The Oxidation and Corrosion of ODS Alloys

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SUMMARY

This paper is a review of the oxidation and hot corrosion of high temperature oxide dispersion strengthened (ODS) alloys. It classifies the environmental resistance of such alloys by oxide growth rate, oxide volatility, oxide spalling, and hot corrosion limitations. Also discussed are environmentally resistant coatings for ODS materials. The report concludes that ODS NiCrAl and FeCrAl alloys are highly oxidation and corrosion resistant and can probably be used uncoated.

INTRODUCTION

Oxide dispersion strengthened (ODS) alloys have long been known to have oxidation resistance that is, in general, superior to that of conventional alloys developed for high temperature applications. This gave rise to the expectation that ODS materials could be used at elevated temperatures without a protective coating to prevent excessive oxidation. Such a belief was based on the early oxidation data on thoria dispersion strengthened nickel (TD-Ni) (ref. 1) and thoria dispersion strengthened nichrome (TD-NiCr) measured in isothermal and cyclic, static air tests. Both alloys were developed by DuPont and later Fansteel during the 1960's. This work seemed to indicate that alloys such as TD-NiCr and DS-NiCr (the Sherritt Gordon Incorporated version of the same alloy) had potential for use uncoated at temperatures as high as 1473 K. TD-Ni, on the other hand, even though exhibiting an oxidation rate slightly lower than pure nickel (Wlodek, 1962; Jones and Westerman, 1963; Pettit and Felten, 1964; and Lowell et al., 1972), still oxidized at a rate which was inadequate for use without a protective coating. Much of this early work has been summarized by Wright (1972).

The inherent oxidation resistance of ODS alloys led to their application in a number of materials systems. One of the most widely investigated potential applications was the thermal protection system (TPS) for the space shuttle which was then in its early stages of design (Gilbreath, 1971; and Klingler et al., 1971). Another potential use was the high pressure turbine first stage vanes for the F-101 engine then under development for the B-1 bomber (Stahl, Perkins, and Bailey, 1972). In the 1980's other engine applications were found for these or similar alloys (Singer and Arzt, 1986). It was soon recognized, however, that all such applications, particularly the first two, required not only exposure to cyclic high temperatures, but also exposure to high gas velocities, which could be in excess of Mach 1. Under these conditions chromium oxide (Cr$_2$O$_3$) which forms on both TD-NiCr and the DS-NiCr had little chance to perform a protective role due to its volatility at temperatures above 1273 K (Goward, 1970; Scruggs, 1970; Kohl and Stearns, 1970; Giggins and Pettit, 1971; Lowell et al., 1971; Gilbreath, 1971; Sanders and Barrett, 1971; Wallwork and Heo, 1971; and Davis, Graham, and Kvernes, 1971).
The recognition of this major shortcoming led to the accelerated development of thoria dispersion strengthened NiCrAl (TD-NiCrAl) in the mid 1970's. This alloy formed a nonvolatile aluminum oxide (Al₂O₃) scale which was expected to be resistant to high gas velocities. At the same time, protection from hot corrosion was added to the list of requirements which led to dispersion strengthened FeCrAl alloys being developed for such applications in the mid 1970's (Allen and Perkins, 1972). While both the TD-NiCrAl and the Yttria strengthened FeCrAl seemed to have considerable promise in high velocity oxidizing environments, another life limiting criterion came into play—the spalling of the protective Al₂O₃ as a result of thermal expansion mismatch stresses.

The object of this paper is to survey the effects of oxidation and hot corrosion on high temperature ODS alloys and discuss the limitations that the environment imposes on the use of these materials. This survey will be primarily limited to those ODS alloys strengthened by either thoria or yttria and to high temperature effects at 1173 K and above. It will deal with both isothermal and cyclic exposures and especially with high gas velocities, i.e., above Mach 0.2. Also discussed will be coating systems that have been devised to overcome some of the lack of environmental resistance that characterizes some highly alloyed ODS alloy systems, e.g., MA6000E (Gedwill, Glasgow, and Levine, 1982). Models for effects such as volatilization and spalling will be evaluated in the context of dispersion strengthening, with emphasis placed upon the models' ability to predict environmental resistance in a quantifiable fashion.

The first part of this paper will discuss the growth of protective oxides and those ODS materials which are limited by oxide growth kinetics. The effects of oxide volatilility will then be examined and discussed in terms of life limitations. This will be followed by an evaluation of the role of scale spalling as a limitation on the use of ODS alloys. The following section will evaluate the effects of hot corrosion; then coatings will be addressed in the context of the peculiar problems that ODS alloys present for their application. Finally, a summary section will attempt to put the environmental effects on ODS alloys into perspective in regard to other material systems for use in high temperature, environmentally active applications.

