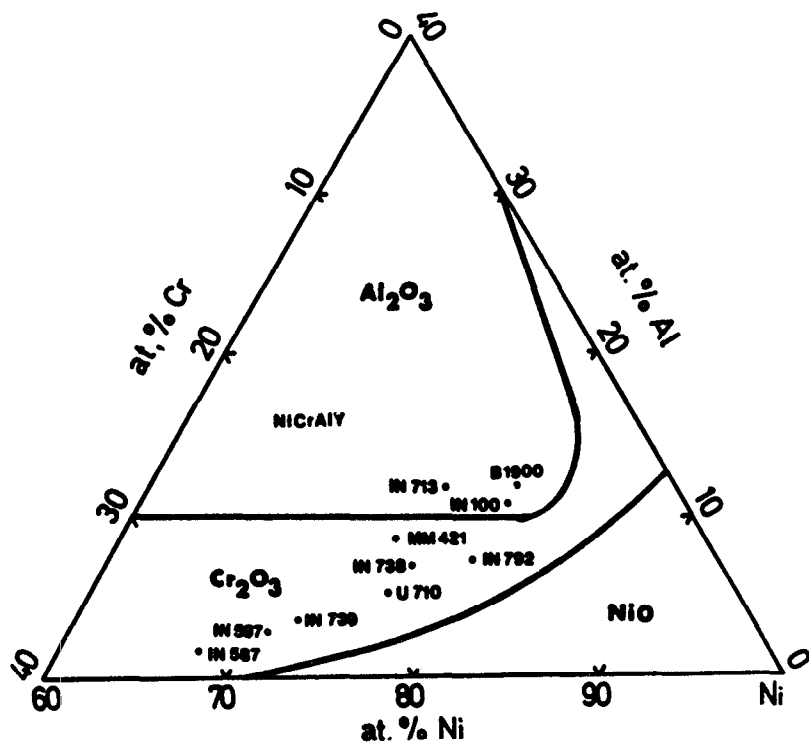used) and a subsequent stage of more rapid attack.

Figure 6. Diagram showing the type of oxide scales formed as
continuous layers upon a number of superalloys at temperatures
of about 1100°C (12).

The time over which nickel base superalloys can maintain protective, external scales of alumina or chromia is affected by temperature, the gas environment, and alloy composition. Generally the superalloys remain alumina or chromia formers for longer times as the aluminum or chromium concentrations are increased. Other elements do affect this time. The presence of small amounts of elements such as yttrium or cerium can cause this time to be significantly extended, since the adherence of the oxide scales is improved. Such elements cannot be used in cast superalloys however because low melting phases become stable. The use of oxide dispersions, or the uniform distribution of oxygen active elements in alloys fabricated by hot isostatic pressing, appear to provide a means to obtain the useful characteristics of oxygen active elements without the adverse effect of these elements on the mechanical properties of the superalloys. In Figure 7 the oxidation resistance of some nickel base alloys are compared with 310 stainless steel. The alloy that is an alumina former and contains an oxygen active element is the most oxidation resistant. Generally the chromia formers have better oxidation resistance as the chromium concentration is increased. The progressive development of the lesser protective oxides as the superalloys degrade is illustrated in Figure 8 by comparing metal recession for some nickel- and cobalt- base superalloys (14).
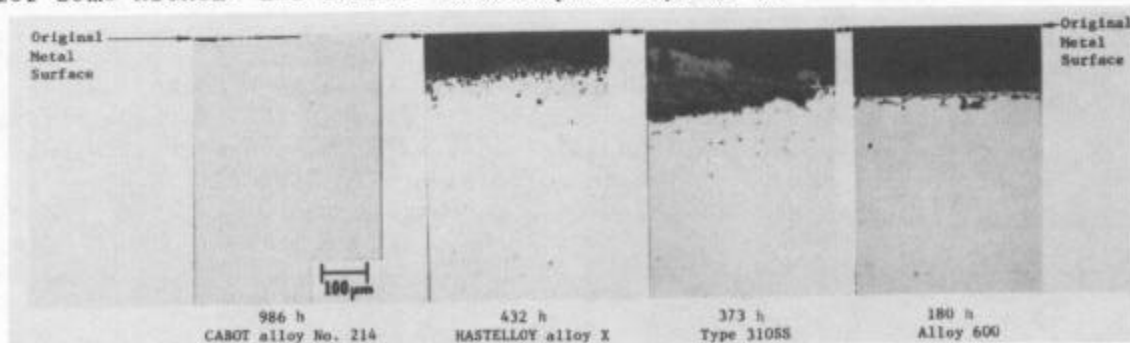

Figure 7. Metal recession of several alloys exposed for times indicated in air at 1150°C (13).

Cobalt and Iron Base Superalloys

The cobalt and iron base superalloys usually cannot be made to contain enough aluminum to permit them to be alumina formers while maintaining the necessary mechanical properties. Such alloys must therefore utilize a Cr_2O_3 scale to achieve oxidation resistance. Hence the oxidation resistances of the cobalt and iron base superalloys are less than those of nickel-base superalloys that are alumina formers. Furthermore, even when considering the nickel-base superalloys that are chromia formers, as degradation begins, namely as the chromia scales become damaged, the less protective oxides formed on the nickel-base alloys contain significant quantities of nickel oxide compared to cobalt and iron oxides on the cobalt-and iron-base alloys, respectively. Since nickel oxides are more protective than cobalt and iron oxides, the drop-off in oxidation resistance is more abrupt in the case of the cobalt- and iron- base alloys compared to nickel-base alloys as shown in Figures 7 and 8.

The oxidation resistance of cobalt- and iron- base superalloys usually increases with the chromium concentrations and the oxidation resistance of alloys with less than about 20% chromium is comparatively poor. Refractory elements such as tungsten and molybdenum have favorable effects on the selective oxidation of chromium in these alloys but when chromium is no longer selectively oxidized the oxidation of these refractory elements results in increased oxidation due to the development of less protective phases in the oxide scales (15).

660

In all of the superalloys, carbides, when present are preferentially attacked. The only protective scale that can be formed over the carbides is chromia and often this scale is not protective due to cracking. Carbides in superalloys are therefore sites of excessive oxidation, Figure 9. In order to minimize this type of degradation the carbides in the superalloys should be small and discontinuous.
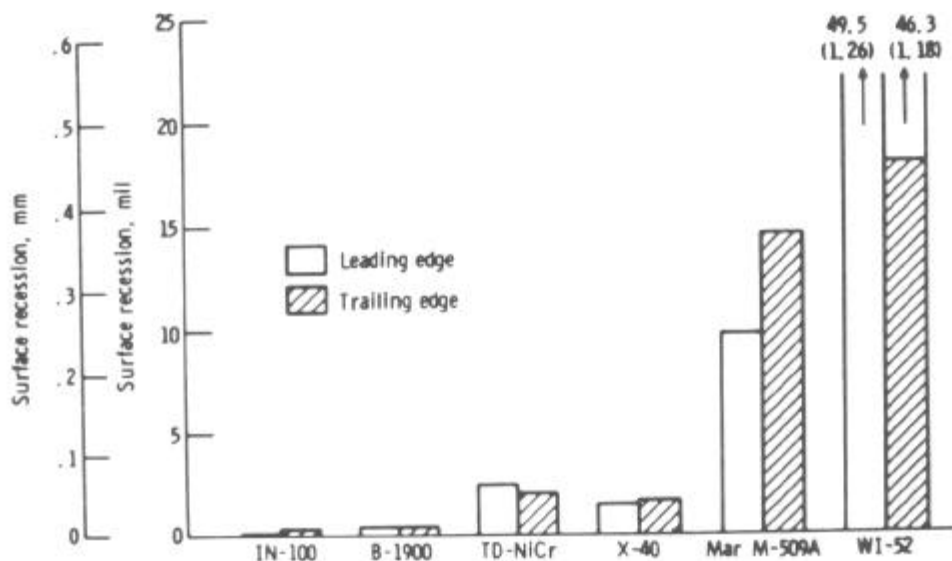

Figure 8. Summary of surface recession measurements after 100 hours at 2000° F (1093°C) using burner rig oxidation test (14).
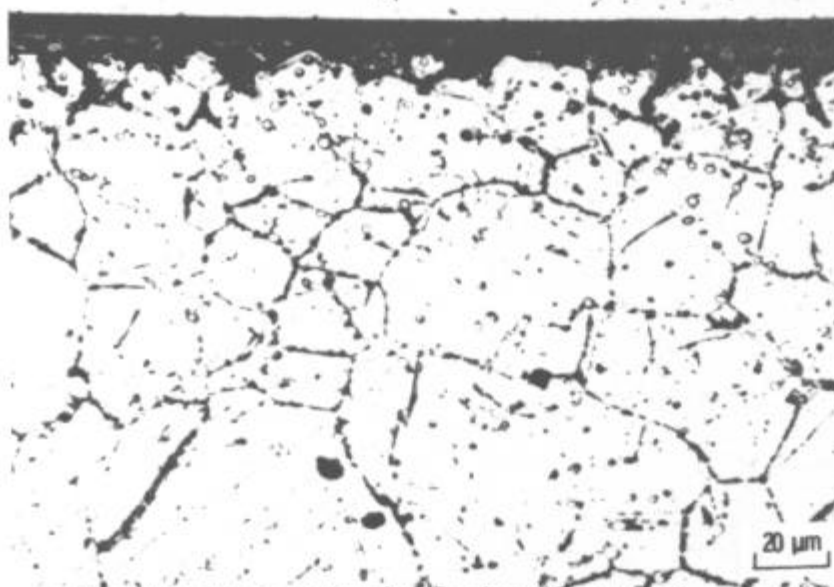
Figure 9. Straight oxidation in burner rig of alloy HA-188 at 900°C for 100 hr. at temperature. Note the thin retained scale and grain-boundary corrosion (16).

Corrosion In Mixed Gas Environments

In some applications for superalloys at elevated temperatures the gas environment contains other reactants in addition to or in place of oxygen. For example alloys used in recuperators are subjected to hot gases that may contain sulfur, carbon and chlorine in addition to oxygen. Moreover, alloys used in nuclear reactors can be exposed to gases that contain carbon with

negligible amounts of oxygen. The problem of achieving, and maintaining, resistance to degradation induced by such environments is more difficult when the gas does not contain oxygen. This condition arises because oxide phases are generally more suitable as barriers to exhibit high temperature corrosion since; oxide scales are more amendable to formation via selective oxidation, oxide scales are more effective diffusion barriers to separate the alloy form the environment, and such scales can be made more adherent to the superalloy substrates (17-19).

Corrosion of Superalloys in Mixed Gases Containing Oxygen

In gases that contain sulfur, carbon, chlorine, as well as oxygen, virtually any alloy that will be resistant to such environments will be one upon which continuous scales of either alumina or chromia are formed over the alloy's surface. Hence, the degradation will be similar to that of these alloys in pure oxidation with one very significant difference. Even though an oxide scale is formed which separates the alloy from the gas, some of the other reactants (e.g. sulfur, carbon, nitrogen, chlorine) do eventually begin to react with the alloy and affect its degradation. The time over which these other reactants affect the degradation process is dependent upon a number of factors, in particular, alloy composition, gas composition especially the pressure ratios of oxygen to the other reactants, and factors which degrade the protective nature of the oxide scale (e.g. thermal cycling, erosive particles). Regardless of the time over which the degradation proceeds, the sequence is strikingly similar. Initially an oxide scale of alumina or chromia is formed. Eventually, particles of phases consisting of metallic elements and the other reactants begin to form in the alloy beneath the external oxide scale. These phases form in the alloy just beneath the oxide scale as shown in Figure 10a. These particles form in such locations since the oxygen activity in the alloy is low because oxygen is consumed by external oxide scale formation. These other reactants gain access to the alloy by either dissolving in the oxide scale and diffusing through it, or by cracks or other defects in these scales. As the exposure time is increased more of these second reactant phases are formed until the external oxide scale can no longer be formed via selective oxidation. At this point more rapid degradation ensues which usually is manifested by the formation of even more second reactant phases Figure 10b. The means by which the second reactant phases render the selective oxidation process ineffective include depletion of the alloy of the elements necessary for selective oxidation, as well as producing nonprotective oxide scales when they react with oxygen. Typical results of mixed gas corrosion are presented in Figure 11 where protective oxides are stable initially but with time much less protective corrosion products are formed due to the formation of second reactant phases.

