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LOS ALAMOS SCIENTIFIC LABORATORY
OF THE UNIVERSITY OF CALIFORNIA o LOS ALAMOS NEW MEXICO

STUDIES ON THE ALPHA-TO-BETA AND BETA-TO-ALPHA PHASE TRANSFORMATION OF PLUTONIUM

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STUDIES ON THE ALPHA-TO-BETA AND BETA-TO-ALPHA PHASE TRANSFORMATION OF PLUTONIUM

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ABSTRACT

The alpha-to-beta and beta-to-alpha phase transformations of plutonium were observed by measuring changes in electrical resistivity. Specimens of different thicknesses were heated from ambient temperature by immersion in agitated, constant-temperature baths. The bath temperature ranged from 123° to 200°C. These specimens were then cooled by immersion in baths at temperatures ranging from ambient to -196°C. A thermocouple was imbedded whenever possible in each specimen. The density of each specimen was determined before and after each run.

The alpha-to-beta transformation is essentially completed in fractions of a minute after specimens at ambient conditions are immersed in baths preheated to 165°C. The beta-to-alpha transformation is essentially completed in less than 3 min. after the immersion of thin specimens into baths at ambient temperature. The time required for these transformations is influenced by specimen purity, history and geometry, bath temperature and other factors.

ACKNOWLEDGMENTS

The authors are indebted to F. W. Schonfeld, Group Leader of the Plutonium Physical Metallurgy Group of this Laboratory, and R. M. Brick and M. Fleming, consultants to the Laboratory, for their suggestions and discussions and to C. F. Metz, Group Leader of the Analytical Chemistry Group of this Laboratory, for analytical data on plutonium.

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INTRODUCTION

The kinetics of the alpha-to-beta and beta-to-alpha phase transformation of plutonium have been studied by various investigators.[1-6] There has been general agreement that the kinetics, among other parameters, are affected by impurities in the metal.[7] With the advent of kilogram quantities of high purity electrorefined plutonium at the Los Alamos Scientific Laboratory in 1960,[8] exploratory discussions and experiments were undertaken to determine which of the several intrinsic properties of plutonium would be most suitable for this study.

There appeared to be readily measurable changes in three properties accompanying the transformation of interest: (1) volume (~9.6%),[9] (2) electrical resistivity (~23%)[10] and (3) thermoelectric power (~23%).[11] Although tests were made on, and considerations given to, transducers as a means of measuring the volume change, it was concluded that such a system without inertia would be difficult to develop. Thermocouples using binary systems of plutonium with tantalum and platinum were made and calibrated. Both systems performed well. However, it was felt that the junction beads from sample to sample might not be reproducible. Preliminary experiments showed that electrical

resistivity measurements were reproducible on "identical" specimens treated in the same manner. Suitable instrumentation was also available for making precise measurements.

Of next concern in this study was the method of heating and cooling the specimen. Ideally the transformation should be studied under nearly isothermal conditions; however, the poor thermal conductivity of the metal and the difficulty of fabricating extremely small area sections precludes this. Therefore, it is necessary to impose a thermal gradient upon the system and attempt to observe changes as a result of this transient. Thin (0.04-in.-thick) specimens were heated from ambient temperature into the beta-phase region by an electrical discharge of 100 μsec duration. Transformation appeared to be extremely rapid, but the determination of the degree of transformation achieved in this system is difficult.

Experiments were undertaken by which variously dimensioned specimens of plutonium were heated or cooled in baths. The electrical resistance of the specimen and the output of an attached thermocouple were measured as a function of time. Figure 1 shows the electrical resistivity of alpha- and beta-phase plutonium as a function of temperature based on data obtained by Group CMF-5[12] of this Laboratory for plutonium of comparable purity to the material used in this study. A calculation of electrical resistivity for a typical run in this study is shown in the Appendix.

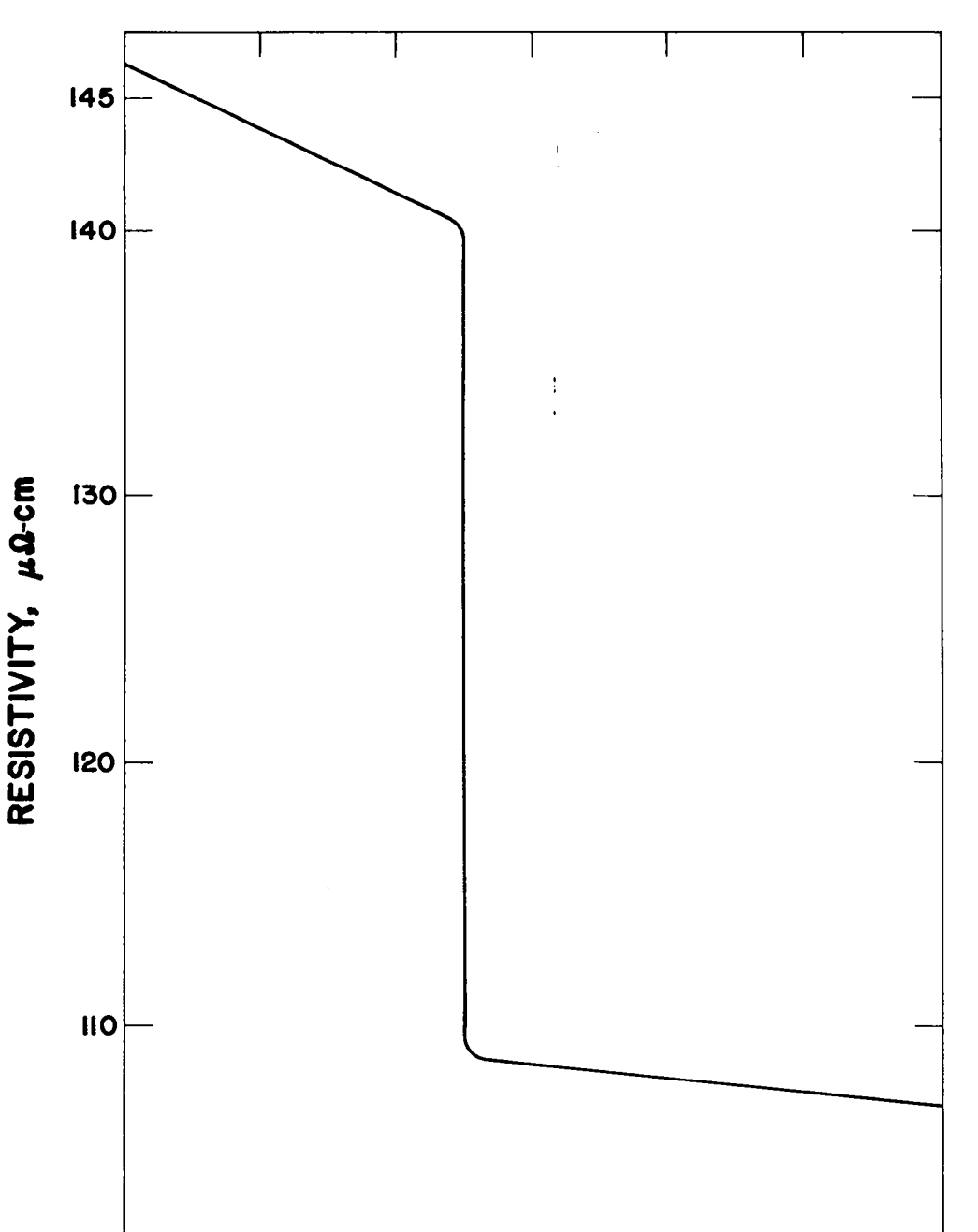

Fig. 1. Electrical resistivity of plutonium vs. temperature.