ALLOYS LIMITED BY OXIDE GROWTH RATES

The kinetics of oxide scale growth were initially elucidated by Wagner (1940) and later expanded by Hauffe (1965). Their work demonstrated that these kinetics were rate limited by the diffusion of anions and/or cations through the oxide scale with the result that the instantaneous growth rate was determined by the diffusion rate of the ions and the thickness of the oxide layer. The growth of oxide scales can therefore be expressed by the following equation:

\[
\text{Oxide thickness} = k_{ox}^{1/2} t^{1/2}
\]

where \( k_{ox} \) is defined as a growth constant, usually called the parabolic scaling constant as the equation as derived is a parabola, and \( t \) is the time. This equation is more commonly expressed as:

\[
\text{Oxide thickness} = k_{ox}^{1/2} t^{1/2}
\]
\[ \frac{\Delta M}{A} = k_p^{1/2}t^{1/2} \]  
\[ (2) \]

where \( \Delta M/A \) is the specific weight gain usually expressed in milligrams per square centimeter. In this case \( k_p \) is the growth constant in terms of weight gain of oxygen.

Assuming that the rate controlling process remains the same during scale growth (i.e., the same scale composition), the temperature \( (T) \) dependence of \( \ln k_p \) is linear in \( 1/T \) with an activation energy equal to that of the diffusing species:

\[ k_p = k_p^0 \exp\left(-\frac{\Delta E}{RT}\right) \]  
\[ (3) \]

An Arrhenius plot for various metals and alloys meeting the above criterion is shown in figure 1, based upon table IX. Here data for the most important ODS materials are presented together with several nondispersion strengthened alloys for comparison.

Typical derived \( k_p \) values for TD-NI at various temperatures as determined by several investigators particularly Wodek (1962); Manning, Royster, and Braski (1963); Pettit and Felten (1964); and Lowell, Grisaffa, and Deadmore (1972) are shown in figure 1. While this alloy is a NiO former and the presence of thorla seems to lower the \( k_p \) slightly in comparison to pure nickel, the degree of improvement is still not sufficient to allow TD-NI to be used uncoated at temperatures above 1273 K. Analysis of the remaining data indicates that the alloys with the lowest \( k_p \)'s are those which form single oxide scales of either Cr2O3 or Al2O3. Typical of these are TD-NiCr and TD-NiCrAl respectively. While there is some diffusion evidence that a scale composed entirely of nickel chromite or nickel aluminate spinel would have small \( k_p \) values, all attempts to form such a scale have failed (Goward, 1970). Even though oxidized TD-NiCrAl scales are often found to have small amounts of nickel aluminate spinel, it is generally believed (e.g., Barrett and Lowell, 1975) that the excellent oxidation resistance of this and similar alloys is primarily a result of Al2O3 formation containing small amounts of Cr3+ ions in solution.

The results of figure 1 demonstrate that, in general, the addition of an oxide dispersoid to an alloy decreases the scale growth rate, e.g., slightly in the case of TD-NI but by a factor of two or more in the case of TD-NiCr. The mechanism of this rate reduction in TD-NiCr has been studied by several investigators including Giggins and Pettit (1971); Stringer, Wilcox, and Jaffe (1972); and Michaels (1976). While the exact mechanism is still subject to some dispute, clearly the rate reduction is due to a lowering of the rate of ion transport either into or through the scale. In the case of transport through the scale, it has been postulated by Giggins and Pettit (1971) that the dispersed oxide becomes entrapped in the scale reducing diffusion through the scale or alternatively (Michaels, 1976), absorption by the scale of cations from the dispersoid could also reduce diffusion through the scale. Davis, Graham, and Kvernes (1971) suggested that diffusion of chromium through NiCr alloys was decreased by oxide dispersions thus reducing the rate of chromium transport to the metal-scale interface and restricting chromia scale growth. Any of the above mechanisms could account for the observed reductions in oxide
growth rate, but the present authors lean toward the absorption of cations from the dispersoid in the growing scale as the most likely mechanism.

In general, most ODS alloys have good to excellent isothermal oxidation resistance even as compared to coated superalloys (fig. 1). The major exception is TD-Ni. Coatings for improved environmental resistance for use on this alloy have had indifferent success.

