NASA TECHNICAL NOTE

NASA TN D-5834

c. 1

NASA TN D-5834

FURNACE AND HIGH-VELOCITY OXIDATION OF ALUMINIDE-COATED COBALT SUPERALLOY WI-52

by Salvatore J. Grisaffe, Daniel L. Deadmore,
and William A. Sanders

Lewis Research Center
Cleveland, Ohio 44135

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • MAY 1970

1. Report No.
NASA TN D-5834

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle
FURNACE AND HIGH-VELOCITY OXIDATION OF ALUMINIDE-COATED COBALT SUPERALLOY WI-52

5. Report Date
May 1970

6. Performing Organization Code

7. Author(s)
Salvatore J. Grisaffe, Daniel L. Deadmore, and William A. Sanders

8. Performing Organization Report No.
E-5307

9. Performing Organization Name and Address

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio 44135

10. Work Unit No.
129-03

11. Contract or Grant No.

12. Sponsoring Agency Name and Address

National Aeronautics and Space Administration
Washington, D.C. 20546

13. Type of Report and Period Covered

Technical Note

14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

Aluminide-coated WI-52 was cyclic oxidation tested in furnace-air and in high-velocity combustion gas environments at temperatures from 1900° to 2100° F (1038° to 1149° C). Cycle frequencies were varied from 1 to 100 hours in furnace tests while 1-hour cycles were used in the high-velocity tests. At all exposure temperatures, increased cycling accelerated coating degradation because the protective aluminum oxide scale spalled during cooling. Spalling depleted the coating of aluminum and permitted less protective oxides to form. In high-velocity tests, coating life decreased from 300 hours at 1900° F (1038° C) to 12 hours at 2100° F (1149° C).

17. Key Words (*Suggested by Author(s)*)

Protective coatings
Oxidation
Cobalt alloys

18. Distribution Statement

Unclassified - unlimited

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
Unclassified	Unclassified	25	$3.00

*For sale by the Clearinghouse for Federal Scientific and Technical Information
Springfield, Virginia 22151

FURNACE AND HIGH-VELOCITY OXIDATION OF ALUMINIDE-COATED COBALT SUPERALLOY WI-52

by Salvatore J. Grisaffe, Daniel L. Deadmore, and William A. Sanders

Lewis Research Center

SUMMARY

Aluminide-coated WI-52 cobalt alloy was oxidation tested in both furnace and high-velocity burner rig environments at temperatures of 1900°, 2000°, and 2100° F (1038°, 1093°, and 1149° C). Furnace exposures utilizing 1-, 2-, 5-, 20-, and 100-hour cycles were conducted for total times ranging from 27 to 608 hours. To study the influence of gas velocity, 1-hour test cycles were applied in a Mach 1 test apparatus fueled by natural gas. Originally the coating consisted of a cobalt aluminide (CoAl) surface layer and a diffusion zone between it and the WI-52. At all temperatures, the degradation of the coating was dependent on both exposure time and the number of exposure cycles. The thickness of the CoAl layer gradually decreased as it degraded to a cobalt solid solution. The protective alumina scale was replaced with $CoAl_2O_4$, $CoCr_2O_4$, and then, when the coating had failed, CoO. Degradation was best followed by metallographic analysis including measurement of the thickness of the CoAl layer. Weight change and X-ray diffraction provided supplementary information.

From the results of this investigation it appears that the times to coating failure in the high-velocity tests decrease by an order of five for each 100° F (55° C) increase in test temperature over the range studied (300 hr at 1900° F (1038° C), 60 hr at 2000° F (1093° C), and 12 hr at 2100° F (1149° C)). There is a linear relation between the log of coating life and test temperature. Furthermore, when furnace tests are conducted at the same cycle period (1-hr cycles) as the high-velocity tests at or above 2000° F (1093° C), the weight change data for the two types of tests compare favorably. While the aluminide coating tested has good oxidation resistance at commercial aircraft gas turbine engine conditions now in use, it does not appear to offer sufficient long time protection under continuous high temperature service ($>$1900° F (1038° C)) for use in advanced engines.

INTRODUCTION

Many commercial aircraft gas turbine engines use stator vanes of the cobalt alloy WI-52. These parts are aluminized to improve their oxidation resistance in service. Such coated vanes normally operate for times approaching 4000 hours at temperatures in the 1500° to 1800° F (815° to 982° C) range. Uneven combustion in the burner, however, can produce hot spots on the vanes that may reach temperatures several hundred degrees above these values. Such hot spots are one cause of premature coating failure.

The oxidation resistance of one widely used proprietary aluminide coating on WI-52 was studied in this investigation in both cyclic furnace and cyclic high-velocity oxidation tests over the temperature range of 1900° to 2100° F (1038° to 1149° C). These temperatures were selected to allow controlled studies of the degradation of the coating under simulated hot-spot conditions. They also allowed an examination of the potential of relatively simple aluminide coatings for use in advanced engines that will operate at material temperatures in this range.

Both cyclic furnace and high-velocity tests were conducted for two reasons. First, the degradation of aluminide coatings is generally believed to be related to the spallation of the protective aluminum oxide surface scale each time a hot component is cooled to ambient temperature. Because commercial flights usually last only a few hours, the engine is thermally cycled many times in its lifetime. Thus, the effects of the number of test cycles, the length of time at temperature during each exposure cycle, and the exposure temperature are of interest. Secondly, there was a desire to compare the results of low-air-velocity, slow heating-cooling furnace tests and high-velocity, rapid heating-cooling tests, since the former tests are much less costly to conduct. Also, a correlation of such results could lead to establishing an inexpensive, standard oxidation test for coated superalloys.

The effects of temperature, time, and cycle frequency were evaluated using weight change data which were supplemented with microstructural studies of surface oxide scales and coating-substrate cross sections. Surface X-ray diffraction analysis and a limited number of electron microprobe scans were also performed.

MATERIALS

The nominal composition of WI-52 is 21 percent chromium (Cr), 11 percent tungsten, (W), 2 percent columbium (Cb), 2 percent iron (Fe), 0.4 percent carbon (C), 0.25 percent manganese (Mn), 0.25 percent silicon (Si), and the balance cobalt (Co). High-velocity test specimens were cast to shape and ground at the base as shown in figure 1.

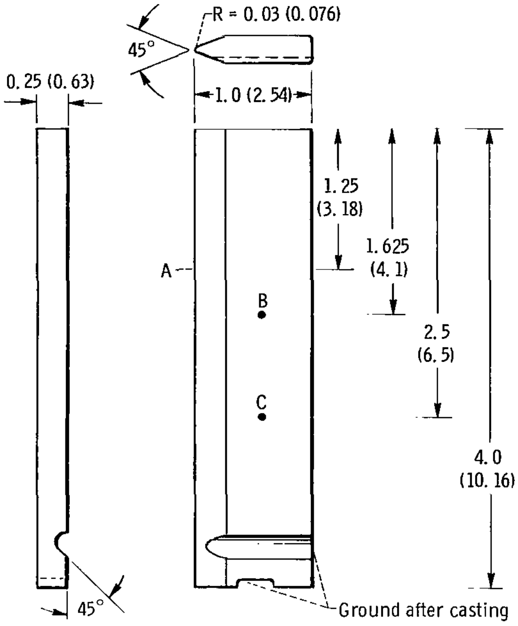


Figure 1. - High-velocity oxidation specimen. Dimensions are in inches (cm); A, B, and C are points for metallographic cross sectioning.

From the large cast bars, small coupons for the furnace tests were cut, much as a loaf of bread is normally sliced. The coupons were approximately 1 by 0.25 by 0.1 inch (2.54 by 0.63 by 0.2 cm). Both the large bars, after grinding the base, and the coupons were sent to the coating vendor and were coated in the same pack cementation run.

The proprietary CoAl coating was deposited to a thickness of about 2.2 mils (5.6×10^{-3} cm). About 1.4 mils (3.6×10^{-3} cm) of the outer layer was the CoAl phase (identified by X-ray diffraction). The diffusion zone beneath the coating was about 0.8 mil (2×10^{-3} cm) thick. These thicknesses were approximately the same on both coupons and bars.

The coated specimens had a golden color and were metallic appearing. Surface examination showed sporadic depressions approximately 0.3 mil (0.7×10^{-3} cm) deep which may have been due to the removal of adherent pack particles. A few grains of the alumina pack material could still be seen clinging to the specimen surfaces.

