[redacted]

[redacted]

UNCLASSIFIED

LOS ALAMOS SCIENTIFIC LABORATORY
of the
UNIVERSITY OF CALIFORNIA

Report written:
April 1953

LA-1539

This document consists of 13 pages

[redacted]

PUBLICLY RELEASABLE
LANL Classification Group
DGL 9/28/95

HIGH TEMPERATURE OXIDATION OF PLUTONIUM AND A PLUTONIUM-GALLIUM ALLOY

by

E. S. Wright
J. T. Waber

Classification changed to UNCLASSIFIED
by authority of the U. S. Atomic Energy Commission,
Per Topic 1.0591 Rev., CG-W-1 1-30-64
(Person authorizing change in classification) (Date)
By 2/25/64
(Signature of person making the change, and date)

TECHNOLOGY--PLUTONIUM

[redacted]

[redacted]

[redacted]

UNCLASSIFIED

[redacted]

TECHNOLOGY-PLUTONIUM **UNCLASSIFIED**

Distributed: AUG 4 1953 LA-1539

Los Alamos Report Library	1-20
Argonne National Laboratory	21-24
Atomic Energy Commission, Washington	25-27
California Research and Development Company	28
Carbide and Carbon Chemicals Company (ORNL)	29-32
Chicago Patent Group	33
Dow Chemical Company (Rocky Flats)	34
duPont Company, Augusta	35-38
duPont Company, Wilmington	39
General Electric Company, Richland	40-43
Hanford Operations Office	44
Iowa State College	45
Knolls Atomic Power Laboratory	46-49
Massachusetts Institute of Technology (Benedict)	50
Patent Branch, Washington	51
Savannah River Operations Office, Augusta	52
Technical Information Service, Oak Ridge	53-67

UNCLASSIFIED

[redacted]

[redacted]

UNCLASSIFIED

ABSTRACT

The oxidation of plutonium in the temperature range from 315 to 400°C and the oxidation of a stabilized delta-phase alloy containing 3.45 atomic percent gallium in the temperature range from 276 to 400°C have been studied. Comparison of the results shows that gallium apparently offers some corrosion protection to plutonium. An alloy containing 98.76 atomic percent aluminum was also studied and the oxidation reaction was found to proceed very slowly at 400°C.

UNCLASSIFIED

[redacted]

[redacted]

1. Introduction

The oxidation of the delta, or face centered cubic, phase of plutonium has been studied by using unalloyed plutonium and a gallium alloy over a range of temperatures in which the delta phase is stable. It appears that gallium does confer oxidation resistance to the metal. The unexplained phenomenon of an arrest during oxidation of the gallium alloy which was first observed at room temperature was also observed in the range of 300 to 400°C.

2. Materials Employed

The plutonium used was chiefly hot-extruded alpha ribbon approximately 0.020 in. thick, but in a few experiments extruded wire, approximately 0.070 in. in diameter and 0.5 in. long, was used. The alloy specimens were pieces of rolled sheet approximately 0.5 in. x 0.125 in. x 0.020 in. thick. The composition of the metal stock is shown in Table 1. The oxygen used for these studies was obtained from the thermal decomposition of reagent grade potassium permanganate at approximately 275°C. Doubly-distilled mercury and reagent grade sulfur were used in the vapor thermostat.

TABLE 1

COMPOSITION OF THE METAL EMPLOYED

	Unalloyed	Alloyed
Carbon	115-125	30-40
Iron	110	-
Silicon	80	25
Calcium	< 3	< 3
Vanadium	<20	ND*
Nickel	40	90
Cobalt	< 5	ND*
Aluminum	20	25
Lead	15	10
Chromium	10	1
Oxygen	120-150	140

*Not detectable.

3. Procedure

The specimens were electropolished after fabrication and stored in evacuated bulbs until used. At that time, the specimens were abraded with 0 and 3/0 emery paper to remove whatever tarnish film was present. The specimen was then immediately measured, weighed,

[redacted]

[redacted]

and sealed within the reaction system, and the system was evacuated.