EXPERIMENTAL PROCEDURES

Plutonium Metal

The two purity levels of plutonium used are called "high purity" and "good purity." The former was obtained by the electrorefining process,[13] the latter by the bomb-reduction method.[14] Typical analytical data are shown in Table 1. The as-received metal was vacuum cast into calcium fluoride-coated graphite molds and machined[15] to shape.

Plutonium Specimen

Two geometries of plutonium specimens were prepared: One was in the form of a right hollow cylinder, 2.7 in. in diameter and 0.250 in. long. The wall thicknesses of the various cylinders used were 0.010, 0.020, 0.040 and 0.080 in. A 1-in.-long arc was removed from each cylinder such that the total circumferential length of the specimen was 7.5 in. A nominal 0.014-in.-diameter thermocouple hole was drilled (parallel to the cylinder axis) into the specimen (with a thickness of > 0.020 in.) to a depth of 0.125 in. in the center of the wall, 0.25 in. from one end. Friction clip power leads made of silver-plated steel were attached to each end of the specimen. Potential pick-up leads were attached near each end. These leads had a silver-plated steel knife edge against one side of the cylinder and a Micarta insulator against the other. The distance between the knife edges was set at 6.00 in. The specimen was held in a rack as shown in Fig. 2.

Table 1

Purity of Plutonium Metal

Element	Concentration, ppm by weight — Lot No.[a] J00-1341	H00-1411	H00-1198	H00-1100
Be	< 0.1	< 0.1	< 0.1	< 0.1
Li	< 0.2	< 0.2	< 0.2	< 0.2
Bi	< 1	< 1	< 1	< 1
Sn	< 1	< 1	< 1	< 1
Mo	< 1	< 1	< 1	< 1
Pb	< 2	< 2	< 2	< 2
La	< 10	< 10	< 10	< 10
Na	< 10	< 10	< 10	< 10
Ca	< 10	< 10	< 10	< 10
Co	< 10	< 10	< 10	< 10
Zn	< 10	< 10	< 10	< 10
Zr	< 10	< 10	< 10	< 10
Ga	< 20	< 20	< 20	< 20
U	< 30	< 30	< 30	< 30
Ta	< 35	< 35	< 35	< 35
B	1	< 0.5	< 0.5	< 0.5
Mn	2	< 2	< 2	< 2
Cu	10	< 2	< 2	< 2
Cr	15	< 5	< 5	< 5
Mg	50	< 10	< 10	< 10
Si	55	10	< 10	< 10
Ni	75	< 10	< 10	< 10
Th	245	< 15	< 15	< 15
Al	5	5	30	< 5
C	310	40	20	10
W	5	33	46	32
Fe	60	20	30	< 20
Am[b]	31	180	175	86
Pu, %	99.79	99.93	99.94	99.99
Density, g/cc	~19.51	---	19.62	---

(a) J00 symbolizes "good" purity; H00, "high" purity.
(b) Corrected to February, 1964 (assuming growth rate of 12 ppm/mo.).

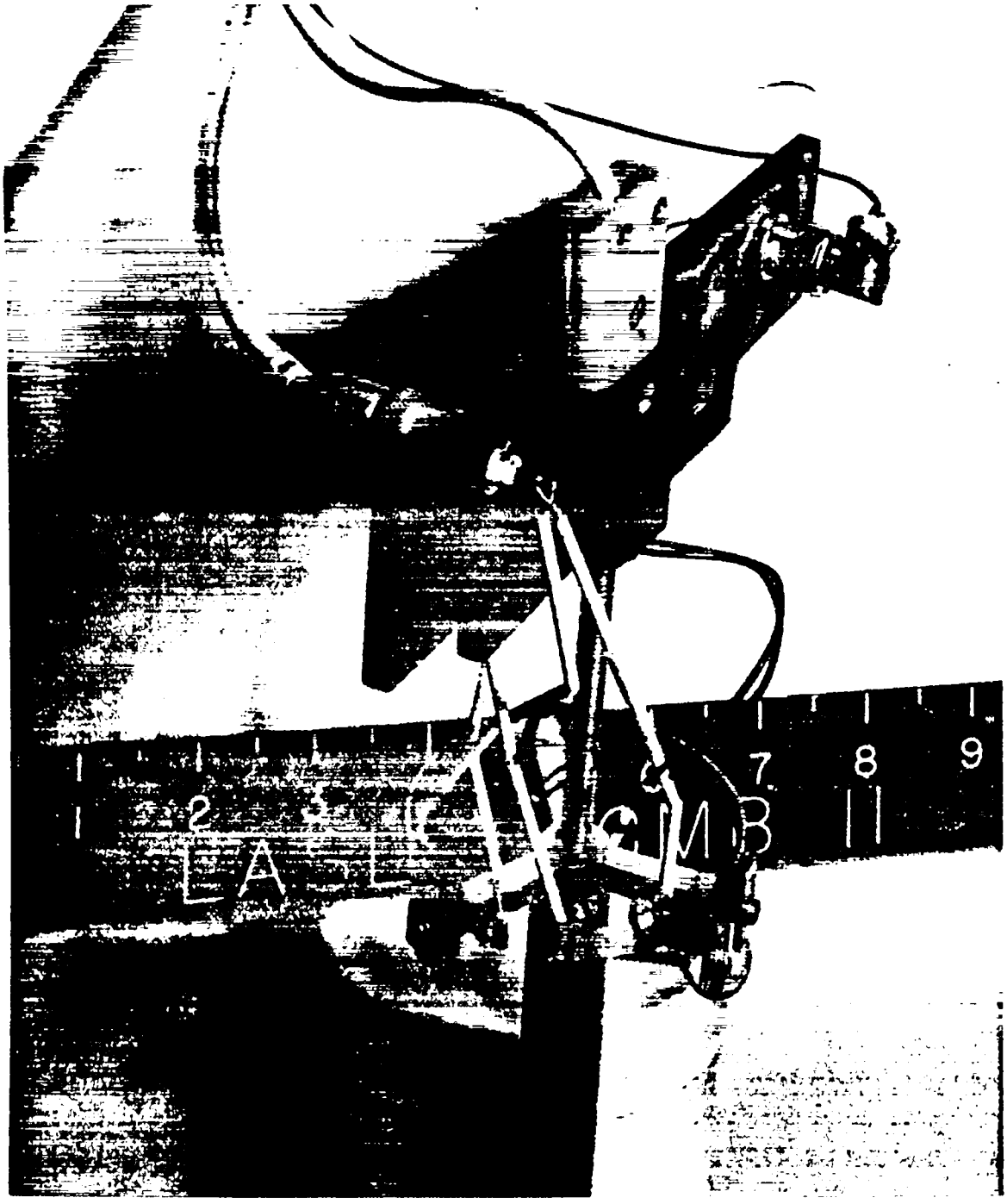

Fig. 2. Plutonium ring specimen with electrical connectors attached.

