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# OBSERVATIONS ON THE CYCLIC AND ISOTHERMAL OXIDATION OF WI-52 AND IN-100

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16. Abstract

Alloys WI-52 and IN-100 were oxidized isothermally and cyclically at 1900° and 2000° F (1038° and 1093° C) in static furnace air. Exposure cycles of 1, 2, 5, 20, and 170 hr for total oxidation times of up to 340 hr were used. Weight and thickness change measurements were used to evaluate the oxidation behavior. Spalled scale compositions were determined for WI-52. Both alloys spall in cyclic oxidation and are sensitive to cycle frequency. Alloy WI-52 spalls much more and exhibits much greater metal consumption with increased cycle frequency than does IN-100.

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# OBSERVATIONS ON THE CYCLIC AND ISOTHERMAL OXIDATION OF WI-52 AND IN-100

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## SUMMARY

Isothermal and cyclic oxidation tests on WI-52 and IN-100 were performed under static furnace conditions at 1900° and 2000° F (1038° and 1093° C). Tests included exposure cycles of 1, 2, 5, 20, and 170 hours for total oxidation times of up to 340 hours. Oxidation behavior was evaluated primarily by weight and thickness change measurements. Supplemental metallographic and X-ray diffraction examinations were made on cycled specimens. The composition of the spalled WI-52 scales was also quantitatively determined by X-ray diffraction.

For the first few cycles WI-52 gained weight up to a maximum of 1 to 2 milligrams per square centimeter with little spallation. A few cycles later spallation increased and a net weight loss was soon evident. Shortly thereafter a linear loss rate was established. The time to reach the linear rate loss region was decreased by increasing the cycle frequency or temperature. The rate of weight loss in the linear region was also increased by increasing the cycle frequency or temperature. Furthermore, increased cycle frequency increased the metal thickness loss.

Alloy IN-100 gained weight in cyclic oxidation. The weight gain, however, was less than that gained in isothermal oxidation due to slight spallation of surface oxides. At 2000° F (1093° C) a maximum in the gain curve was followed by a slight decrease. However, a net weight loss was not achieved even after 140 hours of testing. The time to reach this maximum gain is decreased by increasing the cycle frequency or temperature. Increased cycle frequency increases the metal thickness loss of IN-100. However, IN-100 is much more oxidation resistant than WI-52 and less sensitive to thermal cycling.

## INTRODUCTION

Nickel and cobalt superalloys are widely used as turbine blade and stator vane materials for aircraft gas turbine engines. To evaluate the oxidation resistance of these materials under conditions approaching engine service, Mach 1 combustion gas tests have been conducted in a burner rig from 1800° to 2000° F (982° to 1093° C) (ref. 1). That study showed that the frequency of thermal cycling and the cooling rate exert a significant influence on the oxidation rate of the alloys tested. For example, with 1-hour exposures at 2000° F (1093° C) followed by air blast cooling (below 200° F (93° C) in 1 min) for a total of 100 hours, the weight loss of the cobalt alloy WI-52 was about 2.5 times greater than when 10-hour exposures were followed by free air cooling (below 200° F (93° C) in 5 min). Under similar conditions the weight loss of the nickel alloy IN-100 was 1.6 times greater under the more severe thermal cycling. The dynamic conditions used in reference 1 are necessary for studying gas turbine materials under simulated engine conditions. However, in order to gain more insight into the oxidation of these alloys, it is sometimes necessary to conduct simpler laboratory tests.

This report covers the results of such an effort. The effects of time, temperature, and cycle frequency were determined under static furnace conditions for the superalloys WI-52 (cobalt base) and IN-100 (nickel base). Weight and thickness change measurements were primarily used to follow the alloy's oxidation behavior at 1900° and 2000° F (1038° and 1093° C). These were supplemented with X-ray diffraction analyses of the residual surface scales and the spalled oxides. Also, limited metallographic studies were made.

## MATERIALS AND TEST PROCEDURES

### Specimens

Sheet specimens of WI-52 and IN-100 were vacuum cast by a commercial vendor to approximately 1 by 2 by 0.11 inch (2.5 by 5.0 by 0.27 cm) dimensions. All IN-100 specimens were heat treated at 1550° F (843°C) for 12 hours and air cooled. The WI-52 specimens received no heat treatment. The chemical compositions of the resulting castings are presented in table I along with the nominal composition range for each alloy. The values for both alloys fall within the nominal casting specifications. Typical microstructures of the as-received alloys are illustrated in figure 1.

The sheet specimens were cut in half to make two coupons for testing. Each coupon was 1 by 1 by 0.11 inch (2.5 by 2.5 by 0.27 cm). These coupons were surface ground to provide plane and parallel surfaces for more accurate thickness measurements. The surfaces of most specimens were then hand lapped under water on 600 grit emery paper to a final thickness of 0.10 inch (0.25 cm). This resulted in a surface roughness of 20 to 30 microinches ($50$ to $76\times10^{-6}$ cm). Several specimens of WI-52 were machine polished on a velvet wheel charged with 1/2 micron diamond paste. This gave a surface roughness of 2 to 3 microinches (5 to $7.5 \times 10^{-6}$ cm). A 0.050-inch- (0.15-cm-) diameter hole was electric discharge machined near one end of each specimen.

## Testing

During the course of preliminary testing, which involved resting the specimens on high purity alumina boats, it was found that IN-100 reacted extensively with the boat at the points of contact, while WI-52 showed no reaction. Also it was noticed that on cooling the spallation of the oxides on WI-52 continued for some time after cooldown. Therefore, the final weight of the specimen decreased with time at room temperature. The amount of spallation was rapid at first and then slowed, but even 24 hours after removal from the furnace some spallation was still occurring. No similar phenomenon was detected for IN-100.

The previous observations led to the adoption of a modified test procedure. The specimens were suspended in a vertical tube furnace by a platinum wire with which neither alloy reacted. Here, the test specimens were weighed (both IN-100 and WI-52) 45 minutes after removal from the furnace.

Oxidation testing was carried on as follows: The initial thickness of the test specimen was measured with a micrometer and the specimen was weighed to ±0.1 milligram. The specimen was then attached to one arm of a recording balance (sensitivity of 0.1 mg) by a platinum wire and the preheated vertical tube furnace (5 cm diameter by 65 cm length) was raised until the specimen was at the center of a 2-inch- (5-cm-) long uniform hot zone. The furnace temperature was controlled to $\pm 5^{\circ}$ F ($\pm 3^{\circ}$ C) by a thermocouple placed 0.25 inch (0.62 cm) from the specimen. This couple was protected by an alumina protection tube. Only natural convection was employed to change the air in the tube which was open to the atmosphere at both ends. In the case of the isothermal measurements the weight change of the specimen was continuously recorded while at the test temperature. In the case of cyclic oxidation, the specimen, after a prescribed exposure time at temperature (cycle time), was removed from the furnace and suspended by the platinum wire in a covered beaker. After cooling for 45 minutes, the specimen was weighed. The covered beaker served as a spall catcher, if spalling occurred on cooling. The weight change was then the difference between this final weight and the original weight of the specimen. All weight values were divided by the initial metal surface area in square centimeters and are reported as milligrams per square centimeter. The heating and cooling process was repeated a number of times up to total oxidation times of 340 hours. Cycle times of 1, 2, 5, 20, and 170 hours at temperature were used.

Typical heating and cooling curves are presented in figure 2. The temperature was determined by a thermocouple bead (0.1 cm diameter by 0.02 cm thickness) formed from

30 gage wire and spot welded to the center of the 1 by 1 inch (2.5 by 2.5 cm) face of a test specimen. A type R thermocouple was used. The results for each alloy were the same.

Usually the weight change of the specimen in cyclic testing was not followed while at temperature. However, in the case of 2-, 5-, and 20-hour cyclic tests on WI-52 at 2000° F (1093° C) the weight change of successive cycles was recorded continuously.