The apparatus used for the tests is shown in Fig. 1. A small magnesia crucible was used to hold the specimen within the Pyrex reaction bulb to prevent the specimen from reacting with the Pyrex. A Princeton mercury-vapor pump, backed by a Welch Duo-seal mechanical pump, was used to evacuate the system.

After the system was thoroughly evacuated, the specimen bulb and pre-heat bulb were heated to the reaction temperature by immersing them in the salt bath of the vapor-thermostat apparatus. The bath temperature was determined by the boiling point of the liquid (mercury or molten sulfur) in the vapor-thermostat. The boiling point, in turn, was controlled by a vacuum-operated manostat which regulated the pressure in the thermostat. After the bulbs were thoroughly degassed, the desired pressure of oxygen was admitted to the burette and pre-heat bulb.

The pressure in the system was maintained at the desired level by equalizing the mercury levels in the burette and in the vertical constant-pressure line.

After the pre-heat bulb containing oxygen had been at the reaction temperature for 60 min, it was assumed that the oxygen had attained the reaction temperature, and the reaction was started by opening the stopcock to the specimen bulb. The oxygen passed through the cold stopcock and undoubtedly cooled 20 or 30 degrees before entering the reaction bulb. Apparently very little heat transfer occurred since excessive melting and flowing of the stopcock grease did not occur. Thus both the specimen and the oxygen were nearly at the test temperature when the reaction started. It seems unlikely that the initial induction period is caused by heating the oxygen to the reaction temperature.

The effective heated volume as well as the total volume of the system had been determined by earlier calibration. Therefore the quantity of gas in the system (and thus the amount consumed at any time) could be determined from the equation,

$$V_{STP} = \left(\frac{273\,V_1}{T_1} + \frac{273\,V_2}{T_2}\right)\frac{P}{760}$$

where V_1 varies with the burette reading and represents the effective volume at room temperature, T_1; and V_2 represents the effective volume at the reaction temperature, T_2.

Oxidation rates were determined at 315, 325, 343, and 400°C for plutonium; at 276, 315, and 400°C for the gallium alloy; and at 400°C for the aluminum alloy. The oxygen pressure used in all runs was approximately 590 mm of mercury (0.75 atmosphere).

[redacted]

