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**NASA TECHNICAL
MEMORANDUM**

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OXIDATION BEHAVIOR AT 815C (1500 F) OF 33
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10 000-HOUR CYCLIC OXIDATION BEHAVIOR AT 815⁰ C
(1500⁰ F) OF 33 HIGH-TEMPERATURE ALLOYS

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Abstract

Thirty-three commercial high-temperature Fe-, Ni-, and Co-base alloys were oxidized in air at 815° C (1500° F) for ten 1000-hour cycles. Specific weight change versus time curves were derived and the 10 000-hour surface oxides were analyzed by X-ray diffraction. The alloys were ranked by a combination of appearance and metal loss estimates derived from gravimetric data.

Introduction

Power systems with operating temperatures approaching 815° C (1500° F) and above frequently require wrought alloys that can operate for long times at such temperatures. A critical requirement is that these alloys have adequate oxidation (scaling) resistance. This implies the use of Fe-, and possibly Ni-, and Co-base alloys with sufficient Cr- content to confer this resistance. The alloys used in such power systems will require thousands of hours of operating life with intermittent shut-downs to room temperature. Thus, alloy selection must consider long time cyclic oxidation behavior. However, most oxidation data heretofore available for such alloys are for isothermal (i. e., noncyclic) conditions. As a first approximation, long time (greater than 1000 hr) behavior can be predicted from the isothermal scaling constant k_p derived from shorter time (usually a few hundred hours) weight change/time data.

Intermittent power plant shut-downs, however, offer the possibility that the protective scale will tend to spall (i. e., crack and flake-off) upon cooling, increasing the rate of oxidation attack in subsequent heating cycles. Thus it is critical that for the alloys evaluated for oxidation resistance, a better estimate of their cyclic oxidation behavior be made.

The objectives of this investigation were to oxidize numerous high-temperature alloys at 815° C (1500° F) for ten 1000-hour exposure cycles in static

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air, and from the derived specific weight change versus time data X-ray diffraction analysis, and sample appearance determine if the behavior is significantly different from isothermal oxidation behavior as a result of oxide spalling. A parilinear analysis technique was then used to estimate specific metal loss at 10 000 hours (refs. 1,2). The alloys were then compared on this basis.

Materials and Procedure

Thirty-three alloys in the Fe-, Ni-, and Co-base metal systems were tested in this study. They are listed in table I along with their nominal chemical compositions. The alloys are grouped by base-metal and for the most part include typical high-temperature sheet alloys. The iron-base alloys also include a high-temperature valve steel, designated TRW-valve, and the Ni-base alloys contain a γ/γ' turbine alloy TAZ-8A. Two heater alloys were also tested - a FeCrAl, HOS-875, and a 80 Ni - 20 Cr - Si alloy, DH-243. The remaining alloys are classed as stainless steels in the Fe-base system, except for MULTIMET (N-155) which can be considered a superalloy. The remaining alloys in the Ni- and Co-base systems are also classed as superalloys.

All the alloys were tested as small coupons 12.7 mm wide and 19 to 32 mm long with a 32-mm diameter hanger hole. The thickness of each test coupon depends on the as-received sheet thickness (except for the TRW-valve alloy and TAZ-8A samples cut from bar stock) and are also listed in table I.

The test samples were measured, degreased, ultrasonically cleaned, and weighed to the nearest 0.1 mg. They were then suspended on individual quartz hooks attached to a quartz rod lattice two-tier rack. Two such lattices were used to test duplicate samples in a box furnace with the temperature at 815° C (1500° F). After 1000 hours the samples were removed, cooled to room temperature, and weighed to the nearest 0.1 mg. This procedure was repeated until ten 1000-hour cycles were completed. After final weighing, the samples were photographed, the appearance noted, and finally the sample surface was analyzed by X-ray diffraction in situ to determine the oxide(s) present on each alloy. Specific weight change versus time data was generated for each test sample from the sample weighings and the initial sample area. This gravimetric data was the primary basis for analyzing the oxidation behavior of the alloys.

As a further aid in comparing results the samples were ranked after test as to their general appearance, nature of the oxide, tendency of the scale to spall while handling, etc. This is a subjective relative ranking exclusive of the weight change data with a ranking of 1. (excellent) to 4. (poor) (ref. 4). Both the XRD and ranking criteria will be used later in evaluating the weight change data.

