Sc. Dc-65-1520

MASTER

TECHNICAL REPORT

DISPERSAL OF REACTOR CORE MATERIALS BY REENTRY PROCESSES

by: J. L. Beal, W. R. Brown, and R. L. Pleuthner

CAL No. 114-080-1, Suborder No. 8
(Includes 114-020-2, Suborder No. 2)

QUARTERLY REPORT

Contract No.: Sandia Corporation

P. O. 4804/002 and 4804/008

CAL Project No. AA-1974-Y

April 1965 (Includes October 1964)

APPROVED FOR PUBLIC RELEASE

CORNELL AERONAUTICAL LABORATORY, INC.

OF CORNELL UNIVERSITY, BUFFALO, N. Y. 14221

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

MASTER

CORNELL AERONAUTICAL LABORATORY, INC.
BUFFALO, NEW YORK 14221

CAL REPORT NO. 114-080-1, SUBORDER NO. 8
(INCLUDES 114-020-2, SUBORDER NO. 2)
CAL PROJECT NO. AA-1974-Y

Quarterly Report
DISPERSAL OF REACTOR CORE MATERIALS
BY REENTRY PROCESSES

CONTRACT NO. SANDIA CORPORATION
P.O. 4804, SUBORDER NO. 8
(INCLUDES P.O. 4804/002)

April 1965
(Includes October, 1964)

Prepared By:

J.L. Beal
W.R. Brown
R.L. Pleuthner

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

FOREWORD

This report was prepared by Cornell Aeronautical Laboratory, Inc. of Cornell University, Buffalo 14221, New York on the Sandia Corporation Purchase Order No. 4804/008, Suborder No. 8, "Dispersal of Reactor Core Materials by Re-entry Processes", dated March 3, 1965. This program is being administered under the direction of Mr. L. O. Cropp of the Sandia Corporation. Dr. John L. Beal, Staff Scientist, is Principal Investigator on this project at CAL.

The studies presented in this report were performed during the period August 1, 1964 through October 31, 1964 (Purchase Order No. 4804/002) and during the period February 1, 1965 through April 30, 1965 (Purchase Order No. 4804/008). A report covering the former of these periods was not issued at the customary time. This report is issued both as the current report and, with the agreement of the sponsor, is issued in lieu of that former report.

This report discusses the results of an experimental study of the oxidation of zirconium rods under simulated reentry conditions. It is the ninth report in this series entitled "Dispersal of Reactor Core Materials by Re-entry Processes". The previous reports are as follows.

Preliminary Analysis--July 1962
Contract No. P.O.No.51-1136
Suborder No. 7, Sandia Corporation
CAL Report No. AA-1506-W-1

Quarterly Report--May 1963
Contract No. Sandia Corporation
P.O.No.82-3524, Suborder No. 1
Report No. I08-100, Suborder No. 1
CAL Project No. AA-1738-Y

Second Quarterly Report--August 1963
Contract No. Sandia Corporation
P.O.No.82-3524, Suborder No. 1
Report No. I08-100-2, Suborder No. 1
CAL Project No. AA-1738-Y

Quarterly Report--November 1963
Contract No. Sandia Corporation
P.O. 82-6127, Suborder No. 1
Report No. I10-100-1, Suborder No. 1
CAL Project No. AA-1861-Y

Quarterly Report--January 1964
Contract No. Sandia Corporation
P.O. No. 82-6127, Suborder No. 1
Report No. I10-100-2, Suborder No. 1
CAL Project No. AA-1861-Y

Quarterly Report--April 1964
Contract No. Sandia Corporation
P.O. 82-6127, Suborder No. 1
Report No. I10-100-3, Suborder No. 1
CAL Project No. AA-1861-Y

Quarterly Report--July 1964
Contract No. Sandia Corporation
P.O. No. 82-6127, Suborder No. 9
Report No. I10-900-1, Suborder No. 9
CAL Project No. AA-1861-Y

Quarterly Report--January 1965
Contract No. Sandia Corporation
P.O. 4804, Suborder No. 2
Report No. I14-020-1, Suborder No. 2
CAL Project No. AA-1974-Y

ABSTRACT

Zirconium rods were tested under simulated reentry conditions. Melting phenomena were observed and debris from rapidly ablating rods was collected. Temperature rise rates of the rods were determined by several methods and compared with rates calculated for different intensities of oxidation heating. Based on the tests, a method for computing the oxidation heating effect is suggested.

TABLE OF CONTENTS

	Page No.
FOREWORD	ii
ABSTRACT	iii
SYMBOLS	v
INTRODUCTION	1
TEST CONDITIONS	4
FLIGHT CONDITIONS SIMULATED BY THE TEST	6
TEST MODELS	11
AVERAGE HEAT FLUX AROUND CYLINDER	14
OBSERVATION OF MELTING PHENOMENA	16
TEMPERATURE MEASUREMENT METHODS	24
CALCULATION OF TEMPERATURE RISE	26
RESULTS OF TESTS	30
SUGGESTED METHOD FOR COMPUTING OXIDATION HEATING	38
ABLATION DEBRIS	39
REFERENCES	40

SYMBOLS

A	area
C	specific heat
D	diameter
H	enthalpy
ΔH_{ox}	heat of oxidation per unit of oxygen
M	Mach number
P	pressure
q	heating rate per unit area
q_{av}	average heating rate around cylinder walls
q_s	heating rate at stagnation line of cylinder
r	radius
St	Stanton number
T	temperature
T_{av}	average temperature of rod material
T_w	surface temperature of rod
t	time
u	velocity
u_c	orbital velocity
V	volume
α	thermal diffusivity
ϵ	emissivity
ρ	density
ρ_{SL}	sea level density of air
σ	Stefan-Boltzmann constant
$()_s$ or $()_{stag}$	stagnation
$()_\infty$	free stream

INTRODUCTION

During the burnup of reentering materials, heating by oxidation may be a factor in achieving melting and disintegration of some materials. The work described in this report concerns the oxidation heating of metallic zirconium under simulated reentry conditions.