The second form of plutonium specimen was a rod, 0.200 in. in diameter, 7.5 in. long. Power leads were attached at each end and connectors were used to support the sample from a Micarta block. At 2.25, 2.375 and 2.5 in. from one end, thermocouples were imbedded in the specimen. The first one was on the surface of the rod; the second, 0.050 in. deep and the third, 0.100 in. deep. Potential pick-up leads were positioned 1.25 and 4 in. from the other end. The specimen immersed in an oil bath is shown in Fig. 3.

A freshly machined specimen was used for each run, except where studies were made on multiple runs.

Instrumentation

A Baldwin-Lima-Hamilton type TCA-ES-100, 1-mil wire, bare-tip, Chromel-Alumel thermocouple contained in a 0.014-in.-diameter stainless steel sheath was imbedded in the hole in the specimen between the power and potential pick-up clips.

A constant direct current was fed to the specimen from a Kepco Laboratory Model SC-18-2M regulated power supply.

A potential drop across the specimen and the thermocouple output were simultaneously recorded on a Minneapolis Honeywell Visicorder Oscillograph, Model No. 906C-159XFGH, using chart speeds up to 25 in./min. (Response time for full-scale deflection of this instrument is 20 msec.)

A 1-amp direct current flowing through the 0.040- by 0.250-in. specimen resulted in a 34- to 38-mv potential drop at ambient temperature.

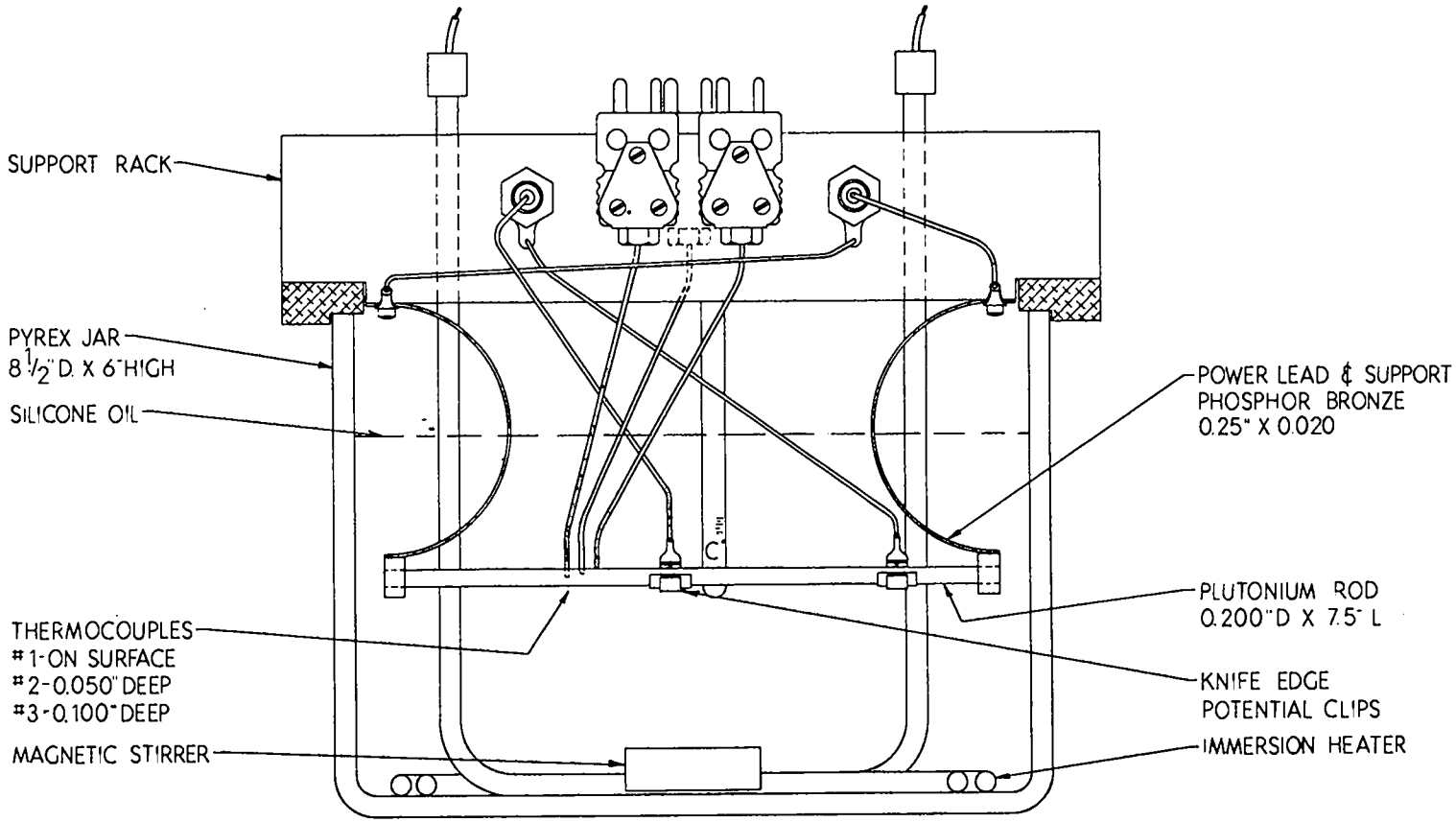

Fig. 3. Plutonium rod resistivity specimen (with electrical connectors attached) in silicone oil bath.

When specimens of other dimensions were used, the current was adjusted to give a 25- to 50-mv drop at ambient temperature. The exact value of the potential drop was not important since the subsequent change was the required measurement. Except in runs where exact current readings were desired, the actual current settings were not calibrated closer than 5%; however, once a setting was established it remained constant within the limits of the power supply (<0.1%) during the run.

Potential-drop-calibration factors of the lines, instrument and cold junction for both the specimen and thermocouple circuits were determined prior to each run. Applying the appropriate corrections, the actual thermocouple voltage values were accurate to 0.05%.

Figure 4 shows the recording instrument and standard gauges used to calibrate the electrical system.