Results and Discussion

Analysis of the Samples

The X-ray diffraction (XRD) results of the surface analysis of each alloy after 10 000 hours are summarized in table II. The alloys are grouped as before and the phases listed are in order of intensity. It is assumed in most cases that oxide with the strongest X-ray intensity controls the oxidation reaction. As is expected for the high-Cr alloys, mostly (Fe, Ni, and Co) Cr_2O_4 spinels (a_0 from 8.30 to 8.45 μm) and Cr_2O_3 control the reaction. Five alloys (TRW valve, 18-8 S/R, HOS-875, IN-702, and TAZ-8A) with appreciable Al (>2%) tend to form Al_2O_3 and in one case, IN-702, also forms an aluminate spinel ($a_0 = 8.15 \mu\text{m}$). It is inferred for these five alloys that the alumina controls the oxidation reaction. These are the two classes of oxidation resistant scales (chromite spinel/ Cr_2O_3 an aluminate spinel/ $\alpha\text{Al}_2\text{O}_3$) discussed previously in cyclic oxidation studies at higher temperatures (refs. 1, 3). Two alloys, however (HAS-N and HAS-b) which had low Cr and no Al formed a third type of oxide which appeared to control oxidation - MoO_2 . The role of the other oxides observed on a given alloy is not clear, but usually those such as NiO indicate spalling has taken place.

Estimation of Metal Loss from Weight Change Data

The ranges of isothermal scaling attack for high-temperature oxidation resistant alloys forming mainly Cr_2O_3 or Al_2O_3 can be predicted from their parabolic scaling constants. These values, representing the upper limits for Cr_2O_3 /chromite spinel and Al_2O_3 /aluminate spinel control, were estimated from the parabolic scaling constant k_p plotted in Ref. 3. The limiting k_p values at 815° C were 1.1×10^{-3} and $4 \times 10^{-5} \left(\text{mg}/\text{cm}^2\right)^2/\text{hr}$, respectively, for Cr_2O_3 and Al_2O_3 forming alloys. As described in Ref. 1, the specific amount of metal consumed at any time, W_m in mg/cm^2 , can be calculated by multiplying $\Delta w/A$ in parabolic oxidation by the stoichiometric constant a which is 2.1667 for Cr from Cr_2O_3 and 1.1242 for Al for Al_2O_3 . At 10 000 hours the W_m limit for Cr_2O_3 formers is 7.2 mg/cm^2 with an additional correction for chromia vaporization (ref. 2). This vaporization correction only raises the W_m limit by less than 1 percent. This limiting metal consumption value is the basis of comparison for the 33 alloys. If the estimated 10 000-hour W_m values exceed 7.2 mg/cm^2 after the cyclic test, it is inferred that scale spalling has become a critical factor in oxidation behavior. This W_m estimation technique has been used previously and has shown good agreement with metallographic thickness change estimates (refs. 1, 3).

Of the 33 sets of alloys tested 29 could be fitted to a parabolic (or in one case parabolic) type of specific weight change versus time model equation by regression analysis. This equation, termed the parabolic approximation, is as follows:

$$\Delta w/A = k_1^{\frac{1}{2}} t^{\frac{1}{2}} - k_2 t \pm \sigma \quad (1)$$

where

- k_1 oxide growth constant
- k_2 oxide spalling constant
- t time, hr

For these 29 alloys the R^2 (coefficient of determination) is well over 0.90 and in most cases near 0.99. The σ value (i. e., the standard error of estimate) is quite low, in about 90 percent of the cases less than 0.10 mg/cm^2 . Figure 1 shows a set of observed $\Delta w/A$ time data along with its parabolic approximation regression curve for a typical alloy, 310 S. S. The upper limit k_p specific weight change curve for Cr_2O_3 formers is shown for comparison. For the example given $k_1 = 0.00096 \left(\text{mg/cm}^2\right)^2/\text{hr}$ and $k_2 = 0.000253 \text{ mg/cm}^2/\text{hr}$. The R^2 was 0.996 and $\sigma = \pm 0.05 \text{ mg/cm}^2$.

The above regression data was then used as input for COREST, a computer program which calculates W_m at any time (ref. 2). This program also requires the proper stoichiometric constant a be used which (as discussed above) was estimated from the XRD results. For the 310 S.S. example in Fig. 1, the 10 000-hour $\Delta w/A$ estimate was 0.57 mg/cm^2 . This yields a W_m estimate at 10 000 hours of 8.63 mg/cm^2 assuming that FeCr_2O_4 spinel ($a = 2.4977$) is the major source of the metal consumed. The specific weight change estimates regenerated by COREST fall almost exactly on the regression curve indicating the parabolic model is an excellent fit. It has been observed previously for NiCrAl alloys that the more cyclic oxidation resistant alloys tend to follow parabolic kinetics quite closely (ref. 1).