The study of oxidation under reentry conditions is made difficult by the fact that the state-of-the-art in this general area is not well developed. Test techniques and methods need development. For any particular material, the basic phenomena, such as melting characteristics when oxidizing in high-velocity flow, need to be observed. Zirconium metal was selected for the study partly because it is a metal which oxidizes rapidly and partly because it has interest as the parent material to which zirconium hydride, a fuel rod material, returns as it is heated toward the melting point.

Previous work at this Laboratory on the oxidation of zirconium includes bench tests and plasma jet tests in which oxidation heating was observed quantitatively but under conditions different from reentry. Reference 1 gives results of some of these studies and shows that the oxygen absorbed is a function of the temperature of the surface and the time required to heat to an elevated temperature. In these tests, the heating rate per pound of oxygen absorbed appeared to be abnormally high, near 23,000 Btu/lb oxygen, when compared with the expected value, which is near 14,500. It was thought that this high value might have been associated with some abnormality (such as excessive ionization) of the plasma jet stream used in the tests.

In other tests, very rapid ablation was observed to have been initiated quickly when the flow density was abnormally high, compared with reentry, and rapid ablation was not initiated when the temperature rise rate was slow. It was desired to learn more about the initiation of rapid ablation.

The previous tests of oxidation of zirconium rods in the Plasma Jet Facility used a very low stream velocity, of the order of 200-300 ft/sec. The free stream had high ambient enthalpy. This condition was used because it permitted ready adjustment of the heating rate in the range of interest. Other than average heating rate, which was determined by the temperature rise of the specimens, the stream properties, including its uniformity, were very poorly known.

The plasma jet tests left much lacking in the simulation of the high-velocity conditions of reentry. Besides heating rate, the supply of oxygen to the interface by boundary layer diffusion, is important. In case plasma jet heating rates are made high by the use of low-density flow at higher-than-normal enthalpy (this method is easy to use with a plasma jet although it was not used in these tests), then the oxygen supply by diffusion through the boundary layer is low. In the extreme, this would prevent study of reaction-controlled oxidation of a material inasmuch as all of the very limited amount of oxygen supplied by diffusion would react and the oxidation rate would be a stream property and not a material property.

The low velocity of the plasma jet did not, of course, simulate the type of boundary layer flow associated with hypersonic flow. This would be of importance in the distribution of heating rate over the body. This velocity consideration could have been overcome by modifications of the plasma jet but it would have left the stream density low which, as mentioned above, would limit the oxygen supplied by diffusion.

Other parameters, such as dynamic pressure and shearing stress level, may also be important. At the low-velocity of the plasma jet tests, these were only trivial.

In order to obtain better simulation of reentry conditions, tests were performed in the Wave Superheater Hypersonic Tunnel. The conditions and simulation are discussed in the following section.

Spinning circular rod specimens were tested in transverse flow. Several methods for observing surface temperature were tried simultaneously. Motion picture records of the specimens and their melting were made. The heating characteristics of the stream were determined and, from this, the time-temperature histories expected without oxidation heating and with several degrees of oxidation heating were calculated. In each test, an oxidizing and a nonoxidizing model were observed simultaneously. The two models were identical except that the nonoxidizing model was protected by a thin layer of glass which was fused to the surface.

The tests were made on rods of varying diameter in order to vary the heating time, with the thought that this would be important in initiating rapid ablation. An attempt was made to capture debris particles from rapidly ablating rods.

TEST CONDITIONS

The tests were performed in the Mach 6 test section of the Wave Superheater Hypersonic Tunnel. The nominal tunnel conditions were: 1900-2000 Btu/lb total enthalpy, 0.9 atm stagnation pressure, 5.8 tunnel Mach number, and 14 seconds test duration. Conditions vary slightly from test to test. The following values are based on Test 704 and may be taken as representative of the series.

M_{∞}	5.78
u_{∞}	9300 ft/sec
P_{∞}	1.76×10^{-2} atm
T_{∞}	1070°R
ρ_{∞}	6.05×10^{-4} lb/ft ³
H_{∞}	269 Btu/lb
P_s	0.813 atm
T_s	5710°R
ρ_s	5.41×10^{-3} lb/ft ³

Heat flux and pressure measurements were made in several of the tests and from these total enthalpy was computed. The heat flux measurements were made on the stagnation line of a 0.5-inch cylinder whose axis was at 90° to the stream direction.

TABLE 1
TEST CONDITIONS

Test No.	P_s psi	<u>Gage No. 1</u>		<u>Gage No. 2</u>	
		q_s Btu/ft ² sec	H_s Btu/lb	q_s Btu/ft ² sec	H_s Btu/lb
704	12.1	330	2220		
735	Taken as identical to #704, based on post-run analysis				
885	13.4			352	1981
886	13.8	371	2035	361	1982
897	13.48	Taken as similar to Test 899, based on post-run analysis			
898	13.15	320	1872	331	1895
899	13.13	363	2038		

Note 1: Gage No. 1 located 0.5 inch from end of 0.5-inch-diameter rod, Gage No. 2 located 1 inch from end of rod.