Bath

A glass bell jar was used to contain the bath fluid. Dow Corning No. 200 fluid (silicone oil) was used at ambient and higher temperatures. The bath was agitated by a magnetic stirrer and heated by an immersion heater. The bath temperature was controlled to 1°C by conventional methods. A certified mercury-in-glass thermometer was inserted in the bath. The temperature of the bath under ambient conditions was not controlled.

Liquid nitrogen was used as a bath fluid for one run.

Figure 5 shows a ring specimen in a bath.

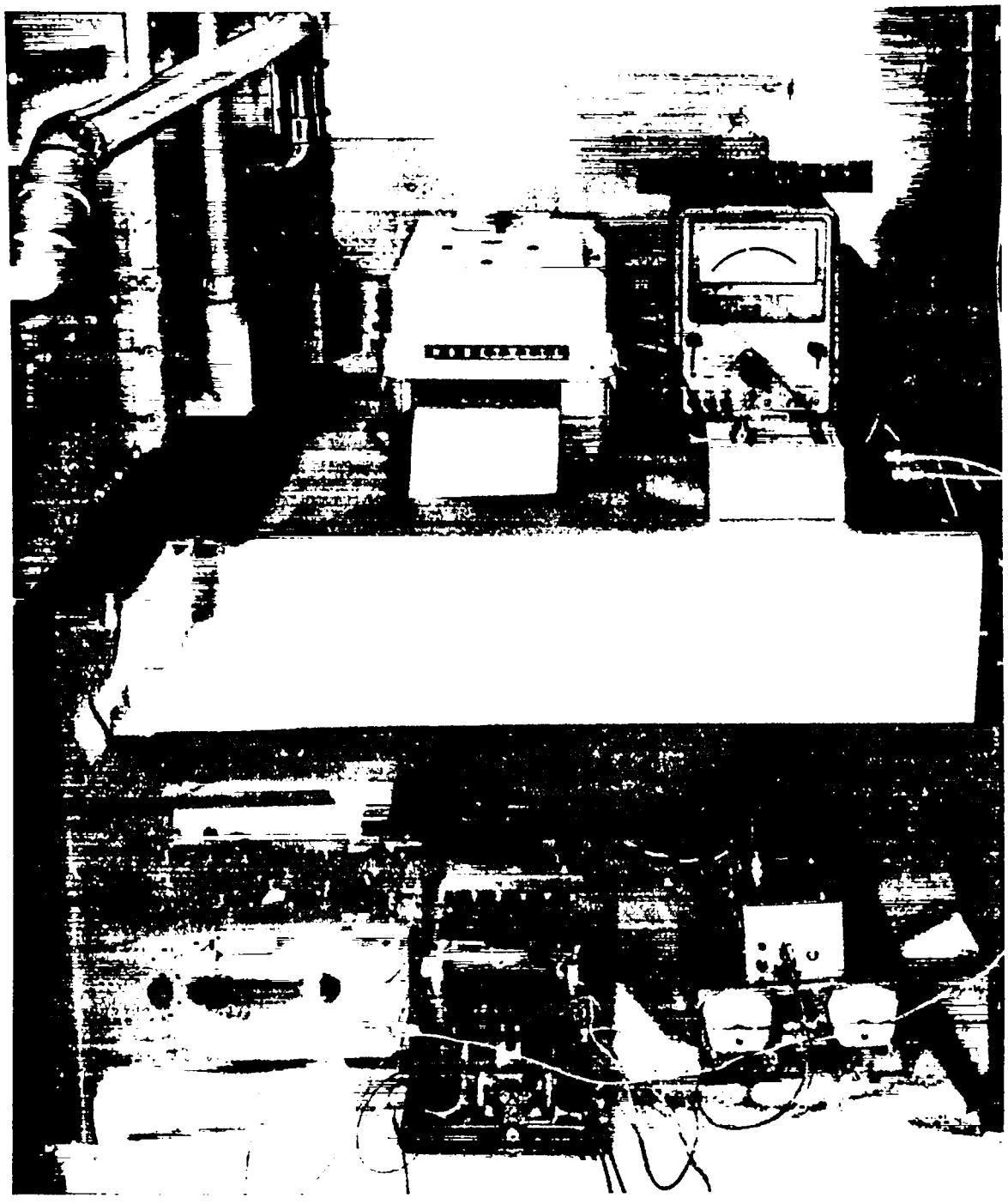

Fig. 4. Potential-drop and thermocouple recording and calibration equipment.