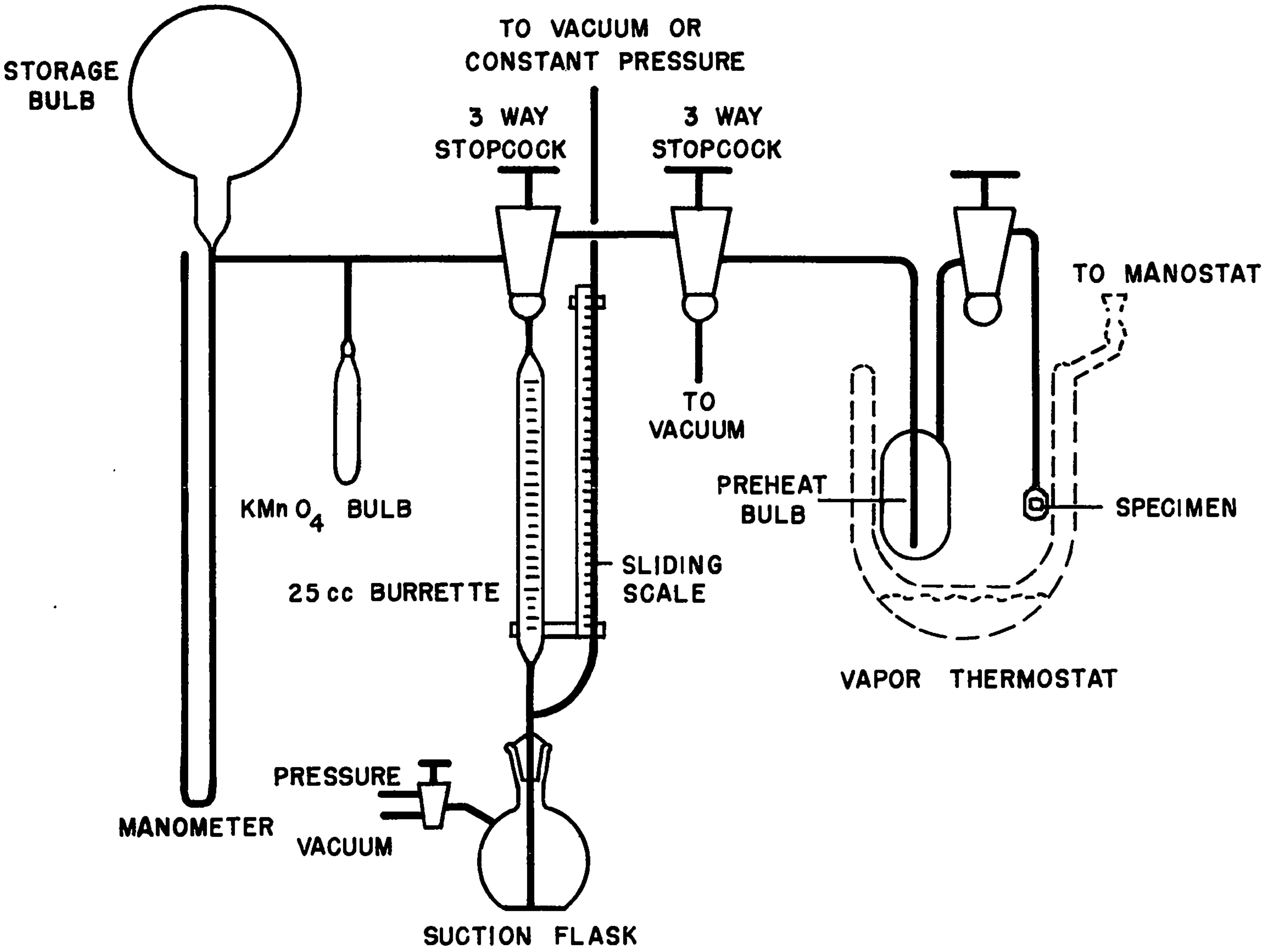

Fig. 1. Oxidation apparatus.

[redacted]

4. Results

The absorption data were plotted on logarithmic coordinates as the logarithm of weight gain in milligrams of oxygen per square centimeter of apparent surface area of the specimen versus the logarithm of elapsed time in hours. The data for the plutonium runs made at 343 and 400°C (see Fig. 2) and for all of the runs made using the alloyed metal gave well-defined straight lines for the initial stages of oxidation. This suggests that the oxidation proceeds according to the equation

$$W = kt^n \qquad (1)$$

where W represents weight gain and t the elapsed time. Since

$$\log W = \log k + n \log t \qquad (2)$$

the slope of the line representing the plotted data is equal to n and the intercept of the line with $t = 1$ is equal to k. The leveling off, near the ends of the runs, of the curves in Fig. 2 (and in Fig. 3) is a result of the specimen being consumed.

For the runs made with plutonium at 315 and 325°C, the data appeared to follow such a law during the early stages of oxidation but exhibited a marked deviation before the runs were half completed. However, if plotted as in Fig. 3 on semi-logarithmic coordinates with weight gain in milligrams per square centimeter versus the logarithm of time in hours, the data points fall in a straight line nearly to the end of the run except during the early stages of the reaction. These data suggest that this reaction follows a logarithmic law of the type

$$W = k_1 \log (k_2 t + k_3) \qquad (3)$$

where W is the weight gain in milligrams per square centimeter and $(t + k_3/k_2)$ represents hours. For reactions following a logarithmic law, it is necessary to add a positive constant such as k_3 to the elapsed time since $W = -\infty$ at $t = 0$ if k_3 is neglected. The constant added to the time scale causes the data points to fall in a straight line, whereas omission of the constant leads to an asymptotic curve. The constant is equivalent to a pre-exposure of k_3/k_2 hours and may indicate the effect of an initial oxide film.

For the runs made with plutonium at 315 and 325°C, the data points, except for the early ones, fell in straight lines without the addition of an increment to the time scale. Attempts to add any significant increment to bring the early data into agreement with the line caused the straight lines to become curved, concave downward. This suggests that the increment, k_3, of the equation is insignificantly small in this case. Values of the constants for plutonium are given in Table 2, while those for the gallium alloy are listed in Table 3.