Note 2: From post-run analysis, the heat flux and enthalpy for Test 897 were taken as similar to those for 899.

FLIGHT CONDITIONS SIMULATED BY THE TEST

Simulation of Heating Rate Per Pound

The rate of heating by oxidation is influenced by the rate at which the temperature of the model is raised. This makes the convective heating rate per pound of model be the dominant parameter to be considered in relating the test condition to flight conditions.

In Test 898, for example, the average heating rate on the sidewalls of the 0.25-inch-diameter model is computed to be $122 \text{ Btu/ft}^2 \text{ sec}$ when the model temperature is 2500°R . This is in the temperature region where the oxidation heating rate is expected to start being appreciable. For a zirconium rod of this diameter, there are 2.12 lbs of model per square foot of sidewall area. The convective heating rate is, therefore, 57.5 Btu/lb sec . In this respect, the test condition and the quarter-inch models simulate any flight condition with which the sidewall convective heating rate is 57.5 Btu/lb sec at 2500°R . Similarly, the half-inch test model simulates any flight condition in which the heating rate is 20.3 Btu/lb sec .

Convective heating for flight was computed by the equations of Ref. 2. For a 0.25-inch-diameter rod, the sidewall heating was so computed at $464 \times 10^4 (\rho/\rho_{\text{SL}})^{.5} (u/u_c)^{3.15} \text{ Btu/ft}^2 \text{ sec}$ when the model is at low temperature. This value was reduced by the enthalpy difference ratio for 2500°R . The altitude-velocity combinations which result in a convective heating rate of 57.5 Btu/lb sec for a 0.25-inch rod when it is at 2500°R are shown on Fig. 1. A similar line is shown for a heating rate of 20.3 Btu/lb sec . Similar lines are also shown for a one-inch-diameter rod.

Figure 1 SIMULATION OF HEATING RATE PER POUND

Simulation of Shearing Stress Level

In the test, the value of the shearing stress level, $St_{av} \rho u^2$, is given by $q_{av} u / \Delta H$ and, based on the heat flux and enthalpy of Test 898, is approximately

$$St_{av} \rho u^2 = \frac{320 \times .381}{(1872 - 131)} \frac{\text{Btu/ft}^2 \text{sec}}{\text{Btu/lb}} \times \frac{1}{32.2 \text{ ft/sec}^2} \times 9300 \frac{\text{ft}}{\text{sec}} = 20 \text{ lb/ft}^2$$

for the half-inch model. For the quarter-inch model, it is 28 lb/ft^2 .

For flight conditions, the shearing stress level is computed from the equation

$$\begin{aligned} St_{av} \rho u^2 &= \frac{(1.74 \times 10^4 \times 0.269 \times 778 \text{ ft lb/ft}^2 \text{sec}) \left(\frac{1 \text{ ft}}{D/2} \right)^{.5} \left(\frac{\rho}{\rho_{SL}} \right)^{.5} \left(\frac{u}{u_c} \right)^{3.15} u}{u^2 / 2 \text{ ft}^2 / \text{sec}^2} \\ &= (396 \text{ lb/ft}^2) (1 \text{ ft}/D)^{.5} (\rho/\rho_{SL})^{.5} (u/u_c)^{2.15} \end{aligned}$$

From this, the flight altitude and velocities which yield the maximum and minimum shearing stress levels of the tests were computed. They are shown on Fig. 2.

Figure 2 SIMULATION OF SHEARING STRESS LEVEL

Reaction-Controlled Oxidation Conditions

It was desired in this study of oxidation that sufficient oxygen be supplied by diffusion to the solid-air interface so that rate of the chemical reaction would be the limiting process rather than the rate of diffusion through the boundary layer. Illustrating with the values in Test 898, the calculated diffusion rate is $0.21 \text{ St}_{\text{av}} \text{ pu}$ or $0.0150 \text{ lb oxygen/ft}^2 \text{ sec}$.

Whether this supply was sufficient to keep the study in the reaction-controlled region is known only from the results of the oxidation heating studies discussed later. In order to define the region of the study, however, it is mentioned here that the maximum oxidation heating rates found experimentally correspond to less than one half of the above-mentioned oxygen supply rate. From this, one can say that the studies are in the reaction-controlled region.

TEST MODELS

The models consisted of cylindrical zirconium rods whose diameters were 0.5, 0.375 and 0.25 inch. They were supported at one end only and the opposite end was in the test stream. Each was placed with its axis at 90° to the stream direction and each was rotated about its central axis at a nominal rate of 600 RPM.

The smaller diameter models were tapered from 0.5-inch diameter at their supported end, as shown in Fig. 3. It was found by experience that tungsten support rods are required. Without them, the rods became bent severely before phenomena of interest occurred. With the half-inch and 3/8-inch models, the support rod was 1/4-inch diameter. With the 1/4-inch model, the support rod was 1/8-inch diameter.

Two models were tested simultaneously. They were identical except that one model was coated to prevent oxidation and the other was bare to permit oxidation. By this, the influence of oxidation heating was noted. Figure 3 shows the 1/4-inch model both before and after test.

The coating used to prevent oxidation was that described in Ref. 1. It was applied by dipping the rod into a water solution of sodium silicate. The rod was first oxidized lightly both to control its emissivity and to aid adherence. The coating was dried and fired sufficiently to fuse the sodium silicate to the surface. The resultant coating was of the order of two mils thick. From previous tests in the plasma jet, this coating was found to adhere and to prevent oxidation. At the high temperatures attained in the tests, the coating became a thin layer of molten glass.

