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High Temperature Cyclic Oxidation Furnace Testing at NASA Lewis Research Center

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HIGH TEMPERATURE CYCLIC OXIDATION FURNACE TESTING
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ABSTRACT

A standardized method of testing the cyclic oxidation resistance of various alloys in static air up to 1200°C has been developed and routinely used at the NASA Lewis Research Center. Test samples are automatically raised and lowered into a resistance wound furnace for a series of fixed-interval heating and cooling cycles. Spall catchers collect the accumulated spall from each sample. The samples are weighed intermittently to generate specific weight change with time data. At various test times the samples and the accumulated spall are analyzed by X-ray diffraction. A computer program is used to print out the specific weight change versus time data and the X-ray data in tabular form and to plot the specific weight change versus time data in a publishable format. The data are also organized and indexed. So far several hundred Fe-, Ni-, and Co-base alloys have been tested using this basic procedure and will form the basis of a series of cyclic oxidation handbooks to be published by NASA. Such specific weight change/time data have been used to estimate the oxidative metal consumption by several computer modeling techniques both to rank alloys and to estimate life.

INTRODUCTION

The bulk of the high-temperature oxidation literature is concerned with isothermal testing. This has lead to a large body of both oxide growth and transport property data. However, the vast majority of applications for high temperature materials are cyclic. It has been shown [1], that during cyclic oxidation, the degree of spalling is as important as the growth rate of the oxide in the determination of total metal consumption. Because Lewis is NASA's aircraft engine and power technology laboratory, oxidation studies at the Lewis Research Center have focused on cyclic furnace and burner rig testing of gas turbine alloys. The primary goal of this oxidation research is to establish the mechanisms of material degradation so as to formulate accurate cyclic oxidation models for predicting hot component life [2]. In addition some convenient method of ranking or comparing alloys in cyclic testing is needed.

The purpose of this paper is to describe the cyclic oxidation test procedures used at Lewis, the method of evaluation, and the scope of the alloys and conditions tested and to present an example of how a given test alloy is evaluated.

As these studies have proceeded, standard testing procedures were developed [1-6], and a large body of cyclic oxidation data have been collected for a great many alloys. While some of these data have been reported as the results of specific investigations, the existing data are being collected and organized into a series of oxidation handbooks to be published shortly.
TEST PROCEDURES

The cyclic furnace oxidation test facility at NASA-Lewis consists of three types of furnaces as summarized in Table 1: (1) a FeCrAl alloy ribbon wound resistance furnace, (2) a silicon carbide rod furnace, and (3) a muffle furnace. Types 1 and 2 are identical mechanically and automatically cycle the samples in the same manner. They differ only in their upper temperature limits and in the symmetry of the heating elements. The muffle furnace (Type 3) was used to manually test a large number of samples at lower temperatures for much longer cycle times (e.g., 1000 hr).

Most of the test samples were in the form of a standard machined coupon 1.0 to 1.27 cm wide by 2.29 cm long with a standard thickness of 0.22 mm. A 0.32-mm-diameter hanger hole was drilled in the sample 0.32 mm from the top. In certain cases other size samples were used. These included 2.54-cm-square by 0.64-cm thick samples [3], small 0.32-mm-thick teardrop samples cut from Mach 0.3 burner rig bars [6], and even 7.62-cm long, 0.64-cm-diameter tensile bars. If only sheet samples were available in thicknesses of 0.32 cm or less, the coupon thickness kept was the same as the received sheet. After the samples were machined to size they were scribed for identification, measured by micrometer, ultrasonically cleaned in tri-chlorethylene, rinsed in distilled water, dried, and then weighed.

In the automatic cyclic rigs of Types 1 and 2 (Fig. 1) individual samples, usually in the form of small coupons, are suspended from Pt-13 percent-Rh hanger wires. These are lowered into the center of the hot zone of the furnace and raised out again by a pneumatic piston controlled by reset timers. As the samples leave the furnace, they are stopped 12.7 cm above the top of the furnace inside tubular shields. A piston-driven plate containing small cups slides under the samples and each cup catches the spall from the individual samples. The individual tubular shields and cups reduce cross-spall contamination to a minimum. This type rig is shown schematically in Fig. 1 for the ribbon wound resistance furnace. The thickest samples cool to an ambient temperature of 66°C in about 12 min in their position above the furnace. The samples are usually held out of the furnace for a minimum of 20 min by the cooling cycle timer before the spall catcher retracts and the samples are returned to the furnace as the control switches to the heating cycle timer. The cycles are automatically totaled both by a mechanical and electrical counter. An electronic reset cycle counter is used with the two cycle timers to hold the samples out of the furnace after any given number of cycles so they can be weighed or examined. The test temperature is monitored by a vertically mounted Pt Pt-13 percent Rh thermocouple probe adjacent to a hanging coupon in one of the six tubes.