One phenomenon exhibited in all of the gallium runs was an arrest occurring during the oxidation reaction (see Fig. 4). Also, such arrests have been noted during the oxidation of

[redacted]

[redacted]

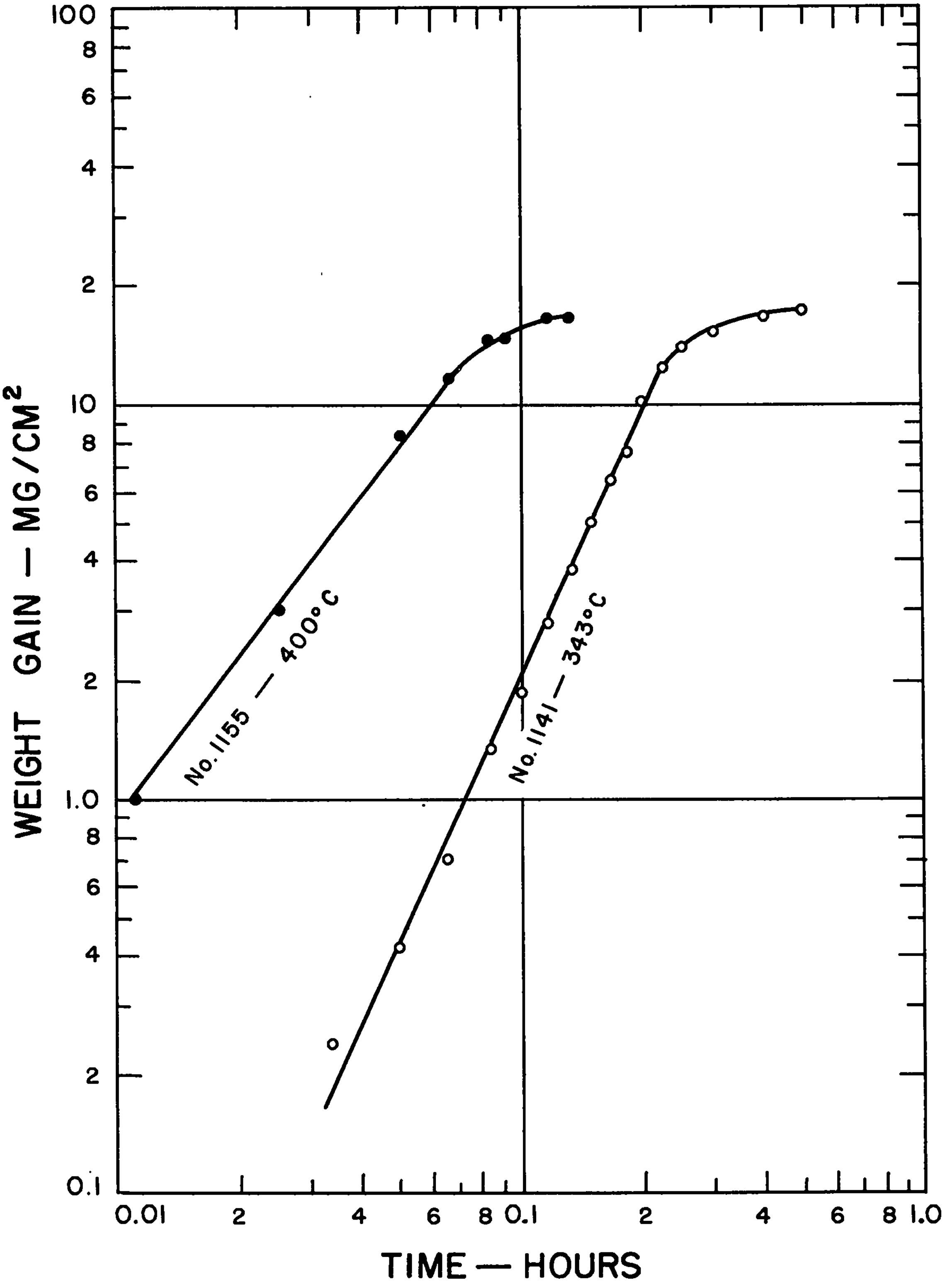

Fig. 2. Oxidation of plutonium.