The bare and coated rods were supported from the top of the test section. They were injected into the test stream after the stream had been started. At the end of the test, the 3/8-inch and 0.25-inch models were withdrawn from the stream and were contained in a surrounding can into which helium was supplied at a positive pressure. The helium was

a. BARE MODEL BEFORE TEST

b. BARE MODEL AFTER TEST

c. COATED MODEL BEFORE TEST

d. COATED MODEL AFTER TEST

Figure 3 ONE-QUARTER-INCH DIAMETER MODEL, TEST 899

used in order that the models could cool without further oxidation. The 0.5-inch rod was tested before the jig for the helium environment was constructed.

A 0.5-inch-diameter rod, not rotating and mounted from the floor of the test section, contained a pressure tap and two heat flux gages. A nonrotating, 0.5-inch-diameter tungsten rod was injected into the stream along with the rotating models. Its function was to provide a collecting surface which could subsequently be examined for impurities in case test anomalies raised question about stream purity.

The rods injected from the top were placed in such manner that they did not interfere with each other with respect to flow and that each could be viewed through the side window.

AVERAGE HEAT FLUX AROUND CYLINDER

The average heating around the entire circumference of a cylinder in the Wave Superheater Hypersonic Tunnel tests was determined by placing a series of heat transfer gages around a 0.5-inch-diameter cylinder. Their positions are shown on Fig. 4. The conditions in this test, No. 705, were the same as those previously listed for Test 704. The results of the measurements are shown on Fig. 4. The curve was drawn through the higher of the two 45-degree test points since it is in better agreement with a previous calibration test and also because it agrees with theory for front face heating of a cylinder. The average heat flux around a cylinder is so determined to be 38.1% of the stagnation line heat flux.

It is noted that this experimentally determined value agrees exactly with Ref. 2 which states that the average sidewall heating of a cylinder in crossflow is 26.9 percent of the stagnation point heating of a sphere of the same diameter. By theory, the stagnation point heat flux of a sphere is $\sqrt{2}$ times larger than the stagnation line heating of a cylinder of the same diameter. It follows from these that the average heat flux around a cylinder is $26.9 \sqrt{2}$, or 38.1, percent of the stagnation line heat flux.

NOTES:

1. HEAT FLUX CORRECTED TO 560° R COLD WALL
2. AVERAGE HEAT FLUX ~ 125.6 BTU/SEC FT² OR 38.1% OF STAGNATION HEAT FLUX
3. MEASURED STAGNATION PRESSURE ~ 1720 PSF (0.814 ATM)
4. SPECIMEN DIAMETER 0.50-INCH CYLINDER IN CROSSFLOW

Figure 4 HEAT TRANSFER MEASUREMENTS AROUND CYLINDER

OBSERVATION OF MELTING PHENOMENA

A most revealing observation occurred with the 3/8-inch-diameter zirconium model, Test 897. Near the end of the test, at 13.4 seconds, a few drops of molten metal were seen to run from the end of the rod and be carried away by the stream. The cold model, after removal from the test rig, appeared, on first observation, to have lost no material and to be exactly the same diameter as before the test. This appearance of being intact is shown in Fig. 5c. Upon further examination, it was discovered that much material had been removed from the last 0.5 inch of this model. Its outer surface was a layer of zirconium oxide which was sufficiently strong to remain intact. Upon attempting to section it, some of the oxide shell was broken and the voids beneath were revealed.

Figure 5a is a photograph of the end showing where some of the shell has been broken away to expose a large void between the shell and the central tungsten rod. Figure 5b is an end-on view which also reveals voids. Figure 5c is a section showing the large void beneath the intact surface. Presumably much or all of the zirconium was molten and held inside of a "cup" of solid zirconium oxide. The shape of the void is influenced by the fact that the model was spinning at 600 rpm while it was cooling and solidifying.

Figure 5d is a photomicrograph of a thin section near the end. It consists of an outer layer of zirconium oxide, typically 47 microns thick, and a metal phase containing dissolved oxygen.

The ability to form a structurally strong oxide shell which contains the molten metal agrees with the phenomena observed in previous plasma jet tests. In them, the attainment of the melting point was indicated by a certain sudden change in appearance of the surface (decided to be the seepage of liquid metal through fissures in the oxide layer) but the models did not show any gross appearance of melting until temperature became much higher.

(a) END OF UNCOATED MODEL FROM RUN NO. 897 WITH PORTION OF OXIDE SHELL BROKEN AWAY (7.7X)

(b) SAME AS 5a EXCEPT END-ON VIEW (7.7X)

Figure 5 MELTING OF 3/8-INCH BARE ROD

(c) CROSS SECTION OF MODEL END SHOWING VOIDS AND THIN SHELL AT "A" (7.7X)

MELT = MOLTEN METAL WHICH "CRAWLED UP" THE OUTSIDE OF THE MODEL FROM THE END
 ZrO_2 = ZIRCONIA LAYER WITH WHITE STREAKS OF MOLTEN METAL
 $Zr+O$ = SOLID SOLUTION LAYER
 $Zr+O+W$ = RESOLIDIFIED MELT

(d) POINT "A" OF 5c AT 200X MAGNIFICATION

Figure 5(Cont.) MELTING OF 3/8-INCH BARE ROD

Figure 6 is a photograph of a specimen from such a plasma jet test. The entire specimen became molten and a vapor bubble was formed in the center; the liquid was contained in the oxide shell which formed on the surface. Surface temperatures as high as 5000°R were sometimes indicated before molten loss became apparent.

The nonoxidizing rod in Test 797 did not melt.