TEST APPARATUS AND PROCEDURES

Furnace Testing

Two general types of furnace tests were used in this investigation. One utilized a

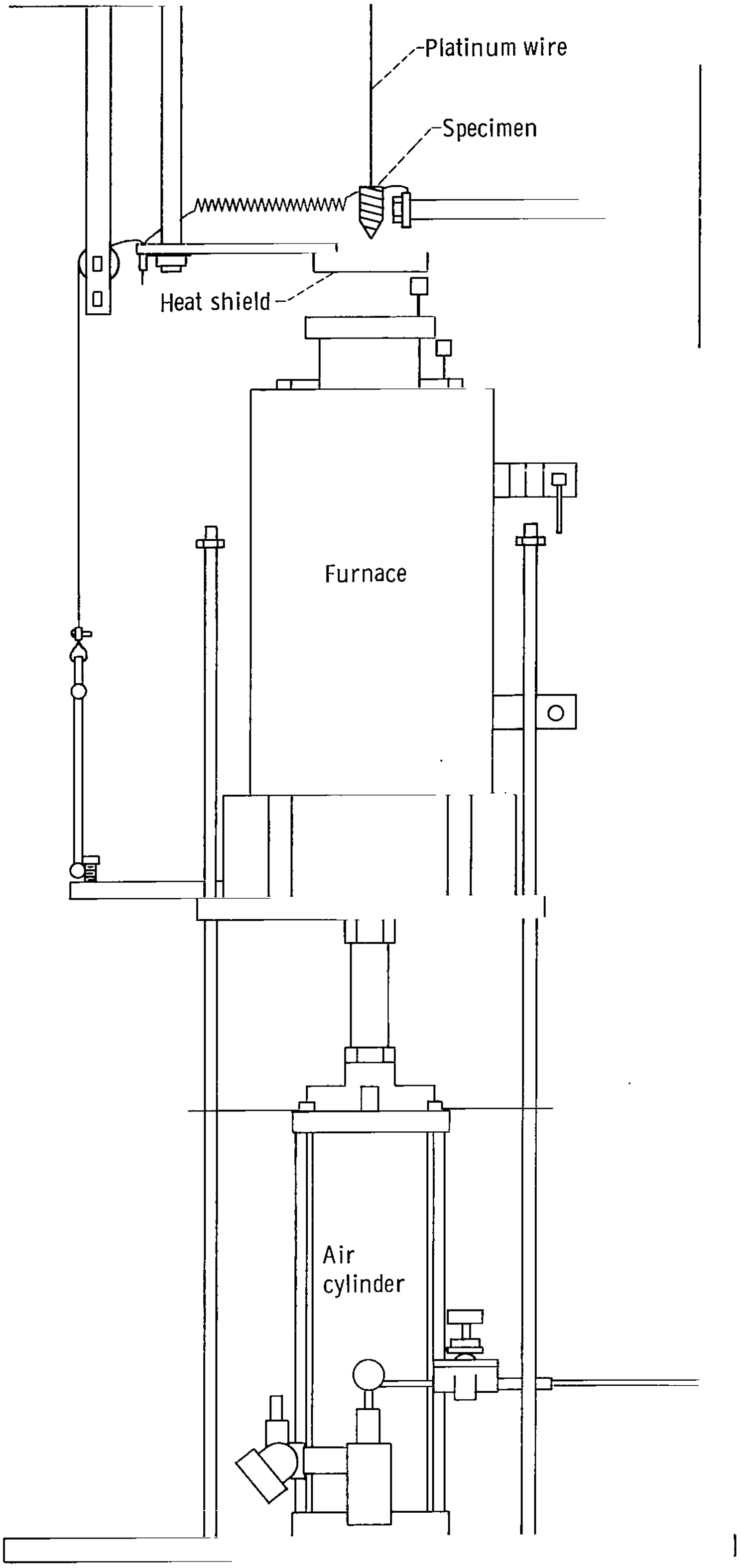


Figure 2. - Automatic cycling furnace.

multitube horizontal furnace. Here individual coupons were rested against one edge of high-purity alumina boats and the specimens were turned after each cycle. On each manual cycle, the boats were slowly inserted and later slowly removed from $1\frac{1}{2}$-inch- (3.8-cm-) diameter high-purity alumina tubes through which air flowed at 2 standard cubic feet per hour ($\sim\frac{1}{2}$ L/min). The other type of tests was conducted in vertical tube furnaces. Here the specimens were suspended in platinum wire harnesses and the furnace slowly raised or lowered around the specimen on each cycle. Only natural convection was employed to change the air in the tubes. In some cases, such furnaces were automated so that many short time (1 to 5 hr) exposure cycles could be achieved without the necessity of constant attendance by support personnel. A schematic diagram of the automatic cycling furnaces employed is shown in figure 2. The specimen hangs from a platinum wire. A heat shield blocks direct radiation and convection currents from the furnace allowing the specimen to cool to about 200° F after 10 minutes out of the furnace. Two timers operate the air solenoid valves which raise and lower the furnace. One controls the time in the up position - at temperature; the other the time in the down position - cooling.

All furnaces were controlled to $\pm 10^{\circ}$ F (5° C). Total specimen exposure times at test temperature ranged from 27 to 608 hours. The cycle times (i.e., the times at temperature between uniformly timed cooling cycles) were 1, 2, 5, 20, or 100 hours. Test temperatures were 1900°, 2000°, and 2100° F (1038°, 1093°, and 1149° C).

On an intermittent basis, the cooled specimens were lightly brushed and weighed.

In this report, the temperature, total exposure time, number of equally timed exposure cycles, and the furnace type are presented in abbreviated form. For example, 1900/100/50(V) means

1900 = exposure temperature, $^{\circ}$F

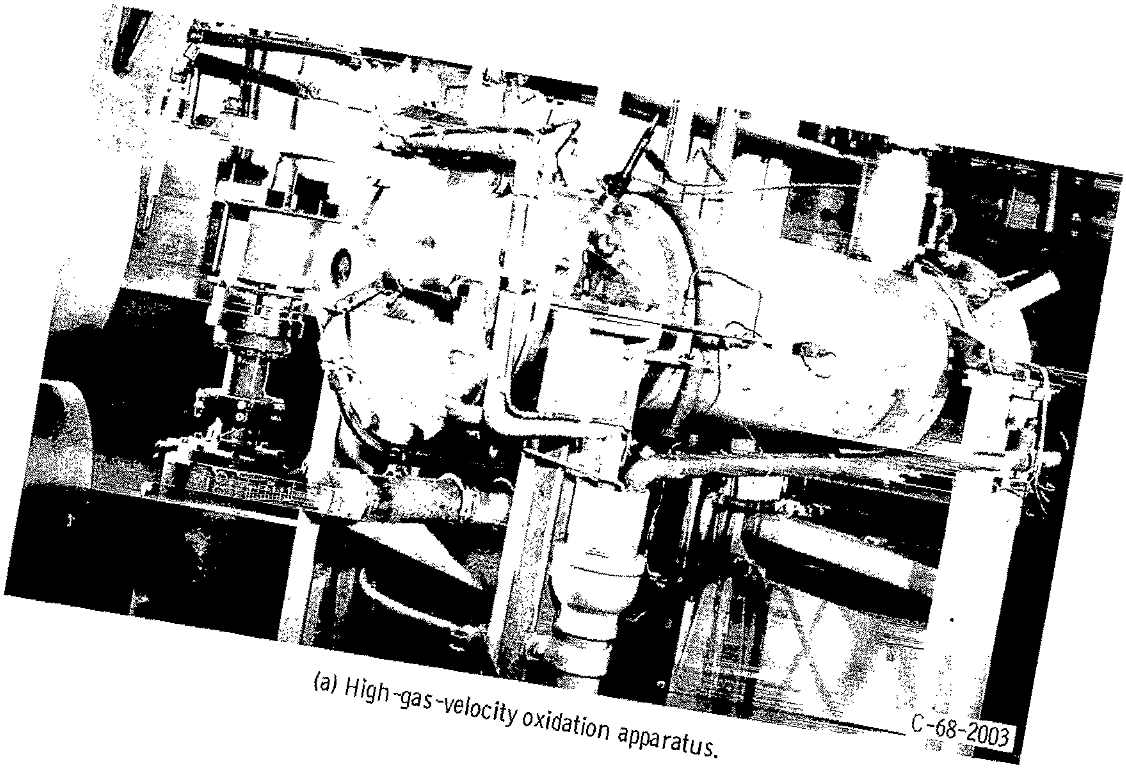
100 = total time at temperature, hr

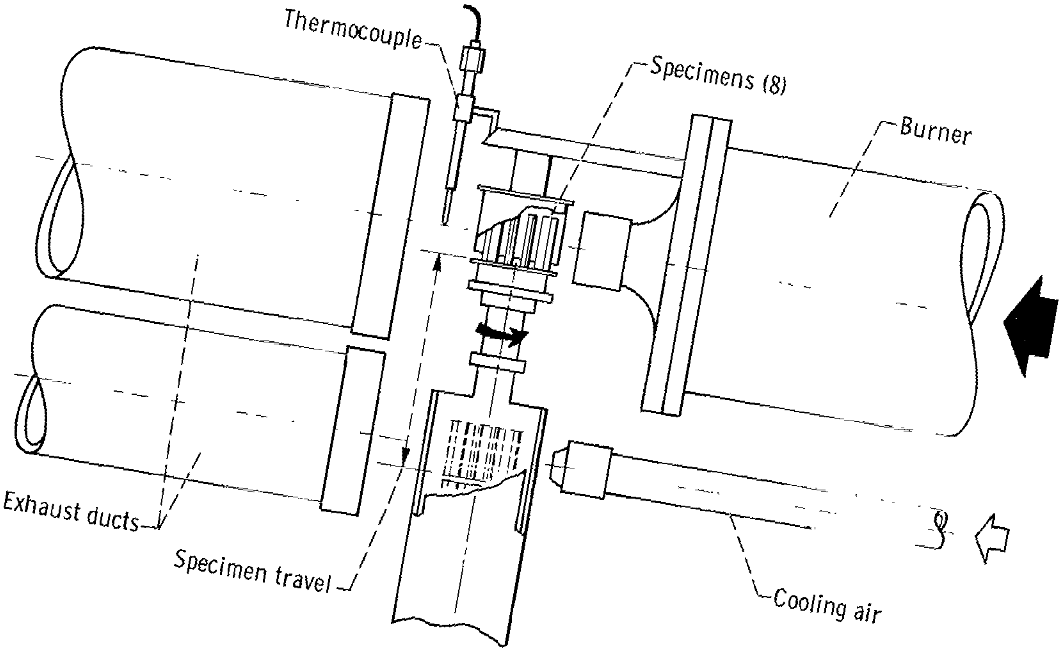
50 = number of equally timed exposure cycles; i.e.,

$$\frac{100\ \text{hr exposure}}{50\ \text{cycles}} = 2\ \text{hr/cycle}$$

and

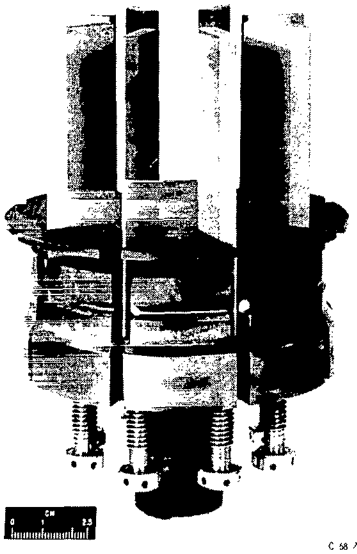
( ) = furnace type (V, vertical; H, horizontal tube)


(a) High-gas-velocity oxidation apparatus.