Selected spall products were quantitatively analyzed for phases present by X-ray diffraction using nickel oxide (NiO) as an internal standard (see appendix A for details). The surfaces of selected specimens were also examined by X-ray diffraction at room temperature for determination of constituents present. After completion of cyclic testing, several specimens were mounted in epoxy, cut in half, and polished. The metal thickness was measured microscopically at five randomly selected sites on the cross section and an average value was calculated. In the case of WI-52 the thickness of the residual metal was measured from the oxide-metal interface on one side to the metal-oxide interface on the other. This includes the subsurface depleted zones. In the case of IN-100 two residual metal thickness measurements were made, one between the oxide-metal interfaces as for WI-52 and the other between the metal-depleted zone interfaces. The reported metal thickness loss in centimeters is thus the difference of the original metal thickness before oxidation and the residual metal thickness after oxidation. The overall precision of the metal thickness loss determination is ±0.0005 centimeter as determined by measuring a test specimen with the micrometer as usual and then (without oxidizing) mounting, sectioning, and remeasuring microscopically.

## RESULTS AND DISCUSSION

### Alloy WI-52

Metallography. - Figure 3 presents a typical cross-sectional photomicrograph of WI-52 oxidized at 1900° F (1038° C) (thirty 2-hr cycles). Note the fragments of heavy, multiphase oxide surface layer and the oxide penetration along the interdendritic carbide networks in the depleted zone.

Weight and thickness change. - The weight change data for ground-lapped WI-52, furnace tested under isothermal and cyclic conditions at 1900° and 2000° F (1038° and 1093° C), are presented in figures 4 to 9. The isothermal weight change data at 1900° and 2000° F (1038° and 1093° C) are presented in figures 4 and 5, respectively. At 1900° F (1038° C), WI-52 gains weight approximately linearly with time (slope of 0.05 $mg/cm^2/hr$). Considerable spalling of the oxide scale occurred on cooling the specimen to room temperature at the end of the run. At 2000° F (1093° C), the isothermal weight gain is also approximately linear (slope of about 0.075 mg/cm$^2$/hr). This specimen also spalled heavily on cooling at the end of the run. Figure 5 compares the present isothermal data with literature data taken from references 2 and 3 at 2000° F (1093° C). The ground-lapped data of reference 2 correspond to the results of this study. However, the results given in reference 3 (as-cast surface) are larger (slope about 0.34 mg/cm$^2$/hr). Part of this disagreement may be due to the difference in surface preparation since reference 2 has shown that the weight gain of WI-52 is sensitive to surface preparation.

Cyclic oxidation weight change data are also included in figures 4 and 5 for 1900° and 2000° F (1038° and 1093° C) exposures, respectively. At both temperatures, regardless of cyclic frequency, the specimens initially gained weight. During this initial period little or no spallation was observed. However, once a peak weight gain of 1 to 2 milligrams per square centimeter was reached, spallation increased and a few cycles beyond this peak the specimens showed a net weight loss. Soon this loss was linear with time at all cycle frequencies. Spallation of the oxide scale was extensive and often explosive in nature in this linear weight loss region.

From the cyclic data presented in figures 4 and 5, several interesting aspects of the cyclic oxidation behavior of WI-52 can be seen. First, the time to reach the beginning of the linear weight loss region was shorter for higher frequency cycling and for the higher test temperature. Second, after the weight loss became linear the slopes became more negative with an increase in cycle frequency or temperature. These slopes and the time to the start of the linear region are tabulated in table II along with burner rig data from reference 1. All the weight change data given in reference 1 are in milligrams; in order to normalize these data to unit surface areas so that they can be compared with the present data, a surface area of 30 square centimeters was used. This is the area of the burner rig blade specimen estimated to be at or near the maximum test temperature. This value of 30 square centimeters, however, is only approximately one-half the total surface area of a burner rig specimen and the remaining one-half is at a temperature between room temperature and the test temperature. Some weight change would also occur in this cooler area, but this change is considered to be small. Thus, only approximate comparisons can be made of the furnace and burner rig data. Also, the burner rig data in table II are for a different heat of WI-52 that was cast into wedge-shaped burner rig bars and tested in natural gas combustion products with periodic air-blast cooling. This air-blast cooling reduced the interior temperature of the burner rig specimen (0.25 in. (0.63 cm) thick) to 200° F (93° C) in 1 minute, while the surface of the furnace test specimens required 4 minutes to reach this temperature (see fig. 2). Again, these factors make comparisons only approximate. The burner rig data show much larger negative slopes than the furnace test data. If the same cycle frequency and exposure temperatures (2000° F (1093° C)) are used, the burner rig slope is -8.1 against -4.6 milligrams per square centimeter per hour in this test. However, the time to the onset of the linear loss region is approximately the same for 1-hour cycles at 2000° F (1093° C) - that is, 20 hours for burner rig against 15 hours in the furnace test. It appears that combustion gas, high velocity, and more rapid cooling have an accelerating effect on the cyclic oxidation weight loss of cobalt alloy WI-52, but very little effect on the time to the onset of the linear loss region at 2000° F (1093° C).

Since lapping leaves considerably surface residual stress and polishing removes some of this stress, the influence of surface preparation on cyclic weight change in furnace test conditions was also investigated for 20-hour cycles at 2000° F (1093° C). A ground-polished specimen was tested. It was found that the weight change results were the same as those given in figure 5 for the ground-lapped specimen. However, a difference was observed in the composition of the spalled scales. This difference is discussed later.

An additional and arbitrary way of looking at the cyclic data is to plot the cycle frequency against the time to reach a given weight loss. A loss value of 80 milligrams per square centimeter was chosen since this is the maximum value for which data are available at all frequencies. A log-log plot is presented in figure 6. Burner rig data points for 1-hour cycles from reference 1 are also included in this figure for comparison. In addition, the 1-hour cyclic furnace test and burner rig results are compared in table III. The results from figure 6 and table III indicate that in the burner rig tests the same weight losses occur in about one-third to two-thirds the time that they occur in furnace tests. These results indicate that high velocity combustion gases and/or quench cooling have an accelerating effect on the oxidation of WI-52.

To further examine the cyclic behavior of WI-52 at 2000° F (1093° C), the weight gains at the test temperature for the 2-, 5-, and 20-hour cycles were continuously recorded. The results are presented in figures 7 to 9. In the case of the curves presented in figure 7 for 20-hour cycles, increasing cycles through at least the third cycle (60 hr of test) produced increasingly rapid initial weight gains and larger final gains. After the third cycle, the weight gain behavior seems to become stable; that is, there is little difference in the shape of the weight gain against time curves for additional cycles. The time (60 hr) to the beginning of this consistency of the kinetic behavior corresponds closely to the beginning of the linear weight loss region in figure 5. Figure 8, for 5-hour cycles, shows decreasing weight gain with time in the second and third cycles which is indicative of increasing oxidation protection of the oxide scale. Further cycling, however, produces a reversal in behavior and larger weight gains. After the sixth cycle the weight gain behavior seems fairly consistent from cycle to cycle although there is some continued small increase in the weight gain with time through the twelfth cycle. Once again the time (30 hr) to the beginning of the more or less consistent kinetic behavior corresponds closely to the beginning of the linear weight loss region in figure 5. Weight gain during the fifteenth, twentieth, and thirtieth 2-hour cycles are presented in figure 9. These cycles are all within the linear loss region and a consistency of weight gain would therefore be expected.

In a complex alloy system the weight change data cannot be translated to the more useful information of loss of load bearing cross section. For this reason the weight change data were supplemented by metallographic measurements of the change in residual alloy thickness after several oxidation exposures at both 1900° and 2000° F (1038° and 1093° C). These data are presented in figure 10. In order to determine the influence of cycling on the metal thickness loss all specimens received the same total exposure time at the test temperature. This was arbitrarily chosen as 60 hours. The boundaries between which the final thickness measurements were made are shown schematically by the insert in figure 10. No measurements were made between the depleted zones because of the difficulty in locating these interfaces. Figure 10 shows that at 1900° F (1038° C) increasing the number of cooling cycles from 3 to 30 results in a doubling of the metal thickness loss (i. e., from 0.006 to about 0.012 cm), while at 2000° F (1093° C) the thickness loss increases by a factor of about 4 (i. e., from about 0.01 to approximately 0.04 cm). Thus, at both temperatures, as shown by the thickness losses, increased cycle frequency significantly increases the extent of oxidation attack on WI-52. A comparison with burner rig data can be made for 1-hour cycles at 2000° F (1093° C). The burner rig data from reference 1 for sixty 1-hour cycles indicate a thickness loss of 0.14 against 0.05 centimeter for the present tests. This once again shows the more severe attack in the simulated engine tests.