In the tests of 0.25-inch rods (Tests 898 and 899), both the oxidizing and nonoxidizing specimens were melted and their major portions were so destroyed during the test. Melting was first observed as a very intermittent process in which one or two small drops of burning metal were carried away. This was soon followed by the start of rapid continuous melting from the end of the rod, leaving the tungsten support rod essentially bare, as may be seen in Fig. 3. In Test 898, the oxide layer may be seen to shift its position as an entire unit and soon thereafter (about one revolution at 600 rpm) to be moved downstream. In Test 899, the phenomenon is somewhat similar but is not exactly repeated. Several stages of the melting process are illustrated in Fig. 7.

The loss of material from the end of the unoxidizing (coated) models proceeded at a much more uniform rate than the oxidizing models. With the latter, the period of uniform ablation was short and was followed by massive losses of material. Presumably the liquid was first retained by an oxide skin and then was quickly lost when the skin was destroyed. Similar behavior has previously been noted in the plasma jet tests.

NOTE: THE 1/4-IN. CYLINDRICAL SPECIMEN WAS SECTIONED ALONG ITS CENTRAL AXIS AND PHOTOGRAPHED AT 10X. THE SPHERICAL VAPOR POCKET AT CENTER INDICATES THAT MELTING HAD BEEN COMPLETE.

Figure 6 PLASMA JET SPECIMEN AFTER TEST

(a) START OF RAPID ABLATION OF UNCOATED 1/4" DIAMETER MODEL
TIME $\approx$ 5.39-SEC (A = GLASS-COATED MODEL, B = UNCOATED MODEL, C = TUNGSTEN MONITOR ROD)

(b) TIME $\approx$ 5.79-SEC RAPID ABLATION IN PROGRESS. A REFLECTED IMAGE APPEARS ABOVE AND TO THE RIGHT OF THE REAL IMAGE

← FLOW DIRECTION (IMAGES 0.34 x ACTUAL SIZE)

(c) TIME $\approx$ 5.80-SEC
CONTINUED RAPID ABLATION

(d) TIME $\approx$ 5.94-SEC
OXIDE SKIN STARTS TO
BREAK FROM MODEL

Figure 7 MELTING PHENOMENA FROM MOTION PICTURE RECORDS

(e) TIME ≈ 6.23 -SEC
HIGH RATE OF MELT RELEASE
AS OXIDE SKIN IS PEELED OFF

(f) TIME ≈ 6.24 -SEC
PORTION OF OXIDE SKIN
VISIBLE IN WAKE

(g) TIME ≈ 8.97 -SEC
COATED MODEL BEGINNING
TO ABLATE AT (D)
UNCOATED MODEL HAS
ABLATED UP TO POINT (E),
LEAVING TUNGSTEN SUPPORT
ROD

(h) STOPPED DOWN PHOTOGRAPH
TAKEN LATE IN RUN, SHOWING
MELT RUNNING DOWN TUNGSTEN
ROD AND LEAVING BOTTOM OF
ROD AS DROPS

Figure 7 (Cont.) MELTING PHENOMENA FROM MOTION PICTURE RECORDS

The times, taken from motion picture records, of certain phenomena, are as follows:

Test	898	899	897	735
Diameter, inch	0.25	0.25	0.375	0.500
Oxidizing Specimens:	time in seconds*			
Start of very sporadic loss	4.6	3.4	13.3	no melting at any time
Start of essentially continuous loss	5.4	5.1		"
Massive loss including main body of oxide layer	5.9**	6.25**		
0.25-inch lost from end	5.9**	5.5		
0.50-inch lost from end		6.25**		
Nonoxidizing Specimens:				
First loss and start of essentially continuous loss	9.0	7.3	no melting at any time	
0.25-inch lost from end	9.65			
0.50-inch lost from end	10.30	8.80		
1.00-inch lost from end	11.70	10.40		

* The time recorded in this series is from the start of injection of the models into the stream. Injection is completed in approximately 0.42 seconds. In correlating with calculated temperatures, the start of heating was arbitrarily taken at 0.1 sec after the start of injection.

** The major part of the specimen material was lost at about this time.

TEMPERATURE MEASUREMENT METHODS

The surface temperature of the bare zirconium rods was viewed by a Thrmidot Radiation Thermometer, Model TD-6 Series, with fast response (95% response in 0.03 seconds). This is a wide-band, infrared pyrometer utilizing a photoconductive (PbS) detector. Its spectral response lies between 1.5 and 2.8 microns. Actually, only the sensing device of the standard model is used and the optical system and output recording system were assembled specifically for use in Wave Superheater Hypersonic Tunnel tests. The system is described in more detail in Ref. 3. This instrument and readings from it are sometimes referred to subsequently in this report by the symbols TD1.

This thermometer, and the two instruments described immediately hereafter, viewed the rods from the side through a window. They were focused on an area of 1/8-inch diameter which was 0.5 inch from the end. Calibrations through the window were performed before and after each test. In only one case did the two calibrations differ and then the difference was minor. The direction of rod rotation was such that the surface material being viewed had passed through the leading edge one-quarter revolution previously.

The surface temperature of the coated rod was viewed in an identical manner by a second Thrmidot Radiation Thermometer (TD2) similar to the above except that its response was slower, 95% response in 0.3 seconds.

The bare rod was also viewed by a Brown Radiamatic Total Radiation Pyrometer. Its sensing unit is a thermopile. It was used with an optical system which focused on a 1/8-inch area one-half inch from the end of the rod and similar to the TD1. From previous use, the unit is considered to be slow in response, lagging by one half to one second. This instrument and its readings are subsequently referred to by the symbols BRP.