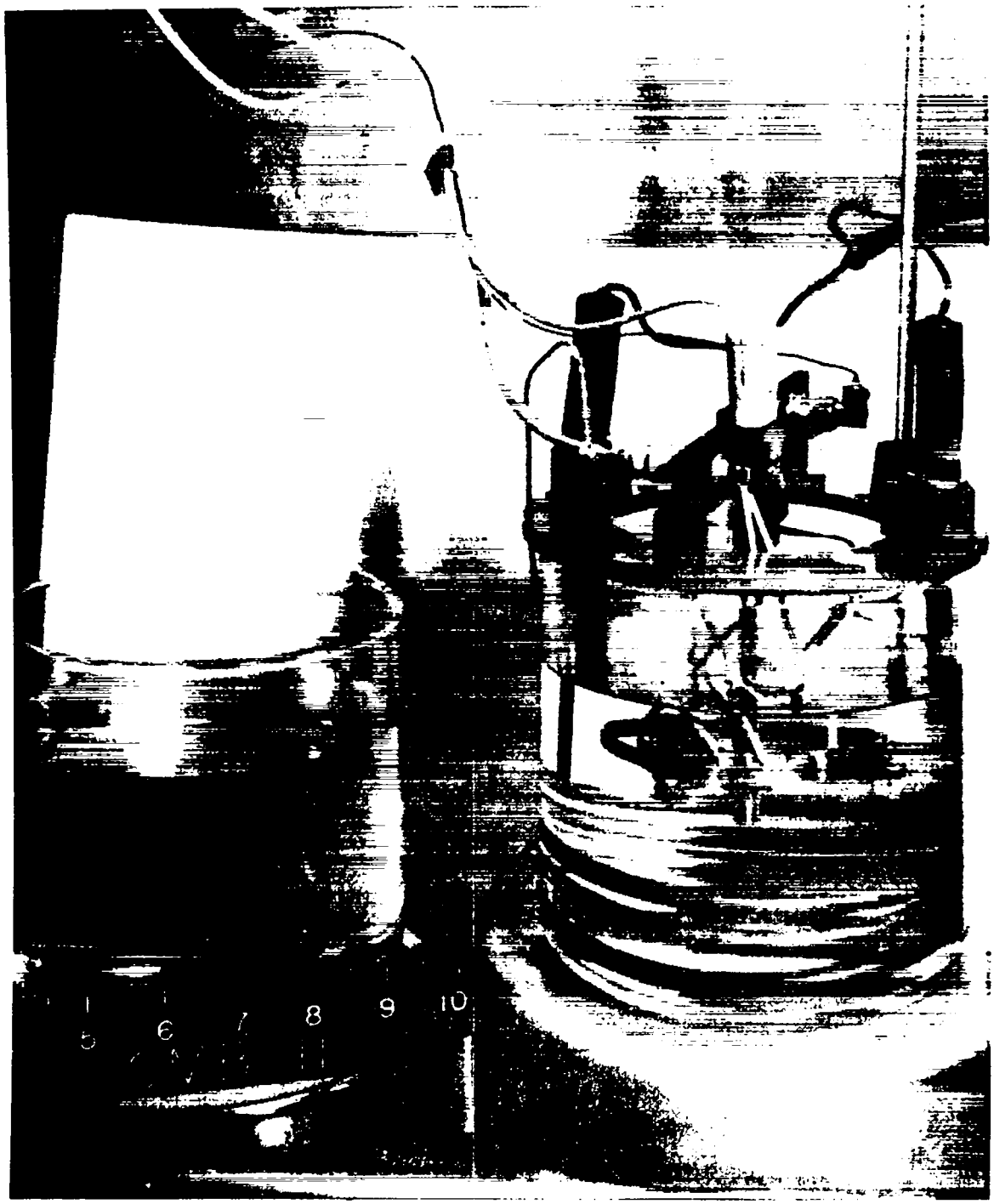

Fig. 5. Plutonium ring specimen in silicone oil bath.

Density

The density was determined by the Archimedian method. The immersion fluid was Matheson, Coleman & Bell BX1020 bromobenzene. The bath was stirred and contained a calibrated mercury-in-glass thermometer. A precision ground steel ball was used as a primary standard. The accuracy of this method has been determined to be 1 part in 10^4.

The density of most specimens was determined just prior to, and within 24 hr after, each run. Subsequently, readings were made on the specimens as a function of time.

EXPERIMENTAL DATA AND DISCUSSION

The temperature and potential-drop data for the various runs are summarized in Table 2. Detailed experimental results are shown graphically and discussed in the following order.

Figure 6 shows the rate of change in electrical resistivity (as measured by potential drop) as a high purity ring specimen is slowly heated and cooled.

Figures 7 through 14 show data for the alpha-to-beta phase transformation of plutonium, and Figs. 15 through 25 are concerned with the beta-to-alpha phase transformation.

Initial experiments were made in which a plutonium ring was placed in a bath at ambient temperature and the bath was slowly heated and cooled. The temperatures of the bath and specimen and the potential drop in the specimen were observed. One such run is shown in Fig. 6. In this case, the

Table 2

Summary of Temperature and Potential-Drop Data for Alpha-to-Beta and Beta-to-Alpha Phase Transformation Studies on Plutonium

Run No.	Specimen Size,[a] in.	Initial Temp., °C	Hot Bath Temp., °C	Initial Potential Drop, mv	Potential-Drop Change at Hot Bath Temp., mv	Cold Bath Temp., °C	Sample No.[b]
2[c]	0.040 x 0.250 x 6	37.5	160	39	10.6	64	H00-1198-1
17	0.010 x 0.250 x 6	31	165	51	13.7	26	J00-1341-29
18	0.020 x 0.250 x 6	32	165	35	9.1	--	J00-1341-31
19	0.020 x 0.250 x 6	31	165	35	8.7	37	J00-1341-31
12	0.040 x 0.250 x 6	27	165	34.5	9.1	34	J00-1341-21
21	0.080 x 0.250 x 6	31	165	29	7.7	22	J00-1341-33
23	0.040 x 0.250 x 6	22.5	123	35.3	8.1	26	J00-1341-24
16	0.040 x 0.250 x 6	31	130	35	8.6	34	J00-1341-23
8	0.040 x 0.250 x 6	29	130	35	9.2	25	H00-1198-5
4	0.040 x 0.250 x 6	27	165	36	9.5	27	H00-1198-7
11	0.040 x 0.250 x 6	32	165	37	9.1	36	H00-1198-11
24	0.040 x 0.250 x 6	23	165	36.5	9.6	-196	H00-1198-10
15	0.040 x 0.250 x 6	34	200	38	10.1	35	H00-1198-9
37	0.010 x 0.250 x 6	28	165	33	8.9	28	H00-1411-52
35	0.020 x 0.250 x 6	25	165	30	8.0	26	H00-1411-51
39	0.080 x 0.250 x 6	29	165	26	7.6	30	H00-1411-50
27	0.040 x 0.250 x 6	--	165	--	--	86	H00-1198-12
33	0.200 dia x 2.75	30	165	9	2.5	32	H00-1100-1

(a) For resistance measurement
(b) H00 symbolizes high purity; J00, good purity.
(c) Specimen placed in silicone oil bath which was heated and cooled at ~ 3°C/min.

Piece No. H00-1198-1
Cross section: 0.040 by 0.250 in.
Current: 1 amp
Initial potential drop: ~39 mv at 37.5°C over 6-in. length