The relative corrosion resistance of the superalloys in mixed gases containing oxygen does follow that for these alloys in oxygen because both types of degradation are dependent upon the ability of the alloys to form protective oxide scales via selective oxidation. There are some significant differences, however, which arise depending upon the other reactants that are present in the gas. When sulfur is present in the gas, nickel sulfide phases result in the formation of especially nonprotective scales, hence nickel base superalloys can have very poor corrosion resistance in such mixed gas environments. It has also been found that chromium can be used to inhibit the onset of the effects produced by second reactants such as sulfur and carbon. The superalloys with high chromium concentrations therefore have better resistance to the degradation that can occur in gases containing sulfur and carbon (17).
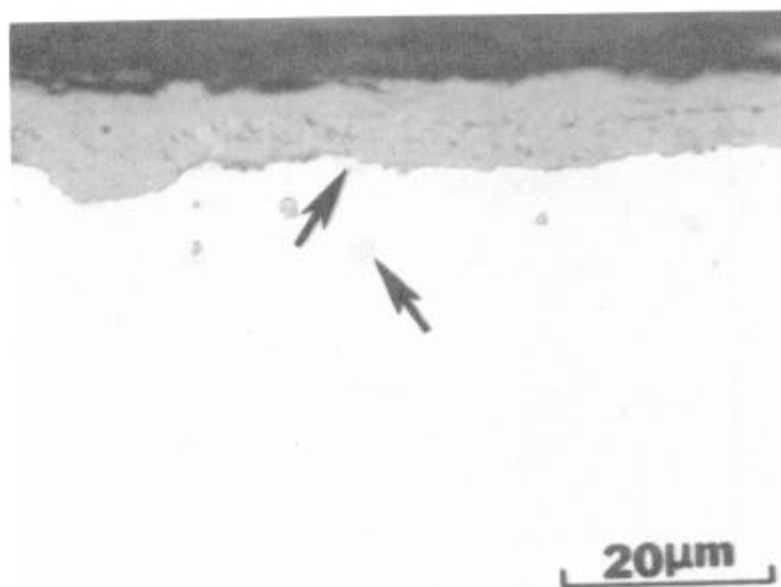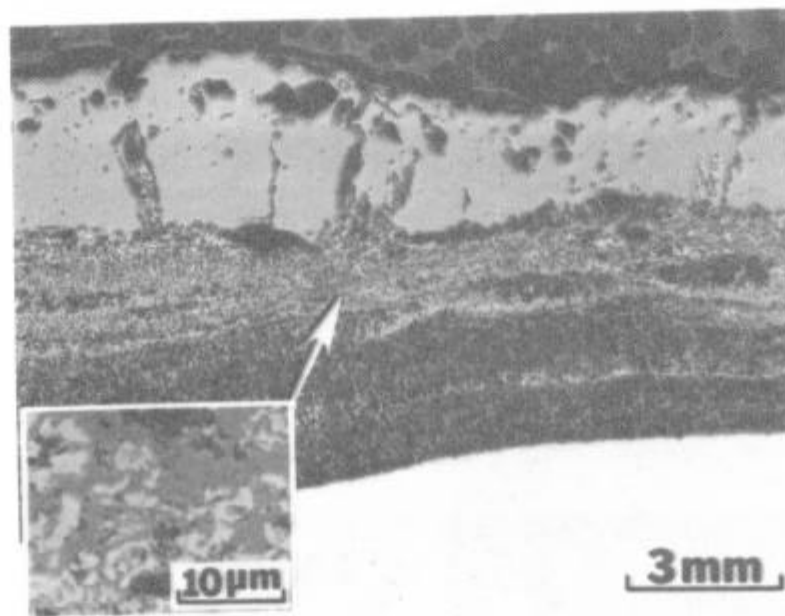
Figure 10. Photomicrographs showing typical microstructures developed during cyclic oxidation of Fe-15Cr at 900°C in flowing argon-5%SO_2. (a) During the earlier stages (<200 hr) an external Cr_2O_3 scale covers the alloy surface and chromium sulfide particles (arrows) are formed within the alloy beneath the scale. (b) As more severe attack occurs the reaction product is composed of an oxide and sulfide mixture beneath an outer zone of iron oxides (350 hr.).

It is worth noting that air is a mixed gas environment. While nitrogen does not generally produce effects as difficult to combat as sulfur or carbon, this element does produce effects similar to carbon and sulfur. In Figure 12 photographs of Ni-25Cr-6Al specimens after cyclic oxidation in air and oxygen are presented. Particles of nitrides in the alloy beneath
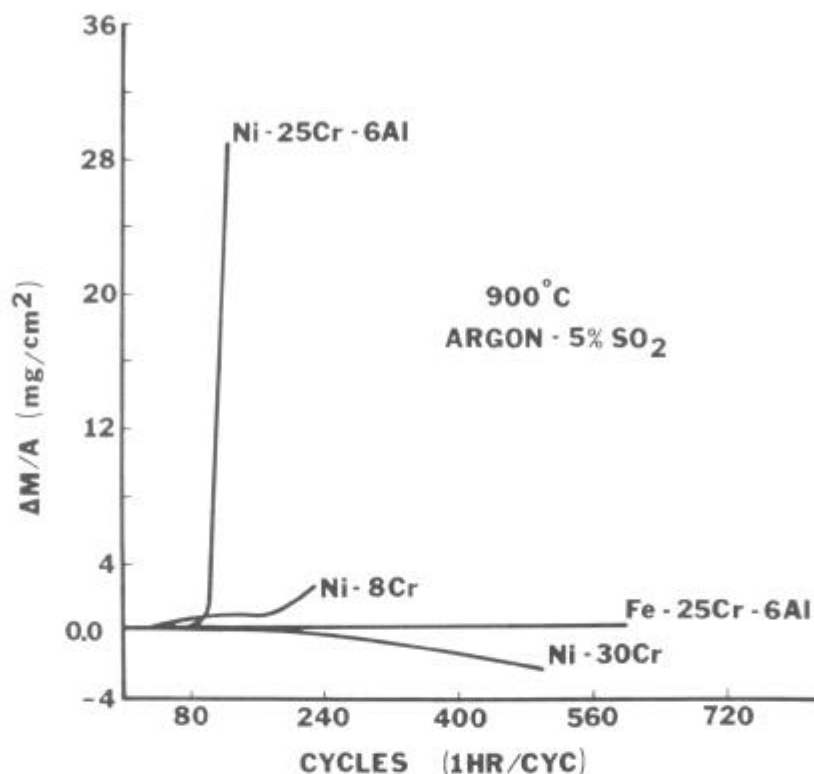
Figure 11. Typical weight-change vs. time data obtained for the cyclic (cooled to approximately room temperature) oxidation of alloys in an argon-5% SO_2 gas mixture. Protective oxides of Al_2O_3 or Cr_2O_3 were formed initially on all of the alloys but only the Fe-25Cr-6Al maintained a protective scale throughout this test.

the oxide scale were evident in the specimen tested in air. These particles are believed to have affected the degradation of this alloy and similar effects have been observed during the cyclic oxidation of superalloys such as B-1900 and IN 738.
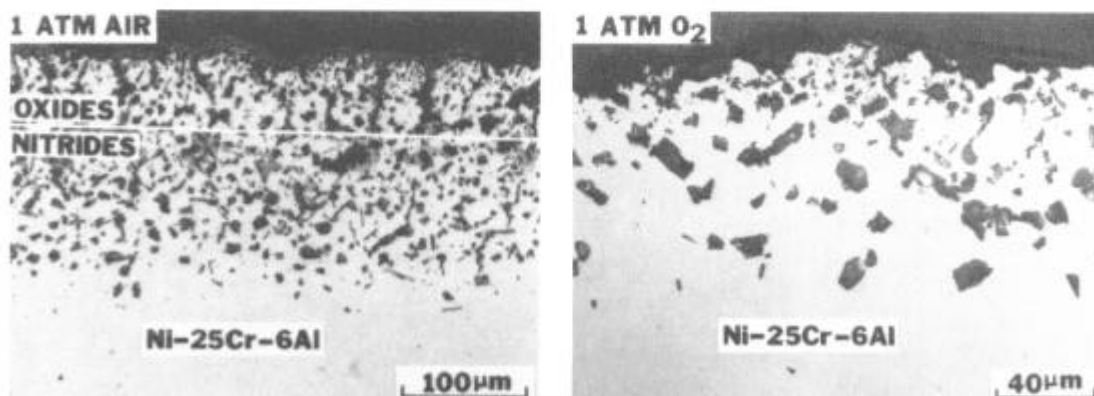
Figure 12. Comparison of microstructural features that developed after 350 hours of cyclic oxidation (50 min. at temperature) 10 min. in cold zone of furnace) at 1000°C in air and oxygen.

Corrosion of Superalloys in Gases Containing No Oxygen

Not much data is available on the corrosion of alloys in gases that do not contain oxygen. The degradation of the superalloys in such gas mixtures will follow the same sequence as discussed in this paper for mixed gases containing oxygen but of course some other scale besides an oxide will initially be formed upon the surfaces of the alloys. It is important to emphasize that most of the available superalloys have been developed to achieve resistance to degradation induced by oxygen. Their compositions are therefore appropriate for selective oxide formation, not necessarily sulfide, carbide or nitride formation. Hence, such alloys can have extremely poor corrosion resistance when exposed to gases that do not contain any oxygen. For example, Meier et al (20) have studied the attack of Incoloy 800 in argon-CH_4 and H_2-CH_4 gas mixtures at 850°C. Carburized zones were detected very much greater than the metal affected zones observed for this alloy exposed to air at 850°C.

Hot Corrosion

In some environments in which superalloys are used, the gas composition is such that, not only are other reactants in addition to oxygen present, but conditions are also conducive to the formation of condensed phases upon the surfaces of the alloys. The development of condensed phases on superalloys represents an especially undesirable situation from a corrosion point of view because of the effects which deposits can have on the protective oxide scales that superalloys have been designed to have formed to develop resistance against attack. Deposit-modified corrosion is called hot corrosion. This type of superalloy degradation is especially severe when the condensed phase is liquid. Depending upon the environment a variety of condensed phases may be formed. Since this type of degradation is often encountered when superalloys are subjected to combustion gases, the deposits often contain sulfates or chlorides with metallic consistituents of sodium, calcium, magnesium or potassium. The sources for these contaminants are the fuel and the air necessary for combustion. Cases where hot corrosion has been observed are gas turbines, fire side corrosion of boiler tubes, and incinerators.

Since there is a variety of conditions that can induce hot corrosion of superalloys, a number of mechanisms have been developed to account for this type of degradation. At present there is a need to attempt to describe the hot corrosion of superalloys in a way such that these different mechanisms can be considered in relation to each other rather than as completely different and unrelated corrosion processes (21).