ALLOYS LIMITED BY OXIDE VOLATILITY

As discussed in section 2, TD-NiCr is an alloy with sufficient oxidation resistance to allow its use uncoated at temperatures to 1473 K; thus it was considered for use in the TPS of the space shuttle. However, many investigators also recognized that chromia, the protective oxide scale, was volatile in the presence of oxygen (Goward, 1970; Scruggs, 1970; Kohl and Stearns, 1970; Giggins and Pettit, 1971; Lowell et al., 1971; Gilbreath, 1971; Sanders and Barrett, 1971; Wallwork and Hed, 1971; and Davis, Graham, and Kvernes, 1971) which could be a serious problem at the velocities expected for TPS applications. The pertinent chemical reaction was shown to be (Kohl and Stearns, 1970):

\[ \text{Cr}_2\text{O}_3(s) + \frac{3}{2} \text{O}_2(g) \rightarrow 2\text{CrO}_3(g) \]  

(4)

At temperatures below 1473 K in still or slowly moving air, this reaction proceeds at a relatively low rate. However, as the air flow increases, the reaction products can be swept away and the reaction rate can increase to the limiting Langmuir rate (Dushman, 1962). Such losses of chromia can be further aggravated by the presence of water vapor which results in the formation of \( \text{Cr}_2(\text{OH})_3 \) (Kohl and Stearns, 1970) a gaseous species which is even more volatile than \( \text{CrO}_3 \). Additionally exposure to partial pressures of atomic oxygen at high reentry velocities would even further accelerate chromia vaporization (Fryburg, Kohl, and Stearns, 1972). For any mechanism which drives equation (4) to the right, the net effect has been observed to be that the rate of \( \text{CrO}_3 \) formation can exceed the rate of formation of \( \text{Cr}_2\text{O}_3 \) and thus protective scale formation is compromised. With the reduction in the rate at which a protective chromia scale forms, scale thickening is diminished and transport across the scale remains high and metal consumption is increased. This effect can be described by:

\[ \Delta W = k_p t^{1/2} - k_v t \]  

(5)

where \( k_v \) is the rate of loss of a volatile species. A typical example of such behavior is plotted in figure 2. Plotted in the figure is the measured specific weight change for the case where volatility is minimal in static air. For comparison, specific weight gain curves are also plotted for slowly moving air as well as for high velocity air (>Mach 1). In the latter case the rate of loss can approach that calculated from the Langmuir equation. For the case of slowly moving air the weight change is positive at first, goes through a maximum and ultimately approaches a constant negative rate at which point the oxide scale growth rate is exactly balanced by the loss via oxidative vaporization. For the case of high velocity air the rate of loss is so great that effectively no chromia scale formation can be supported.
A more important measure of the practical implication of the oxidation process is the rate at which metal is consumed. This is plotted in figure 3, for the data used in figure 2, and presents a more graphic demonstration of the effect of volatility. It is evident that the effect of the vapor loss via CrO₃ is to keep the rate of metal consumption at a high, constant value. This is in contrast with alloys whose protective scale is nonvolatile and consequently whose metal consumption rate steadily diminishes with time.

This process of oxidation controlled by volatility has been modeled extensively by Barrett and Pressler (1976) resulting in a computer program called COREST. This program allows one to calculate and accurately predict the weight change and metal consumption from a knowledge of \( k_p \) (assuming parabolic growth) and \( k_v \) or simply two sets of weight change/time values. The accuracy of this model is primarily determined by the accuracy with which the values of \( k_p \) and \( k_v \) are known or can be determined. While \( k_p \) is primarily a function of temperature and can be measured with considerable precision, \( k_v \) is a function of oxygen pressure, flow rate, and geometry as well as temperature and can, in general, be measured only indirectly. The presence of ThO₂ does not affect this \( k_v \) value, (Wright, 1972). However, the limiting highest rate can be calculated from the vapor pressure of CrO₃ using the Langmuir equation as shown by Kohl and Stearns (1970). This rate is reached when the gas velocity exceeds about Mach 0.2. Even in slowly moving air the effect of CrO₃ formation on oxidation kinetics becomes noticeable above 1273 K (Lowell et al., 1971). An example of the application of COREST is plotted in figure 4 for TD-NICr tested in static air. In this figure predicted and measured specific weight change data are plotted and the agreement is seen to be good after the first 10 hr.

The deleterious effects of oxide volatility at high velocities are most easily demonstrated in burner rig tests, e.g., (Lowell and Sanders, 1972; Timbres, Norris, and Clegg, 1972; and Johnston and Ashbrook, 1974), or arc jet facilities, e.g., (Centolanzl et al., 1971; Gilbreath, 1972; Land, Williams, and Perkins, 1972; Tenney, Tang, and Herring, 1974; and Young, Tenney, and Herring, 1975). A burner rig is an apparatus in which material is exposed to combustion gasses exhausted through a convergent nozzle. In burner rig tests gas velocities are commonly between 0.3 and 1.0. Burner rig test results obtained by Lowell and Sanders (1972) on TD-NICr are shown in figure 5. At short times (<1 hr) metal loss is dominated by the formation and volatilization of a chromia scale. At about 1 hr chromium loss from the metal exceeds the replenishment of chromium via diffusion through metal. This results in the formation of other, less protective oxides—NiO and NiCr₂O₄. From that point onward the rate is lower than the initial rate, because these oxides are less volatile, but the rate is still unacceptably large.