As the system was originally designed, it was thought that all of the spall could be collected and be used with the sample weight change in mass balance calculations to directly estimate metal loss [4]. Some of the spall, however, particularly the fine particle size oxide (usually associated with samples with excellent cyclic oxidation resistance) is always lost as finely suspended dust in the air which is circulated by convection currents over the furnaces. On the other hand, samples with poor cyclic oxidation resistance usually spall massively as large flakes or particles of oxide(s). In some cases this can lead to cross-spall into adjacent spall cups [4]. For this reason, in the proposed handbook presentation the collected spall will be used for identification purposes rather than a quantitative measure of weight loss due to spalling, as was done in some of the earlier reports from this laboratory [3,4]. In the roughly 5 percent of the tests where cross-spall was detected, the X-ray spall data were corrected.
Over 90 percent of the automatic cyclic runs involved a series of 1-hr exposures in the furnace followed by a minimum of 20 min out of furnace, while the samples cooled to ambient temperature, here, approximately 66° C. The standard weighing cycle(s) were 1, 15, 30, 45, 60, 75, 90, 100, 115, 130, 145, 160, 175, 190, and 200 hr. If the tests were continued they were weighed every 50 hr out to 1000 hr and every 100 hr out to 3000 hr, which was the longest test time at this cycle frequency. Other exposure cycles used on occasion for special tests were 0.05, 1, 10, 20, and 50 hr. Generally, if the exposure times were less than 1 hr, the cooling cycle times were usually reduced to times approaching the heating times so as not to excessively prolong the test.

The samples were weighed to the nearest 0.1 mg during each weighing cycle. The specific-weight-change-with-time data were then computed from the original sample weight and area based on the original sample measurements. A comparison of the specific-weight-change data of replicated samples indicated the variability of the tests. As was discussed [4], the within run and between run variation for a wide variety of alloys was under 10 percent.

The test rigs were designed fail-safe so that if for any reason the furnace, control, thermocouple, air supply, or cycle devices failed, the samples would be protected by automatic removal from the furnace if they were in the exposure part of the cycle or held out of the furnace if they were in the cooling mode. The test could not be continued until the conditions were corrected. This is especially critical when test times of more than 2000 hr have been invested in a given set of samples.

Generally speaking, the FeCrAl ribbon wound furnaces had lifetimes of between 5000 and 10 000 hr, operating steadily at temperatures of 1100° and 1200° C. The silicon carbide furnace life was on the order of 3000 to 4000 hr at temperatures above 1200° C. The 99-percent Al2O3 ceramic liner tubes and 17-gage thermocouple lasted for about 10 000 hr.

The box muffle furnaces were used in cyclic oxidation testing for long-time, low-cycle-frequency testing. Up to 144 coupon samples suspended individually in a quartz lattice (see Fig. 2) could be tested. The samples were exposed for ten, 1000-hr cycles. At the end of each 1000-hr cycle, the lattice was removed manually, and the samples were cooled to room temperature. The coupons were weighed and then remounted on the lattice and reloaded into the furnace for the next cycle. In this type of test the individual sample spall could not be collected. The specific weight change data as a function of time were computed in the same manner as the shorter automatic cyclic data. Two box muffle furnaces were used. One was held at 816° C (1500° F), and the other at 982° C (1800° F). These furnaces had extremely long, stable operating lives (greater than 24 000 hr) at these test temperatures since they were well below the 1200° C operating limit for this model furnace. Reference 5 gives an example of a cyclic oxidation study run in this type of test rig.