X-ray diffraction. - Additional information was derived from X-ray diffraction analyses of the residual oxide scale (in situ) and the spalled oxide scale. After each 20-hour cycle at 2000° F (1093° C) the in situ surface scale on the ground-lapped and ground-polished specimens was found to contain chromium oxide ($Cr_2O_3$), cobalt tungstate ($CoWO_4$), a spinel ($CoCr_2O_4$), and cobalt oxide (CoO). These results remained constant for each cycle and agree with the 1-hour cycle burner rig results reported in reference 1. The spalled material was analyzed by an internal standard procedure described in appendix A. This procedure yields approximately quantitative results. The analyses of the spalls from the ground-lapped and ground-polished specimens are presented in table IV for each of the 20-hour cycles. These results indicate that the spall was predominately $CoCr_2O_4$ and CoO with lesser amounts of $Cr_2O_3$ and $CoWO_4$. The composition did not change markedly with cycling in either case. However, the ground-polished spalls contained greater amounts of $Cr_2O_3$, CoO, and $CoWO_4$ but less $CoCr_2O_4$ than the spalls from the ground-lapped specimens. This difference in scale composition may be due to differences in surface stress, roughness, or chemical contamination resulting from the surface preparation. Table V compares the spall compositions for 20-hour-cycle ground-lapped and ground-polished specimens to those of 5- and 2-hour cyclic tests for a total of

60 hours of exposure at 2000° F (1093° C) in each case. Here, increased cycle frequency results in a decrease in $Cr_2O_3$ (four for 20-hr cycles to (not detected for 2-hr cycles), a slight drop in $CoCr_2O_4$ (50 to 40), and an increase in $CoWO_4$ (11 to 27). The tungsten probably comes from the interdendritic carbide networks in the alloy. So the increased $CoWO_4$ content with increased cycle frequency indicates that the attack of these carbide networks increases in importance with increased cycle frequency.

A quantitative knowledge of the phase content of the spall along with measured weight change data allows the calculation of an oxygen balance. This is presented and briefly discussed in appendix B as confirmatory and auxiliary information.

### Alloy IN-100

Metallography. - Figure 11 shows a thin multiphased oxide on the surface of IN-100 with local nodules of oxide penetrating somewhat into the depleted surface layer. This depleted layer probably forms due to depletion of Cr, Al, etc., near the surface.

Weight and thickness change. - Isothermal and cyclic furnace oxidation weight change data for the nickel base alloy IN-100 at 1900° and 2000° F (1038° and 1093° C) are presented in figures 12 and 13, respectively. These isothermal data will be compared to some literature information at both temperatures. Isothermal furnace oxidation data at 1900° F (1038° C) are presented in reference 4. The weight gain values given are 0.96 milligram per square centimeter at 64 hours, 4.0 milligrams per square centimeter at 112 hours, and 9.76 milligrams per square centimeter at 304 hours. These values at 112 and 304 hours are larger than the isothermal results of this study which are presented in figure 12. The experimental method used by reference 4 caught any spall that may have occurred during oxidation and was weighed with the specimen. This could account for the larger values given by reference 4 since the method used in the present investigation did not catch and weigh any spall that might have been lost during oxidation. However, no visually detectable amount of spall was observed at the bottom of the furnace tube in the present work nor were discontinuities in the weight change recording detected which would result from small losses. Isothermal furnace oxidation data from reference 5 at 2000° F (1093° C) for two heats of IN-100 are presented in figure 13 for comparison. The present results fall between the literature values which indicate some variation from heat to heat.

In any event, the present isothermal weight gain data for IN-100 is less than that of WI-52 at both temperatures. For example, IN-100 gained approximately 1.8 milligrams per square centimeter in 100 hours at 2000° F (1093° C) while WI-52 gained about 7 milligrams per square centimeter.

It is evident from figures 12 and 13 that the total cyclic weight gain of IN-100 at both temperatures is less than that for the isothermal test. This is due to spallation on cooling. The amount of spall produced in each cycle was so small that a very close examination of the spall catcher was required to visually detect its presence. It is further noticed at both temperatures that the greater the cycle frequency, the greater the spalling, which is reflected in a smaller net weight gain. At $1900^{\circ}$ F ($1038^{\circ}$ C) at 2 and 20 hour frequencies the specimens still show an increasing net weight gain even at the longest time (140 hr). However, at $2000^{\circ}$ F ($1093^{\circ}$ C) a peak gain is reached with a subsequent decrease at both cycle frequencies. The time to reach the peak is shorter for the higher cycle frequency. In general, at both temperatures, the shape of the curves for IN-100 resemble the shape of the initial or very short time (10 hr) portions of the corresponding cyclic curves for WI-52. The linear portion of the cyclic weight change curves corresponding to the linear weight loss region of WI-52 is not reached at $1900^{\circ}$ F ($1038^{\circ}$ C) for either cycle frequency, at least up to the maximum oxidation time of 140 hours, so no comparison can be made to WI-52. At $2000^{\circ}$ F ($1093^{\circ}$ C) there is a final portion of the weight change curves, at least for 2-hour cycles, that may correspond to the linear weight loss region of WI-52. If it is assumed that this is the case, for 2-hour cycles the slope of the loss region is -0.008 milligram per square centimeter per hour. This is considerably smaller than the -4.4 milligrams per square centimeter per hour (table II) for WI-52 - in fact, about 550 times smaller. In cyclic furnace oxidation it can be concluded that IN-100 is more spall resistant than WI-52.

A rough comparison of the present furnace weight change results to burner rig results reported in reference 1 can be made. For example, after sixty 2-hour cycles (120 hr) of furnace testing at $2000^{\circ}$ F ($1093^{\circ}$ C) the specimen exhibits a net weight gain, while burner rig testing for sixty 1-hour cycles (60 hr) produces a weight loss. Thus, while cyclic furnace tests of WI-52 are conservative as to weight change by a factor of 2 or 3, a similar comparison for IN-100 shows the furnace test to give weight gains, while the burner rig tests produce weight losses.

Metal thickness loss of IN-100 is presented in figure 14 for $2000^{\circ}$ F ($1093^{\circ}$ C). As in the case of WI-52, all specimens received the same total exposure of 60 hours so that the cyclic effect could be directly evaluated. Two thickness measurements were made for IN-100. The reference lines are shown in the schematic diagram in figure 14. The thickness loss resulting from measurement A includes the effect of the depletion zones, while measurement B was made from scale-metal interfaces which excludes the effect of the depletion zones. Both curves show an increase in thickness loss with increased cycle frequency as was observed for WI-52. The relatively large difference between the thickness loss arrived at by the A and B measurements may be significant for thin sheet materials. The thickness losses of IN-100 are smaller than WI-52. For example, after thirty 2-hour cycles at $2000^{\circ}$ F ($1093^{\circ}$ C), with the thickness data A which correspond to those used for WI-52, IN-100 lost approximately 0.0009 centimeter while WI-52 had a loss of 0.04 centimeter.

X-ray diffraction. - Since so little spall developed from the IN-100 tests only in situ surface diffraction was made on this material. The furnace results are presented in table VI for the specimen given sixty 2-hour cycles at 2000° F (1093° C). Also contained in table VI are data for IN-100 tested for sixty 1-hour cycles in the burner rig at 2000° F (1093° C) as reported in reference 1. The MO (NiO) was present in the surface of the burner rig specimen, but it is absent from the surface of the furnace test specimen. It is noticed that $Cr_2O_3$ and $TiO_2$ are absent from the burner rig specimen surface. The absence of $Cr_2O_3$ from the surface of the burner rig test specimen may be attributed to the high velocity environment producing vaporization loss. The difference in NiO and $TiO_2$ contents cannot be explained at this time.