The Hot Corrosion Degradation Sequence

When superalloys undergo hot corrosion degradation, this process almost always consists of two stages. For example as shown in Figure 13, for IN 738, initially this alloy is degraded at a relatively slow rate but eventually much faster rates of degradation ensue. The B-1900 specimen appears to have undergone rapid attack from the onset of the weight change measurements but expansion of the time scale would show that this alloy also has a much slower initial stage of corrosion. Fryburg et al. (22) have observed that the hot corrosion of B-1900 consists of an initial slow stage which is followed by a much more severe stage of attack. Such behavior is really not surprising because even under pure oxidation conditions a similar sequence is followed as is evident in Figure 5. It is a fact that all corrosion resistant alloys degrade via such a sequence and it is the result of using
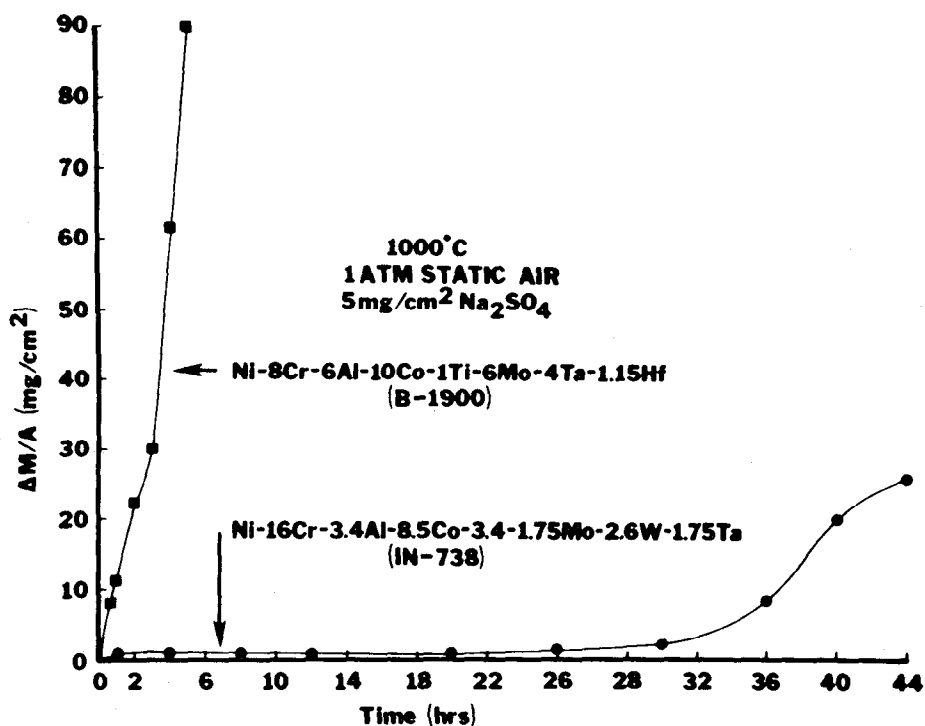
Figure 13. Comparison of weight change versus time data for the Na_2SO_4- induced hot corrosion in air of B-1900 and IN 738.

selective oxidation to develop oxidation or corrosion resistance. The conditions causing hot corrosion therefore do nothing more than shorten the time for which the superalloys can form protective alumina or chromia scales via selective oxidation.

In order to discuss the hot corrosion of superalloys in a general manner it is convenient to place emphasis on the two stages, namely, to call the first an initiation stage during which the alloys are behaving much as they would have behaved in the absence of the deposit, and to identify the second as a propagation stage where the deposit has caused the protective properties of the oxide scales to become significantly different than what they would have been had no deposit been present. The deposit can therefore be viewed as having two effects. It affects the time for which the alumina or chromia scales are stable as protective scales upon the superalloys and it causes the properties of the corrosion products to be different after the selective oxidation process is no longer operative. Such conditions are depicted schematically in Figure 14.
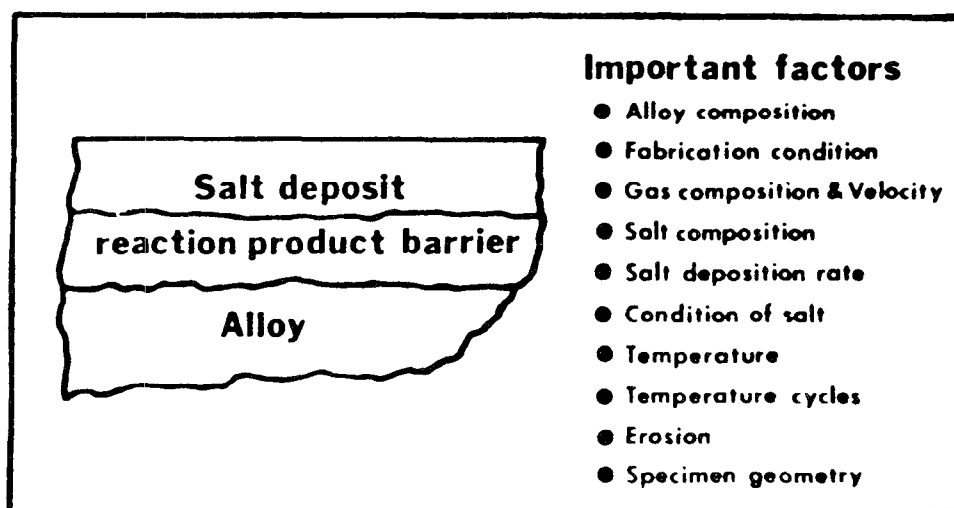
The Initiation Stage of Hot Corrosion

During the initiation stage of hot corrosion superalloys are being degraded at rates similar to those that would have prevailed in the absence of the deposit. Obviously in attempting to develop resistance to hot corrosion one should strive to have the superalloys remain in the initiation stage as long as possible. However in extremely harsh conditions this is not possible and many superalloys exhibit very small or nondetectable initiation stages, Figure 13.

While the nature of the processes which take place during the initiation stage are not fully understood (23), it is apparent that during this stage

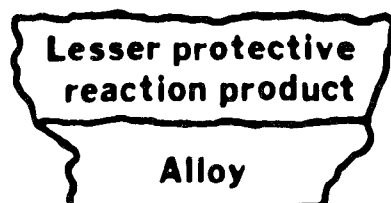# HOT CORROSION CHRONOLOGY

Initiation stage

Important factors

- Alloy composition
- Fabrication condition
- Gas composition & Velocity
- Salt composition
- Salt deposition rate
- Condition of salt
- Temperature
- Temperature cycles
- Erosion
- Specimen geometry

Salt deposit

reaction product barrier

Alloy

Propagation stage

Lesser protective reaction product

Alloy

Figure 14. Schematic diagram to illustrate the conditions that develop during the initiation and propagation of hot corrosion attack and to identify the factors that determine the time at which the transition from the initiation stage to the propagation stage occurs.

the deposit is beginning to affect the alloy in certain ways. In order to illustrate these effects it is necessary to use alloy systems which are related to, but not actually superalloys. In Figure 15 data is presented for a Ni-30Cr-4Al alloy which was cyclicly oxidized when covered with a Na_2SO_4 deposit. This alloy remained in the initiation stage for over 300 hours but after less than forty hours sulfides were detected in this alloy and the amount of sulfides in this alloy progressively increased with time. In view of such results it seems reasonable to propose that during the initiation stage the superalloys are being preconditioned by the deposits in a way that determines the time after which selective oxidation is no longer possible and which also determines the type of corrosion product scale that will be formed as the alloy enters the propagation stage.

Numerous factors affect the time at which the hot corrosion process moves from the initiation stage into the propagation stage. These same factors also play the dominant role in determining the type of reaction
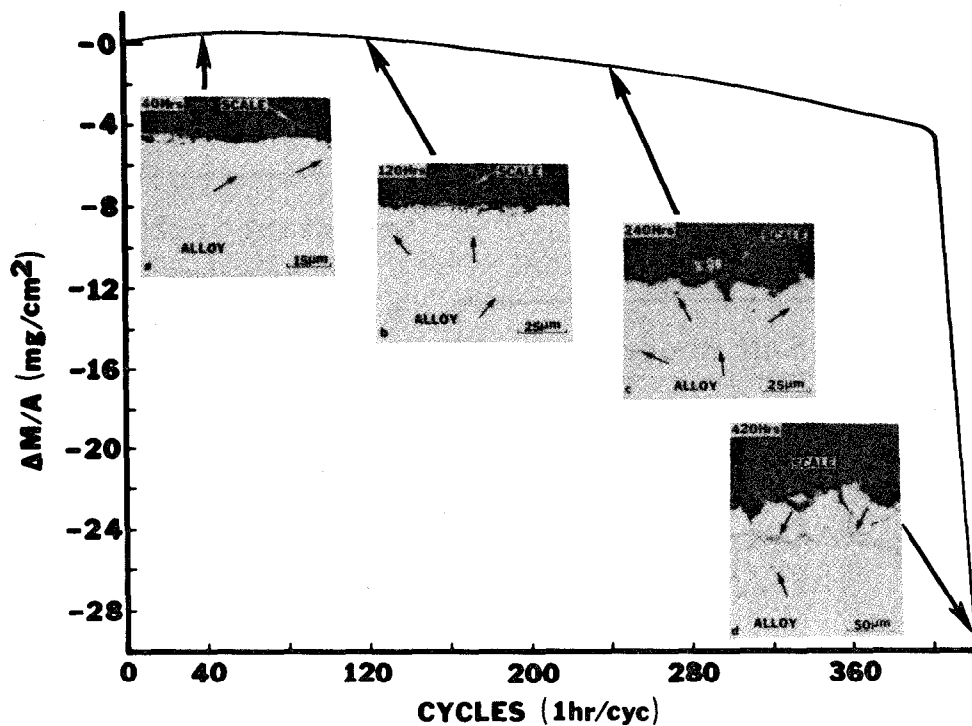
Figure 15. Weight change versus time data and corresponding micro-
structural features for the cyclic hot corrosion of Na_2SO_4- coated
(applied every 20 hrs.) Ni-30Cr-4Al in air. The amount of sulfide
particles (small black arrows) increases until the oxidation of the
sulfide phases significantly affects the rate of attack.

product that is formed in the propagation stage. This fact is responsible
for the variety of hot corrosion processes that have been observed when
superalloys are exposed to different environments. The factors which have
been found to be important are:

   ·alloy composition

   ·alloy fabrication condition

   ·gas composition and velocity

   ·deposit composition and its physical state

   ·amount of deposit on superalloy

   ·temperature

   ·temperature cycles

   ·erosion

   .specimen geometry

In the present paper it will not be attempted to describe how each of these
factors affect the initiation of hot corrosion attack. It is sufficient to
emphasize that these factors can influence the hot corrosion process in
different ways and when their effects are taken into consideration, much
of what could be considered anomalous behavior is reasonably coherent.

   In the following discussion of the propagation mode, only deposits of
Na_2SO_4 on superalloys will be considered. However, consideration of other
deposits would not change the content of what is presented but only add

668

variations of a similar fundamental theme. Similarly gas mixtures contain-
ing oxygen and different amounts of SO_3 will be used to illustrate the in-
fluence of the gas on the hot corrosion process.

The Propagation Modes of Hot Corrosion

The propagation stage of the hot corrosion sequence is the stage for
which the superalloy must be removed from service since this stage always
has much larger corrosion rates than for the same superalloy in the
initiation stage. The microstructural features that are developed however
are highly indicative of the particular propagation mode via which de-
gradation of the superalloy is taking place. Consequently much more data
is available on the propagation stage of hot corrosion compared to the in-
itiation stage. In fact, during the initiation stage often no microstructural
features are evident to indicate that hot corrosion is a factor in the de-
gradation process.

Deposit-Induced Effects. Before describing the types of propagation
modes by which superalloys undergo hot corrosion attack, it is of value to
examine how deposits upon the surfaces of superalloys may affect their
corrosion behavior. In Figure 16 a deposit of Na_2SO_4 is depicted schemat-
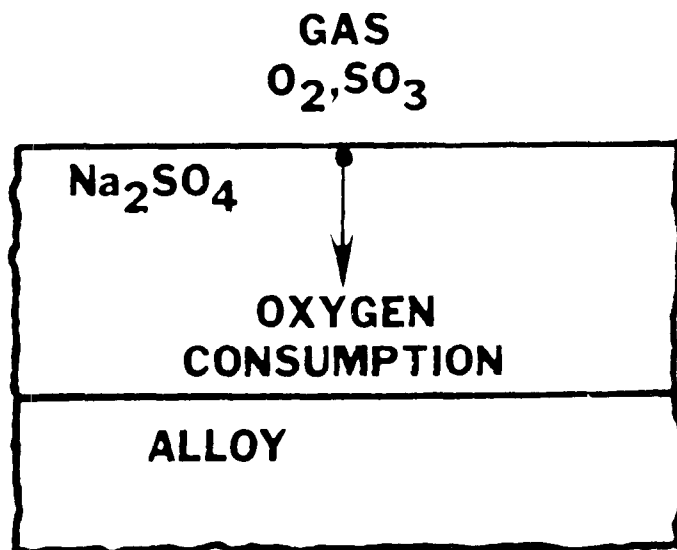ically upon the surface of a superalloy.