**X-RAY DIFFRACTION**

At the completion of each oxidation test and after the samples were removed and then weighed, the surface oxide scale on each alloy was analyzed by an X-ray diffractometer while a powder pattern was run with a Guinier deWolfe camera on the sample spall. In addition in selected long-time tests, the sample(s) and the spall were analyzed at selected intermediate times. In both types of analyses the observed phases were listed in order of dif-
fraction pattern intensities. The observed alloy phases were also listed when detected either as underlying a thin oxide or exposed due to scale spalling. The various phases formed in cyclic oxidation of these types of alloys are listed in Table II.

FORMA: AND DISCUSSION

This large body of data was handled by means of a computer program termed "HANDBOOK" which was used to process and organize all of the gravimetric and X-ray data. It also plotted the data graphically and listed them in a standard format as part of a 16-mm film or "ZETA" plotter subroutine package. In addition the program was used to store, organize, and index the output data.

The observed weight values were transferred to IBM cards along with the appropriate run number, alloy designation, test temperature, initial sample thickness, initial sample weight, and length of cycle. The weights and their corresponding times were also input. All the information was keyed to the run number and position of the sample in the cyclic furnace during a run. Here specific sample weight change data in mg/cm² are plotted and listed with time in hours. In addition the output is stored for indexing and classification. This graphics package can also, if needed, plot up to nine sets of data on a single figure. At the end of each plot the X-ray diffraction data are summarized also. A typical sample run output from "HANDBOOK" is shown in Fig. 3.

EVALUATION OF CYCLIC OXIDATION SPECIFIC WEIGHT CHANGE DATA

Cyclic oxidation data are obtained at room temperature by weighing between heating cycles and at the end of the test. The measured specific weight change (ΔW/A) may be positive or negative and is the vector sum of weight gained from oxygen uptake due to oxide formation and metal weight loss due to oxide spalling or vaporization. However, the desired quantity to be estimated is total specific metal consumption defined as Wₘ. While Wₘ is related to ΔW/A and the specific weight of the retained oxide, Wᵣ, by

\[ \Delta W/A = W_r - W_m \]  

Wᵣ is in general not known and Wₘ must be determined by mathematical analysis or by metal thickness measurement. The latter process is time consuming, expensive, destructive of the sample, and often not accurate enough [4,9]. Therefore, mathematical inference from 1 is the way primarily used by this laboratory for evaluation of Wₘ, although some selected thickness change measurements were made primarily to verify the validity of the gravimetric approach. It should be noted that, if much spalling has occurred, Wᵣ becomes << Wₘ and ΔW/A = − Wₘ. For example, early Mach 1.0 burner rig studies at Lewis used the final ΔW/A values to compare test alloys using the implicit relationship Wₘ = − ΔW/A [9,10].

In general, all cyclic oxidation processes pass through several stages, although the time required for each stage is a function of the alloy composition, temperature, and cycle severity (i.e., frequency).

In high temperature Fe-, Ni-, and Co-base alloys there are two basic types of alloys: One, usually containing 12 weight percent Cr or more, protects by forming mainly Cr₂O₃ (chromia) as the protective oxide and
fails as more and more chromite spinel and base metal oxide such as Fe₂O₃, NiO, and CoO are formed. This system is complicated by the Cr₂O₃ tending to vaporize off as CrO₃ above 1000°C with longer times and high exposure gas velocities such as those used in Mach 0.3 to Mach 1.0 burner rigs. For this reason more emphasis at Lewis in recent years has focused on alloys of the other basic type: those alloys with Al contents greater than about 4 weight percent with Cr levels greater than about 5 weight percent. These alloys form protective scales or mainly nonvolatile Al₂O₃ at temperatures up to 1200°C. This scale tend to fail less drastically, particularly in Ni- and Fe-Base alloys. In addition, small, deliberately added or "tramp" additions of such reactive elements as Zr, Y, and Si tend to increase the adherence of both types of oxides. Those elements inhibit drastic, or cracking-to-bare-metal, spallirg of the protective scales when cooled repeatedly in a cyclic test. For this reason most of the recent and future alloy oxidation work at LeRC involves basic alumina forming alloys and coatings with reactive element additions.