(b) Schematic of apparatus.

Figure 3. - High-gas-velocity oxidation apparatus.



(c) Specimen holder assembly.

Figure 3. - Concluded.

High-Velocity Testing

Figure 3 shows a picture (a), a schematic diagram (b), and a photograph of the specimen holder assembly (c) of the Mach 1, natural gas fueled test apparatus described in reference 1. The combustion gas from this apparatus is mostly air since the air to fuel ratio is approximately 30 to 1. Eight bar specimens rotate in the hot gas stream with the wedge portions closest to the nozzle. To provide rapid cooling (~100° F/sec or 55° C/sec), the rotating fixture is lowered into the path of Mach 1 cooling air. Temperatures are measured using a slip ring thermocouple arrangement connected to a dummy specimen in the rotating fixture and are controlled by a stationary control thermocouple downstream of the test bars. Temperature checks are made by a calibrated optical pyrometer. Specimen temperatures are maintained within ±15° F (8° C) during test.

At intervals of approximately 20 hours, the specimens are removed from the holder, weighed, and inspected. Testing is stopped when visual changes (black cobalt oxide) and/or weight changes (rapid loss of weight with time) indicate that the coating has definitely failed.

After testing, the bars are cross sectioned at points A, B, and C shown in figure 1 to provide metallographic cross sections at various temperature regions.

In this report, the suffix B will be used together with the temperature/time/cycle notation to designate a high-velocity test.

Additional Evaluation

Both surface and cross-sectional metallographic analyses were performed on the tested furnace coupons and on the high-velocity test bars using bright field and polarized light illumination. Normally, examination was made at ×250.

X-ray diffractometer scans were made on as-coated and selected as-tested furnace coupons using nickel filtered copper K-alpha radiation (40 kV, 40 mA). The resultant chart intensity data for the major diffraction peak of each phase detected were compared after various exposures.

RESULTS AND DISCUSSION

Furnace Testing (1900° F; 1038° C)

Figure 4 represents the weight change against time data for both uncoated WI-52 (2- and 20-hr cycles) and for aluminide-coated WI-52 (1-, 2-, 20-, and 100-hr cycles). Uncoated specimens gained weight for the first few cycles and then spalled heavily. Generally, the coated specimens spalled slightly on the first cycle and experienced a weight loss. Thereafter, generally, the coated specimens gained weight. After 200 hours at 1900° F (1038° C) little difference existed in weight change (-0.05 to 0.4 mg/cm^2) regardless of how many cycles had been applied. Only after about 420 hours of testing did

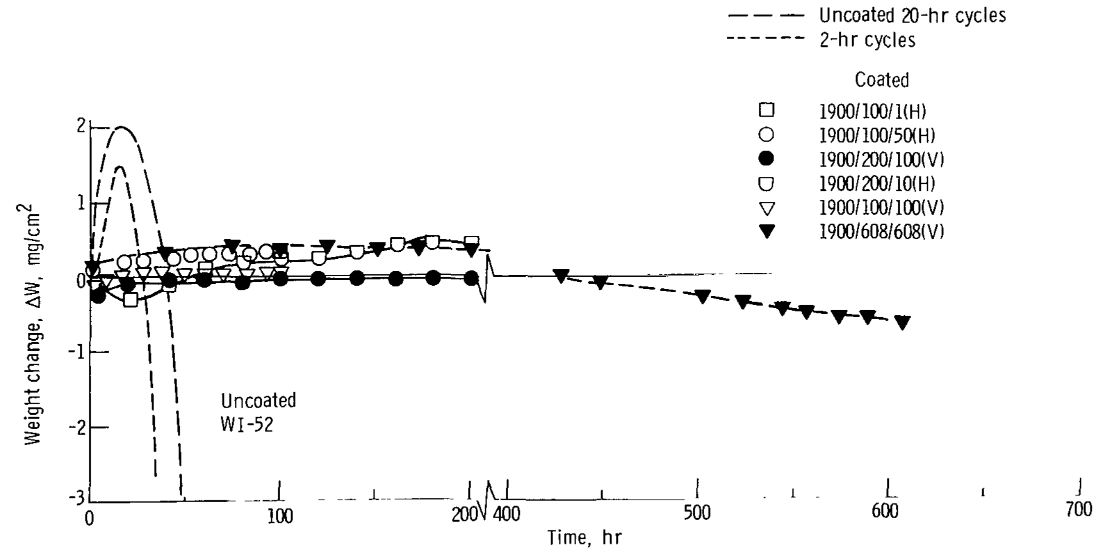


Figure 4. - Effect of cycle frequency and exposure duration on furnace oxidation resistance of aluminized WI-52 at 1900° F (1038° C).

TABLE I. - CHART INTENSITIES OF MAJOR DIFFRACTION PEAKS FOR PHASES OBSERVED AFTER AIR EXPOSURE OF ALUMINIDE COATED WI-52 AT 1900° F (1038° C)[a]

Exposure condition	Peak intensity		
	Strong	Medium	Weak
As-received	CoAl (diffuse)	-------	-------
1900/100/1(H)	CoAl	-------	Al_2O_3
1900/100/5(H)	------------	CoAl Al_2O_3	-------
1900/100/50(H)	------------	CoAl Al_2O_3	-------
1900/200/10(H)	------------	Al_2O_3 CoAl Cobalt solid solution	-------
1900/608/608(V)	------------	Cobalt solid solution Al_2O_3	CoAl $CoAl_2O_4$

[a] If more than one phase had the same intensity group rating, the more intense phase is listed first.

the 1900/608/608(V) specimen again begin to spall to the extent that a net weight loss was observed.

X-ray diffraction studies on selected specimens are summarized in table I. Here, the chart peak intensity for the major peak of each phase detected is presented for the various exposure conditions. The as-received material showed a strong but rather diffuse pattern for CoAl. After the 1900/100/1(H) exposure the CoAl pattern became sharper and a weak peak for aluminum oxide (Al_2O_3 - alpha corrundum structure) was detected. The 1900/100/5(H) and the 1900/100/50(H) specimens showed about the same intensities for both CoAl and Al_2O_3. After 1900/200/10(H), some cobalt solid solution was observed and further testing with more cycles, 1900/608/608(V), also resulted in the detection of a spinel phase of relatively low lattice parameter which is indexed to be $CoAl_2O_4$.

Contrary to the weight change data (fig. 4), microscopic examination of the external surface scales on the coupons after various exposures showed detectable differences. From the golden metallic color in the as-coated condition, the 1900/100/1(H) specimen developed a thin white oxide scale, which, based on X-ray diffraction, was alumina. Increasing cycles during 100 hours of exposure or increasing time beyond 100 hours caused this thin scale to develop blue areas. The cobalt aluminate spinel ($CoAl_2O_4$) phase is blue. A typical polarized light surface photomicrograph of a more severe ex-