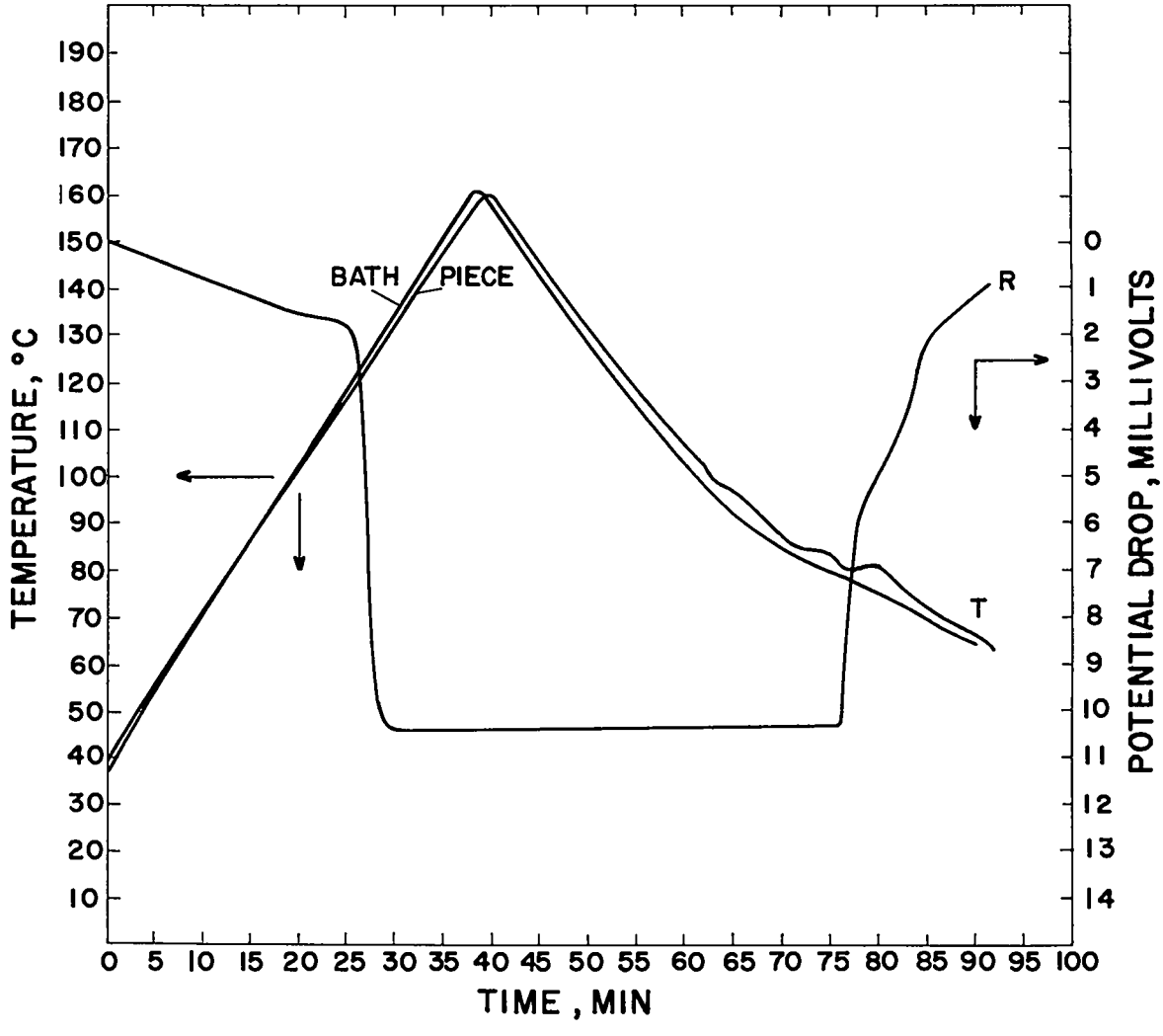

Fig. 6. Temperature and potential drop vs. time for heating high purity plutonium from 37.5° to 160°C in silicone oil and cooling to 64°C at ~3°C/min (Run No. 2).

high purity specimen had a cross section measuring 0.040 by 0.250 in. The silicone oil bath was heated from 37.5° to 160°C at a rate of 3°C/min and then cooled to 64°C at approximately the same rate. The potential drop, which reflects the resistivity change, was measured over a 6-in. length through which was flowing a constant current of 1 amp.

The following points are of interest: The potential-drop curve decreases linearly until 20 to 21 min, at which time it exhibits a change in slope. The temperatures of the bath and the center of the specimen are 106° and 102°C, respectively. After 24 min, the curve breaks down sharply, and the bath and central specimen temperatures are 118° and 114°C, respectively. These temperatures are, therefore, limiting values for the alpha-to-beta phase transformation of this specimen.

The transformation to beta phase was completed (24.6% total change in the potential drop) by the time the bath temperature reached 140°C, as evidenced by the constancy in the potential-drop curve as the bath and specimen were further heated to ~160°C.

Upon cooling the specimen, the beta-to-alpha phase transformation did not start until the central specimen temperature was ~80°C. At this point the potential-drop curve rose rapidly.

Alpha-to-Beta Phase Transformation

A typical result showing the specimen temperature and potential drop as a function of time after the immersion of plutonium into a

pre-heated silicone oil bath is given in Fig. 7. The high purity ring specimen (with a cross section of 0.040 by 0.250 in.) was heated from 32° to 165°C. The thermocouple in the center of the specimen indicated a temperature increase up to about 126°C and then a sudden decrease before rising to bath temperature. The potential drop through a 6-in. length of specimen with a 1-amp direct current showed an immediate rapidly declining rate followed by a lesser rate before a second rapidly declining rate.

Complete alpha-to-beta transformation had occurred in less than 0.35 min. Assuming a transformation temperature of 110°C, 12.4% of the total potential drop is due to heating the alpha-phase material.

By the time (greater than 0.4 min) the temperature in the center of the specimen reached bath temperature, transformation had been completed. Therefore, isothermal conditions cannot be achieved in immersion-type experiments.

The data in the previous run on high purity plutonium are compared in Fig. 8 with those obtained under the same experimental conditions using good purity plutonium. The specimens (with a 0.040- by 0.250-in. cross section) at ambient temperature were immersed in a silicone oil bath at 165°C.

It is evident that the temperature rise was faster in the high purity material until the break occurred in the temperature curve. (This faster heating may be due to the higher density of the high purity plutonium.) However, the temperatures of the two were the same

Piece No. H00-1198-11
Cross section: 0.040 by 0.250 in.
Current: 1 amp
Initial potential drop: ~37 mv at 32°C over 6-in. length