Four remaining alloys: 409 S. S., 430 S. S., 347 S. S., and DH-243 presented a more difficult analytical problem. 409 S. S., 347 S. S., and DH-243 were characterized by a specific weight loss at 1000 to 2000 hours and a increasing weight loss thereafter, while 430 S.S. showed an initial weight loss followed by a weight gain. These four alloys required special modification of the parabolic approach and were treated to give the most pessimistic W_m estimates for the four alloys.

The maximum of the measured (duplicate) W_m values are presented visually in Fig. 2 as bar graphs. These are grouped by alloy base. The upper limit for isothermal Cr_2O_3 control after 10 000 hours is shown as well. Also shown on the bar graph are the visual rankings for each alloy ranging from 1.0 - excellent to 4.0 - poor. The controlling oxide is also indicated.

Comparison of Alloys

Of the 33 alloys tested and plotted in Fig. 2, 12 exceed the upper isothermal limit of 7.2 mg/cm^2 for Cr_2O_3 /chromite spinel formation after 10 000 hours of cyclic exposure. This indicates spalling is a significant factor influencing metal consumption in these alloys.

Most of the ferritic and austenitic Fe-base alloys that depend on Cr_2O_3 /chromite spinel formation due to high Cr contents tend to exceed this upper limit or are close to it. On the other hand the three ferritic iron-base alloys TRW - valve, 18-8 S/R, and HOS-875 that depend on Al_2O_3 formation fall well below this upper limit and have thin adherent oxides with no visible traces of spalling.

The largest group of alloys tested covered a broad range of Ni-base super-alloys. From a basic 80 Ni - 20 Cr heater alloy (DH-243) to a γ/γ' turbine alloy TAZ-8A. As expected, the two alloys with low Cr and high Mo, HAS-B and HAS-N show poor cyclic oxidation resistance and the presence of MoO_2 which appears to control oxidation. In addition to these two low Cr alloys only two other Ni-base alloys, DH-243 and IN-750X exceeded the upper limit of 7.2 mg/cm^2 . The best Ni-base alloys can be considered to have good to excellent oxidation resistance with little visible effects of spalling. The two Ni-base Al_2O_3 forming alloys, IN-702 and TAZ-8A (ranked 1.5 and 1.0, respectively) are well below the 7.2 mg/cm^2 .

The four Co-base alloys tested were Cr_2O_3 /chromite spinel controlled and behaved similarly with S-57 having the lowest W_m estimate and a 1.0 ranking indicating excellent cyclic oxidation resistance.

In general the alloys with the poorest resistance tended to spall in patches to bare metal. HAS-B, 321 S.S., and 409 S.S. show this behavior the most. DH-243 spalls to bare metal and shows bright specks after cooling to room temperature. Most of the alloys ranking near 2, like 210 S.S. spall leaving small pock marks on the surface of the oxide. For alloys with excellent spall resistance no effects of spalling are usually visible and the derived k_2 values are near the $10^{-5} \text{ mg/cm}^2/\text{hr}$ range. In this range k_2 approaches the estimated static vaporization rate for Cr_2O_3 at 815° C (ref. 2).

An attempt to correlate the cyclic oxidation behavior in detail with alloy composition has not been completely successful. If it were simply a matter of high

enough Cr, DH-243, and 310 S. S. should have superior resistance. A minimum of about 16 percent seems necessary for Cr_2O_3 /chromite spinel to control cyclic oxidation. Al is decidedly beneficial and if enough is present for Al_2O_3 formation either exclusively or with Cr_2O_3 (as in HOS-875), excellent cyclic oxidation resistance seems assured.

Summary of Results

Thirty-three high-temperature Fe-, Ni-, and Co-base alloys were tested for ten 1000-hour cycles in static air at 815°C (1500°F). The cyclic oxidation behavior of these alloys was compared to calculated long-time isothermal behavior at 815°C for the general class of Cr_2O_3 and Al_2O_3 forming alloys. The following results were obtained:

(1) Direct comparison of the two types of oxidation could be made based on specific metal loss estimates at 10 000 hours W_m using parilinear analysis for most of the oxidation data.