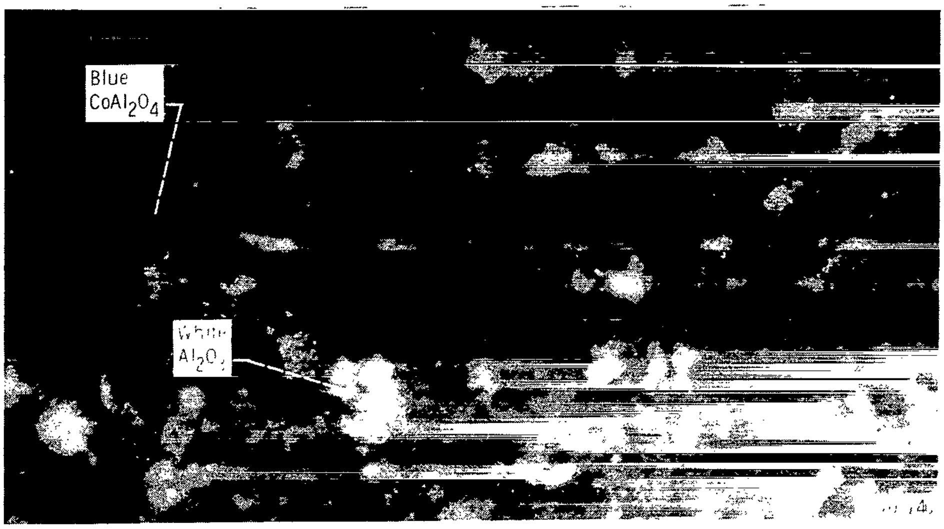


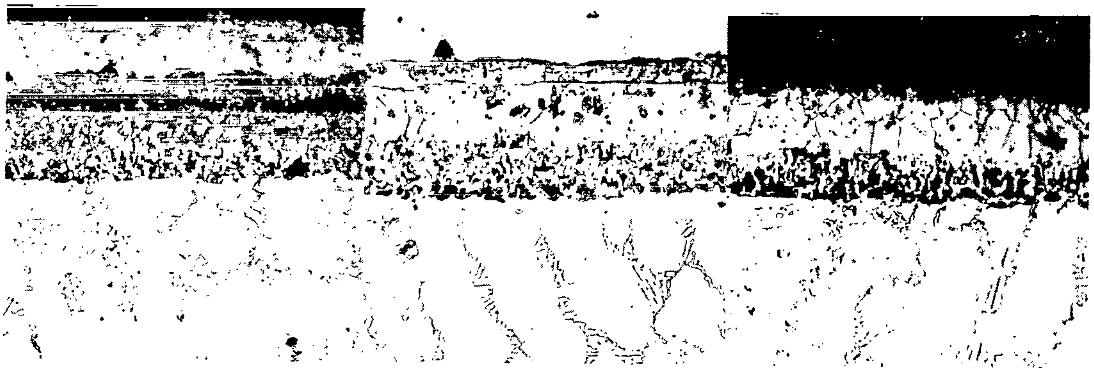
Figure 5. - Polarized light photomicrograph of 1900/200/10(H) specimen surface. X250.

posure condition (1900/200/10(H)) is presented in figure 5. Here, the white alumina areas are clearly distinguished from the blue $CoAl_2O_4$ background (black in reproduction). While X-ray diffraction did not detect the $CoAl_2O_4$ spinel until after the 1900/608/608(V) exposure, it was observed metallographically even on the mildly exposed 1900/100/5(H) specimen.

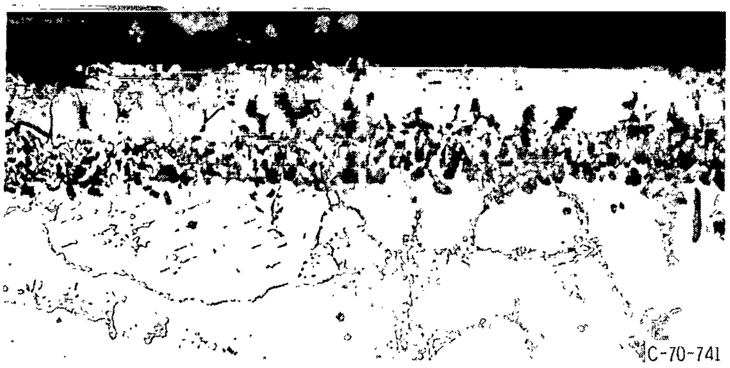
Metallographic analysis was conducted on cross sections of tested specimens exposed for various times and cycles. Figure 6 presents typical photomicrographs of some of these cross sections and a schematic drawing identifying the major microstructural features observed. For all specimens furnace tested at 1900° F (1038° C), table II summarizes thickness data for the various coating layers observed - aluminum depleted solid solution zone between the oxide and CoAl, CoAl layer, diffusion layer under the CoAl, and aluminum interdiffusion zone in the substrate. These data represent average measurements made from ×250 photomicrographs.

Several aspects of the metallographic data are worthy of note. Initially, the CoAl layer increases slightly in thickness. When the number of cycles and the cycle times are increased, which promotes spalling of the aluminum oxide scales, the CoAl layer appears to become thinner while the multiphase diffusion zone remains about the same. Also, while some cracks are shown in the as-deposited coating, cracks heal or appear less prone to form in the exposed specimens.

A white phase is seen randomly above the CoAl layer in the 1900/200/10(H) specimen. In the 1900/608/608(V) specimen this phase is a continuous layer ~0.2 mil or ~5 microns thick. This is believed to be the cobalt solid solution phase detected by X-ray diffraction on the latter specimen. Since none of the other specimens gave simi-



As-received 1900/100/1(H) 1900/100/50(V)



1900/200/10(H) 1900/608/608(V)

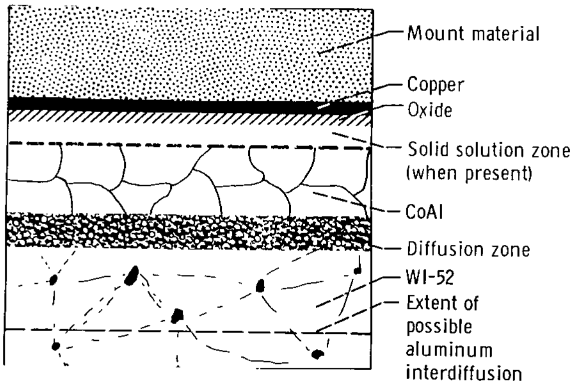


Figure 6. - Selected cross sections of aluminized WI-52 after cyclic furnace exposures at 1900 F (1038° C). X250.

TABLE II. - COATING ZONE THICKNESS DATA AFTER

1900° F (1038° C) FURNACE EXPOSURE

Furnace exposure condition	Approximate zone thickness, mils (cm)			
	Solid solution zone beneath oxide	CoAl zone	Diffusion zone	Observed aluminum interdiffusion zone
As-received	0	1.4 (0.0036)	0.8 (0.002)	0
1900/100/1(H)	↓	1.8 (0.0046)	1.2 (0.003)	↓
1900/100/5(H)		1.6 (0.0041)	1.0 (0.0025)	
1900/100/50(H)		1.4 (0.0036)	0.8 to 1.0 (0.002 to 0.0025)	
1900/200/10(H)	Trace	1.2 to 1.4 (0.003 to 0.0036)	0.8 to 1.0 (0.002 to 0.0025)	
1900/200/100(V)	Trace	1.4 (0.0036)	1.0 (0.0025)	1.0 (0.0025)
1900/608/608(V)	0.2 to 0.4 (0.0005 to 0.001)	1.0 (0.0025)	1.2 (0.003)	1.6 (0.0041)

lar X-ray diffraction responses, the response is not due to the substrate. This belief is confirmed by mass absorption calculations which show that X-rays diffracted by the substrate would be absorbed by a CoAl layer greater than 0.6 mil (1.5×10^{-3} cm). Furthermore, as will be presented in the following section, limited electron microprobe scans show that this white layer has a higher cobalt concentration and lower aluminum concentration than the CoAl layer; again indicating the solid solution.

Furnace Testing (2000° and 2100° F (1093° and 1149° C))

In figure 7, the weight change against furnace exposure time plots are presented for uncoated (2- and 20-hr cycles) and aluminide coated WI-52 tested under 1-, 2-, 5-, 20-, and 100-hour cyclic conditions at 2000° F (1093° C). The uncoated WI-52 lost weight rapidly after only a modest period of weight gain. In contrast to figure 4, the cycle frequency has a definite effect on coating weight change. As the number of cycles in a given total exposure time increases, the time to experience a net weight loss decreases. Figure 7 also shows that for the same test conditions, the results for either the horizontal or vertical tube furnace tests agree satisfactorily (compare the two curves for 20-hr cycles and the two for 2-hr cycles).

Table III contains the X-ray diffraction data obtained on selected specimens after the test. Here, as in the 1900° F (1038° C) exposure, the isothermal specimen alone

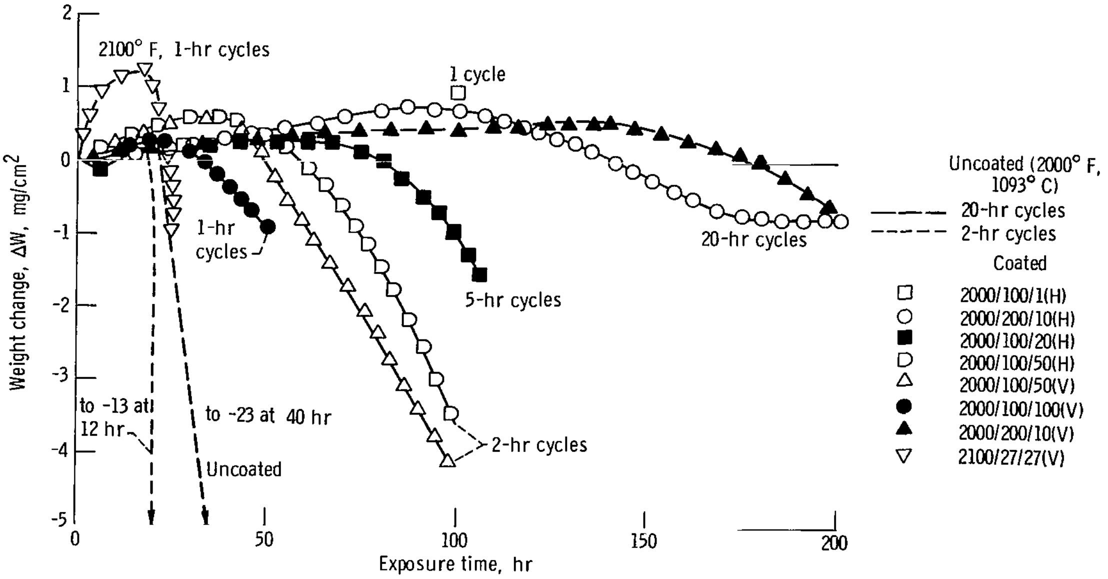
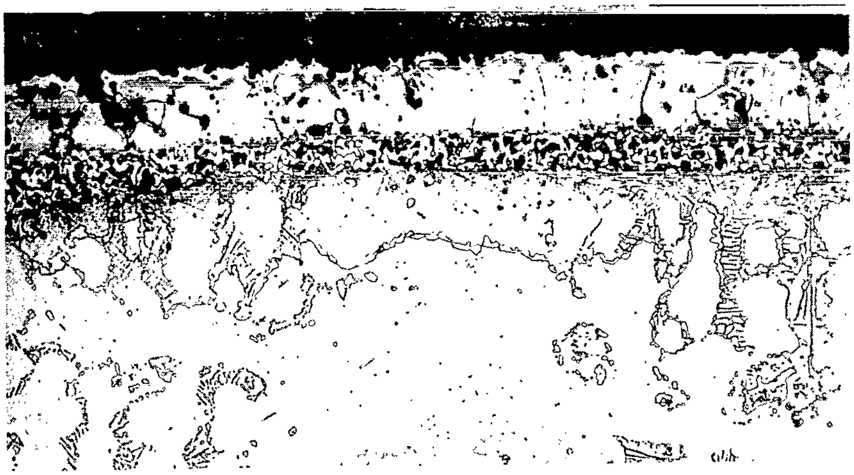