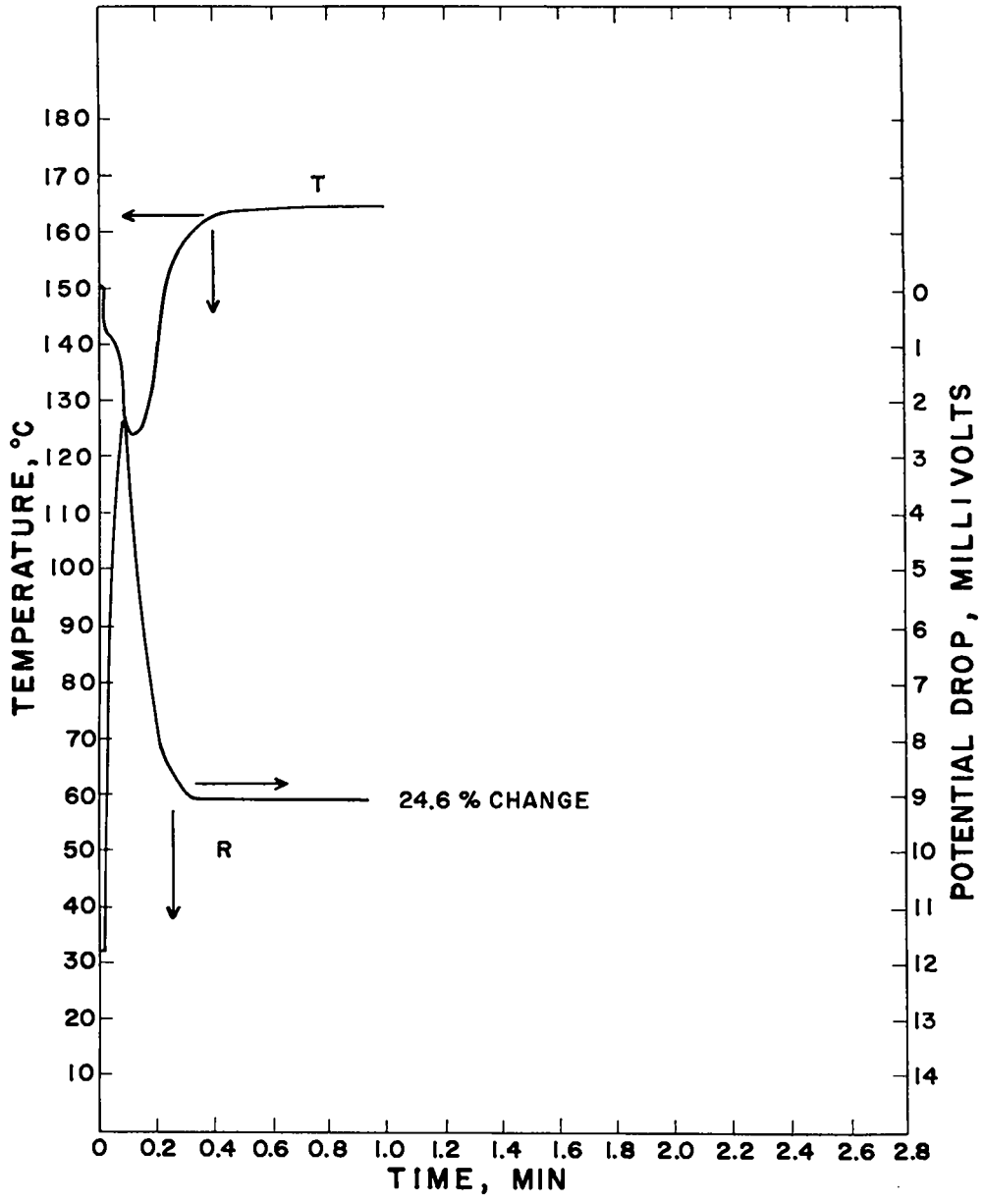

Fig. 7. Temperature and potential drop vs. time for high purity plutonium heated from 32° to 165°C by immersion in silicone oil (Run No. 11).

Run No.	11	12
Plutonium purity	High	Good
Piece No.	H00-1198-11	J00-1341-21
Thickness, in.	0.040	0.040
Height, in.	0.250	0.250
Current, amp	1.0	1.0
Initial potential drop, mv (6-in. length)	~37	~34.5
Initial temperature, °C	32	27

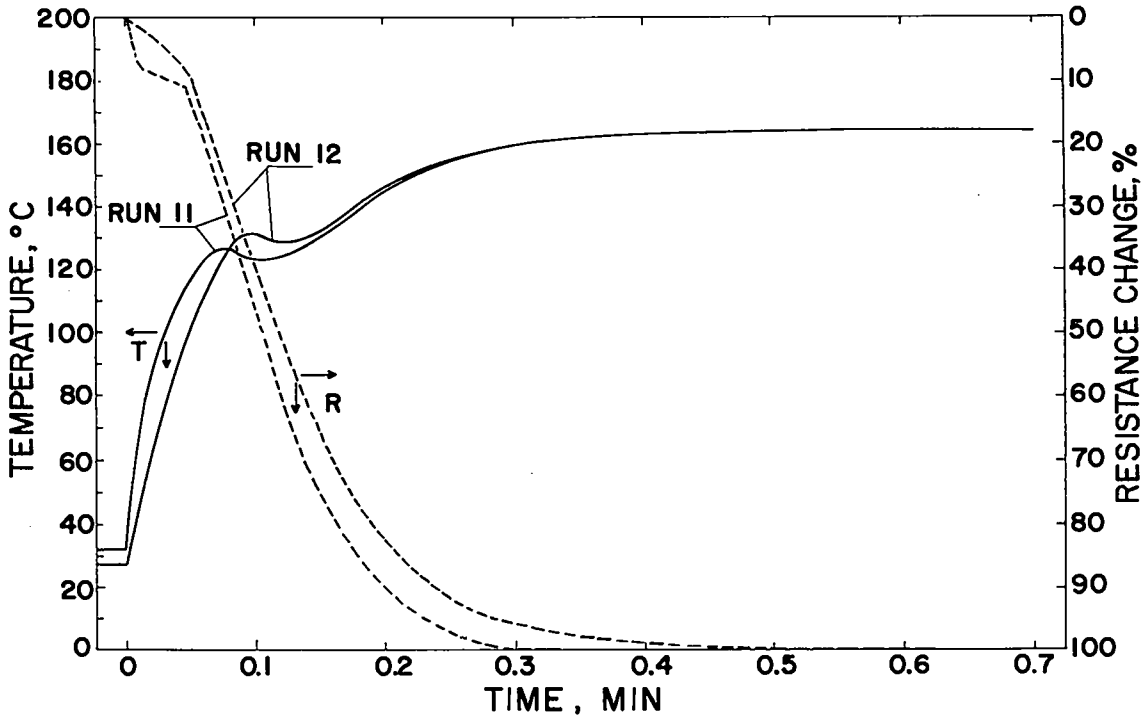

Fig. 8. Temperature and resistance change vs. time for high purity and good purity plutonium heated from ~30° to 165°C by immersion in silicone oil (Run Nos. 11 and 12).

after about 0.3 min. These breaks in the temperature curves represent a period when the heat flow characteristics were reversed and not the start of beta-phase transformation.

The resistance change[a] curve shows that the high purity specimen was transformed to beta phase in about 0.35 min while some 0.6 min were required for the good purity material. Also of interest is the first part of the resistance change curves. The resistance of the high purity specimen decreased rapidly, followed by a horizontal break and again decreased rapidly, whereas the good purity material had a gradually changing resistance. This was characteristic of these two purity levels in these immersion heating experiments.

High purity plutonium ring specimens with the same dimensions (0.040 by 0.250 in.) were separately heated from ambient temperature to 130°, 165° and 200°C by immersion into preheated silicone oil. Figure 9 shows their resistance change as a function of time. Ninety percent of the total resistance change was achieved in 0.12 min for the specimen immersed in the bath at 200°C compared to 0.29 min for the bath at 165°C and 1.42 min for the bath at 130°C.

Figure 9 illustrates the point that the faster the specimen is heated the more rapidly it transforms.

(a) In this and most of the following figures, the potential drop has been converted to resistance and plotted as a percentage change in which 0% represents the initial ambient condition, and 100%, complete transformation to beta phase.