## SUMMARY OF RESULTS

Isothermal and cyclic furnace oxidation tests were performed on cobalt alloy WI-52 and the nickel alloy IN-100 at 1900° and 2000° F (1038° and 1093° C). Weight and metal thickness changes were measured. The tests included exposure cycles of 1, 2, 5, 20, and 170 hours for total oxidation times of up to 340 hours. Supplemental metallographic and X-ray diffraction analysis were also made.

The following results were obtained:

1. In cyclic furnace exposures, followed by relatively slow cooling (about 4 min to reach 200° F (93° C)), both IN-100 and WI-52 showed increased spalling of surface oxides with either increased exposure temperature or cycle frequency. However, WI-52 spalled much more extensively than IN-100. For example, when 2-hour exposures at 2000° F (1093° C) were used, after a total of 50 hours WI-52 lost 130 milligrams per square centimeter while IN-100 still showed a net weight gain of about 0.7 milligram per square centimeter; WI-52 also showed much greater metal consumption. The trends in the furnace oxidation behavior of both alloys with increased cycle frequency and temperature were somewhat similar to those observed in a previous burner rig study which involved much more rapid cooling after each exposure cycle.

2. The oxides formed on WI-52 were CoO, $CoCr_2O_4$, $CoWO_4$, and $Cr_2O_3$ under all furnace test conditions and these were the same oxides observed to form on WI-52 in previously reported burner rig tests. On IN-100, $NiAl_2O_4$, $NiCr_2O_4$, $Cr_2O_3$, $Al_2O_3$, and $TiO_2$ formed in the furnace tests, but in the previous burner rig studies $Cr_2O_3$ and $TiO_2$ were not present while NiO type oxides were detected.

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# APPENDIX A

## QUANTITATIVE X-RAY DIFFRACTION ANALYSIS OF SPALLS

The X-ray quantitative analysis of the spalled material followed the procedure described in reference 6. A standard specimen for each phase present in the spall was prepared by mixing powder of that phase (90 percent by weight) with powder of the internal standard, which was NiO (10 percent by weight). The ratio of the X-ray intensity of a particular peak for the phase to that of a chosen peak for NiO was then determined. This ratio can then be used in determining the amount of the phase in any unknown powder specimen to which 10 percent by weight of NiO has been added and the corresponding intensity ratio determined. The spall specimens were so small in some cases that a special powder mixture method was necessary to produce specimens that gave sufficient X-ray intensities. In this method the spall was ground, mixed with the NiO, and then blended with mineral oil. This slurry was spread on a glass slide for X-ray diffraction. A standard specimen using this method was made up from high purity phases to check this mixing procedure. The actual amounts of the phases mixed in the standard specimen and those determined from X-ray intensity ratios are presented in table VII. It was found that the $CoWO_4$ peaks gave very poor reproducibility with mineral oil samples. This yielded inaccurate intensity ratios, and, therefore, it was thought that $CoWO_4$ was better determined by difference (for the standard specimen in table VII this gives 17 percent compared to 15 percent actually present against 9 percent by direct determination). At the levels the phases are present in most of the spalls it is estimated that the phases may be present within the following weight percentages: $Cr_2O_3$, ±25 percent of the value reported; $CoCr_2O_4$, ±10 percent of the value; CoO, ±10 percent of the value; and $CoWO_4$ (by difference), ±25 percent of the value reported.

# APPENDIX B

## CALCULATION AND DISCUSSION OF OXYGEN BALANCE

The oxygen balance is defined as the ratio of oxygen lost in the spall to the total oxygen gained by the specimen. This ratio will be calculated from the data for the third 20-hour cycle at 2000° F (1093° C) for WI-52. First, the oxygen content of the spalled scale is calculated (see table VIII) assuming each oxide to be stoichiometric.

The weight of spall collected was 37 milligrams per square centimeter. Now the oxygen loss is

$$37\ \mathrm{mg/cm^2}\ \text{of spall} \times 25.1\ \text{wt \% oxygen in spall} = 9.2\ \mathrm{mg/cm^2}\ \text{of oxygen lost}$$

The amount of oxygen gained, taken from figure 7, for the third cycle is 9.5 milligrams per square centimeter. So the ratio

$$\frac{\text{Oxygen loss}}{\text{Oxygen gained}} = \frac{9.2}{9.5} \times 100 = 97\ \text{percent}$$

which is the oxygen gained during oxidation that appears in the spall on cooling. Therefore, only 3 percent of the oxygen gained remains behind on the specimen. This 3 percent is probably distributed between the unspalled scale, the subscale region, and errors in the determinations. The result of this calculation agrees with the visual observation of nearly complete loss of the surface scale on cooling this specimen.

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5. Wasielewski, G. E.: Nickel-Base Superalloy Oxidation. Interim Rep. No. 2, General Electric Co., June 30, 1966. (Work done under Contract AF33(615)-2861.)
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## TABLE I. - CHEMICAL COMPOSITION[a] OF AS-CAST WI-52 AND IN-100

| Element | WI-52 | | IN-100 | |
|---|---|---|---|---|
| | Actual analysis | Nominal range | Actual analysis | Nominal range |
| C | 0.47 | 0.4 to 0.5 | 0.17 | 0.15 to 0.20 |
| Mn | .27 | .5 max. | <.1 | .5 max. |
| Si | .27 | .5 max. | <.1 | .5 max. |
| S | .02 | .04 max. | .003 | .015 max. |
| Cr | 21.1 | 20.0 to 22.0 | 9.7 | 9.0 to 10.0 |
| Fe | 2.1 | 1.0 to 2.5 | .11 | 1.0 max. |
| Co | Balance | Balance | 15.2 | 14.0 to 16.0 |
| Ni | .4 | 1.0 max. | Balance | Balance |
| W | 11.2 | 10.0 to 12.0 | ------- | ------- |
| P | .01 | .04 max. | ------- | ------- |
| Ta+Nb | 1.73 | 1.5 to 2.5 | ------- | ------- |
| Mo | ---- | --------- | 3.2 | 2.7 to 3.3 |
| Al | ---- | --------- | 5.6 | 5.3 to 5.7 |
| Ti | ---- | --------- | 4.3 | 4.0 to 4.4 |
| Zr | ---- | --------- | .06 | .03 to 0.09 |
| B | ---- | --------- | .01 | .01 to 0.02 |
| V | ---- | --------- | .92 | .9 to 1.1 |

[a] In weight percent.

## TABLE II. - SLOPE OF WEIGHT LOSS CURVES IN LINEAR OXIDATION REGION AND TIME TO START OF LINEAR LOSS FOR WI-52

| Temperature | | Cycle time, hr/cycle | Time to start of linear loss, hr | Slope of linear loss, mg/cm$^2$/hr |
|---|---|---|---|---|
| °F | °C | | | |
| 1900 | 1038 | 20 | 100 | -1.3 |
| 1900 | 1038 | 2 | 40 | -1.8 |
| [a]1900 | [a]1038 | [a]1 | [a]40 | [a]-2.8 |
| 2000 | 1093 | 170 | 300 | -0.44 |
| 2000 | 1093 | 20 | 40 | -1.7 |
| 2000 | 1093 | 5 | 25 | -2.9 |
| 2000 | 1093 | 2 | 20 | -4.4 |
| 2000 | 1093 | 1 | 15 | -4.6 |
| [a]2000 | [a]1093 | [a]1 | [a]20 | [a]-8.1 |

[a] Burner rig data from ref. 1.

### TABLE III. - COMPARISON OF TIME TO LOSE 80 mg/cm$^2$ IN CYCLIC FURNACE AND BURNER RIG TESTS USING 1-HOUR CYCLES

| Temperature | | Time, hr | |
|---|---|---|---|
| °F | °C | Furnace test | Burner rig test |
| 1900 | 1038 | [a]63 | 45 |
| 2000 | 1093 | 33 | 12 |

[a]Extrapolated from fig. 6.