The formation of a volatile oxide, CrO₃, prevents the use of TD-NICr in thick sections, but is even more deleterious for thin sheet (~0.03 cm) applications such as were envisioned for the TPS. Such thin section tests were run in arc jet facilities by the investigators cited above at hypersonic velocities with enhanced degradation results as anticipated. In the arc jet test some atomic oxygen was also present so the results contain effects of both high velocity and enhanced oxidation rate due to the atomic oxygen. Gilbreath (1971) found in oxidizing TD-NICr at 1373 K that in terms of 10 hr metal recession values obtained in flowing oxygen exceed static oxygen values by a factor of 10 and with atomic oxygen (at unspecified concentrations) present a factor
of 30. As with the burner rig results, within a very short time a chromia scale could not be maintained and the thickness losses were unacceptable even for the relatively short periods (50 hr) needed. In addition to the overall metal loss, the remaining metal was structurally weakened by the presence of Kirkendahl voids resulting from the diffusion of chromium into the scale and the condensation of vacancies around the dispersed oxide particles.

This section has concentrated on TD-NiCr, however, the conclusion that this alloy is not suited to high gas velocity applications at temperatures above 1273 K is equally valid for any ODS alloy, (e.g., MA-754 and IN-853 from table I) which relies upon the formation of a chromia scale for its oxidation protection. Chromia forming alloys can also suffer from enhanced oxidation due to the spalling processes discussed in the next section. However, in high velocity environments the effects of oxidative vaporization are so great that they often mask any effect of spalling, e.g., Lowell and Sanders (1972). Attempts were made by alloying TD-NiCr with 2 to 4 percent manganese to form a scale over the volatile chromia consisting of a MnCr$_2$O$_4$ spinel Klingler et al. (1971) and Timbres, Norris, and Clegg (1972). While this approach was to some degree successful (Gilbreath, 1972), it was abandoned in favor of the alumina forming TD-NiCrAl as will be discussed in the following section.

ALLOYS LIMITED BY OXIDE SPALLING

TD-NiCrAl was specifically developed to overcome the effects of oxide volatility. In contrast to TD-NiCr which forms chromia as its protective scale, TD-NiCrAl forms an alumina scale which presents no volatility problems at temperatures up to at least 1473 K which is considered to be the useful strength limit for this alloy. In addition neither the presence of water vapor nor atomic oxygen is an important factor in the oxidation process Goward (1970) and Gilbreath (1972). Also, as was demonstrated above, the growth rates of scales on this alloy are among the lowest for any metallic material (Fig. 1 and table II). For alloys which form alumina scales the life limiting factor becomes spalling of the protective oxide during cooling from the oxidizing temperature. This includes many of the ODS alloys in table I. Those with compositions of >4 wt % aluminum have alumina as an important scale component; these alloys range from slight variations on TD-NiCrAl like MA-953 to the highly alloyed MA-6000E or MA-755E.

Spalling occurs as a result of thermal expansion mismatch stresses developed between the metal and the oxide (Lowell and Deadmore, 1980). As the alumina grows at temperature, only negligible stresses are developed. Upon cooling the thermal contraction of the metal is much greater than that of the oxide (18×10$^{-6}$ and 10×10$^{-6}$ K, respectively). The result is that the oxide is subjected to stresses that are proportional to the difference in thermal expansion coefficients of the metal and the oxide times the difference between the oxidizing temperature and the temperature to which the material is cooled, i.e.

$$\sigma = \Delta\alpha \times \Delta T$$

(6)

where $\sigma$ is the stress generated in the scale, $\Delta\alpha$ is difference between the thermal expansion coefficients of the scale and the alloy, and $\Delta T$ is the difference between the heating and cooling temperatures. If the stress generated
in the scale exceeds the compressive strength of the oxide, part, or all of the scale will spall. The effect of this process is in some ways analogous to the volatility process. Some, or all of the protective oxide is lost on each cooling cycle and the metal consumption rate may be greatly increased.