Figure 16. Schematic diagram showing a Na_2SO_4 deposit upon
an alloy separating the alloy from the gas phase.

As indicated in this Figure the superalloy will react with elements in the
deposit providing that the deposit prevents free access of the gas. Since
superalloys always contain elements that have high affinities for oxygen,
an oxygen gradient is established across the deposit. Hence, an important
effect of the deposit is to separate the superalloy from the gas environ-
ment. This situation usually results in a lower oxygen activity over the
surface of the alloy than what would have been established in the absence
of a deposit. Moreover, the activities of other reactants in the gas are
increased. Such conditions cause selective oxide formation to be more
difficult when a deposit is present upon the surface of the superalloy.
This does not mean that an oxide barrier will not be formed initially.
However as the exposure time increases and the scale is damaged by thermally
induced stresses, eventually less   protective oxides will be formed sooner
in the case of the superalloy with foreign deposits on its surface.

Another effect of deposits on the corrosion of superalloys is that the protective oxide scales formed on the superalloys may dissolve in the deposits. This condition can lead to especially undesirable conditions when the deposit is a liquid. In certain cases conditions can exist where the protective scale dissolves into the liquid deposit at one interface and precipitates at another interface as a nonprotective layer. Such processes have been called fluxing reactions of the protective oxide barrier by the deposit. (24-26)

The effects produced by deposits on superalloys can be described somewhat more effectively by using thermodynamic stability diagrams such as the one presented in Figure 17. In this Figure conditions are depicted that could develop when a deposit is formed on an alloy such as shown in Figure 16. As a result of oxygen depletion the sulfur pressure over the alloy can be increased and the deposit also may become either basic or acidic
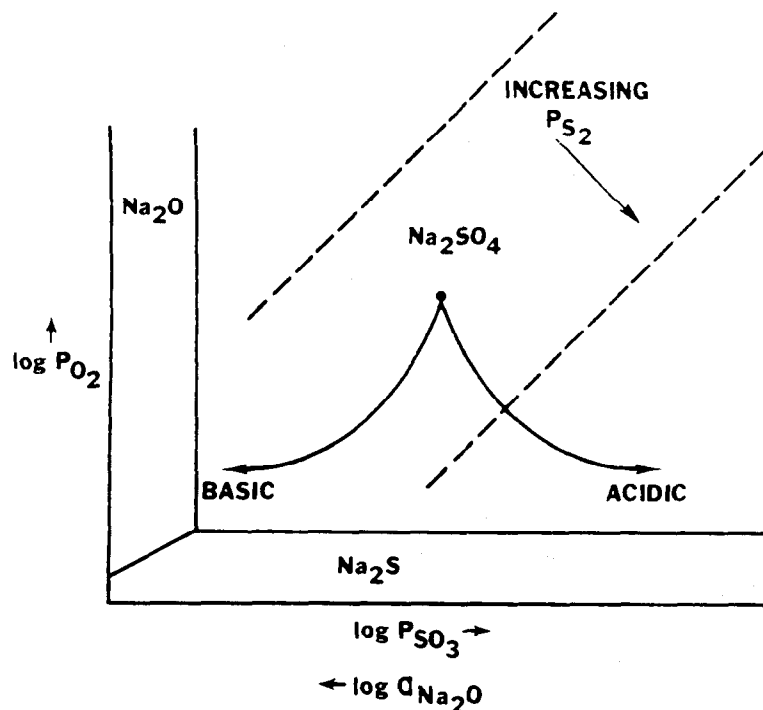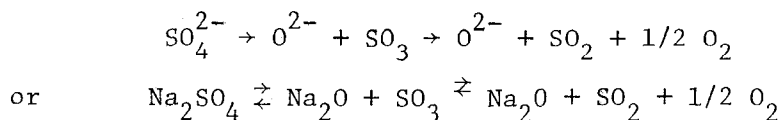

Figure 17. Thermodynamic stability diagram for the Na-O-S system showing how composition of Na_2SO_4 may change due to alloy reacting with the deposit.

in regards to its initial composition. Basic conditions arise because of reactions of the type (24,25).

$$SO_4^{2-} \rightarrow O^{2-} + SO_3 \rightarrow O^{2-} + SO_2 + 1/2 \ O_2$$

or
$$Na_2SO_4 \rightleftarrows Na_2O + SO_3 \rightleftarrows Na_2O + SO_2 + 1/2 \ O_2$$

As the liquid becomes more basic protective oxide scales may react with the deposit via the following reactions,

$$Al_2O_3 + O^{2-} \rightleftarrows 2 \ AlO_2^-$$

or
$$Na_2O + Al_2O_3 \rightleftarrows 2Na \ AlO_2$$

670
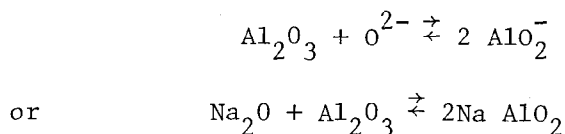
The deposit can also become acidic by reacting with certain oxides in the corrosion product (22,26),

$$MoO_3 + SO_4^{2-} \rightleftharpoons MoO_4^{2-} + SO_3$$
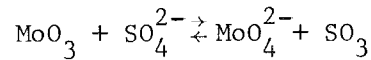
or via equilibration with SO_3 in the gas. Reactions of the following type are then possible between protective oxide barriers and the deposit,

$$Al_2O_3 + 3 SO_3 \rightleftharpoons 2 Al^{3+} + 3 SO_4^{2-}$$
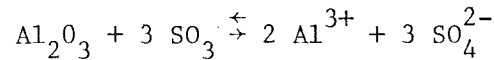
The phase stability diagrams can be used to attempt to account for the different corrosion product morphologies that are observed during the hot corrosion of superalloys by supposing that the deposit exists over a range of compositions as shown in Figure 18. In order to estimate the phases that may be formed in the corrosion product it is necessary to superimpose upon the Na-O-S diagram phase boundaries for the elements present in the super-alloys. Such superposition of thermodynamic stability diagrams usually represents assumptions of conditions that are not completely valid for the systems being studied. Nevertheless the diagram presented in Figure 18 that was constructed by superposition of Na-O-S, Ni-O-S, Cr-O-S and Al-O-S diagrams is consistent with the microstructure developed during the hot corrosion of the Ni-8Cr-6Al alloy shown in Figure 19.

Types of Propagation Modes. In view of the effects that a deposit may have on the corrosion of a superalloy the hot corrosion propagation modes for superalloys can be divided into two general classifications, namely, propagation modes involving fluxing reactions and those that require a component from the deposit to subsequently affect the corrosion behavior of the superalloy. The possible salt deposition effects are shown schematically in Figure 20 where the salt deposit is considered to be innocuous when it is porous and the gas has free access to the superalloy.

The salt fluxing reactions for superalloys may be either acidic or basic in nature. Moreover it is important to emphasize that the propagation stage for a given superalloy may consists of a sequence of several different propagation modes. For example in the case of the superalloy B-1900 the propagation stage consists of basic fluxing followed by acidic fluxing whereas IN 738 has a propagation stage composed of basic fluxing, sulfi-dation (i.e. salt component alloy reaction involving sulfur) and finally acidic fluxing (22,27,28).

The Basic Fluxing Mode. Basic fluxing reactions occur because sulfur is removed from the Na_2SO_4 and consequently oxide ions are produced which react with the protective oxide scale (24). It is important to notice that the concentration of oxide ions available for basic fluxing is limited by the amount of the deposit present upon the surface of the superalloy. Hence basic fluxing reactions are not self-sustaining but require a continuous source of Na_2SO_4 in order for this type of degradation to proceed indefinitely. In Figure 21 data are presented for two alloys exposed to a large amount of Na_2SO_4. The Ni-8Cr-6Al has undergone hot corrosion via basic fluxing and typical microstructural features developed as a result of this type of hot corrosion are shown in Figure 22. The Ni-15Cr-6Al did not undergo hot corrosion attack because a protective alumina scale developed on this alloy and consequently a large oxygen gradient was not established across the Na_2SO_4 layer. With continued exposure the Ni-15Cr-6Al alloy will undergo a similar propagation stage. Thermal cycling of this alloy will shorten its initiation stage.
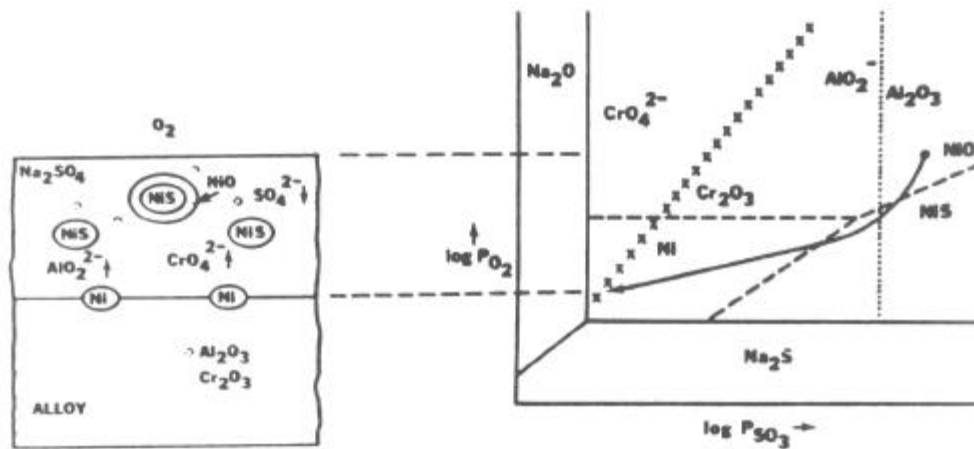
Figure 18. Schematic diagrams correlating stability diagram to corrosion microstructure to illustrate the Na_2SO_4 - induced hot corrosion of a Ni-8Cr-6Al alloy in air. Oxygen depletion occurs, and sulfide formation results in the production of oxide ions which react with Al_2O_3 and Cr_2O_3.
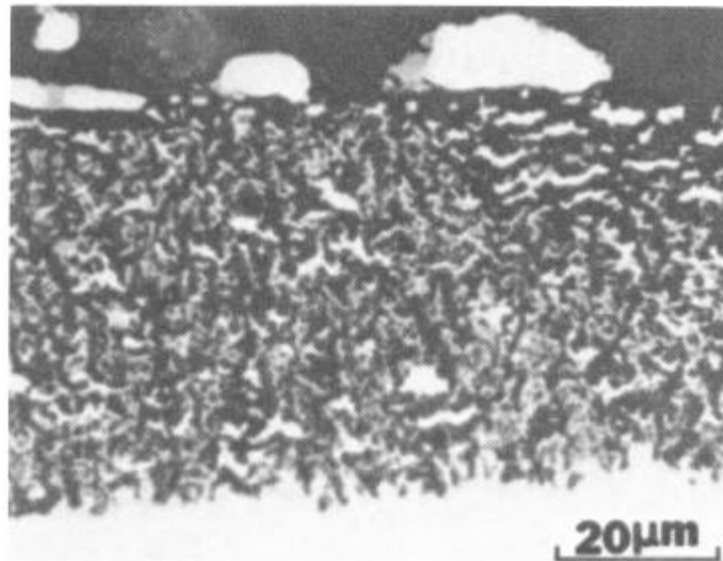

Figure 19. Microstructural photomicrograph showing features of Ni-8Cr-6Al specimens after exposure at 1000°C in air to 5 mg/cm^2 Na_2SO_4 for 2 minutes. Degradation occurs via basic fluxing and is consistent with schematic diagrams of Figure 18.