The above instruments were calibrated for temperature on the basis of a 0.725 value for the emissivity of the rods. This value is reported in Ref. 1.

Lamps of known temperature were installed in the test section where they were viewed by a motion picture camera. It was expected that they would be a useful aid in viewing the motion picture record. The lamp temperatures were 2830, 3380, 3940 and 4330°R as determined by optical brightness readings corrected for an emissivity of tungsten at 0.65 microns of 0.43. It was subsequently found that interpolation could be made and some temperatures were assigned by visual comparison of the rods and lamps as photographically recorded.

CALCULATION OF TEMPERATURE RISE

Inasmuch as the direct measurement of temperature by the several methods tried was not entirely satisfactory, as discussed in a later section, temperature rise of the specimens was computed from heat flux. The heat input computed is that to an infinitely long cylindrical rod in crossflow with the rod spinning. This situation does not fit the conditions of the models perfectly, inasmuch as end conditions are ignored, but it is believed to be acceptably close. A check on the calculation is available in those cases where an unoxidizing zirconium rod reaches the melting point.

The average heat input to the cold wall was taken as 38.1% of the measured stagnation line heating. The measurements were made by a heat transfer gage on the stagnation line of a 0.5-inch-diameter cylinder. For other diameters, the heat flux was taken as inversely proportional to the square root of diameter. As the model temperature increased, the heat flux was reduced and made proportional to the difference in enthalpy at the stagnation condition and the wall condition.

The appropriate specific heat for use from room temperature to the melting point of zirconium is questionable. Transition from alpha to beta zirconium occurs at 1143°K and 1140 Cal/gm are absorbed in the transition. This heat of transition is approximately 8% of the total enthalpy gain in attaining the melting point. In the rapid heating of these tests, it seems probable that transition would occur over a range of temperature. With radial temperature gradients, transition would also tend to occur over a range of time. Inasmuch as it is impossible to be exact in distributing this heat of transition, it seemed well to use an average specific heat over the entire range. The figure used is 0.087 Btu/lb°R.

Interest is in the surface temperature, and this is higher than the average temperature. It can be computed from standard equations that the maximum difference between the surface temperature and the average temperature is quickly attained when the heating rate is constant. For a 0.25-inch zirconium rod, this maximum difference is attained in approximately

0.15 second. If a time-temperature curve can be well represented by straight-line segments of at least this duration, this maximum difference may be used. This was judged to be the case in these tests. The increase in average temperature was computed, for a short time interval, from the heat input and the surface temperature increment was then added.

Radiation loss was computed using emissivity as 0.725, taken from Ref. 1.

The equations used in computing temperature of a nonoxidizing model are as follows.

$$\left(\frac{dT_{av}}{dt} \right)_{\text{convection}} = q_{s.5 \text{ inch}} \left(\frac{D.5 \text{ inch}}{D} \right)^{\frac{1}{2}} (0.381) \frac{H_{\text{stag}} - H_{\text{wall}}}{H_{\text{stag}} - H_{\text{cold wall}}} \frac{1}{(C_p V/A)} \quad (1)$$

$$\left(\frac{dT_{av}}{dt} \right)_{\text{radiation}} = - \frac{\sigma \epsilon T_w^4}{(C_p V/A)} \quad (2)$$

$$T_w - T_{av} = 0.125 \frac{r^2}{a} \frac{dT_{av}}{dt} \quad (3)$$

The computations were programmed for a 7044 computer and performed in steps of approximately 10°R .

The results for the 0.25-inch rod in Test 898 are shown by the lower line (the line marked $\Delta H_{\text{ox}} = \text{zero}$) of Fig. 8. It may be seen that the temperature so calculated is very close to the melting point of zirconium at the time that rapid melting of the unoxidizing rod was observed to start. It had been expected that slight adjustment of the inputs might be required to make the calculated and observed times agree, but this was not necessary in Test 898.

For the oxidizing model, the heat addition by oxidation was added to the above equations. It is based on Equation 6 of Ref. 1, and is

Figure 8 TEST 898, 1/4-INCH-DIAMETER ZIRCONIUM ROD

$$\left(\frac{dT_{av}}{dt}\right)_{\text{oxidation}} = \frac{7.8 \times 10^{-4}}{2t^{1/2}} \left[\left(\frac{T_w}{1000} - 2 \right)^2 + \frac{2t}{1000} \left(\frac{2T_w}{1000} - 4 \right) \left(\frac{dT_{av}}{dt} \right) \right] \frac{\Delta H_{ox}}{(C_p V/A)} \quad (4)$$

In this, t is time in seconds from the start of heating, T is temperature in degrees Rankine, ΔH_{ox} is the heat of reaction of oxygen with zirconium in Btu/lb oxygen and $(C_p V/A)$ is heat capacity per unit area in Btu/ft² °R.

Three values of ΔH_{ox} were used in the calculations, 14,500 Btu/lb, 18,750 and 23,000. These are also shown plotted on Fig. 8. The value 14,500 was used because it is the heat of reaction of oxygen and zirconium in forming zirconium dioxide. The value 23,000 was used because it best fit the data of Ref. 1. The value 18,750 was used as an intermediate point.

In Test 899, a reduction of approximately 6% in both H_{stag} and q_s was required in order that the calculated value of temperature at the observed time of rapid melting agree with the melting point. Without this adjustment, the calculated temperature was 120°R too high. The lines for oxidation heating use these adjusted inputs.

In Test 897, the unoxidizing 3/8-inch model did not melt, and there was, therefore, no check between the observed and calculated time of melting. Inasmuch as the inputs for Tests 897 and 899 were based on the same experimental data, the inputs used for the calculation of Test 897 were similarly adjusted.