The severity of the attack is determined by two major factors. The first is the temperature difference between oxidation and cooling; the greater this difference beyond that needed for the initiation of spallling, the greater the amount of spalling per cycle. This effect is illustrated in figure 6 for TD-NiCrAl as compared to a chromia forming alloy, IN-601 and another alumina forming alloy, FeCrAl. In this figure the specific weight change is shown after 200 1-hr cycles at 1473 K as a function of cooling temperature. These data were obtained in a cyclic furnace test using slowly moving air. Until the difference between the oxidizing temperature and the cooling temperature exceeds about 1100 K the weight change of the TD-NiCrAl is the same as that for an isothermal test. When the difference exceeds 1100 K, spallling was observed and increased as the temperature difference increased. The weight change of the IN-601 showed the same trends, but spallling was observed at smaller values of $\Delta T$, probably the result of the lower compressive strength of chromia. Because of the significantly lower coefficient of thermal expansion of the FeCrAl alloy and consequently reduced stress in the oxide, no spallling was observed even with a $\Delta T$ of 1400 K.

The second factor affecting the severity of spallation is the adherence of the scale to the alloy. If the oxide is strongly adherent, fracture will occur within the scale; if the oxide is weakly adherent, fracture will take place at the metal/oxide interface with much more serious consequences. The resultant exposure of bare metal on the next heating cycle will cause a greatly accelerated metal consumption rate. The effects of the two types of spallling are shown in figure 7 from Barrett, 1988) for stoichiometric beta nickel aluminate with and without an addition of 0.1 at % zirconium. Here cyclic oxidation test results are plotted for the alloy without zirconium, which does spall to bare metal, and the aluminate with zirconium, which spalls within the oxide. The former displays a negative weight change almost from the beginning while the latter has a positive weight change throughout the duration of the test only a modest weight loss.

The mechanism of oxide adherence or nonadherence has been the subject of a very large number of investigations. The model which seems to explain most, but perhaps not all of the observations, is that of Smeggil (1986) and Smialek (1987). Both propose that nonadherent alumina scales result from segregation of sulfur at the oxide/metal interface resulting in the disruption of the oxide/metal bond. It has been long known that small amounts of active element additions such as yttrium, zirconium and silicon were effective in promoting adherence between the oxide and the metal. Smialek proposes and appears to have convincing evidence that the function of these additions is to effectively prevent trace sulfur impurities from segregating at the metal/oxide interface. This is accomplished either by chemical combination of the active element and the sulfur, or a reduction of the amount of diffusion of sulfur to the surface of the metal.

The additions of oxide dispersions also are known to have a beneficial effect on oxide adherence. While the mechanism is not established, and it is
difficult to understand how the oxide particles prevent the sulfur from reaching the oxide/metal interface, the fact remains that alumina scales on TD-NiCrAl are adherent and do spall primarily within the scale whether yttrium is present in the alloy or not.

Because of the analogy of the accelerated attack of the spalling process to that of oxide volatility, the first attempts at modeling this attack used a COREST base (Barrett and Pressler, 1975). Equation (3) was replaced by:

\[
\frac{\Delta W}{A} = k_1^{1/2}t^{1/2} - k_2t
\]

where \( k_1 \) was assumed to be a measure of scale growth analogous to \( k_p \) and \( k_2 \) was an empirical spalling constant, analogous to \( k_v \). In practice, specific weight gain data is fit by multiple linear regression to obtain estimates of \( k_1 \) and \( k_2 \). \( k_1 \) and \( k_2 \) were then combined into one value, \( K_a \), which was shown to be an indication the degree of susceptibility to cyclic oxidation.

While this model has been successfully applied to a number of studies aimed at ranking alloys (see particularly Barrett and Lowell (1977) and subsequent reports Barrett and Lowell (1978); Barrett, Khan, and Lowell (1981); and Barrett and Lowell (1982)) it was recognized that its empirical nature severely limited its predictive utility. The use of this type of equation assumes that the amount of spall per cycle is a constant, clearly an unwarranted assumption with the possible exception of systems in which the oxide spalls completely on every cycle. Thus the concept that \( k_2 \) represents a constant spall rate, which has no physical significance, is the major flaw in this approach.

As an alternative approach, the COSP model was developed (Lowell, Smailuk, and Barrett, 1983; and Lowell et al. (1988)). It makes two basic assumptions: (1) the growth of an oxide scale during each heating cycle is determined by the amount of oxide on the material at the start of the cycle and, (2) the amount of oxide spalled upon cooling from each heating cycle is proportional to the total amount of oxide on the material at the end of the heating cycle. Inputs to the model are the growth kinetics of the scale and an expression for the dependence of spalling on scale thickness. The latter has been experimentally determined for alumina and chromia scales as shown in figure 8.