While basic fluxing reactions require a source of Na_2SO_4 for this type of degradation to continue indefinitely, a number of mechanisms have been proposed whereby large amounts of degradation can occur by a small amount of deposit due to a solution and reprecipitation process (25,29,30). In the present paper it is sufficient to note that protective scales formed upon superalloys can be destroyed via a process that involves the production of oxide ions in the deposit. In most practical cases the salt deposition is such that the time during which the desired protective scale is stable on the superalloy is significantly reduced compared to the time this scale would have been stable had no deposit been present.

The Acidic Fluxing Mode. The acidic fluxing reactions involve the

INITIATION STAGE

Salt
Reaction product
Alloy

PROPAGATION STAGE

Possible salt deposition effects

Inocuous   Salt fluxing reactions   Salt component - alloy reactions

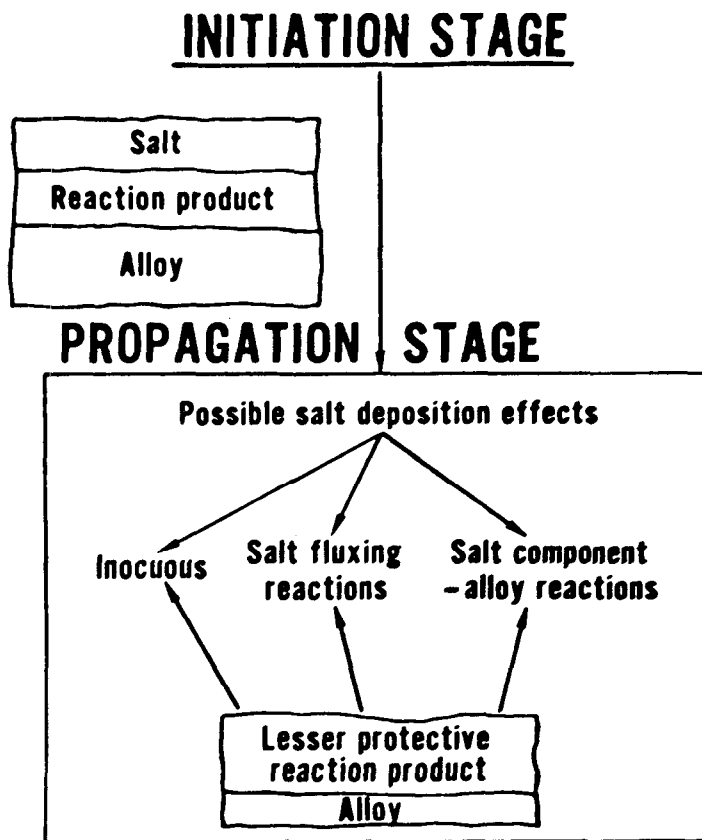**Lesser protective reaction product**

Alloy

Figure 20.   Schematic diagram to illustrate the general categories of protective scale breakdown to a lesser protective reaction product when a salt deposit is present during the corrosion process.

development of nonprotective reaction products on superalloys as the result of a liquid deposit on the surface of the superalloy which has a deficiency of oxide ions. The deficiency of oxide ions in the Na_2SO_4 can arise due an acidic component present in the gas (31-34), or an acidic phase formed as an oxidation product upon the superalloy. When the acidic component is present in the gas (e.g. SO_3) the nonprotective oxide scale ensues due to rapid transport of certain ionic species in the acidic melt (33,34). If the melt becomes acidic due to a formation of an oxide from an element in the superalloy, the attack becomes self-sustaining even with a small amount of Na_2SO_4 (22,26). The refractory elements Mo, W and V form oxides that cause Na_2SO_4 to become acidic and hence these elements when oxidized in the presence of a Na_2SO_4 deposit on superalloys usual cause catastrophic self-sustaining hot corrosion via acidic fluxing. This fluxing need not involve solution and reprecipitation of oxides such as Al_2O_3 or Cr_2O_3 since the MoO_3 or WO_3 that is formed is incorporated into the Na_2SO_4 via the formation of compounds such as Na_2MoO_4, $Na_2MoO_4 \cdot MoO_3$, $Na_2MoO_4 \cdot 2MoO_4$ where these phases are liquid and have a high solubility for Al_2O_3 and Cr_2O_3. The degradation microstructures observed when elements in the alloy have caused acidic fluxing always have the oxide of the causative element as a more or less continuous zone in the corrosion product as shown in Figure 23.

Modes Involving a Component From the Deposit. Superalloy degradation propagation modes can consist of mechanisms where certain elements in the deposit accumulate in the alloy or the deposit and eventually cause a non-protective oxide scale to be formed. Two elements that produce such effects
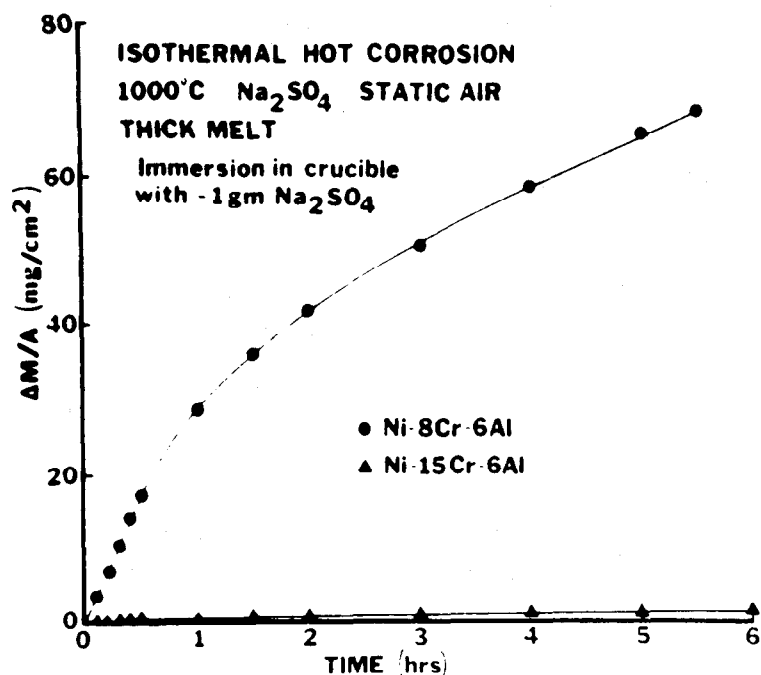
Figure 21. Weight change versus time data showing that increased chromium concentration in Ni-Cr-Al alloys extends the initiation stage for hot corrosion attack induced by large deposits of Na_2SO_4 in air. The Ni-8Cr-6Al alloy is in the propagation stage whereas the Ni-15Cr-6Al is still in the initiation stages.

are sulfur and chlorine.

Some typical results obtained with sulfur are presented in Figure 24. In this Figure cyclic oxidation data of a Ni-25Cr-6Al alloy are compared for cyclic oxidation in air after the alloy was pretreated at regular intervals with Na_2SO_4 or by exposure in an H_2S-H_2 gas mixture. In normal oxidation at 1000°C a protective scale of Al_2O_3 is stable for more than 120 hours. However, for the specimens which were pretreated with Na_2SO_4 or in the H_2S- containing gas, sulfides accumulated in the alloy with microstructures similar to that shown in Figure 15, and after about 10 hours these sulfides resulted in the formation of nonprotective oxide scales. Sodium sulfate deposits are especially effective in causing the hot corrosion of some superalloys by sulfur induced effects. It is worth mentioning that some of the first cases of hot corrosion of superalloys in gas turbines involved sulfur induced degradation (35,36). Consequently this type of degradation was called sulfidation. To this very day, hot corrosion and sulfidation are used by some as synonymous. It is important to note that sulfidation is a specific form of hot corrosion but all hot corrosion attack does not take place via sulfidation.

In many of the deposits formed upon superalloys chloride ion can be present. It is well documented that chloride ion in deposits does cause oxide scales such as alumina and chromia to become more susceptible to cracking and spalling (37). Also when chloride ion is present volatile chlorides of aluminum and chromium can be formed (34). Such products usually are formed at the point where the oxygen pressure in the deposit has been reduced to low levels. Hence chlorides are formed but as they move away from the alloy into regions of higher oxygen pressure they are converted to nonprotective oxides. Typical microstructural features are presented in Figure 25 where nonprotective
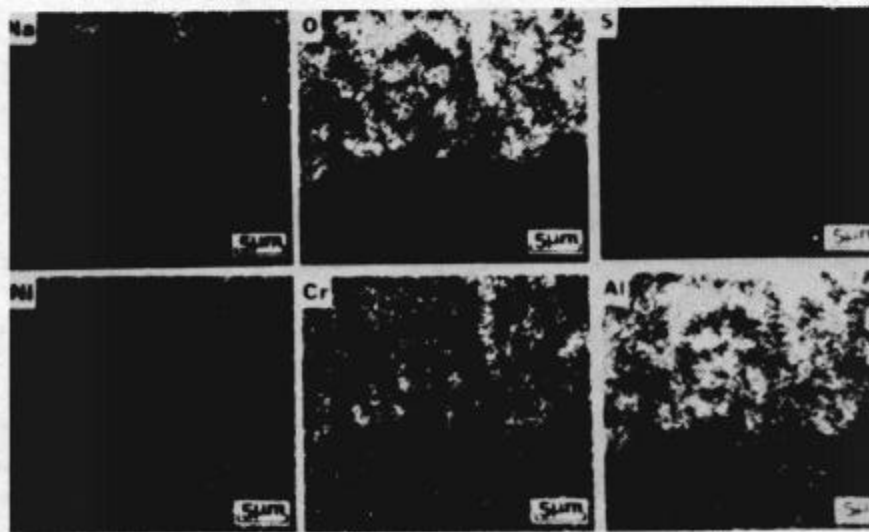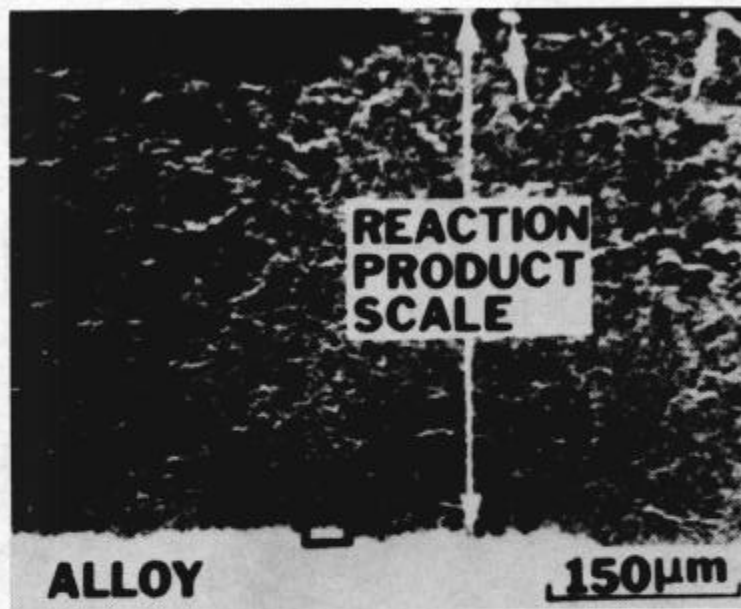
Figure 22. Upper photograph is photomicrograph of Ni-8Cr-6Al alloy that has undergone basic fluxing. The x-ray images show the distribution of different elements in the corrosion product at the corrosion front-alloy interface.

corrosion products are usually separated from the alloy by a zone composed of internal oxides with some porosity. A schematic diagram to illustrate the effects that can occur due to the presence of chloride in Na_2SO_4 deposits is presented in Figure 26.