### TABLE IV. - QUANTITATIVE X-RAY ANALYSIS OF SPALLED SCALES FROM GROUND-LAPPED AND GROUND-POLISHED WI-52 FOR 20-HOUR CYCLES AT 2000° F (1093° C)

| Cycle | Phase content of spall, wt % | | | |
|---|---|---|---|---|
| | $Cr_2O_3$ | $CoCr_2O_4$ | CoO | [a]$CoWO_4$ |
| Ground-lapped | | | | |
| 1 | 3 | 50 | 34 | 13 |
| 2 | 2 | 50 | 37 | 11 |
| 3 | 4 | 50 | 35 | 11 |
| 4 | 3 | 45 | 45 | 7 |
| 5 | 2 | 45 | 36 | 17 |
| 6 | 3 | 47 | 39 | 11 |
| Ground-polished | | | | |
| 1 | 11 | 22 | 54 | 13 |
| 2 | 3 | 29 | 59 | 9 |
| 3 | 3 | 21 | 56 | 20 |
| 4 | 4 | 23 | 51 | 22 |

[a]By difference.

TABLE V. - QUANTITATIVE SPALL COMPOSITION BY X-RAY DIFFRACTION FOR 2000° F (1093° C) TESTS

[Total exposure in each test, 60 hr.]

| Surface condition and cycle | Phase content of spall, wt % | | | |
|---|---|---|---|---|
| | $Cr_2O_3$ | $CoCr_2O_4$ | CoO | [a]$CoWO_4$ |
| Ground-lapped | | | | |
| 20-hr cycles (3rd cycle) | 4 | 50 | 35 | 11 |
| 5-hr cycles (12th cycle) | 2 | 46 | 32 | 20 |
| 2-hr cycles (30th cycle) | [b]ND | 40 | 33 | 27 |
| Ground-polished | | | | |
| 20-hr cycles (3rd cycle) | 4 | 21 | 56 | 19 |

[a] By difference.

[b] Not detected.

TABLE VI. - IN SITU X-RAY DIFFRACTION RESULTS FOR IN-100 TESTED AT 2000° F (1093° C) FOR 60 HOURS

| Furnace test (2-hr cycles) | Burner rig test[a] (1-hr cycles) |
|---|---|
| Spinel, $a_o$ = 8.1Å ($NiAl_2O_4$)[b]<br>Spinel, $a_o$ = 8.3Å ($NiCr_2O_4$)[b]<br>$\alpha$ - $Cr_2O_3$<br>$\alpha$ - $Al_2O_3$<br>$TiO_2$ | $\alpha$ - $Al_2O_3$<br>Monoxide (probably NiO)<br>Spinel, $a_o$ = 8.10Å<br>Spinel, $a_o$ = 8.3Å |

[a] Ref. 1 data.

[b] Suggested in ref. 5.

TABLE VII. - COMPARISON OF A STANDARD COMPOSITION TO ITS COMPOSITION DETERMINED BY X-RAY ANALYSIS

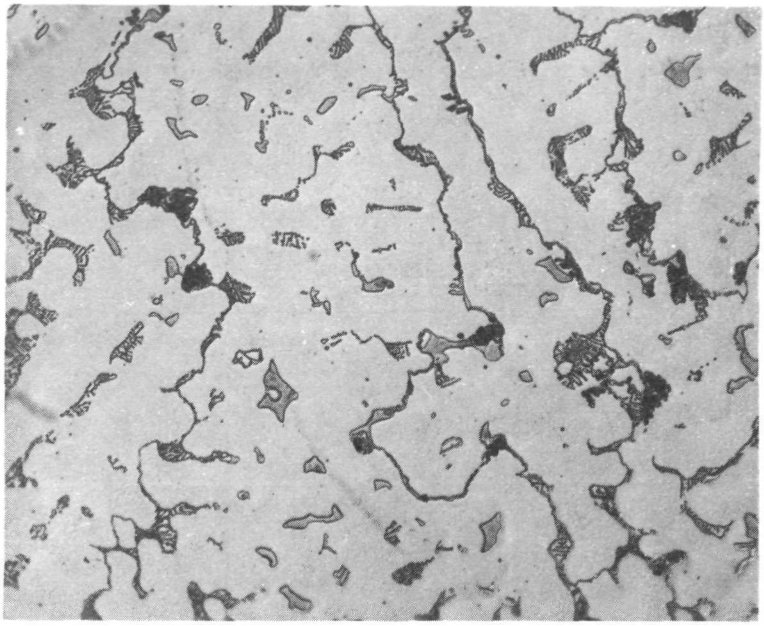
| | $Cr_2O_3$ | $CoCr_2O_4$ | CoO | $CoWO_4$ | Total |
|---|---|---|---|---|---|
| Composition of standard, wt % | 5.5 | 39.5 | 40 | 15 | 100 |
| Composition determined by analysis, wt % | 3 | 40 | 40 | [a]9[b](17) | [a]92 |

[a] Direct determination.

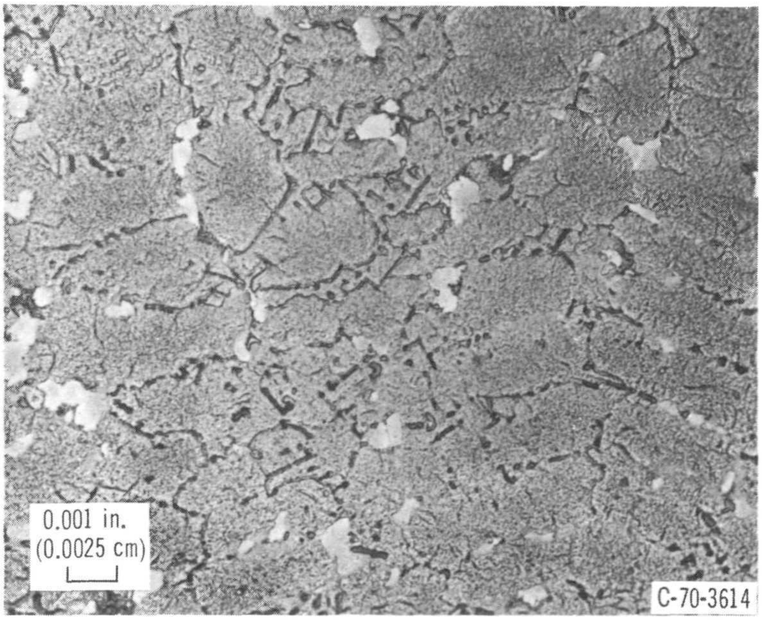
[b] By difference.

TABLE VIII. - CALCULATION OF OXYGEN CONTENT OF THE SPALLED SCALE

| Spall composition, wt % | Oxygen in oxide, wt % | Oxygen in spall, wt % |
|---|---|---|
| 4 $Cr_2O_3$ | 31.6 | 1.3 |
| 50 $CoCr_2O_4$ | 28.2 | 14.0 |
| 35 CoO | 21.3 | 7.5 |
| 11 $CoWO_4$ | 20.9 | 2.3 |
| | | Total 25.1 |



(a) WI-52.



(b) IN-100.

Figure 1. - Typical microstructures of as-received alloys. X250.