In cyclic oxidation testing during the early stage of oxidation, most of the weight change is due to oxide formation so a ΔW/A versus time plot is nearly parabolic. As the weight gain per unit time decreases, the amount of oxide loss from spalling becomes a major factor, and the slope of the ΔW/A versus time curve falls to zero and then becomes negative after a maximum ΔW/A value is achieved. At longer times the net weight gained during heating approaches the loss due to spalling, and the curve becomes nearly linear with a nearly constant negative slope as Wₚ approaches an asymptotic thickness. This assumes that the oxidation kinetics are not altered by subscale alloy depletion or other mechanistic changes. If such changes do occur, they may either accelerate or decelerate these processes and change the basic ΔW/A versus time curve. A typical curve with no mechanism change is shown as Fig. 4(b) and is termed paralinear. It can be compared with a parabolic curve 4(a) plotted directly above it. Comparable Wₚ plots are also shown. A large number of cyclic test run data have been fitted, with success, to the paralinear kinetic model [4, 11-15]. In such a treatment the specific weight change is expressed as

$$\Delta W/A = k_1^{1/2} t^{1/2} - k_2 t$$

(2)

where k₁ and k₂ are scale growth and scale loss constants, respectively, and t = time. The relative values of k₁ and k₂ determine the times to reach maximum value of ΔW/A, the crossover time (i.e., the time when the ΔW/A values drop to zero), and a final, constant negative slope. The value for k₁ is a function of temperature and alloy composition, while k₂ is a function of temperature, cycle severity, and the alloy composition, especially the small concentrations of Y, Zr, etc., which increase oxide adhesion. Mechanism changes will, in general, affect both k₁ and k₂.

The experimental ΔW/A versus time data are fitted to Eq. (2) by multiple linear regression and if the fit is "good" (i.e., the coefficient of determination, R², is 0.90 or greater), an attack parameter, Kₐ, is assigned to the data. The attack parameter has been defined as

$$K_a = (k_1^{1/2} + 10 k_2)$$

(3)
This parameter has been used in several studies at this laboratory to compare or rank alloys in terms of oxidation resistance [11, 13-16]. The fitted curve supplies input parameters to a computer program termed COREST derived from a set of defining differential equations [12]. If the controlling oxide scale is known, all three parameters from Eq. (1) can be generated as a function of time. Then $W_m$ is the ultimate corrosion or oxidation parameter since it is the total metal consumed in the total oxidation process. Also for the same type of scale former, there is a direct relationship between $K_{ax}$ and $W_m$ derived at a given test time [16].

This whole estimation procedure depends on how well the oxidation process is approximated by Eq. (2). In actual testing, deviations from Eq. (2) may occur due to mechanism changes. An attempt is being made at Lewis to actually simulate on a computer each oxidation cycle of parabolic scale growth at temperature followed by spalling on cooling. This program called COSP includes COREST as a special approximating case [17]. Figure 5 shows these various estimation techniques for a coating type alloy Ni-14Cr-14Al-0.12Zr tested for 3000 1 hr exposure cycles at 1100°C in static air. The sample was air cooled for a minimum of 20 min between cycles. The observed $\Delta W/A$ data values are shown as circles with the dashed line showing the fit to Eq. (2) as:

$$\Delta W/A = 0.15500t^{1/2} - 0.004108t^{0.28}$$

with an $R^2 = 0.970$. This gives a $K_{ax}$ of 0.19607 and a crossover time of 1424 hr from Eq. (2) by setting $\Delta W/A = 0$ and solving for $t$. Since X-ray diffraction analysis indicates that Al$_2$O$_3$ is the major oxide, at least up to about 2000 cycles, its stoichiometric constant can be used as input to COREST along with the calculated final and cross-over $\Delta W/A$, time data sets. The COREST generated values, shown as a solid line on Fig. 5, fall almost on the dashed curve on the plot. The corresponding $W_m$, time estimates are shown on Fig. 6. Note these always increase monotonically with time. COSP can use the identical input on a discrete cycle model and generate the identical $\Delta W/A$ and $W_m$ estimates.

It has been shown, however, that the spalling rate is not necessarily constant from cycle to cycle as the parabolic model implies, but rather increases as the scale thickness increase (i.e., the spalling rate is a percent function of the scale thickness [17]). If the isothermal scaling constant for this alloy [18] is used as input for COSP along with the spalling rate of 0.0138 percent the resultant $\Delta W/A$ versus time and $W_m$ versus time values can also be plotted on Figs. 5 and 6.