Figure 7. - Effect of cycle frequency and exposure duration on furnace oxidation resistance of aluminized WI-52 at 2000° F (1093° C) and 2100° F (1140° C).

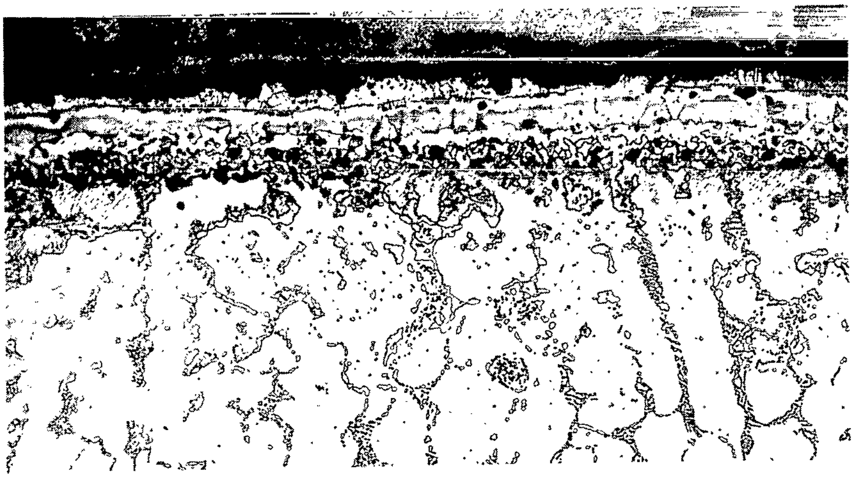
TABLE III. - CHART INTENSITIES OF MAJOR DIFFRACTION PEAKS FOR PHASES OBSERVED AFTER AIR EXPOSURE OF ALUMINIDE COATED WI-52 AT 2000° F (1093° C)[a]

Exposure condition	Peak intensity			
	Strong	Medium	Weak	Not detected
As-received	CoAl (diffuse)	------	------	----
2000/100/1(H)	CoAl	Al_2O_3		
2000/100/5(H)	Co solid solution	Al_2O_3	CoAl	----
2000/50/50(V)	---------------	Co solid solution	CoAl	----
2000/100/50(V)	---------------	Al_2O_3 $CoAl_2O_4$ Co solid solution	$CoAl_2O_4$ Al_2O_3 Trace of $CoCr_2O_4$	CoAl
2000/200/10(H)	---------------	$CoAl_2O_4$	Co solid solution Al_2O_3 Trace of $CoCr_2O_4$	CoAl

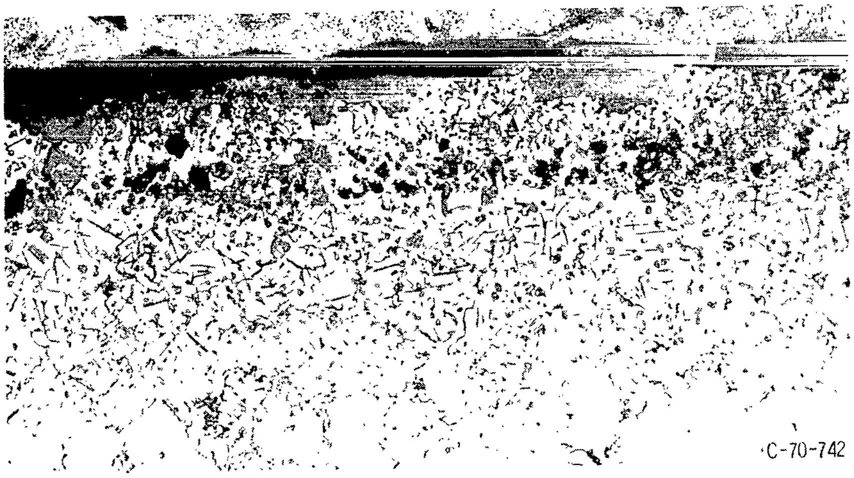
[a] If more than one phase had the same intensity group rating, the more intense phase is listed first.



Exposure condition, 2000/100/5(H).



Exposure condition, 2000/100/50(V).



Exposure condition, 2000/200/10(H).

Figure 8. - Degradation of aluminized WI-52 at 2000° F (1093° C) with increasing cycles or exposure time. X250.

showed only CoAl and Al_2O_3 (2000/100/1(H)). The 2000/100/5(H) specimen showed the additional cobalt solid solution phase which had been detected by X-ray diffraction only after longer times at 1900° F (1038° C). Increasing time and cycles resulted in the detection of $CoAl_2O_4$ (2000/50/50(V)). And the two specimens having either the most cycles (2000/100/50(V)) and/or the most exposure (2000/200/10(H)) showed the presence of a trace of $CoCr_2O_4$.

Visually these specimens ranged from white (2000/100/1(H)) to dark blue. They were similar to the 1900° F (1038° C) specimens, but the white Al_2O_3 scale was visibly thicker and the blue $CoAl_2O_4$ more abundant. The two most severely exposed specimens also contained dark green areas with brown islands in them. A previous study (ref. 2) identified such green areas as chromium oxide (Cr_2O_3), although none was detected by X-ray diffraction here, and the brown as a spinel of higher lattice parameter than $CoAl_2O_4$ which contained chromium - cobalt chromate spinel ($CoCr_2O_4$).

Pertinent metallographic cross sections are shown in figure 8. These cross sections illustrate further steps in the degradation of the coating. The thickness data for the various coating layers of all tested specimens are presented in table IV. As can be seen from figure 8, the degradation process is significantly accelerated by temperature

TABLE IV. - COATING ZONE THICKNESS DATA AFTER 2000° F (1093° C)

AND 2100° F (1140° C) FURNACE EXPOSURE

Furnace exposure condition	Approximate zone thickness, mils (cm)			
	Solid solution zone beneath oxide	CoAl zone	Diffusion zone	Observed aluminum interdiffusion zone
As-received	0	1.4 (0.0036)	0.8 (0.002)	0
2000/100/1(H)	0	1.6 (0.0041)	1.2 (0.003)	↓
2000/100/20(V)	0.2 to 0.4 (0.0005 to 0.001)	1.0 to 1.2 (0.0025 to 0.003)	0.8 (0.002)	↓
2000/100/50(H)	0.4 to 0.8 (0.001 to 0.002)	0.4 to 0.6 (0.001 to 0.0015)	0.8 to 1.2 (0.002 to 0.003)	↓
2000/100/100(V)	0.2 to 0.4 (0.0005 to 0.001)	0.6 (0.0015)	0.8 (0.002)	↓
2000/120/60(V)	0.2 to 0.6 (0.0005 to 0.0015)	0.6 (0.0015)	1.0 (0.0025)	↓
2000/50/50(V)	0.2 (0.0005)	1.0 (0.0025)	0.8 (0.002)	0.6 (0.0015)
2000/200/10(H)	0.8 to 1.6 (0.002 to 0.0041)	0 to 0.8 (0 to 0.002) (Imminent failure)	---------------	4 to 5 (0.01 to 0.0125) (Internal oxidation of aluminum)
2000/200/10(V)	0.4 (0.001)	0 to 0.8 (0 to 0.002)	0.8 to 1.2 (0.002 to 0.003)	3 (0.0008) (Internal oxidation of aluminum)
2100/27/27(V)	0.4 (0.001)	0.4 to 1.0 (0.001 to 0.0025)	1.0 (0.0025)	0