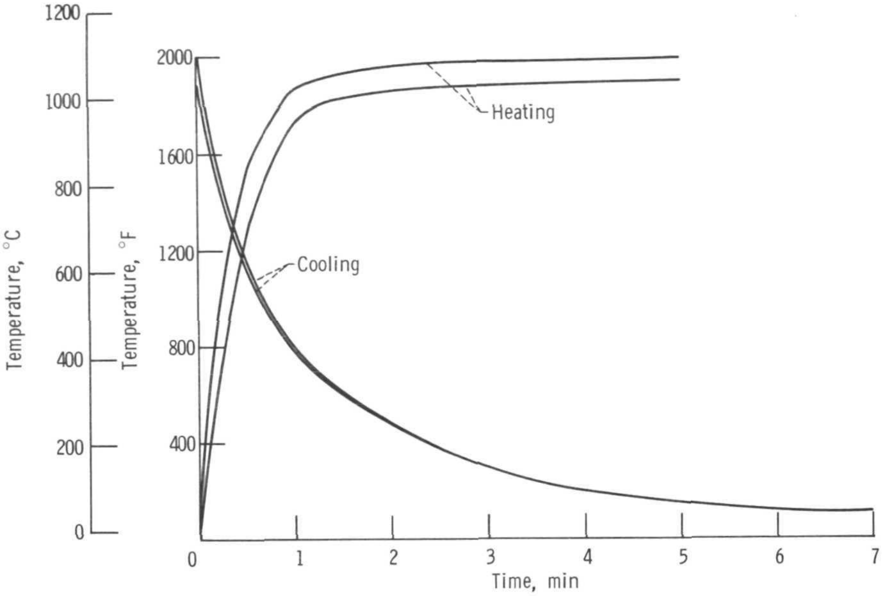


Figure 2. - Typical heating and cooling curves.

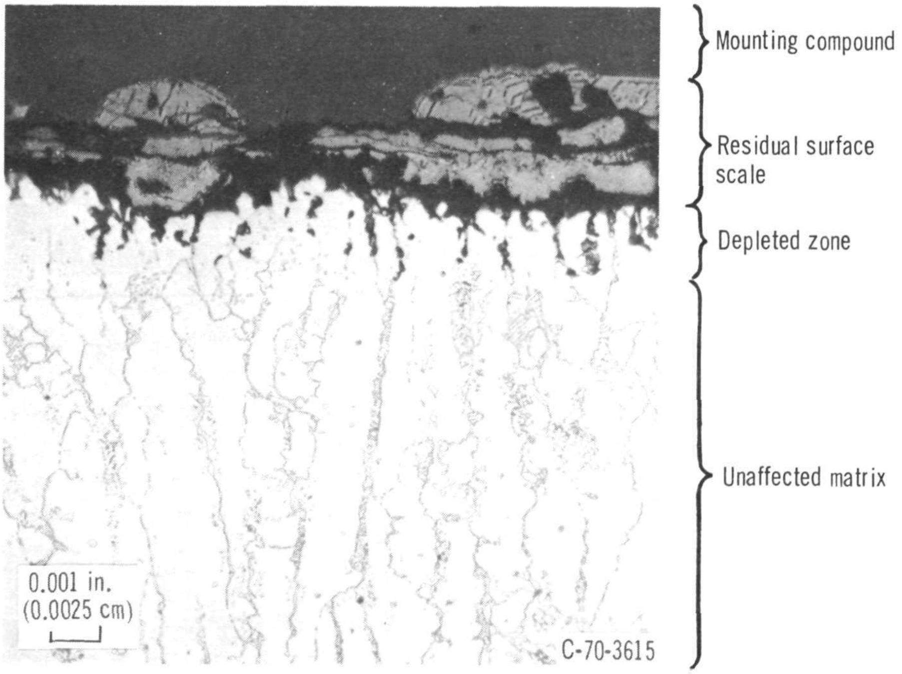


Figure 3. - WI-52 after thirty 2-hour cycles at 1900° F (1038° C). X250.

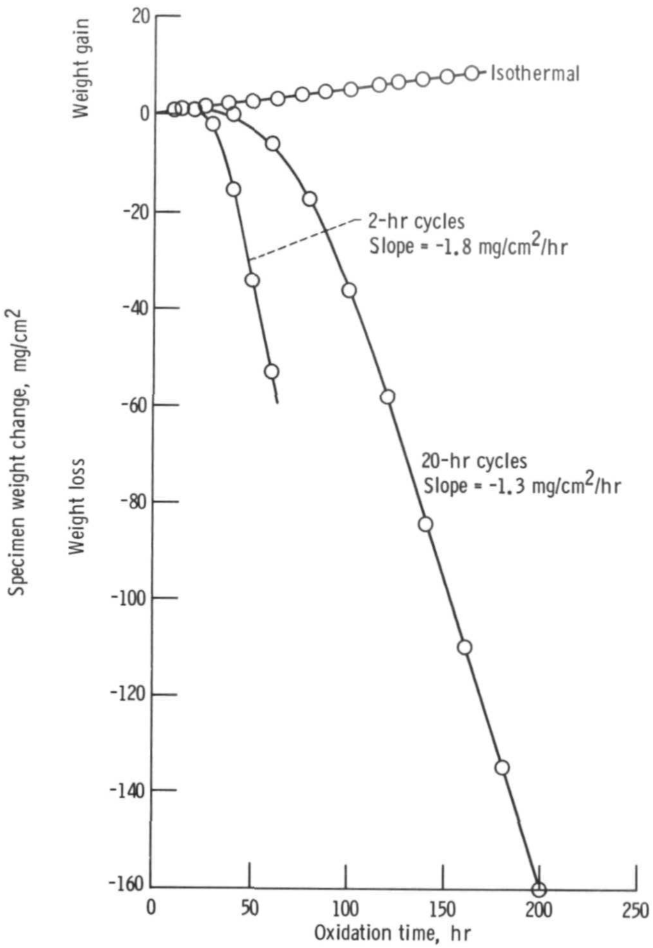


Figure 4. - Weight change of ground-lapped WI-52 specimens during isothermal and cyclic oxidation at 1900° F (1038° C).

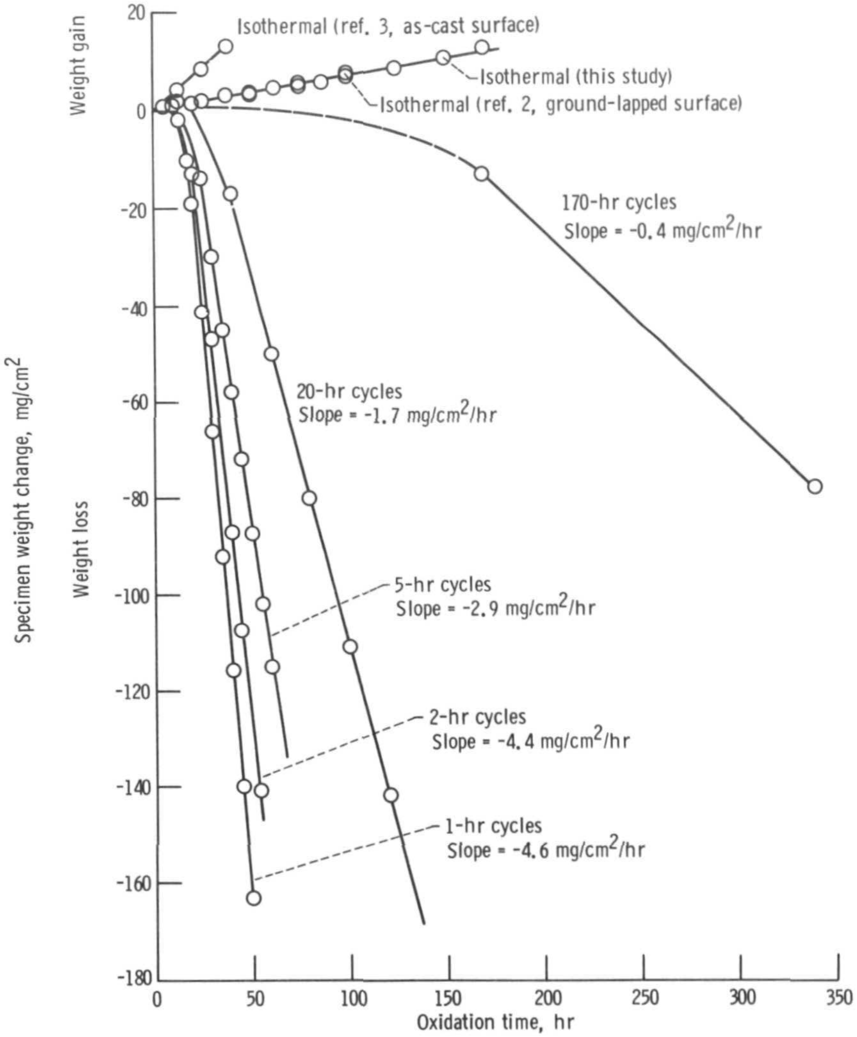


Figure 5. - Weight change of ground-lapped WI-52 specimens during isothermal and cyclic oxidation at 2000° F (1093° C).