Summary of Propagation Modes. In Table III the different hot corrosion propagation modes for superalloys are summarized. These modes are not independent of each other but are interrelated and the particular mode that is followed will be determined by the magnitudes of the parameters identified in Figure 14. The hot corrosion of some superalloys can consist of a sequence of two or more propagation modes. Kohl et al have found that the superalloy B-1900 (22) first proceeds via basic fluxing and then by self-sustaining acidic fluxing. Typical results are presented in Figure 27 for an alloy with the chromium, aluminum and molybdenum concentrations in B-1900 but without any of the other elements. The alloy Ni-8Cr-6Al is degraded via basic fluxing but this type of degradation is not self-sustaining and requires Na_2SO_4 for the attack to continue. Hence the attack stops for
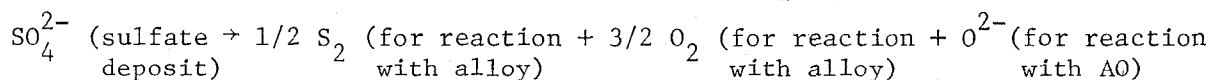
TABLE III

Possible Propagation Modes for Hot Corrosion of
Superalloys by Na_2SO_4 Deposits

| I. Modes Involving Fluxing Reactions	II. Modes Involving A Component of the Deposit
·Basic ·Acidic	·Sulfur ·Chlorine

I. Fluxing Modes

A. Basic Processes

1. Dissolution of Reaction Product Barriers, (i.e. AO) Due to Removal of Sulfur and Oxygen from the Na_2SO_4 by the Metal or Alloy:

$$SO_4^{2-} \text{ (sulfate} \rightarrow 1/2 \text{ } S_2 \text{ (for reaction} + 3/2 \text{ } O_2 \text{ (for reaction} + O^{2-} \text{(for reaction}$$
$$\text{deposit)} \quad \text{with alloy)} \quad \text{with alloy)} \quad \text{with AO)}$$

Reaction between AO and oxide ions can follow 2 courses:

(a) Continuous dissolution of AO

$$A(alloy) + 1/2 \text{ } O_2 + O^{2-} \rightarrow AO_2^{2-}$$
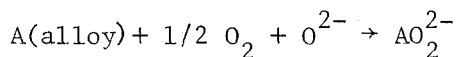
Na_2SO_4 is converted to Na_2AO_2 and attack is dependent on amount of Na_2SO_4 initially present.

(b) Solution and reprecipitation

$$A(alloy) + 1/2 \text{ } O_2 + O^{2-} \rightarrow AO_2^{2-} \text{(solution)} \rightarrow AO \text{(precipitate)} + O^{2-}$$
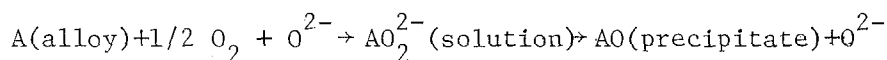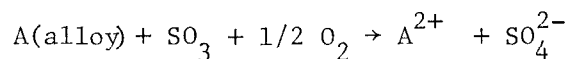
A supply of SO_3 is required in order for attack to proceed indefinitely, otherwise attack will stop when melt becomes sufficiently basic at precipitation site.
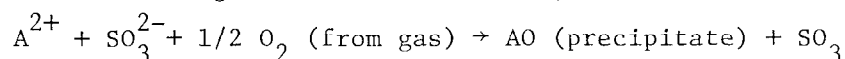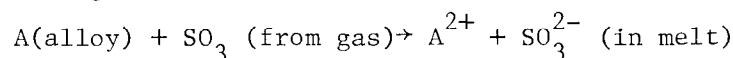
TABLE III (CONTINUED)

B. Acidic Processes

    1. Gas Phase Induced

        (a) Formation of ASO_4 in Na_2SO_4:

$$A(alloy) + SO_3 + 1/2\ O_2 \rightarrow A^{2+} + SO_4^{2-}$$

            Continuous solution of ASO_4 in Na_2SO_4 requires continuous supply of SO_3 and O_2 from gas.

        (b) Solution and Precipitation of AO in Na_2SO_4 Due to Reduction of SO_3:

$$A(alloy) + SO_3\ (from\ gas) \rightarrow A^{2+} + SO_3^{2-}\ (in\ melt)$$

$$A^{2+} + SO_3^{2-} + 1/2\ O_2\ (from\ gas) \rightarrow AO\ (precipitate) + SO_3$$
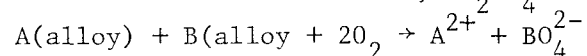
        (c) Nonprotective Reaction Product Barrier formation due to rapid removal of base element (e.g. Co, Ni) from alloy by molten deposit (33).

        (d) Solution and Precipitation of AO as a Result of Negative Gradient in Solubility of AO in Na_2SO_4 as in B.
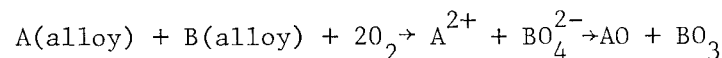
    2. Alloy Phase Induced

        (a) Solution of AO in Na_2SO_4 Modified by Second Oxide from Alloy (i.e. BO_3).
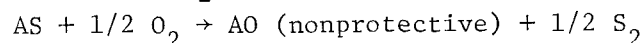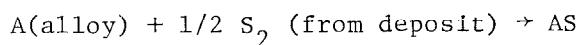
            Sequence:

            i. Modification of Na_2SO_4 by BO_3

$$B(alloy) + 3/2\ O_2 + SO_4^{2-} \rightarrow BO_4^{2-} + SO_3$$
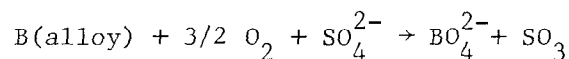
            ii. Solution reaction for AO, Na_2SO_4 becomes enriched in ABO_4

$$A(alloy) + B(alloy + 2O_2 \rightarrow A^{2+} + BO_4^{2-}$$

or

            iii. Solution and repricipitation

$$A(alloy) + B(alloy) + 2O_2 \rightarrow A^{2+} + BO_4^{2-} \rightarrow AO + BO_3$$

II. Salt Component Effects

  A. Sulfur

$$A(alloy) + 1/2\ S_2\ (from\ deposit) \rightarrow AS$$
$$AS + 1/2\ O_2 \rightarrow AO\ (nonprotective) + 1/2\ S_2$$

  B. Chlorine

$$A(alloy) + 1/2\ Cl_2\ (from\ deposit) \rightarrow ACl\ (gas)$$
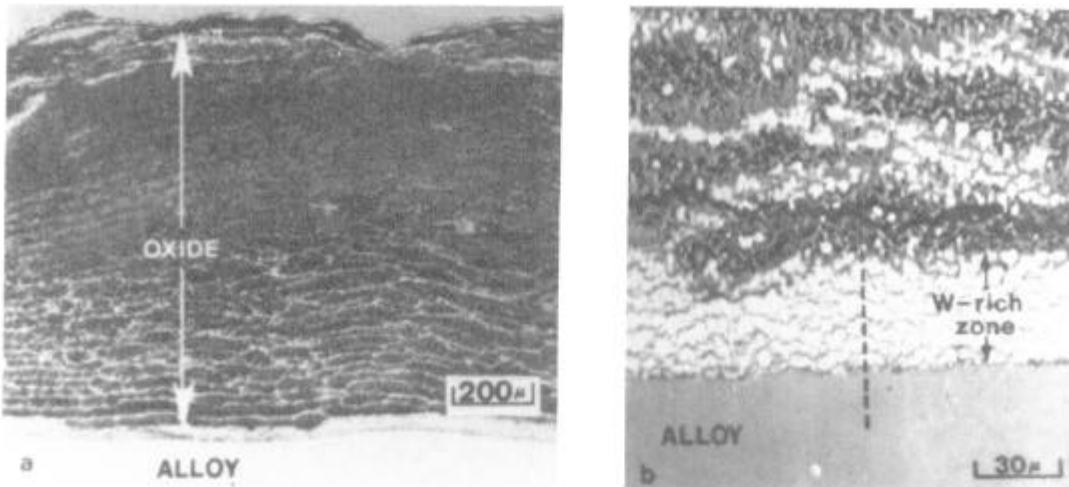$$ACl + 1/2\ O_2 \rightarrow AO\ (nonprotective) + 1/2\ Cl_2$$
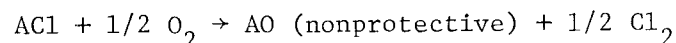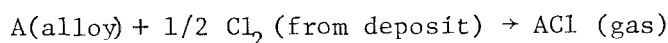
Figure 23. Photomicrographs showing accumulation of refractory metal oxides at corrosion front during alloy-induced acidic fluxing of a Co-25Al-12W alloy.
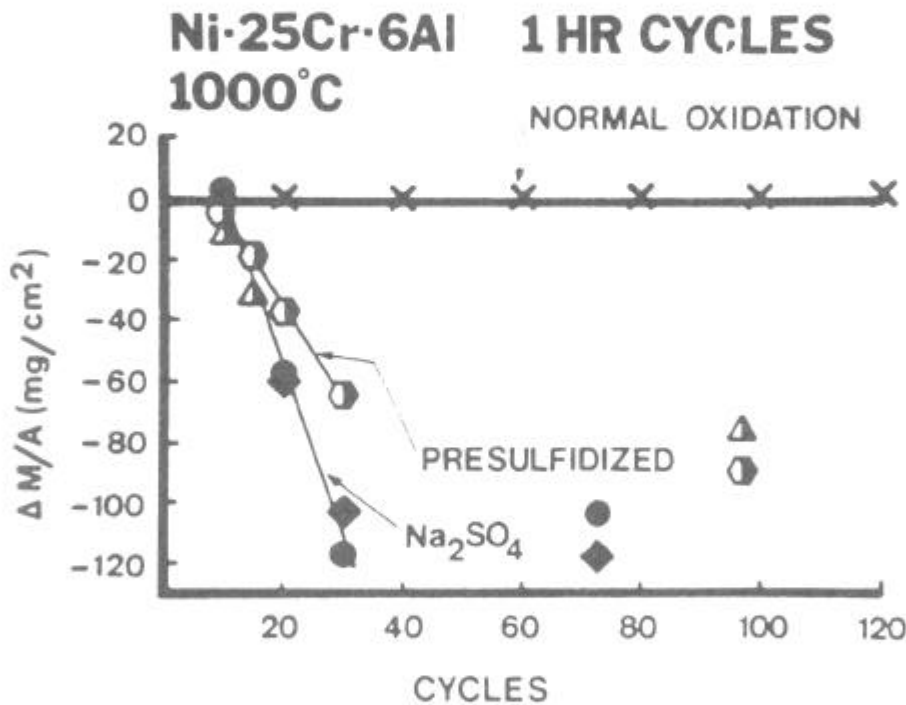

Figure 24. Comparison of the cyclic oxidation data obtained for Ni-25Cr-6Al specimens that were coated with Na_2SO_4 to those presulfidized in an H_2S-H_2 gas mixture. Approximately 5 mg/cm^2 of Na_2SO_4 was added to one specimen after every 5 hrs. of exposure up to 20 hrs. and then after every 10 hr. interval beyond 20 hrs. The presulfidation was performed at the same time intervals that the Na_2SO_4 was applied and the sulfur picked up was equivalent to the sulfur in a 5 mg/cm^2 Na_2SO_4 deposit.