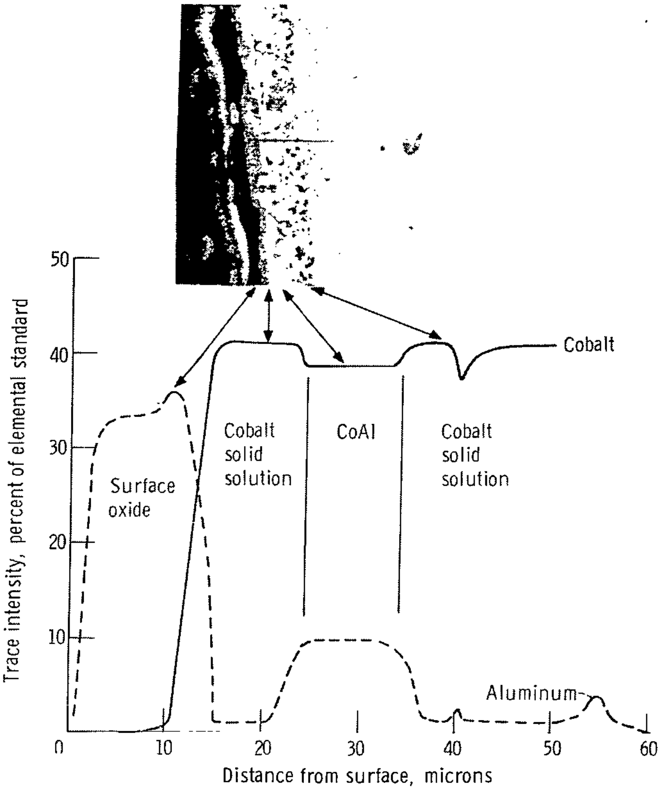


Figure 9. - Electron microprobe trace on cross section of 2000/100/50(V) exposed aluminide coated WI-52 specimen.

and cycling. At 2000° F (1093° C), the cobalt solid solution layer formed on the CoAl after only five 20-hour cycles, 2000/100/5(H), whereas at 1900° F (1038° C), a complete layer was observed only on the 1900/608/608(V) specimen. With further cycling the CoAl became thinner and the cobalt solid solution became more extensive above and below the CoAl - 200/100/50(V). Figure 9 presents a second micrograph of this specimen showing a single microprobe beam path as well as the resultant raw traces for Co and Al, obtained using two spectrometers simultaneously. These are uncorrected traces. They show, however, a relatively low aluminum content in the solid solution zone beneath the oxide, a higher aluminum concentration in the CoAl phase, a decrease in aluminum in the solid solution zone beneath the CoAl, and finally the gradual drop of aluminum to zero in the interdiffusion region. After 200 hours of exposure, figure 8 shows that complete coating failure is imminent (2000/200/10(H)). In areas where some CoAl still remains, no internal oxidation can be observed, and the scale was white (Al_2O_3) and blue ($CoAl_2O_4$). In areas where the CoAl was completely consumed, internal oxidation has taken place to a depth of 4 to 5 mils (10 to 12×10^{-3} cm) (not shown completely in the figure). The scale above these regions was green (Cr_2O_3) and brown ($CoCr_2O_4$).

Similar to the results at 2000° F (1093° C), after only 27 hours at 2100° F (1149° C) a significant portion of the CoAl in the coating had been consumed.

High-Velocity Testing

The weight change data presented in figure 10 represent the total weight change for coated WI-52 tested at 1900°, 2000°, and 2100° F (1038°, 1093°, and 1149° C) using 1-hour exposures. Also plotted are data for uncoated WI-52 similarly tested at 2000° F (1093° C). The simple aluminide coating under investigation survives only 12 hours at 2100° F (1149° C) and 60 hours at 2000° F (1093° C), as shown by the arrows in figure 10 which indicate visual failure. Even at 1900° F (1038° C), the coating visually failed

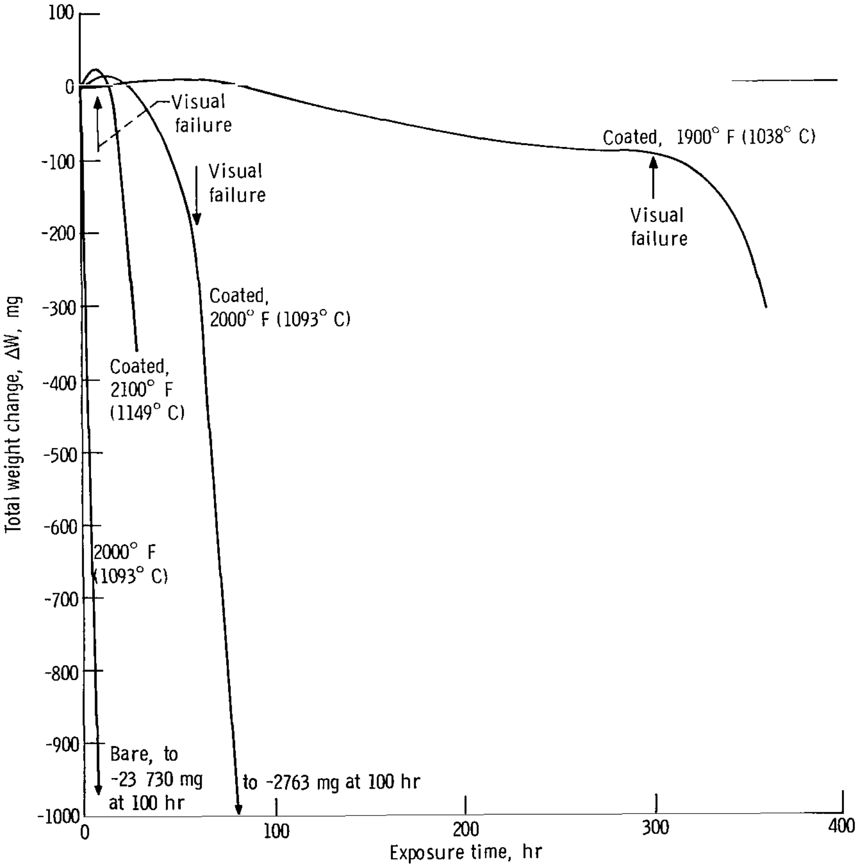
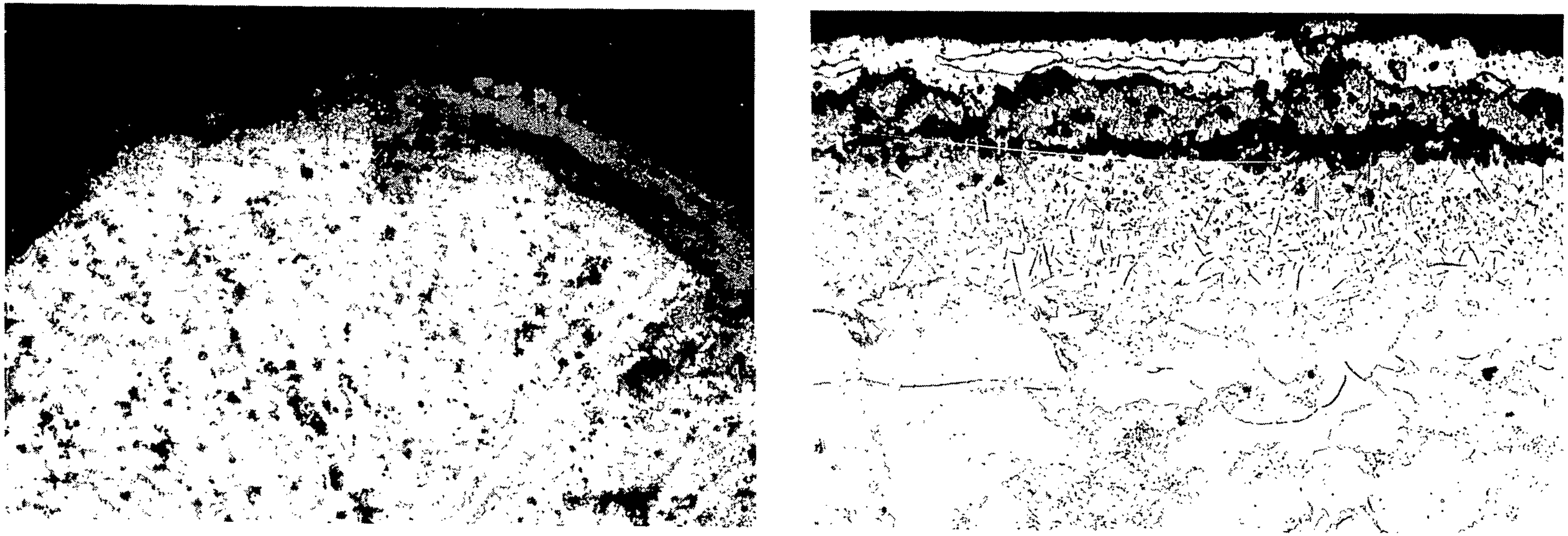
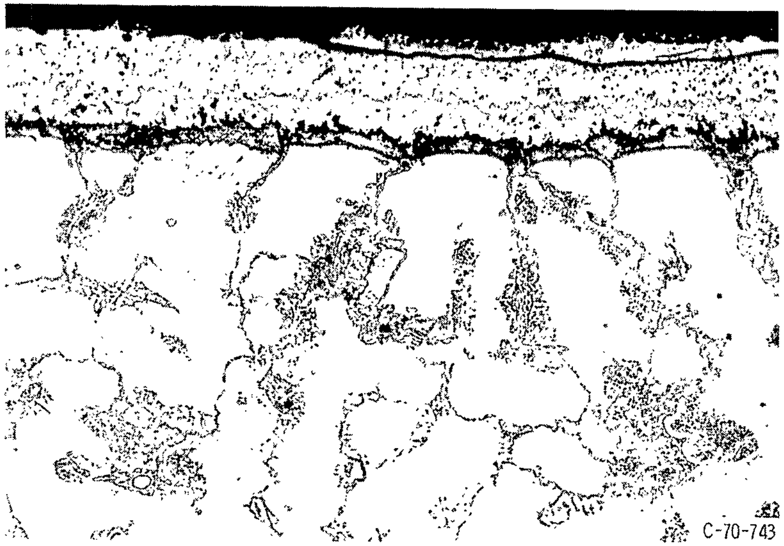


Figure 10. - Effect of temperature on oxidation weight changes of aluminized WI-52 in Mach 1 apparatus for 1-hour cycles.