Using the data of figure 8, the COSP model has been successfully used to predict cyclic oxidation response by utilizing measurements made from isothermal tests (Lowell, Smailuk, and Barrett, 1983). An example of this application is shown in figure 9 which plots cyclic test experimental specific weight change data for TD-NiCrAl. Also plotted are predictions from the COSP model; the agreement is excellent. The major advantages of this model are twofold. By doing one isothermal measurement, one can predict accurately the cyclic oxidation behavior of an alloy for any duration of heating cycle. Equally important is that the model allows calculation of the metal consumed during thermal cycling, a determination hitherto only possible by destruction of the sample. An example of the results of this type of calculation is shown in figure 10.

\(^1\)COREST also computes the specific weight of metal consumed with time (i.e., \( W_m \)). If the \( k_2 \) value derived for COREST is quite small the \( W_m \) values derived by COREST and COSP may not differ significantly.
alloys and as well as their coatings. Figure 11 (Lowell, Deadmore, and Whittenberger, 1982) plots burner rig weight change data for several Ni-base ODS alloys which are Al₂O₃ formers similar to TD-N1CrAl in concept as well as an Fe-base ODS alloy, MA-956. For comparison, data for a MCrAlY coated super-alloy, also an alumina former is plotted. Especially good performance was obtained for the ODS FeCrAl which showed virtually no attack throughout the entire test. This result was probably due to the fact that the thermal expansion of iron base materials is significantly lower than that of their nickel base equivalents (Deadmore and Lowell 1977). This fact means that the thermal expansion mismatch stresses are considerably less and therefore spalling is substantially reduced (see above and fig. 6). Indeed, ODS FeCrAl is one of the best cyclic oxidation resistant materials measured in this type of test. At the other extreme, figure 11 shows the catastrophic weight loss for TD-N1Cr after only a few cycles.

To sum up this section, ODS alloys, which form an alumina protective scale, are excellent in cyclic oxidation as well as in high gas velocity tests. They are therefore able to be used uncoated in most types of oxidation environments at temperatures approaching 1200 °C.

ALLOYS LIMITED BY HOT CORROSION

Hot corrosion is a term usually applied to accelerated oxidation attack which occurs at temperatures where a molten alkali salt is present on the surface of a material, typically ~1173 K. This corrosion process has been delineated for chromia and alumina forming turbine alloys by Fryburg and his coworkers at NASA Lewis (Fryburg et al., 1982; and Fryburg, Kohl, and Stearns, 1984). In the operation of a gas turbine engine the molten salt results from the ingestion of airborne sodium chloride or other alkali salts into the combustor where the salts react with sulfur, which is present at low concentrations in the fuel. This reaction results in the formation of sulfates which condense on the airfoils of the turbine. The molten sulfates flux the protective oxide scale leading to catastrophic attack; in extreme cases, such as can be sometimes found in marine turbines, failure can occur in a few hours.

An excellent simulation of this attack is the burner rig test. Sodium chloride or synthetic sea salt can be injected into the combustor of the burner rig continuously as a water solution. The chloride reacts with the sulfur in the jet fuel used to form sodium sulfate which condenses on the samples after exiting the nozzle, simulating the turbine engine process. The severity of the test can be controlled by the level of salt injection and the temperature. These tests are usually run at the parts per million level of sodium in the air. The temperature most often used in these tests is 1173 K so that the samples are above the melting point of the sulfate (1156 K) but below the dew point (~1300 K at atmospheric pressure).

Hot Corrosion tests have been performed on both chromia and alumina forming ODS alloys. Long time corrosion studies comparing various ODS alloys near 1173 K in burner rig testing have been reported by Lowell and Deadmore, 1977; Benn, 1977; Huber, 1978; Sanford, 1979; Weber, 1980; Glasgow and Santoro, 1982; Huber, 1983; and Kane, 1983. A plot comparing several ODS alloys with IN-792 and MCrAlY coated MAR-M200 is shown in figure 12. Plotted are weight change data for a burner rig hot corrosion test performed at 1173 K on several ODS
alloys as compared to a nickel base superalloy reputed to have reasonably good resistance to hot corrosion (IN-792). All of the ODS alloys were alumina formers and fared quite well compared to IN-792. The two alloys with Ta additions failed (>10 mm/cm² loss) earlier than those without Ta and the ODS FeCrAl survived the entire test without any evidence of accelerated attack. These results suggest that as long as the alumina scale remains intact hot corrosion is minimized; the alloy with the least susceptibility to spallling, MA-956 (ODS FeCrAl) showed the least attack. In fact the micrographs taken at the end of the test and shown in figure 13 indicate that there was no attack at all on this alloy. It seems likely that the early failure of the alloys with Ta additions was due to a disruption of the alumina scale induced by inclusion of Ta into the oxide.

Another alloy comparison study by Huber (1978) showed that yttria dispersion strengthened IN-738 had better hot corrosion resistance than IN-738 without the yttria. Kane (1973) tested several alloys and found that MA-956 had by far the greatest resistance to hot corrosion in comparison to a wide range of ODS and conventional alloys.