one application of Na_2SO_4, Figure 27. The alloy with molybdenum has the initiation of hot corrosion attack delayed because the formation of MoO_3 inhibits the formation of oxide ions in the melt. Eventually however the protective oxide is broken down and oxygen is rapidly removed from the Na_2SO_4 by the alloy. Typical microstructures are presented in Figure 28 and the melt has become highly basic, stage 4. The rapid consumption of
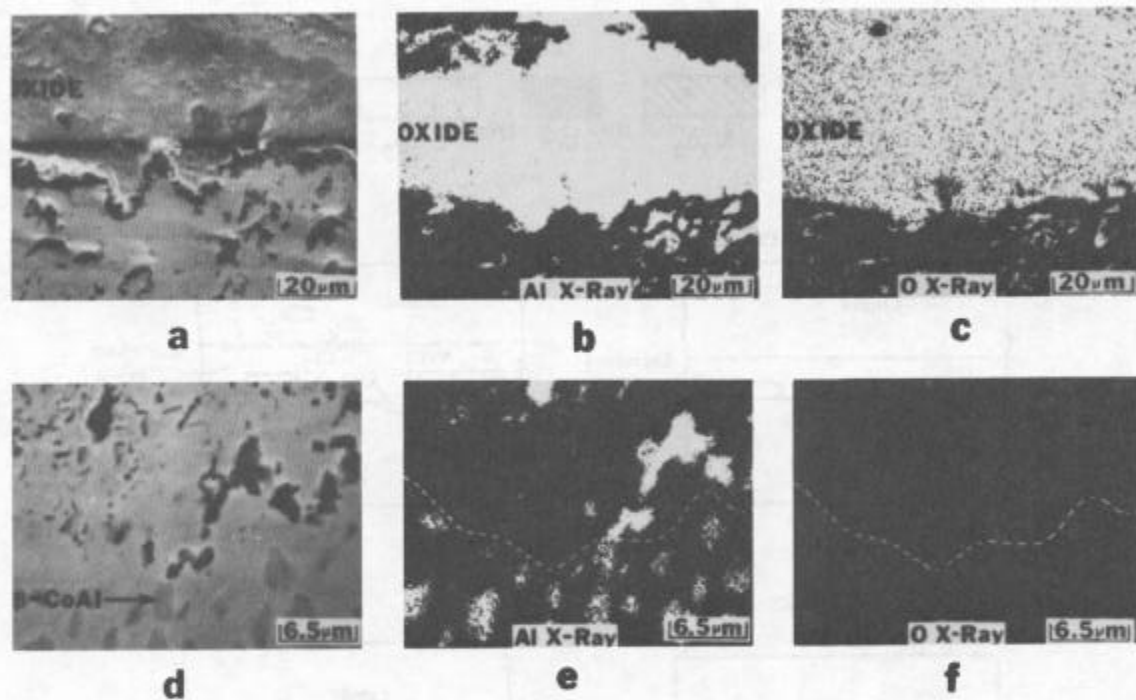
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Figure 25. Microstructural photomicrographs and X-ray images of a Co-25Cr-6Al-.5Y specimen after 100 hrs. of cyclic hot corrosion testing at 900°C where 1 mg/cm^2 Na$_2$SO$_4$-90% NaCl was applied after every 20 hrs. The structural features at the external scale – alloy porous zone interface and at the alloy porous zone – unaffected alloy interface are shown in (a) and (d), respectively. (b) and (c) are X-ray images of the area shown in (a), and (e) and (f) are X-ray images of the area defined in (d). The zone contains oxide particles of aluminum near the oxide scale and particles of aluminum chloride deeper in the alloy.

alloy however, must produce a significant amount of MoO$_3$ and acidic hot corrosion begins to occur as this oxide accumulates in the melt adjacent to the alloy, Figure 28, stage 7. The hot corrosion of IN 738 also proceeds via alloy – induced acidic fluxing and this propagation mode is preceded by other propagation modes one of which must be basic fluxing because the hot corrosion of this alloy by a Na$_2$SO$_4$ deposit is initiated much sooner in an air or oxygen environment compared to a gas which contains some SO$_3$ gas.

Temperature Dependence of the Propagation Modes. Since hot corrosion occurs by different but interrelated propagation modes in discussing the effects of temperature and of different elements it is always necessary to associate comments with specific modes of degradation. The basic fluxing mode needs sulfur incorporation into the alloy in order to make the Na$_2$SO$_4$ basic, hence this mode is usually significant at temperatures above about 900°C and it is most favored in gases containing oxygen. Similar comments apply to sulfur and chlorine induced degradation but chlorine probably causes increased oxide cracking and spalling at temperatures below 900°C. In the case of alloy-induced acidic fluxing this mode is important at all temperatures which liquid deposits can be formed upon superalloys. When MoO$_3$ or WO$_3$ are incorporated into Na$_2$SO$_4$, the resulting phases have melting points significantly below that of Na$_2$SO$_4$ in air (i.e. 883°C). However, the superalloys do not normally form substantial quantities of MoO$_3$ or WO$_3$ at temperatures below 900°C except at carbides. Hence basic fluxing, alloy induced fluxing, and sulfur and chlorine-induced effects normally become significant at about 850-900°C and above.
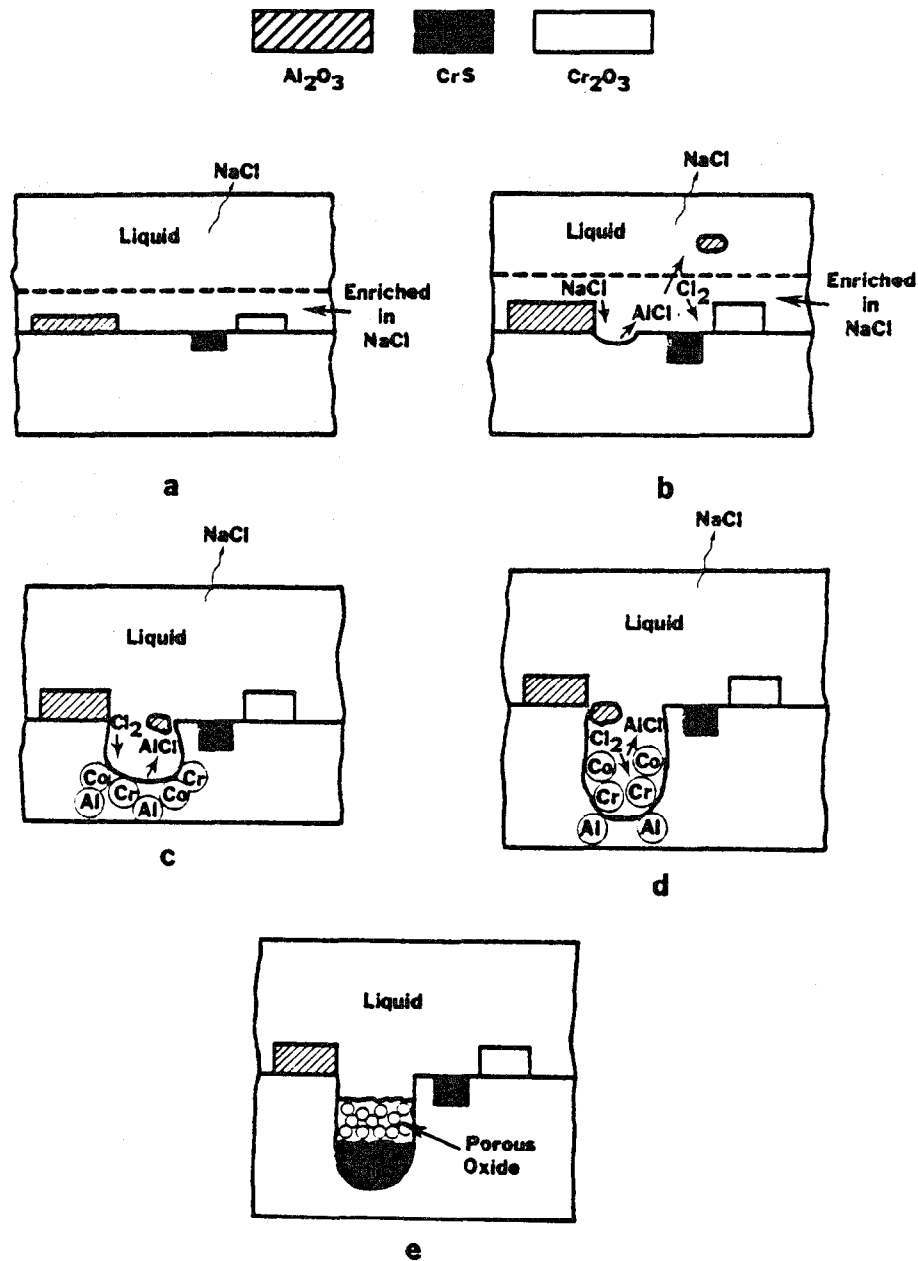
Figure 26. Schematic diagrams to illustrate the hot corrosion
attack of alloys induced by mixtures of Na_2SO_4 - NaCl. Volatile
chlorides are converted to nonprotective oxides as these species
move out to oxygen richer areas.

Gas phase induced acidic fluxing is usually important at temperatures in
the range between 650 and 750°C. This is the case since the SO_3 pressure in
the gas phase decreases as temperature is increased and the SO_3 pressure
required to form the sulfate phases increases with temperature. Consequently
when SO_3 is present in the gas phase, Na_2SO_4 deposits can become liquid at
temperatures as low as about 650°C by incorporation of sulfates such as
$CoSO_4$ and $NiSO_4$.

A diagram that indicates the temperature ranges over which the different
hot corrosion propagation modes are important is presented in Figure 29. It
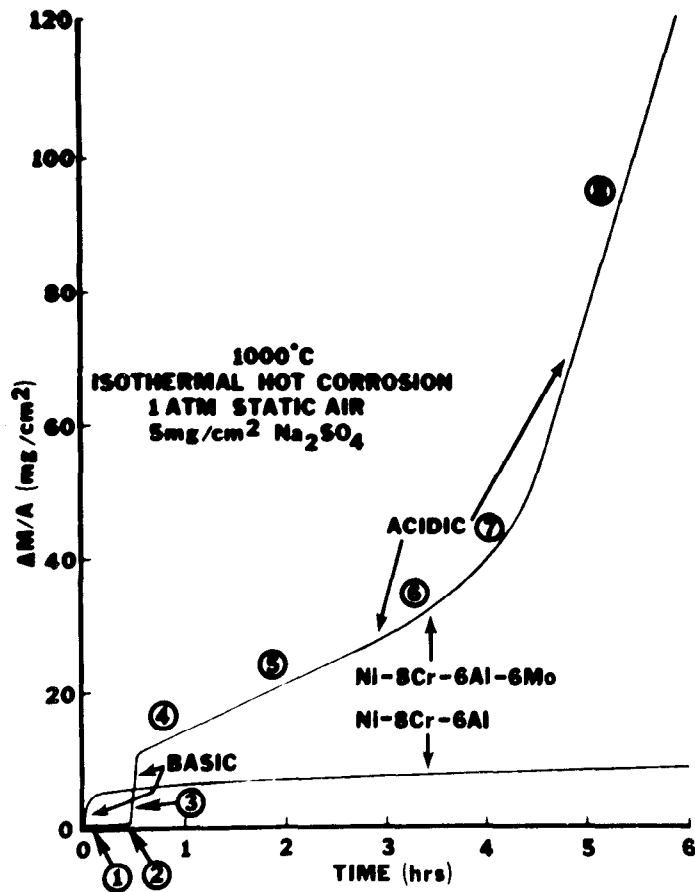can be seen that the attack goes through a maximum at about 700°C and then

Figure 27. Comparison of the isothermal hot corrosion of Na_2SO_4-coated Ni-8Cr-6Al and Ni-8Cr-6Al-6Mo alloys; both alloys have undergone hot corrosion attack. Degradation microstructures for Ni-8Cr-6Al are presented in Figure 19. The circled numbers in the Figure identify various stages during the hot corrosion of the Ni-8Cr-6Al-6Mo and typical degradation microstructures for this alloy are presented in Figure 28.

eventually begins to increase again at temperatures above about 900°C. It is important to emphasize that the low temperature maximum applies to gases containing SO_3 while the degradation for the high temperatures occurs in pure oxygen or in gases with SO_3.