RESULTS OF TESTS

In Test 898, the readings from the two Thermodot instruments were found to oscillate widely in temperature during very short time intervals. Temperature excursions, up and down, as much as 1000°R occurred within brief periods. Some oscillations followed the rotation of the rods and perhaps may be associated with color variations discernible in the motion pictures. Figure 9 shows the temperatures indicated at 0.5-second intervals plus peak temperatures indicated at other times. It was concluded that the large temperature fluctuations are difficult to interpret as real with respect to the heating of the rod and may be associated with a lateral vibration of the rods which prevented the aperture of the instrument from being completely filled by the specimen. Inasmuch as the 1/8-inch area viewed covers a large fraction of the rod diameter, small sidewise motion of the rod may have prevented it from filling the entire aperture of the instrument. This explanation fits the fact that such temperature excursions were greatest with the smallest rods and with the fastest response instrument. On this basis, only the few peak temperatures reported by the Thermodot instruments were considered to have possible validity.

The several types of temperature readings for Test 898 are shown on Fig. 8. Only the peak Thermodot readings marked on Fig. 9 are shown on Fig. 8. Inasmuch as response time of the several types of temperature indicators vary, some shifting of the lines along the time axis should be expected when temperature change is rapid.

For the coated rod (no oxidation heating), there is fair agreement between the temperatures calculated from heat flux measurements, the temperatures obtained by visual comparison and the peak Thermodot temperatures. At the time when melting was noted to occur, the calculated temperature was very close to the melting point of 3830°R . Inasmuch as the calculation of temperature is based on an infinitely long rod, it was expected that some adjustment of the inputs used in the calculation might be required in order that

Figure 9 PLOT OF READINGS OF THERMOTOT RADIATION PYROMETER NO. 1 FOR ONE-QUARTER-INCH BARE MODELS

the observed melting time would agree with the calculated melting temperature. The agreement is so close, however, that adjustment seemed unwarranted. It appears that the calculated temperature-time line can well be accepted as representative of the coated rod.

For the bare (oxidizing) rod, the slopes of the temperature-time lines by the several methods of determining temperature are in fair agreement. For example, at 3500°R , the slopes are 840, 530 and $820^{\circ}\text{R}/\text{sec}$ for the visual comparison method, the Thermodot and the Brown Radiamatic Pyrometer, respectively. These are significantly larger than the slope for the coated rod, which is approximately $200^{\circ}\text{R}/\text{sec}$ at 3500°R . The difference in slopes for the two rods is associated with the oxidation heating rate.

The calculated temperature-time lines have slopes at 3500°R ranging from $316^{\circ}\text{R}/\text{sec}$ for a heating value of 14,500 Btu/lb to $621^{\circ}\text{R}/\text{sec}$ for a heating value of 23,000 Btu/lb. The calculated slope for a heating value of 18,750 Btu/lb is $479^{\circ}\text{R}/\text{sec}$. By a comparison of slopes, one concludes that a heating value near 23,000 Btu/lb, or perhaps slightly higher, best represents the oxidizing situation.

Unfortunately there is little background for judging the continued heating above the melting point. From plasma jet tests, one can expect the surface temperature of the oxide layer to attain temperatures of $4500\text{--}5000^{\circ}\text{R}$ before the skin ruptures when the temperature rise rate is rapid. Clearly, the calculated temperature line based on ΔH_{ox} as 14,500 Btu/lb is too low at the time when continuous melting was observed. Although it is speculative, the best fit appears to be obtained if the calculated line with ΔH_{ox} as 23,000 Btu/lb (or perhaps a line intermediate between it and the 18,750 line) is extended on with slightly increasing slope to about 4500°R at the time of the observed continuous melting.

Test 899 had the same nominal conditions as Test 898. The calculated temperatures and the several types of temperature indications are shown on Fig. 10. The peak Thermodot temperatures appear to be erroneously low.

Figure 10 TEST 899, 1/4-INCH-DIAMETER ZIRCONIUM ROD

In case lateral vibration of the rods is the cause of error, as suggested above, then one must assume that the effect is greater in Test 899 than in Test 898.

Without adjustment of inputs, the calculated temperature of the coated rod was 120°R higher than the melting point of zirconium at the time when continuous melting was observed. A downward adjustment of enthalpy and heat flux by approximately six percent was necessary to obtain agreement, and the calculated curves on Fig. 10 are based on the adjusted values. Two of the three temperatures obtained by the visual comparison method agree with the calculated line.

For the bare rod, the slopes of the lines for the temperatures indicated by the Brown Radiamatic Pyrometer and the visual comparison method are in good agreement although the lines are displaced along the time axis. The slopes are both close to $640^{\circ}\text{R}/\text{sec}$ at 3500°R . The slope of the line calculated with ΔH_{ox} as 23,000 Btu/lb is $700^{\circ}\text{R}/\text{sec}$ and the slope with ΔH_{ox} as 18,750 Btu/lb is 548. As in Test 898, a value of ΔH_{ox} near 23,000 Btu/lb appears to provide the best fit. Again, extension of such a line to approximately 4500°R indicates the observed continuous melting time.

The data associated with the 0.375-inch-diameter rods of Test 897 are shown on Fig. 11. Inasmuch as Tests 897 and 899 are considered to have the same conditions, adjustment of input data mentioned above was also used in the calculation of temperature in Test 897. The calculated temperatures are acceptable in that they agree with the basic melting phenomena observed; that is, the calculated temperature for the coated rod remains below the melting point and it was observed not to melt, and the calculated temperatures for the oxidizing rod rise above the melting point and bare rod melting was observed.