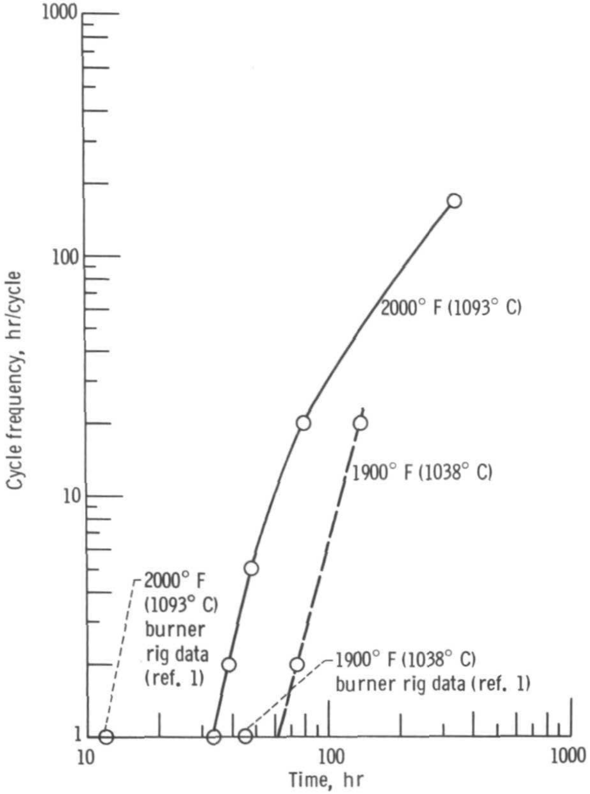


Figure 6. - Relation between cycle frequency and time to loss of 80 milligrams per square centimeter for WI-52. Ground-lapped specimens.

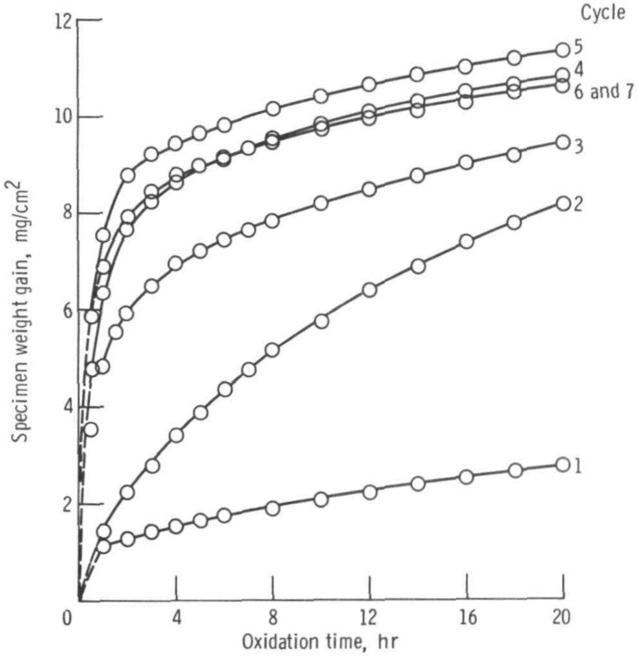


Figure 7. - Weight gain of WI-52 during heating portion of each 20-hour cycle at 2000° F (1093° C) ground-lapped specimen.

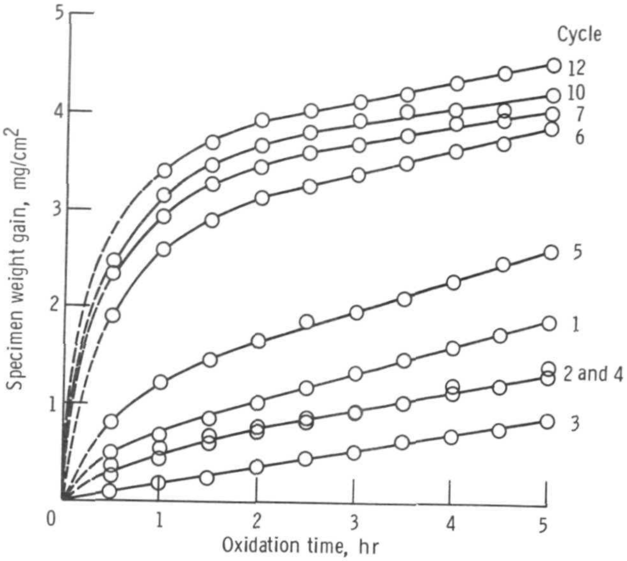


Figure 8. - Net weight gain of WI-52 at 2000° F (1093° C) during heating portion of successive 5-hour cycles for ground-lapped specimen.

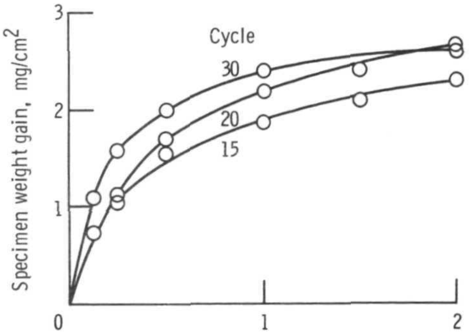


Figure 9. - Weight gain during heating portion of several 2-hour cycles for WI-52 at 2000° F (1093° C) for ground-lapped specimen.

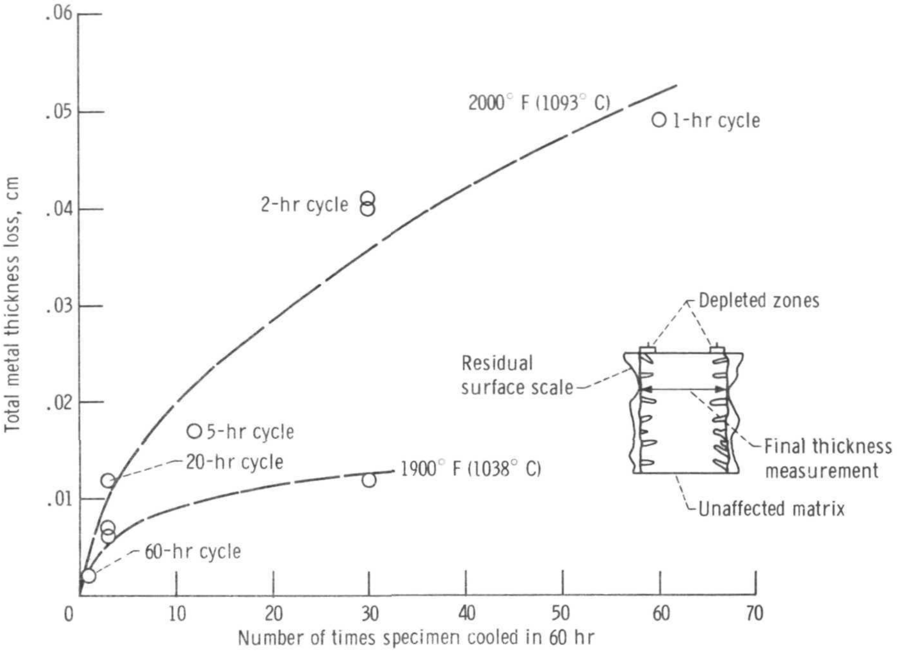


Figure 10. - Effect of cyclic oxidation on total metal thickness loss of WI-52 at 1900° and 2000° F (1038° and 1093° C) for ground-lapped specimens. Original metal thickness, 0.25 centimeter.