(2) Twelve of the alloys indicated higher metal loss estimates in cyclic oxidation due to oxide spalling than the upper-limit W_m value of isothermal Cr_2O_3 scale forming alloys.

(3) To varying degrees, scale spalling in patches to bare metal between heating cycles was responsible for the high metal losses observed.

(4) Cyclic oxidation behavior could not be correlated directly with composition although about 16 percent Cr is necessary to allow Cr_2O_3 /chromite to course cyclic oxidation alloys in which Al_2O_3 /aluminate spinel was found to be controlling, showed excellent cyclic oxidation resistance.

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TABLE I. - NOMINAL ALLOY COMPOSITION AND SPECIMEN THICKNESS

Alloy	Fe	Ni	Co	Cr	Al	Si	C	Mn	Ti	Mo	W	Other	Thickness, mm
409 S. S.	Bal.			11			0.045		0.50				1.49
410 S. S.				11.5 - 13.5		1 Max.	0.15 Max.	1.0 Max.					1.61
430 S. S.				14 - 18		1 Max.	0.12 Max.	1.0 Max.					1.60
TRW-VALVE					32	0.35	0.04	0.1		0.1	0.5		2.44
18-8 S/R		0.1		18	2.0	1 Max.	0.040	0.40	0.40				1.71
HOS-875		0.25		22.5	5.5	0.5	0.05						1.30
304 S. S.		8 - 12		18 - 20		1 Max.	0.08 Max.	2.0 Max.					1.53
310 S. S.		19 - 22		24 - 26		1.5 Max.	0.25 Max.	2.0 Max.					1.62
316 S. S.		10 - 14		16 - 18		1.0 Max.	0.08 Max.	2.0 Max.		2 - 3			1.29
321 S. S.		9 - 12		17 - 19		1.0 Max.	0.08 Max.	2.0 Max.	5xC Min.				1.50
347 S. S.		9 - 13		17 - 19		1.0 Max.	0.08 Max.	2.0 Max.				Cb - Ta, 10xC Min.	1.48
MULTIMET		20	20	21		0.5	0.15	1.5		3	2.5	Cb + Ta - 1.0	2.05
INCOLOY-800		32		20.5		0.35	0.04	0.75					3.10
IN-600	7.2	Bal.		15.8		0.20	0.04	0.20					1.61
IN-601	14.1			23	1.35	0.25	0.5					Cu 0.25	1.30
IN-702	0.35			15.6	3.4	0.20	0.04	0.05	0.7				2.40
IN-617			12.5	22	1		0.07			9			3.05
IN-671					48		0.05		0.35				3.16
IN-750X	6.75			15	0.08		0.04	0.70	2.5			Cb 0.85, Cu 0.30 Max.	1.68
IN-706			1 Max.	16	0.4 Max.	0.35 Max.	0.06 Max.	0.35 Max.	1.75			Cb 2.9 Max., B 0.006 Max.	1.57
HAS-B	5.0		2.5 Max.	1.0 Max.		1.0 Max.	0.05 Max.	1.0 Max.		28		V 0.40 Max.	1.50
HAS-N	5.0 Max.		0.2 Max.	7.0		0.5 Max.	0.06	0.8 Max.		16.5		B 0.01 Max.	1.61
HAS-S	1			15.5	0.2	0.2	0.02 Max.	0.2		15.5		B 0.009, La 0.02	.53
HAS-C-276	5.5		2.5 Max.	15.5		0.02 Max.	0.02 Max.	1.0 Max.		16	3.75	V 0.35 Max.	1.97
HAS-X	18.5		1.5	22		1.0 Max.	0.10	1.0 Max.		9	0.6		2.54
NIMONIC-75	0.50			20.5	0.20	0.45	0.10	0.45	0.35				1.31
RENE-41			11	19	1.5		0.09		3.1	10			.77
DIH-243	1			20		1.5	0.03		2				1.68
TAZ-8A				6	6		0.125				4	B 0.04, Cb 2.5, Zr 1, Ta 8	2.50
I-605		10	Bal.	20		0.5	0.10	1.5			15		1.35
HA-188	1.5	22		22			0.08				14	La 0.08	1.60
H-150	18 - 20	3 Max.		28		0.75	0.05 - 0.12	0.5					1.70
S-57		10		25	3							Ta 5 Y. 5	1.70