An extension of the calculated line based on ΔH_{ox} as 23,000 Btu/lb falls short of the previously mentioned 4500°R temperature at the time of melting. With this larger rod, however, the melting was observed as drops running off from the end which left voids under the oxide skin with this skin remaining intact on the sidewalls. Presumably the melting phenomena were different with this slower heating rod.

BARE ROD:

Δ VISUAL COMPARISON

COATED ROD:

▽ VISUAL COMPARISON

CALCULATED VALUES SHOWN BY
DASHED LINES:

NO. 1	$\Delta H_{ox} = 23,000$ BTU/LB
NO. 2	18,750
NO. 3	14,500
NO. 4	ZERO

Figure 11 TEST 897, 3/8-INCH-DIAMETER ZIRCONIUM ROD

For this test, all methods of temperature indication yield temperatures lower than those calculated with the exception of the final temperature attained by visual comparison. The Thermodot readings do not exhibit the large temperature excursions shown with the smaller rods. It seems necessary to consider them in error, however, inasmuch as they remain below the melting point and melting was observed. The low readings of the Brown Radiamatic Pyrometer seem explainable only as some form of misalignment of its viewing of the rod.

The data on a bare 0.5-inch rod of Test 735 are shown in Fig. 12. This test was performed at an earlier date than the others and the use of a coated rod and of the visual comparison method for temperature was not then employed.

Temperatures were indicated by three methods. The Brown Radiamatic Pyrometer and the slower response Thermodot Radiation Thermometer were used through the side window as in Tests 897-899. The faster response Thermodot Radiation Thermometer viewed the leading edge of the rod by looking through a rotor tube of the Wave Superheater Hypersonic Tunnel.

Although the readings from the two Thermodot Radiation Thermometers agree reasonably well, their temperatures are low compared with the calculated temperatures. The high temperature readings of the Brown Radiation Pyrometer fall in the range of the calculated temperatures. On the basis that this instrument tends to lag in time by about 0.5 second at high temperature, a value of 23,000 Btu/lb for ΔH_{ox} fits its readings quite well. No melting occurred with the 0.5-inch rod.

Figure 12 TEST NO. 735, 0.50-INCH ZIRCONIUM ROD, BARE

SUGGESTED METHOD FOR COMPUTING OXIDATION HEATING

These hypersonic tests confirm, within their limited character for being interpreted accurately, the oxidation heating rates previously reported in Ref. 1. Specifically, a heat effect near 23,000 Btu/lb oxygen also fits these tests. It is suggested that Equation 4, given in a preceding section, be used for computing oxidation heating with ΔH_{ox} taken as 23,000 Btu/lb.

Although the equation developed from a concept of the physical mechanism (that is, a certain amount of oxygen being absorbed and each unit of oxygen developing a certain amount of heat), it should be noted that its final form is, in a sense, an empirical equation which fits, within limits, the data of these high-velocity tests. As such, the constant expressing oxygen absorption and the constant expressing the heat effect per unit of oxygen became combined into one empirical constant.

The above equation is valid only to the melting point of the metal. In rapid heating situations, at least, liquid does not become apparent until temperatures are well above the melting point. This region above 3830°R and before the appearance of liquid drops, is not well defined. It is suggested that the time-temperature line be calculated to 3830°R and then be extended at constant slope with the expectation that liquid drops will appear at about 4500°R in a rapid heating, such as in Test 898, and at lower temperature in slower heating.

ABLATION DEBRIS

The motion picture records of Tests 898 and 899 show very large drops of liquid running down the back of the tungsten support rod after the lower part of the zirconium metal had been removed. These large drops ultimately left the model as large drops and were carried downstream. In all cases noted, they were quickly ruptured by the stream. Their breakup was recorded by the motion pictures but little detail of the process was discernible.

A debris collector was located downstream. It consisted of an evacuated tank with its inlet port, which faced upstream, controlled by a valve. The valve was opened, after rapid ablation was observed, so that the tank was filled with the test gas and debris particles. The valve was closed after two seconds. The debris particles were subsequently washed from the tank with water. Examination of the particles is in progress but is incomplete.

The particles collected on a filter of one-micron pore size have been observed by X-ray diffraction to contain zirconium dioxide (with no metallic zirconium) along with impurities. Iron oxide is a chief impurity. Some of this was removed magnetically. Microscopic examination of the resultant particles, after a firing at 1500°F to remove organic matter, indicates that the largest particle observed is of the order of 60 microns; it is thought to be iron oxide impurity rather than model debris. Most of the particles are very much smaller.

The stable drop size, as indicated by the critical Weber number for these conditions, is computed to be approximately 200 microns. No particles as large as this have been observed. Presumably the drops are shattered to a size very much smaller than the stable size.

It is to be noted that agglomeration may have occurred during the treatment of the particles and any information which may come from this examination will be subject to that consideration.

REFERENCES

1. Beal, J. L.; Brown, W. R.; Vassallo, F.A.: Dispersal of Reactor Core Materials by Reentry Processes CAL Report No. 114-020-1, Suborder No. 2 January 1965.
2. Klett, Robert D.: Drag Coefficients and Heating Ratios for Right Circular Cylinders in Free Molecular and Continuum Flow from Mach 10 to 30 Sandia Corporation Report No. SC-RR-2141 Draft of November 17, 1964.
3. Newton, J. F.: Rotor Tube Pyrometer Operations Manual CAL Hypersonic Tunnel Department December 1, 1963.