The $W_m$ versus time plots in Fig. 6 are the key parameters in estimating oxidation attack. The COREST estimate is more pessimistic than the COSP model $W_m = 14.23 \text{ mg/cm}^2$ versus 9.29 $\text{ mg/cm}^2$, respectively, at 3000 hr. Note in Fig. 5 that all three methods give a good fit to the data out to about 2200 hr. Then the experimental $\Delta W/A$ values breaks gradually downward. This implies a change in mechanism due to the Al level at the metal/oxide interface not being able to sustain Al$_2$O$_3$ formation (i.e., Al depletion).

The critical problem in cyclic oxidation research is attempting to predict at what time this type of break occurs, since it can be defined as incipient failure. This requires a tie-in with bulk diffusion data of Al and other elements in this type of alloy. This diffusion-cyclic oxidation linkage is currently being investigated at Lewis in conjunction with a NASA Grant with Michigan Technological University. It would be possible to use
COSP and a change the scale control of 2000 hr from Al2O3 NiAl2O4. This change would drive the calculated \( \Delta W/A \) values closer to later observed values (Fig. 5). It would also increase the corresponding \( W_m \) values after 2000 hr, as NiAl2O4 is less protective than Al2O3. Although this time this approach is still on a trial and error basis, it looks quite promising for this and similar alloy systems in defining the useful life of Al2O3 forming, oxidation-resistant alloys.

CONCLUDING REMARKS

In summary, the current and future cyclic oxidation work at NASA Lewis Research Center will concentrate on

1. Organizing and publishing the Lewis cyclic test data as a series of oxidation handbooks,
2. Methods of ranking and understanding the oxidation resistance of alumina forming alloys with spall inhibiting additives, and
3. In modeling the cyclic oxidation process in conjunction with aluminum diffusion data to define and predict useful oxidation life.

REFERENCES


### TABLE I - CHARACTERISTICS OF THREE TYPES OF FURNACE USED FOR HIGH-TEMPERATURE CYCLIC OXIDATION STUDIES AT NASA LEWIS RESEARCH CENTER

<table>
<thead>
<tr>
<th>Description</th>
<th>Silicon carbide rod</th>
<th>Box muffle</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 in. ID x 34 in. OD x 24 in. long shell (see fig. 1). 6 to 25 in. long, 99-percent Al₂O₃, 1-3/8 in. ID open end ceramic tubes, vertically mounted on 5 in. ID of furnace. Bottom of tubes closed (static air).</td>
<td>5 in. ID x 34 in. x 36 in. shell. 6 to 39 in. long, 99-percent Al₂O₃, 1-3/8 in. ID open end ceramic tubes, vertically mounted on 5 in. ID of furnace. Bottom of tubes closed (static air).</td>
<td>Blue M box type. Hot zone dimensions 8-1/2 in. wide 12 in. deep, 6 in high. Firebrick chamber walls.</td>
</tr>
</tbody>
</table>

#### Heating elements

| Kanthal A-1 (Fe-22Cr-5.5A-0.5Co) ribbon; open wound; no shunt taps. | 12 1-1/8 in. diam silicon carbide rods. 3 Tier high, 4 in. apart, 4 per level horizontally mounted. | Blue M "Modella" - rated to 1093° C continuous operation. |

#### Test temperature

| To 1200° C, 4 in. test zone ±2° C. 5000- to 10 000-hr avg. furnace life. | To 1500° C, 4 in. test zone ±4° C. 3000- to 4000-hr avg. furnace life. | To 1000° C, hold set point ±1.5 percent. >24 000 hr avg. furnace life. |

#### Test positions per furnace

| 6, Pt-13-percent-Rh hanger wire. | 6, Pt-13-percent-Rh hanger wire. | 144 coupon quartz lattice modules. |

#### Number of furnaces

| 10 | 2 | 2 |
TABLE II. - OBSERVED PHASES FORMED IN THE CYCLIC OXIDATION OF Fe-, Ni-, and Co-BASE ALLOYS AT HIGH TEMPERATURES AS DETERMINED BY X-RAY DIFFRACTION