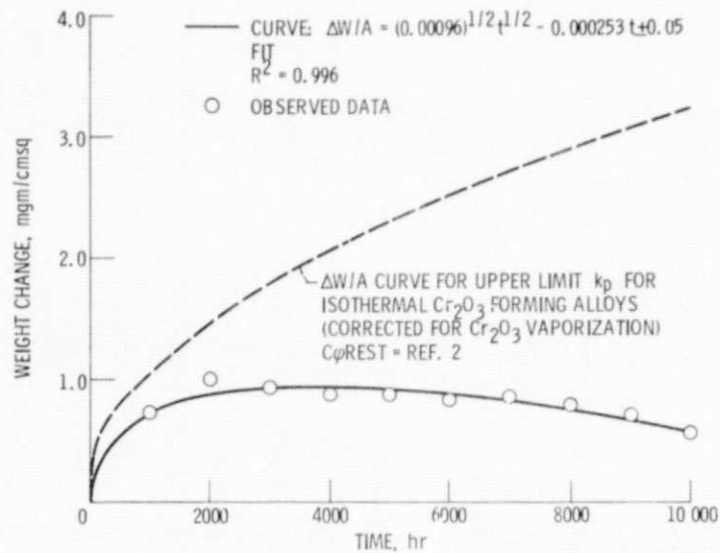


Figure 1. - Comparison of the regression fit of the parabolic model, $\Delta W/A = (k)^{1/2}t^{1/2} - k_2t$, to observed data for ten 1000 hour cycles in still air at 815°C (1500°F) for 310 stainless steel.

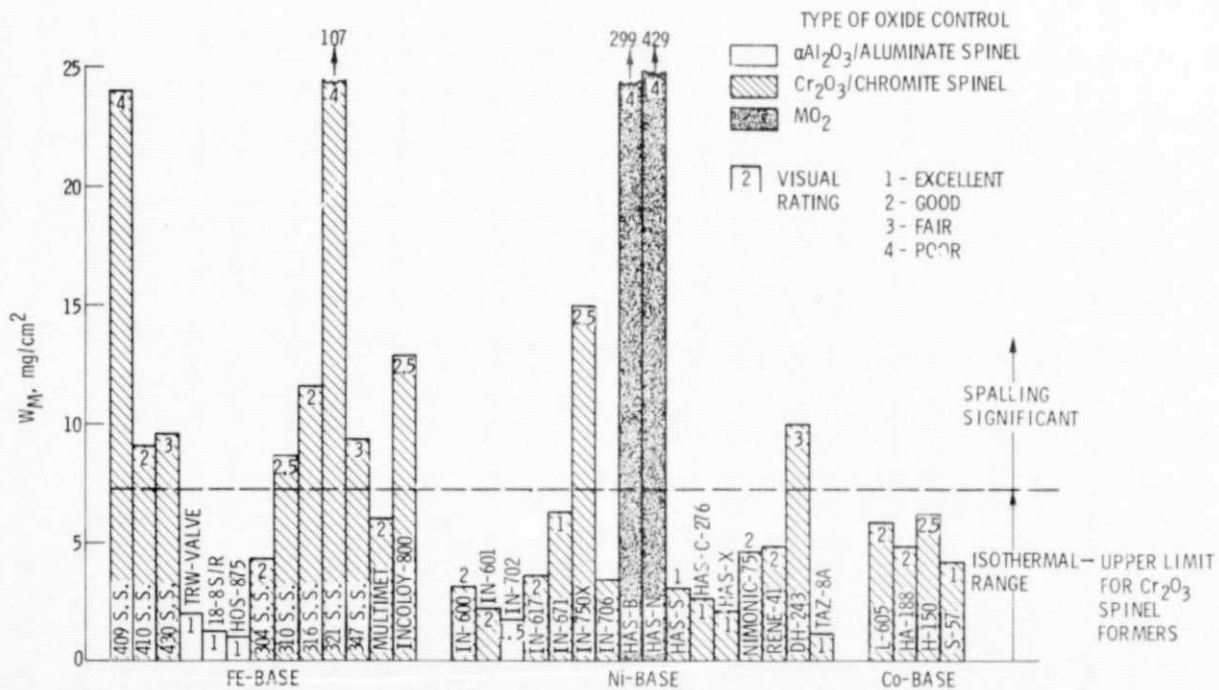


Figure 2. - Specific metal loss estimates, W_M , for 10 - 1000 hour exposures (10 000 hr total) at 815°C (1500°F) in static air for 33 high temperature alloys compared to the W_M limiting value for Cr_2O_3 /chromite forming alloys after 10 000 hours in isothermal oxidation.