The results of the tests described indicate that alumina forming ODS alloys and especially the FeCrAl's (e.g., MA-956) can be used uncoated in even the most aggressive hot corrosion environments. However, it must be pointed out that there may be conditions of extreme temperature excursions where the alumina scale might be broached allowing excessive corrosion to occur.

**COATINGS FOR ODS ALLOYS**

As pointed out earlier, there are some ODS alloys with otherwise attractive properties that cannot be used in aggressive environments without the application of an environmentally resistant coating system. TD-Ni, TD-NiCr and MA6000E all have been shown (see above) to have insufficient resistance to environmental attack. All have been the subjects of coating attempts.

The two most common types of coatings used to resist oxidation and hot corrosion are (1) diffusion coatings usually applied by a pack cementation process and (2) overlay coatings applied either by physical vapor deposition (PVD) or plasma spraying (PS). Of the two general types overlay coating are generally preferred. This is due to the fact that they result in a coating which has much less interdiffusion between the coating and the substrate. The compositions of overlay coatings that can be applied are generally more resistant to environmental attack, especially hot corrosion. The most common type of PVD or PS overlay coating compositions are the MCrAlY where M is nickel and/or cobalt and the role of the yttrium is to promote scale adhesion.

Overlay coatings have been successfully applied to nickel and cobalt base superalloys. The lives of such coatings on superalloys are limited by the rate at which aluminum in the coating is lost by diffusion into the substrate and by scale formation. Such coating systems have been successfully used for tens of thousands of hours and are bill-of-materials for high temperature components in commercial aeropropulsion turbines. However, the use of these systems on ODS alloys has been hampered by porosity formation resulting from interdiffusion between the MCrAlY coating and the ODS substrate. While the formation of porosity also occurs in coated superalloys, it is present to a considerably
thousands of hours and are bill-of-materials for high temperature components in commercial aeropulsion turbines. However, the use of these systems on ODS alloys has been hampered by porosity formation resulting from interdiffusion between the MCrAlY coating and the ODS substrate. While the formation of porosity also occurs in coated superalloys, it is present to a considerably lesser degree (Glasgow and Santoro, 1981). This effect can be tolerated until sufficient porosity forms to cause exfoliation of the coating from the substrate alloy. The microstructure shown in figure 14 demonstrates this effect which is often observed after only a few hundred hours.

Fortunately, considerable progress has been made in the application of overlay coatings on the MA6000E (Glasgow and Santoro, 1981). While these results hold out hope that ODS alloys can successfully be protected from environmental attack by the use properly designed coating systems, further development and more extensive testing are needed before one can have confidence that coatings can be produced with sufficient reliability that they can be used in commercial applications.

CONCLUDING REMARKS

Regardless of whether the environmental attack is one of oxidation or hot corrosion, isothermal or cyclic, or still air or high velocity air, some ODS alloys can find use uncoated. The alloys with greatest resistance are those which form a protective alumina scale, primarily the NiCrAl and FeCrAl alloys with the latter having the most resistance to environmental resistance attack. Indeed the resistance of ODS FeCrAl (MA-956) is equivalent or better than the best coating alloys currently available. Therefore, the use of these alloys in high temperature applications is not limited by either oxidation or hot corrosion at temperatures up to 1473 K. The same cannot be said for nonalumina forming ODS alloys such as TD-NI, TD-NICr, or MA6000E. In order for these alloys to be used under severe conditions, coatings tailored to the peculiar requirements of these alloys will have to be developed.

In sum, ODS alloys, as a class, have better environmental resistance than similar alloys without dispersion strengthening. From an environmental durability standpoint ODS have a great deal to recommend them.

REFERENCES


Lowell, C.E.; et al. (1971) Oxidation of Ni-20Cr-2ThO2 and Ni-30Cr-1.5Si at 800 °C, 1000 °C, and 1200 °C. NASA TND-6290.


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TABLE II. - PARABOLIC SCALING CONSTANT, kp FOR VARIOUS Ni OR  
Fe-Based ODS ALLOYS

[Other studies with Fe-Cr or Ni-Cr plus dispersoids (e.g., TiO2, Y2O3, etc.)  
show complex kinetics above 1273 K due to vaporization of the chromia  
and the effect of the dispersoid in the chromia. The curves are  
approximately paralinear with rate constants difficult to derive. Any kp listed for this  
type of alloy is somewhat questionable. Many investigations just show  
the range of specific weight change/time data.]