(a) Temperature, 1915° F (1046° C); position A; leading edge. X100.

(b) Temperature, 1925° F (1051° C); position B; side. X250.



(c) Temperature, 1640° F (893° C); position C; side. X250.

Figure 11. - Degradation of coating on aluminized WI-52 at three locations after Mach 1 oxidation testing at ~1900° F (1038° C) for 380 hours (1-hr cycles).

within 300 hours. The visual failure criteria was the change in scale color from white or gray-blue to black, indicating the presence of cobalt oxide (CoO) which is the same major oxide that forms on the uncoated WI-52.

Cross sections of appropriate regions (locations A, B, and C in fig. 1) were examined after test. These cross sections are illustrated in figure 11 for a bar tested at 1900° F (1038° C). This figure shows the leading edge of the hot zone (A), the side of the bar in the hot zone (B), and the side of the bar in a cooler zone near the base (C). Observed temperatures measured by an optical pyrometer are also presented. This figure shows how the coatings generally fail at the leading edge, which is the region subjected to the most rapid temperature changes. Once failed, oxidation appears to proceed down the carbide phases and significant loss of load bearing area results. At approxi-

TABLE V. - COATING ZONE THICKNESS DATA AFTER MACH 1 TEST EXPOSURE

AT 1900° F (1038° C), 2000° F (1093° C), AND 2100° F (1145° C)

Mach 1 exposure condition, °F (°C)	Approximate zone thickness, mils (cm)			
	Solid solution zone beneath oxide	CoAl zone	Diffusion zone	Observed aluminum interdiffusion zone
		1900/308/308(B)		
[a]1915 (1046)	(b)	(b)	(b)	(b)
[c]1925 (1051)	0.3 to 0.5 (0.0008 to 0.0012)	Islands only		3.3 (0.0084)
[d]1640 (893)	0	1.2 (0.003)	0.8 to 1.0 (0.0020 to 0.0025)	0.4 (0.001)
		2000/100/100(B)		
[a]1995 (1090)	(b)	(b)	(b)	(b)
[c]2005 (1096)	0.2 to 0.4 (0.0005 to 0.0010)	0.1 to 0.6 (0.0002 to 0.0015)	1.2 to 1.4 (0.0030 to 0.0036)	0
[d]1660 (905)	0	1.2 to 1.4 (0.0030 to 0.0036)	0.6 to 1.0 (0.0015 to 0.0020)	0
		2100/27/27(B)		
[a]2095 (1146)	(b)	(b)	(b)	(b)
[c]2105 (1151)	0.2 to 0.8 (0.0005 to 0.002)	0.6 to 1.0 (0.0015 to 0.002)	0.8 to 1.2 (0.002 to 0.003)	0
[d]1780 (971)	0	1.2 (0.003) cracks	0.6 to 1.0 (0.0015 to 0.002)	0

[a] Leading edge, $1\frac{1}{4}$ in. (3.2 cm) from tip.

[b] Coating failure.

[c] Side of bar, $1\frac{5}{8}$ in. (4.2 cm) from tip.

[d] Side of bar, $2\frac{1}{2}$ in. (6.4 cm) from tip.

mately the same temperature, the coating on the side of the specimen (B) shows imminent failure and considerable internal oxidation which lead to cracking during sample preparation. The cooler region (C), more representative of current commercial engine service temperatures, is still in very good condition. Thickness data for all coating layers at all three temperatures are presented in table V.

Comparison and Evaluation of Test Results

Figure 12 compares the 1-hour cyclic furnace weight change data with the 1-hour cyclic data obtained in the Mach 1 test apparatus. The weight change data shown in figure 10 were converted to milligrams per square centimeter by dividing by 30 square centimeters, the approximate area of the hot zone. These data show that at both 2100° and 2000° F (1149° and 1093° C) the cyclic furnace tests are only slightly less severe than the Mach 1 tests. At 1900° F (1038° C), however, the furnace weight change behavior is significantly less severe than that in the high-velocity apparatus. These differences may well be related to the differences in alumina scale growth rate with temperature. Thick alumina scales are developed at the higher temperatures, and thick scales spall more readily than thinner scales. Thus, at the higher exposure temperatures, both the relatively slow cool down in the furnace tests and the very rapid cool down in the burner tests

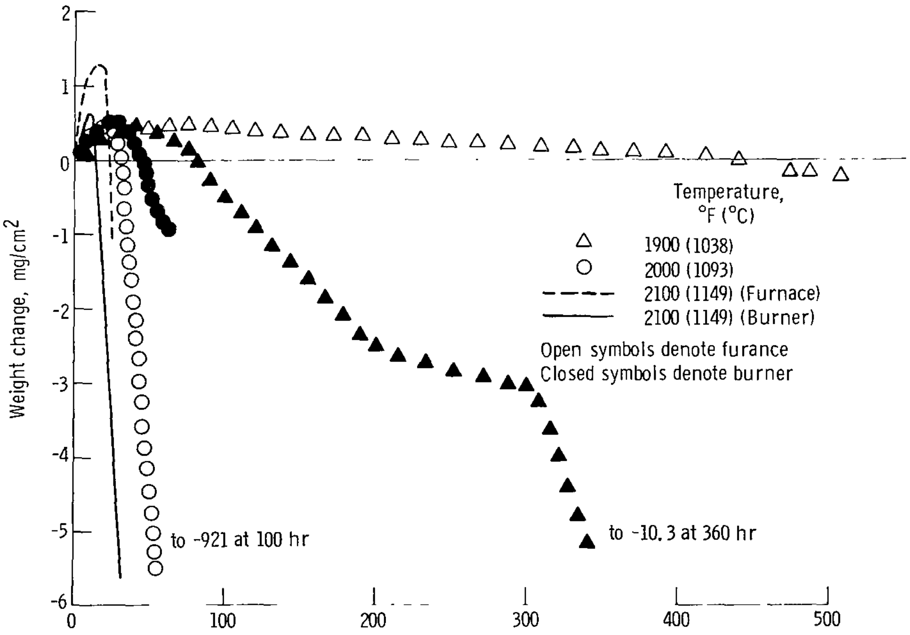


Figure 12. - Comparison of 1-hour cyclic oxidation weight change for furnace and burner rig tested aluminide coated WI-52.

may both have been sufficient to produce significant spalling. Because the 1900° F (1038° C) scales appeared much thinner, only the rapid quench in the Mach 1 cold air stream may have been enough to cause them to spall significantly.

Based on the surface and cross-sectional metallography, coupled with observed weight losses and X-ray diffraction data, the degradation of the aluminide coating is schematically summarized in figure 13. This process is continuous even though for ease of presentation it is shown as a series of steps.

First, white to gray alumina (Al_2O_3 aluminum oxide) forms on the surface of the CoAl phase during oxidation (b). Some interdiffusion and growth of the CoAl layer also occurs in the early stages of testing. With increased time and cycling, spallation of the alumina surface scale takes place, greater amounts of $CoAl_2O_4$ (a spinel oxide-cobalt aluminate) form, and the surfaces appear a gray-blue color (c). Further exposure produces continued spalling of Al_2O_3 and $CoAl_2O_4$. The oxide scale that then grows on the surface contains more of the $CoAl_2O_4$ phase. The loss of aluminum in reforming the $Al_2O_3/CoAl_2O_4$ scale depletes the CoAl of enough aluminum so that a cobalt solid solution layer forms between the external scale and the remaining CoAl phase (d). Then, further spalling and oxide formation remove more aluminum from the coating and the continuous layer of CoAl begins to break into islands surrounded by the solid solution (e). During these stages some aluminum also appears to diffuse inward (as indicated by very subtle etching effects). As the islands of CoAl disappear due to the continued loss of aluminum caused by $CoAl_2O_4$ scale spalling, internal oxidation (to Al_2O_3) of the region enriched by inward diffusion of aluminum occurs. With the aluminum reservoir in the coating nearly depleted, $CoCr_2O_4$ (a spinel oxide-cobalt chromate) and perhaps Cr_2O_3 begin to form in the oxide scale (f). Beyond this stage, as observed on the high-velocity test specimens, the black CoO forms; this oxide spalls severely on thermal cycling.

The degradation of an aluminide coating on a cobalt alloy appears similar to that observed for aluminide coatings on nickel alloys (ref. 3) where spalling of the aluminum rich surface oxides causes aluminum loss from NiAl. This results in the formation of Ni_3Al and eventually a nickel solid solution containing aluminum. Because of the lack of an analog to Ni_3Al in the cobalt system (ref. 4), the process of aluminum depletion producing the solid solution from the monoaluminide appears to be more rapid. This more rapid degradation and the attendant development of less protective oxides than Al_2O_3 is substantiated by the data of reference 5. These data show that several commercial coatings on two cobalt alloys generally fail earlier than commercial aluminide coatings on nickel alloys.