[redacted]

[redacted]

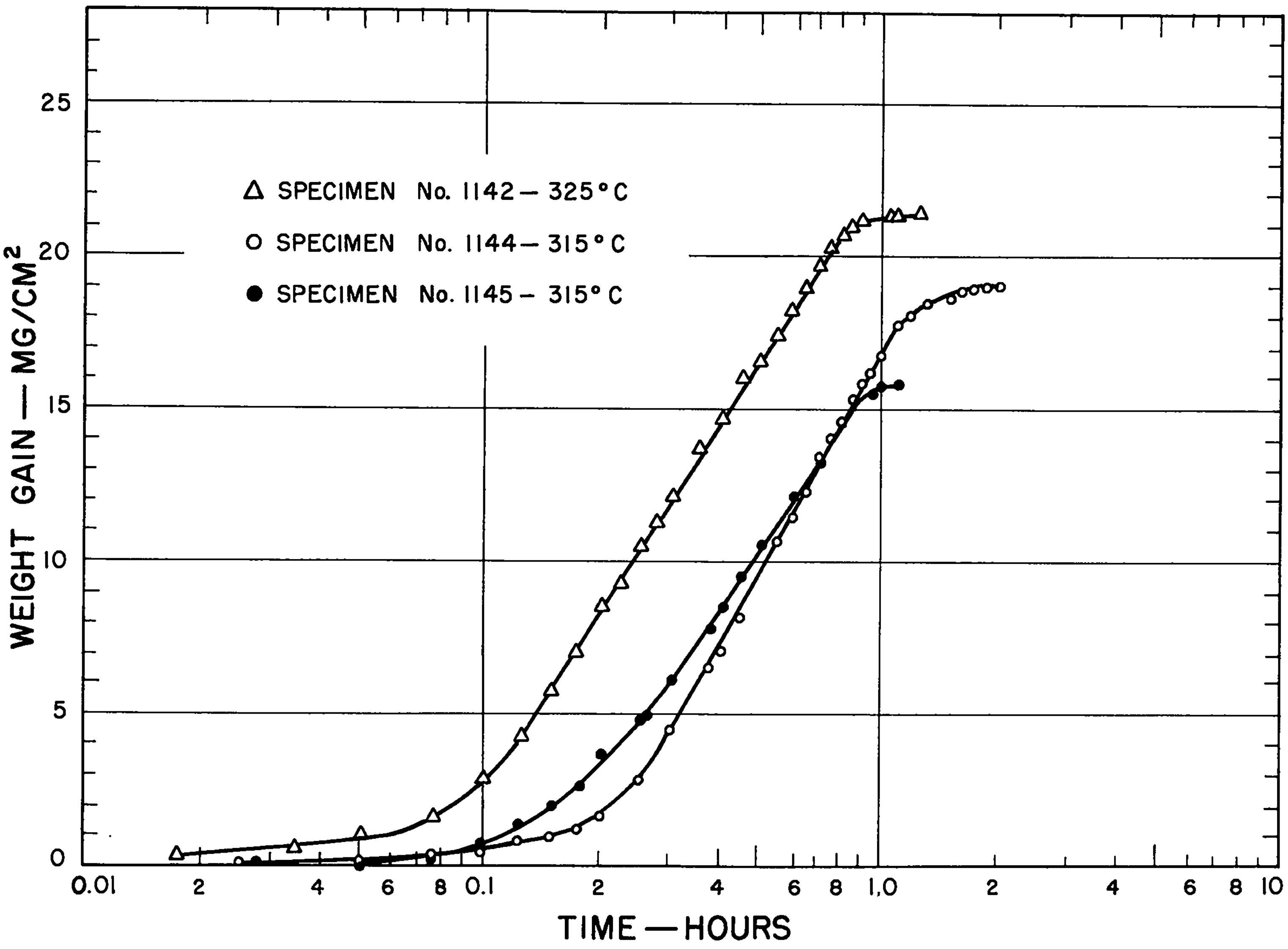

Fig. 3. Logarithmic oxidation of plutonium.