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Reference:
- Wlodek - 1962
- Jones and Westeman - 1963
- Manning, Royster, and Braski - 1963
- Pettit - 1964
- Rosenberg - 1964
- Saegusa - 1966b
- Goward - 1970
- Scruggs - 1970
- Giggins and Pettit - 1971
- Rhee and Spencer - 1971
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- Peck, Bublick, and Berkley - 1972
- Wright and Wilcox - 1974
- Barrett and Lowell - 1975
- Michels - 1976
- Michels - 1977
- Michels - 1978
- Goncal, Whittle and Stringer - 1981
- Nagai and Okebayashi - 1991
- Ramanarayanan, Raghavan, and Petkovic-Luton - 1984

FIGURE 2. - SPECIFIC WEIGHT CHANGE CALCULATED BY PARALINEAR ANALYSIS (COREST) FOR Cr2O3 FORMING ALLOY, Ni-20Cr AT 1473 K IN STATIC AIR, SLOWLY MOVING AIR AND HIGH VELOCITY AIR.

FIGURE 3. - SPECIFIC WEIGHT LOSS, $W_{gt}$ OF Cr CALCULATED BY PARALINEAR ANALYSIS (COREST) FOR AlCr2O3 FORMING ALLOY Ni-20Cr AT 1473 K IN STATIC AIR, SLOWLY MOVING AIR AND HIGH VELOCITY AIR.
FIGURE 4. - ISOTHERMAL OXIDATION OF TD-NiCr AT 1473 K IN STATIC AIR (LOWELL, ET AL., 1971) SHOWING OBSERVED DATA AND THE CALCULATED CURVE FROM A CORRECT PARALINEAR ANALYSIS. $k_p = .006$ AND $k_v = .0145$.

FIGURE 5. - METAL RECESSION AS A FUNCTION OF TEMPERATURE DURING CYCLIC OXIDATION AT 1473 K (LOWELL AND SANDERS, 1972).

FIGURE 6. - EFFECT OF COOLING TEMPERATURE ON SCALE SPALLING DURING CYCLIC OXIDATION AT ELEVATED TEMPERATURE AFTER 200 ONE HOUR CYCLES. EACH CYCLE CONSISTS OF ONE HOUR AT TEMPERATURE FOLLOWED BY SLOW COOLING. (LOWELL AND DEADMORE, 1980).
FIGURE 7. EFFECT OF 0.1 ATOMIC PER CENT ZIRCONIUM ON THE CYCLIC OXIDATION BEHAVIOR OF BETA TiAl. SAMPLES EXPOSED FOR ONE HOUR CYCLES AT 1423 K IN STATIC AIR (BARRATT, 1988).

FIGURE 8. SPALL FRACTION, q, DEPENDENCE ON THE SPECIFIC WEIGHT OF RETAINED OXIDE PRIOR TO COOLING, W, FOR ALUMINA AND CHROMIA FORMING ALLOYS DURING ELEVATED TEMPERATURE OXIDATION.

FIGURE 9. CYCLIC OXIDATION BEHAVIOR OF A Ti-6Al-4V ALLOY (UNPUBLISHED NASA LEWIS DATA) TESTED AT 1473 K FOR ONE HOUR EXPOSURE CYCLES IN STATIC AIR. OPEN SYMBOLS ARE OBSERVED DATA VALUES. THE SOLID LINE REPRESENTS A COSP MODEL COMPUTER FIT USING a = 1, b0 = .002 AND b1 = .003 (LOMELL, SMIALEK, AND BARRATT, 1983).
Figure 10. - Cogor model computer estimates of the specific weight of a consumed, $W_n$, during the cyclic oxidation of a TD-NiCrAl alloy tested at 1473 K under conditions as in Fig. 9.

Figure 11. - Average weight change (duplicate specimens) of several ODS alloys as a function of number of cycles of oxidation testing in a Mach 0.3 burner rig at 1373 K. Each cycle consisted of one hour at temperature followed by three minutes of forced air cooling (Lowell, Deadmore and Whitteringer, 1982).

Figure 12. - Average weight change (duplicate runs) of several ODS alloys as a function of cyclic hot corrosion testing in a Mach 0.3 burner rig at 1173 K. The gas stream was doped with 5 ppm synthetic sea salt. Each cycle consisted of one hour at temperature followed by three minutes of forced air cooling. The samples were washed in distilled water and dried before weighing (Lowell, Deadmore and Whitteringer, 1982).
Abstract

This paper is a review of the oxidation and hot corrosion of high temperature oxide dispersion strengthened (ODS) alloys. It classifies the environmental resistance of such alloys by oxide growth rate, oxide volatility, oxide spalling, and hot corrosion limitations. Also discussed are environmentally resistant coatings for ODS materials. The report concludes that ODS NiCrAl and FeCrAl alloys are highly oxidation and corrosion resistant and can probably be used uncoated.