Comparison of the Hot Corrosion of Different Superalloys

If nickel-, cobalt- and iron- base superalloys are compared, with a few exceptions, there are not significant differences in hot corrosion resistances providing the effects of the alloying elements in the superalloys are considered. First the exceptions will be discussed and then the effects of different alloying elements will be examined.

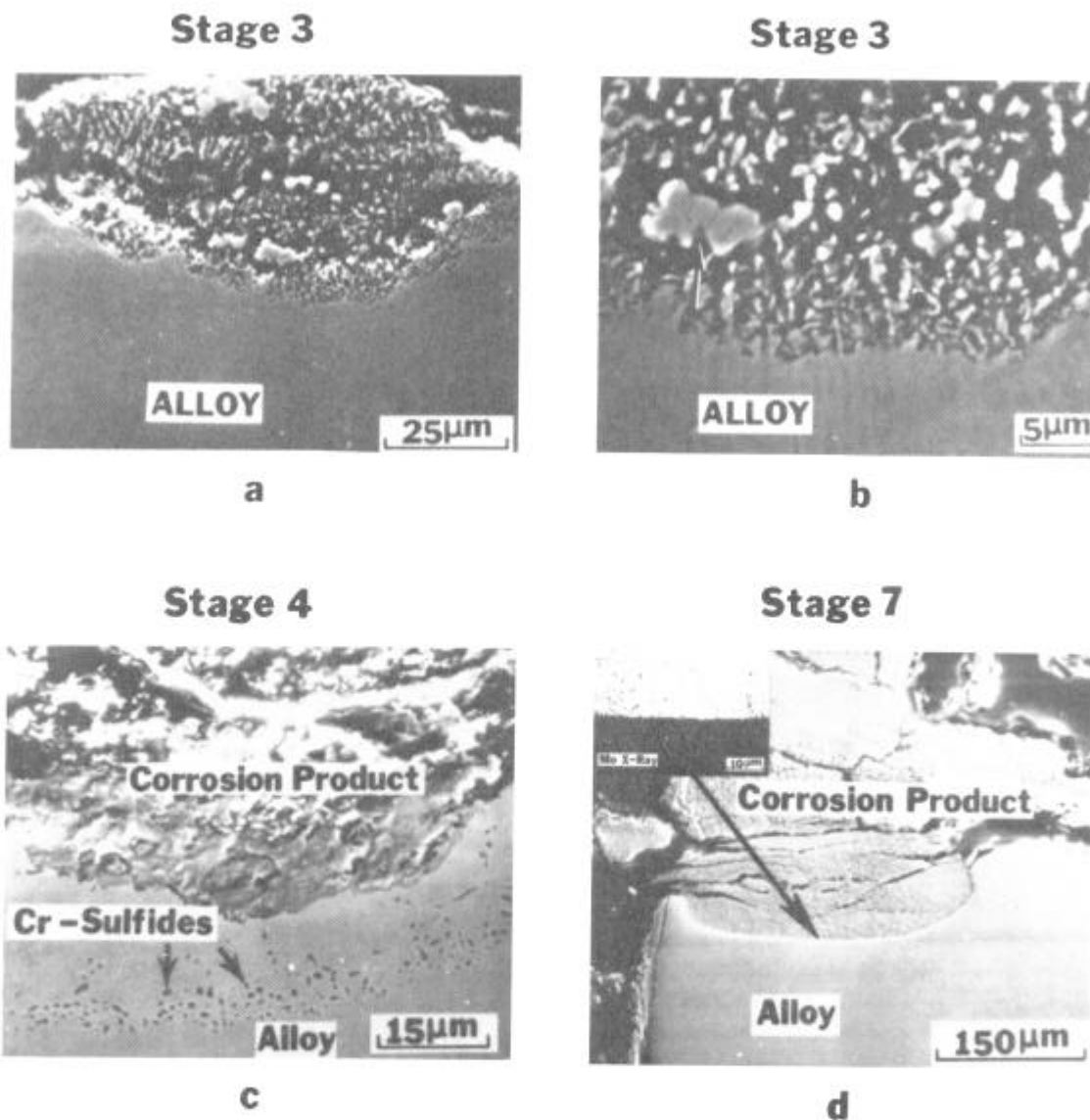When sulfide phases are formed in superalloys, nickel-base alloys are

Stage 3

a

Stage 3

b

Stage 4

c

Stage 7

d

Figure 28. Photomicrographs showing the microstructural features that developed during Na_2SO_4 - induced hot corrosion of Ni-8Cr-6Al-6Mo alloys at 1000°C; (a) and (b) 2 min. in static air, (c) 14.5 min. in flowing oxygen, (d) 1.5 hrs. in static air. Stages 3 and 4 are basic fluxing whereas stage 7 is alloy induced acidic fluxing.

inferior to cobalt and iron due to the formation of nickel sulfide phases which are especially effective in destroying the corrosion resistance of alloys. At low temperatures cobalt alloys do permit liquid phases (i.e. Na_2SO_4 - $CoSO_4$ solutions) to be formed sooner than nickel or iron based alloys, however once liquid phases are present on all of these alloys there is not a significant difference in the hot corrosion rates.

The Effects of Alloying Elements

When discussing the effects produced by alloying elements on the hot corrosion of superalloys it is necessary to associate the comments with an appropriate propagation mode because some elements may produce deleterious effects for one propagation mode and benefical effects for another.

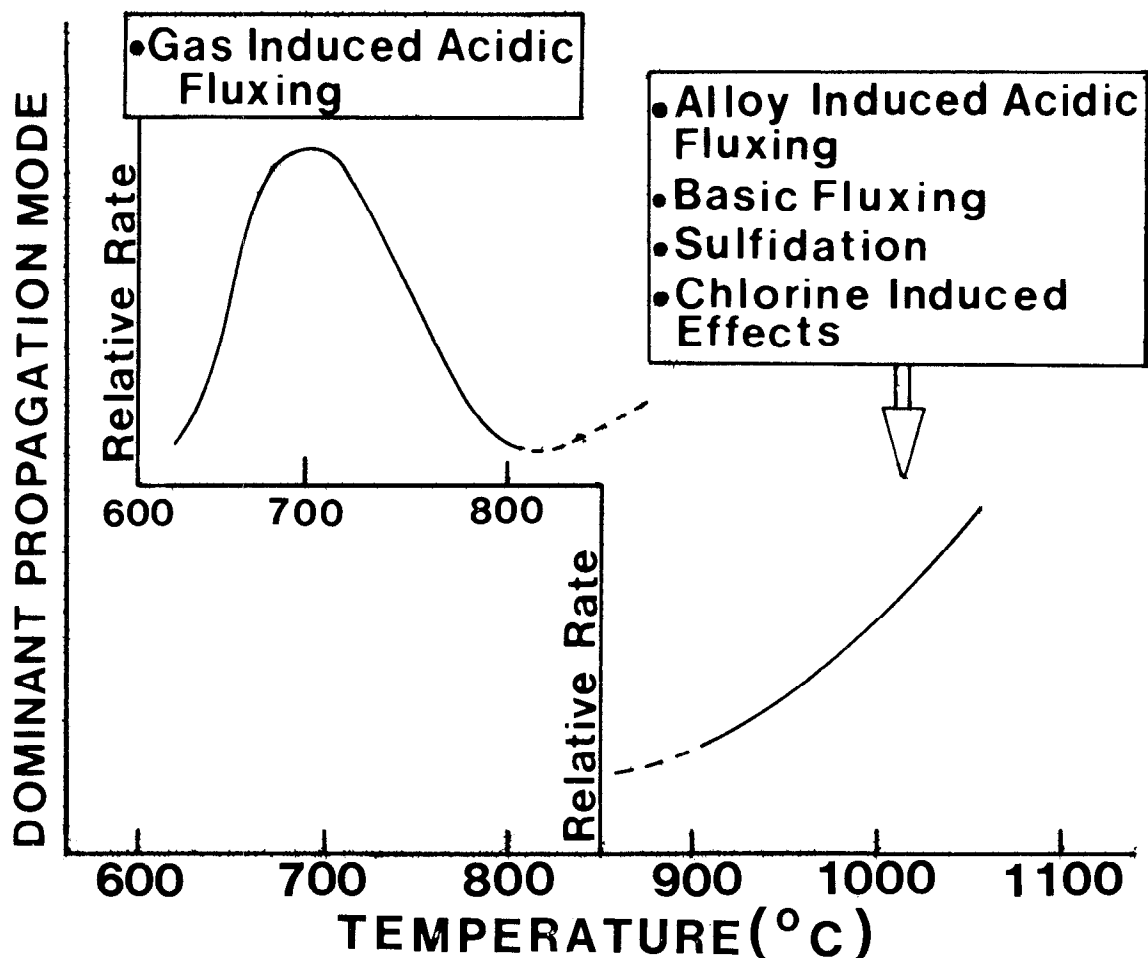Chromium. This element produces beneficial effects on basic fluxing

Figure 29.   Schematic diagram to show temperature regimes over which the different propagation modes are most important.   The rates are relative to a given regime to show temperature effects in that regime.

and both types of acidic fluxing.   Chromium has been shown to inhibit basic fluxing (25).   It also has been found to lengthen the time before alloy – induced acidic fluxing is observed (38).   Chromium has been found to decrease the rate of low temperature hot corrosion of CoCrAlY coatings alloys (39). Chromium also produces beneficial effects on sulfidation – hot corrosion. This element is removed from alloys very rapidly when deposits contain chloride due to the formation of volatile chlorides.

Aluminum.   High aluminum concentrations are desirable in alloys since generally alloys stay in the initiation stage for longer times as the aluminum concentrations are increased.   In the case of sulfidation however nickel-base alloys are especially susceptible to sulfur-induced effects when the aluminum concentrations are between about 1 and 4. percent.   This has not been observed for cobalt- or iron-base alloys.   Also, in the low temperature hot corrosion regime the attack has a preference for the aluminum rich phases in nickel-, cobalt- and iron-base alloys.   It therefore appears that aluminum must be used cautiously when low temperature hot corrosion is a factor.

Molybdenum, Tungsten and Vanadium.   All three of these elements produce

similar effects. They do inhibit the onset of basic fluxing, however, the oxides of these elements are responsible for alloy-induced acidic fluxing. Consequently such elements must be used with great care in any environment that can initiate hot corrosion attack.

Tantalum, Titanium and Niobium. Tantalum and titanium have been reported to produce beneficial effects on hot corrosion. The investigations on the effects produced by these elements have not been very extensive and it is not possible to make any remarks in regards to a specific propagation mode. It seems safe to propose that these two elements do not produce deleterious effects on the hot corrosion resistance of superalloys.

There is a limited amount of data on the effect of niobium on the hot corrosion of superalloys. This element is not desirable when considering the oxidation resistance of superalloys. It also has been reported to adversely effect hot corrosion resistance of alloys but the data is not very definitive.

Carbon. Carbide phases are sites for initiation of hot corrosion attack (3) and hence represent an undesirable condition with regard to hot corrosion resistance.

Manganse, Silicon, Boron, Zirconium. These elements are present in small concentrations in superalloys and it is not apparent that at such concentrations they significantly influence superalloy hot corrosion resistance. It is worth noting that silica scales have been found to be quite resistant to acidic melts, but rather susceptible to degradation induced by basic deposits.

Summary and Concluding Remarks

The principal types of degradation of superalloys, in particular, oxidation, mixed gas attack, and hot corrosion have been examined. It has been shown that all three types of degradation can be viewed as consisting of initiation and propagation stages. These alloys undergo the least amount of degradation in the initiation stage when selective reaction product barriers of alumina or chromia are formed, and must be removed from service due to unacceptable degradation rates when less protective reaction product barriers are formed. The effects of different parameters on the stability of the alumina and chromia barriers has been discussed. While the effects of many parameters are understood more work is required to describe certain effects on a more quantitative level.

Acknowledgements

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