[redacted]

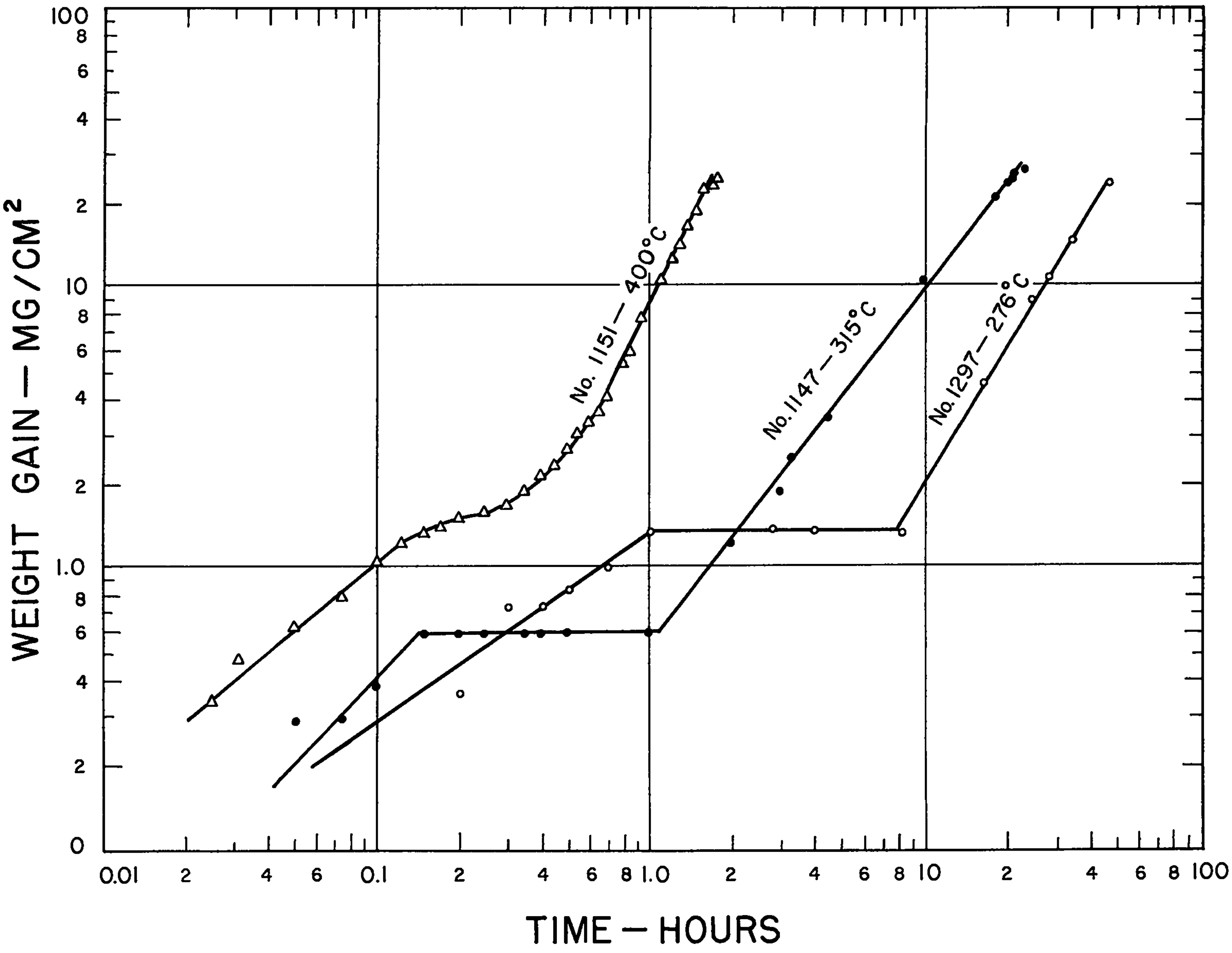

Fig. 4. Oxidation of a plutonium-3.5 atomic percent gallium alloy.