If the time to visual failure in the high-velocity test specimens is plotted logararithmically against exposure time as in figure 14, the three failure points from this study fall on a straight line. Assuming that rapid interdiffusion allows the CoAl layer to reach a thickness of approximately 1.8 mils (4.5×10^{-3} cm) as shown in figure 6, the consump-

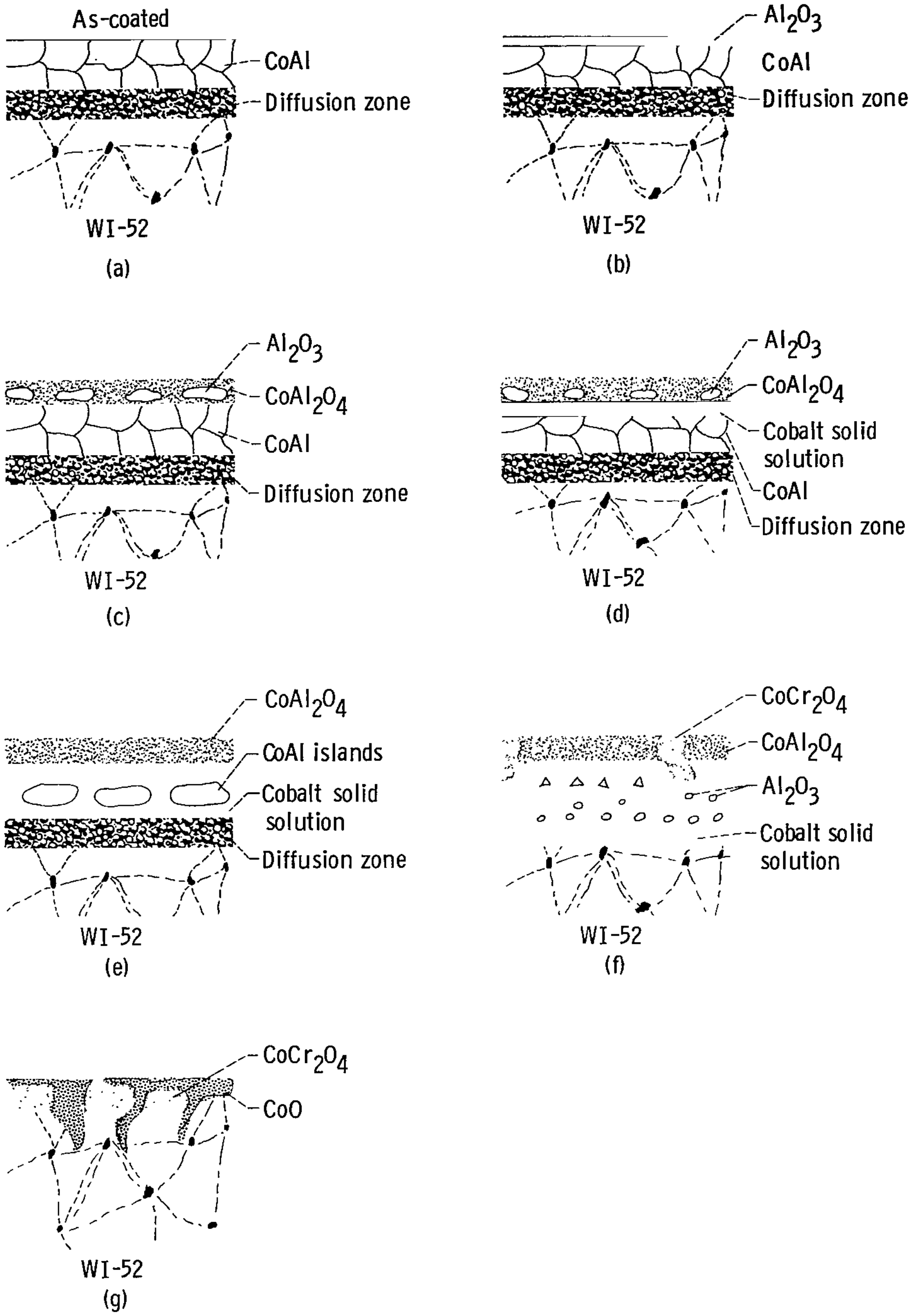


Figure 13. - Schematic degradation of an aluminide coating on WI-52.

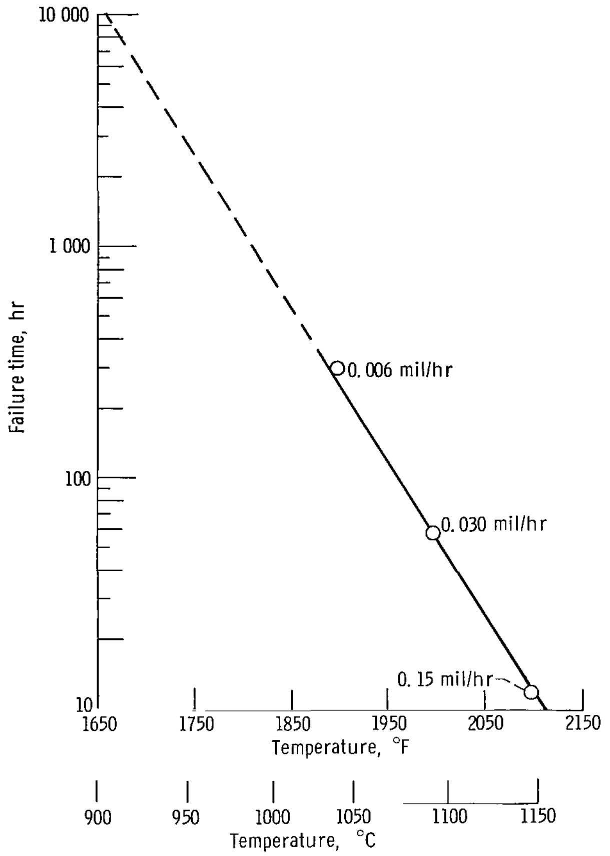


Figure 14. - Effect of temperature on life of aluminide coated WI-52 in high-velocity tests using 1-hour cycles.

tion of CoAl can be determined for the failure time in mils per hour. These approximate values are also shown in figure 14. The times to failure decrease by an order of five for each 100° F (55° C) increase in temperature. If these relations hold true for lower temperature exposure as well, the coating tested would have a life of about 1500 hours at 1800° F (982° C) and about 7500 hours at 1700° F (927° C).

CONCLUSIONS

Cyclic furnace and Mach 1 oxidation tests were performed on cobalt alloy WI-52 coated with a widely used commercial aluminide coating. Furnace test conditions ranged from 608 hours at 1900° F (1038° C) to 27 hours at 2100° F (1149° C). The furnace tests included exposure cycles of 1, 2, 5, 20, and 100 hours. Similarly, Mach 1 high-velocity oxidation test conditions ranged from 360 hours at 1900° F (1038° C) to 27 hours at

2100° F (1149° C) using only 1-hour cycles. The following conclusions can be drawn from the results of these tests and the subsequent metallurgical and X-ray diffraction analyses:

1. The protection provided by the coating in the Mach 1 tests was limited to 300 hours at 1900° F (1038° C), 60 hours at 2000° F (1093° C), and 12 hours at 2100° F (1149° C). Thus, there was an order of five increase in life for every 100° F (55° C) decrease in test temperature. These findings indicate that simple aluminide coatings are not adequate for multithousand-hour service at temperatures above 1900° F (1038° C) in advanced engines.

2. Cycle frequency, at the higher test temperatures of this study, strongly influences the rate of coating degradation. For a given high-temperature exposure time, increasing the cycle frequency decreases the life of the coating.

3. For this coating system, at 2000° F (1093° C) and above, simple furnace tests give results similar to high-velocity tests.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, March 5, 1970,
129-03.

REFERENCES

1. Johnston, James R.; and Ashbrook, Richard L.: Oxidation and Thermal Fatigue Cracking of Nickel- and Cobalt-Base Alloys in a High Velocity Gas Stream. NASA TN D-5376, 1969.

2. Grisaffe, Salvatore J.; and Lowell, Carl E.: Examination of Oxide Scales on Heat Resisting Alloys. NASA TN D-5019, 1969.

3. Goward, G. W.; Boone, D. H.; and Giggins, C. S.: Formation and Degradation Mechanisms of Aluminide Coatings on Nickel-Base Superalloys. Trans. ASM, vol. 60, no. 2, June 1967, pp. 228-241.

4. Hansen, Max: Constitution of Binary Alloys. Second ed., McGraw-Hill Book Co., Inc., 1958.

5. Moore, V. S.; Brentnall, W. D.; and Stetson, A. R.: Evaluation of Coatings for Cobalt and Nickel-Base Superalloys. Vol. 1. Rep. RDR-1474-2, Solar Div., International Harvester (NASA CR-72359), Jan. 31, 1969.

NASA-Langley, 1970 —— 17 E-5307

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546

OFFICIAL BUSINESS

FIRST CLASS MAIL

POSTAGE AND FEES PAID
NATIONAL AERONAUTICS AND
SPACE ADMINISTRATION

[illegible]
[illegible]
[illegible]

[illegible]

POSTMASTER: If Undeliverable (Section 158 Postal Manual) Do Not Return

> *"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."*
>
> —NATIONAL AERONAUTICS AND SPACE ACT OF 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS: Information receiving limited distribution because of preliminary data, security classification, or other reasons.

CONTRACTOR REPORTS: Scientific and technical information generated under a NASA contract or grant and considered an important contribution to existing knowledge.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities. Publications include conference proceedings, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

TECHNOLOGY UTILIZATION PUBLICATIONS: Information on technology used by NASA that may be of particular interest in commercial and other non-aerospace applications. Publications include Tech Briefs, Technology Utilization Reports and Notes, and Technology Surveys.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION DIVISION

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Washington, D.C. 20546