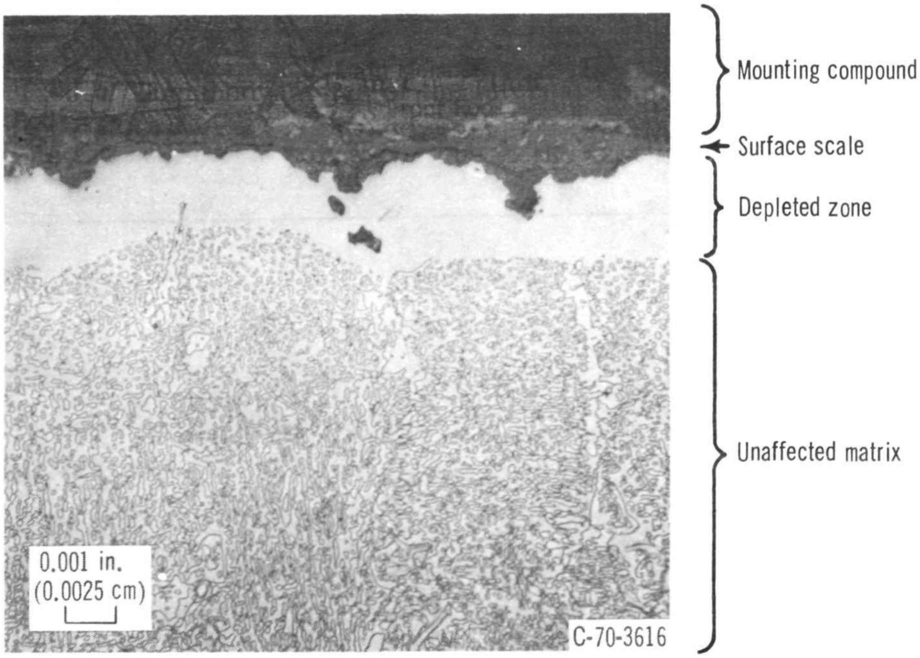


Figure 11. - IN-100 after forty-five 2-hour cycles at 2000° F (1038° C). X250.

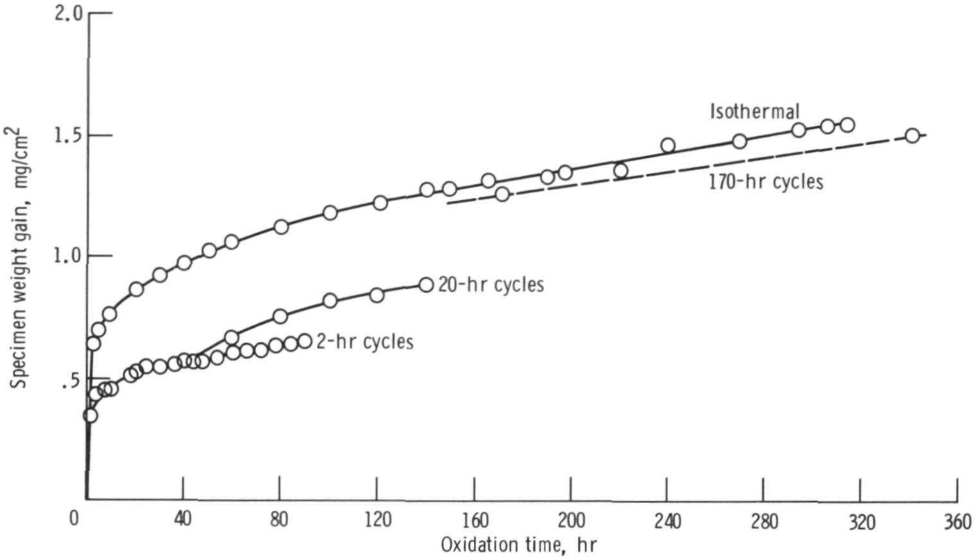


Figure 12. - Effect of cyclic and isothermal oxidation on weight gain of IN-100 at 1900° F (1038° C).

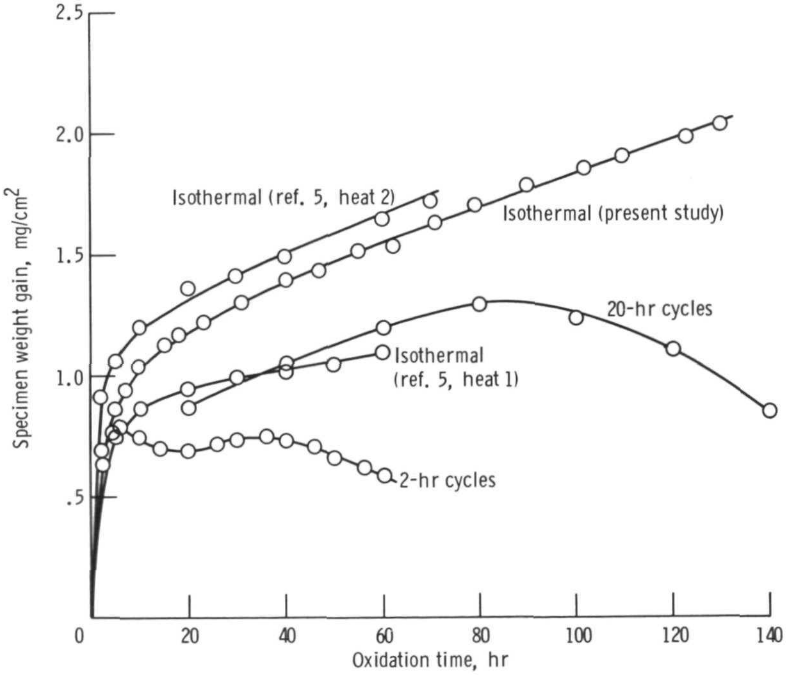


Figure 13. - Effect of isothermal and cyclic oxidation at 2000° F (1093° C) on weight gain of IN-100.

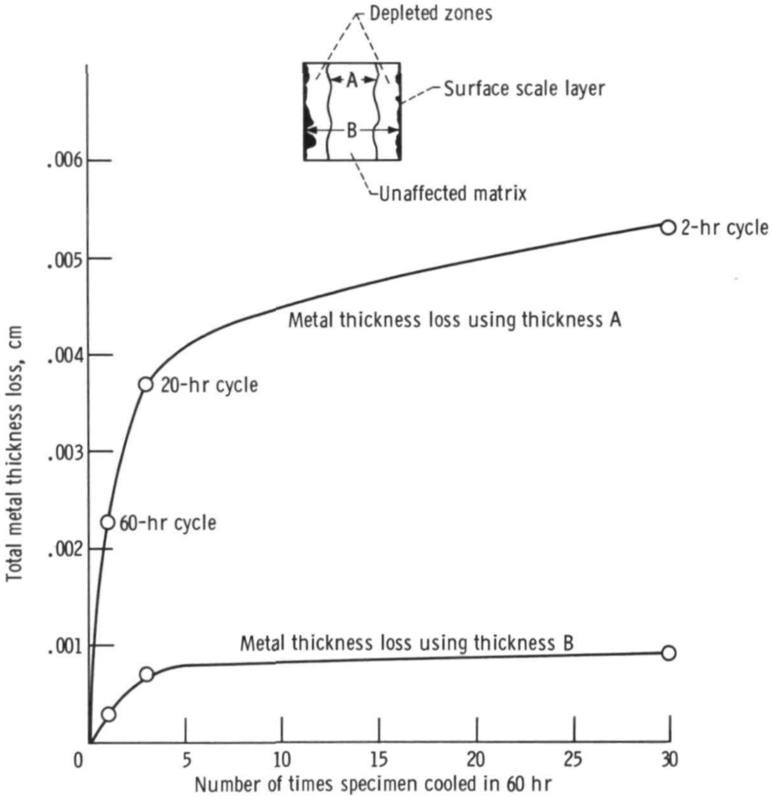


Figure 14. - Effect of cyclic oxidation on total metal thickness loss of IN-100 at 2000° F (1093° C). Original metal thickness, 0.25 centimeter.

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