similar gallium alloys at room temperature. The duration of the arrest decreases with increasing temperature: at 276°C it was evidenced by a period of about 8 hours during which no measurable reaction occurred, while at 400°C it consisted of a temporary decrease in slope and lasted about half an hour. An attempt was made to determine whether the formation of a film, high in Ga_2O_3, might have accounted for the arrests. Specimens were heated to 315°C in oxygen for periods of 1/2, 1, and 2 hours. However, examination of the resulting oxide films with an X-ray spectrometer showed only the presence of PuO_2.

The specimen containing 98.76 atomic percent aluminum (10 weight percent plutonium) was exposed to oxygen at 400°C for 1 week. During that time the specimen underwent a weight gain of only 0.2 ± 0.1 mg/cm^2. No visible change was noted in the appearance of the specimen, and X-ray examination of the surface showed only the presence of aluminum, $PuAl_4$, and weak Al_2O_3.

TABLE 2

CONSTANTS n AND k FOR THE OXIDATION OF PURE PLUTONIUM

Spec. No.	Temp., °C	n		k_1	k_2
		Logarithmic (Eq. 3)			
1139	315	----	(1)	19.2	8.36
			(2)	10.6	62.00
1144	315	----		24.6	4.81
1145	315	----		20.2	6.49
1142	325	----		20.6	12.96
		Exponential (Eq. 1)			
974*	343	1.21		10.5	-
1141	343	2.22		320	-
1155	400	1.38		480	-

*Reaction followed manometrically.

[redacted]

TABLE 3

CONSTANTS n AND k FOR THE OXIDATION OF A 3.5 ATOMIC PERCENT GALLIUM ALLOY

Spec. No.	Temp., °C	Initial		Final		Arrest	
		n_1	k_1	n_2	k_2	Occurrence, mg/cm^2	Duration, hours
1297	276	0.67	1.35	1.69	0.046	1.35	8
1146	315	1.3	8.0	1.36	0.37	0.17	0.45
1147	315	1.04	4.40	1.27	0.53	0.58	0.85
1150	400	0.55	3.80	1.67	12.5	1.45	0.75
1151	400	0.79	6.50	2.02	8.4	1.55	0.25

5. Discussion

A means of comparing the oxidation resistance of alloyed and unalloyed plutonium is to compare their weight gains at two temperatures after both have been tested for the same length of time. Such data for 315 and 400°C are summarized in Table 4, and indicate that gallium offers some corrosion protection to plutonium in the delta range.

TABLE 4

WEIGHT GAINS OF UNALLOYED AND ALLOYED PLUTONIUM AT 315 AND 400°C

Temp., °C	Unalloyed		Alloyed	
	mg/cm^2	hours	mg/cm^2	hours
315	0.8	0.1	0.17	0.1
	0.6	0.1	0.38	0.1
	10.5	0.5	0.17	0.5
	9.5	0.5	0.58	0.5
	15.7	1.0	0.42	1.0
	16.6	1.0	0.58	1.0
400	8.3	0.05	0.62	0.05
	15.5	0.1	1.05	0.1

One notes that, after the arrests shown in Fig. 4, the slope of the lines increases in each of the three runs. Examination of Table 3 shows that the time dependence (n-values) increases after the arrests, and that in each of these five runs the second slopes n_2 are greater than unity. Consequently one concludes that after the arrests the oxidation reaction

[redacted]

[redacted]

accelerates with increasing time.

6. Summary

Studies have been made of the oxidation of unalloyed plutonium and of a gallium alloy over a range of temperatures in which the unalloyed delta phase is stable. The data indicate that small additions of gallium confer protection against oxidation to plutonium at these temperatures. In all of the runs made with the gallium alloy the oxidation reaction underwent an arrest, the duration of which appears to depend on the test temperature. Following the arrest, an accelerating rate of attack was observed. Similar arrests, followed by an accelerating attack, have been observed in room temperature experiments with the gallium alloy.

[redacted]

UNCLASSIFIED

UNCLASSIFIED