<table>
<thead>
<tr>
<th>Oxide phase</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr$_2$O$_3$</td>
<td>Protective scales</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>Protective scales</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td></td>
</tr>
<tr>
<td>NiO</td>
<td></td>
</tr>
<tr>
<td>CoO</td>
<td></td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td></td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td></td>
</tr>
<tr>
<td>SiO$_2$</td>
<td></td>
</tr>
<tr>
<td>ThO$_2$</td>
<td></td>
</tr>
<tr>
<td>HfO$_2$</td>
<td></td>
</tr>
<tr>
<td>Ni(W,Mo)$_2$O$_4$</td>
<td></td>
</tr>
<tr>
<td>Mn$_2$O$_3$</td>
<td></td>
</tr>
<tr>
<td>NiTi$_2$O$_3$</td>
<td></td>
</tr>
<tr>
<td>Ni(W,Mo)$_2$O$_4$</td>
<td></td>
</tr>
<tr>
<td>3Y$_2$O$_3$-5Al$_2$O$_3$</td>
<td></td>
</tr>
<tr>
<td>3Y$_2$O$_3$-5Al$_2$O$_3$</td>
<td></td>
</tr>
<tr>
<td>CoTi$_2$O$_3$</td>
<td></td>
</tr>
<tr>
<td>MoO$_2$</td>
<td></td>
</tr>
<tr>
<td>CoMoO$_4$</td>
<td></td>
</tr>
<tr>
<td>Al$_2$TiO$_5$</td>
<td></td>
</tr>
<tr>
<td>CoWO$_4$</td>
<td></td>
</tr>
<tr>
<td>Oxide spinels</td>
<td>MeM$_2$O$_4$ (Cubic)</td>
</tr>
<tr>
<td></td>
<td>Where Me is Fe, Ni, and/or Co and M is Fe, Cr, Al, and/or Mn</td>
</tr>
<tr>
<td>Lattice parameter, $a_0$</td>
<td>8.05, 8.10, 8.15Å - Aluminate spinels</td>
</tr>
<tr>
<td></td>
<td>8.20 to 8.40Å - Chromite spinels</td>
</tr>
<tr>
<td></td>
<td>8.45 to 8.50Å - Manganate spinels</td>
</tr>
<tr>
<td>Rutile/tri-rutile</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Lattice spacing, $d$, on (110)</td>
<td>3.25 to 3.27Å TiO$_2$</td>
</tr>
<tr>
<td></td>
<td>3.27 to 3.34Å Cr</td>
</tr>
<tr>
<td></td>
<td>(refractory metal)$_2$O$_4$</td>
</tr>
<tr>
<td></td>
<td>3.34 to 3.36Å Fe, Co, Ni (refractory metal)$_2$O$_2$</td>
</tr>
<tr>
<td></td>
<td>Where refractory metal = Ta, Nb, W, Mo</td>
</tr>
</tbody>
</table>
Figure 1. - Schematic representation of high-temperature test apparatus for measuring cyclic oxidation resistance of experimental alloys at NASA Lewis Research Center.

Figure 2. - Quartz lattice module for long cycle time oxidation testing in box muffle furnaces.
Figure 3. A typical page of cyclic oxidation output for a test alloy to be published in a series of cyclic oxidation handbooks from NASA Lewis Research Center.

Figure 4. A comparison of oxidation kinetics, isothermal vs. cyclic exposure in static air for a representative Al$_2$O$_3$ forming alloy for specific sample weight charge, $\Delta W/A$ and specific metal consumed, $W_m$. Based on the mass balance relationship: $\Delta W/A = W_f - W_m$ where $W_f$ is the specific weight of the retained oxide.
Figure 5. - Specific weight change, $\Delta W/A$ vs. time for 3000-one hour cycles at 1100°C in static air for a Ni-14 w/o Cr-14 w/o Al-0.12 w/o Zr alloy.

Figure 6. - Specific weight of metal consumed, $W_m$ vs. time for 3000-one hour cycles at 1100°C with Al$_2$O$_3$ scale control in static air for a Ni-14 w/o Cr-14 w/o Al-0.12 w/o Zr alloy in COSP model 2: $W_m = Q_s W_0^{x1}$ (Ref. 17), where $W_s$ is the specific weight of the oxide spalled and $W_0$ the specific weight of the retained oxide before spalling in a given cycle.