Run No.	8	4	15
Piece No. H00-1198-	5	7	9
Thickness, in.	0.040	0.040	0.040
Height, in.	0.250	0.250	0.250
Current, amp	1.0	1.0	1.0
Initial potential drop, mv (6-in. length)	~35	~36	~38
Initial temperature, °C	29	27	34
Bath temperature, °C	130	165	200

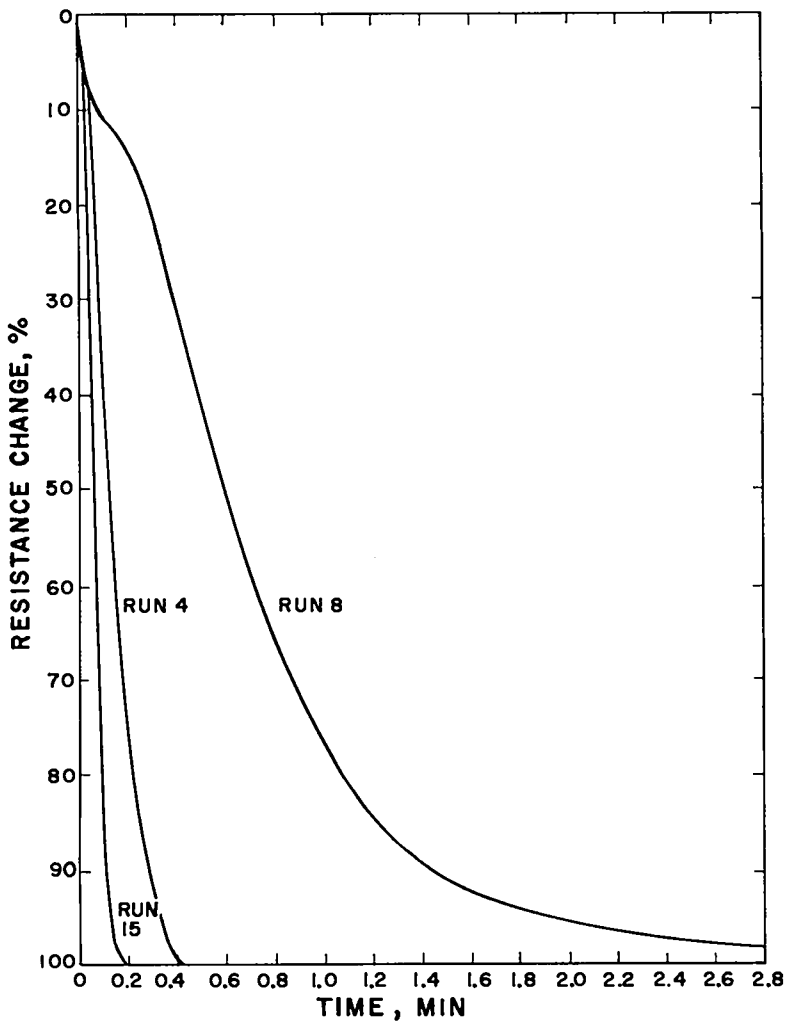

Fig. 9. Resistance change vs. time for high purity plutonium specimens separately heated from ~30° to 130°, 165° and 200°C by immersion in silicone oil (Run Nos. 8, 4 and 15).

The conditions for Run No. 4 shown here and Run No. 11 shown in Figs. 7 and 8 were identical in that these specimens were immersed in a bath at 165°C. The temperature rise curves for the two runs were essentially identical as were the resistance change curves up to 50%; however, there were differences during the final 50% in resistance change. The specimen in Run No. 4 required about 0.42 min for complete transformation whereas that used in Run No. 11 required about 0.35 min. This is probably related to the lower initial density, 19.62 g/cc, compared to 19.59 g/cc.

Figure 10 is a plot of resistance change vs. time for high purity plutonium of various thicknesses heated from ambient temperature to 165°C by immersion in silicone oil. The ring specimens, all 0.250 in. high, had thicknesses of 0.010, 0.020, 0.040 and 0.080 in. Obviously, the thinner specimens heated and transformed more rapidly.

Figure 11, developed from the data given in Fig. 10, gives the time for various resistance changes as a function of the thickness of high purity plutonium heated from ambient temperature to 165°C by immersion in silicone oil. Again, it should be emphasized that the time given includes both that for heating the alpha-phase material and for transformation, and that the resistance change due to alpha heating is about 12.5%. From the caloric standpoint, some 45% of the total heat is required for alpha-phase heating and 55% for alpha-to-beta phase transformation. Because of these facts, the actual time for transformation must be shorter than that required for 100% resistance change.

Run No.	37	35	11	39
Piece No. H00-1411-	52	51	11	50
Thickness, in.	0.010	0.020	0.040	0.080
Height, in.	0.250	0.250	0.250	0.250
Current, amp	0.3	0.5	1.0	1.7
Initial potential drop, mv (6-in. length)	~33	~30	~37	~26
Initial temperature, °C	28	25	32	29

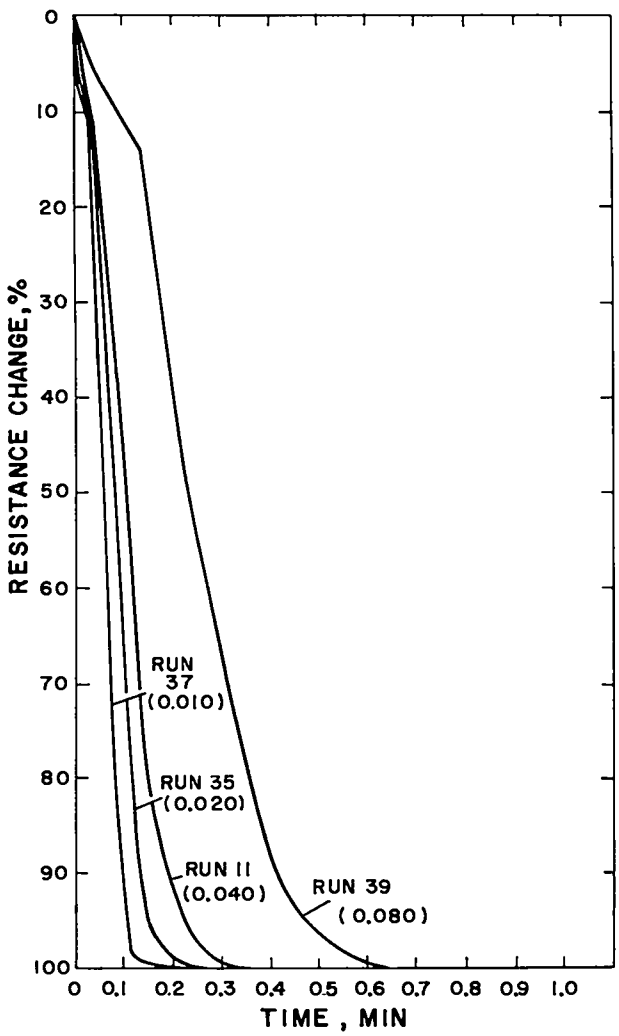

Fig. 10. Resistance change vs. time in bath (not at bath temperature) for high purity plutonium of various thicknesses heated from ~30° to 165°C by immersion in silicone oil (Run Nos. 37, 35, 11 and 39).

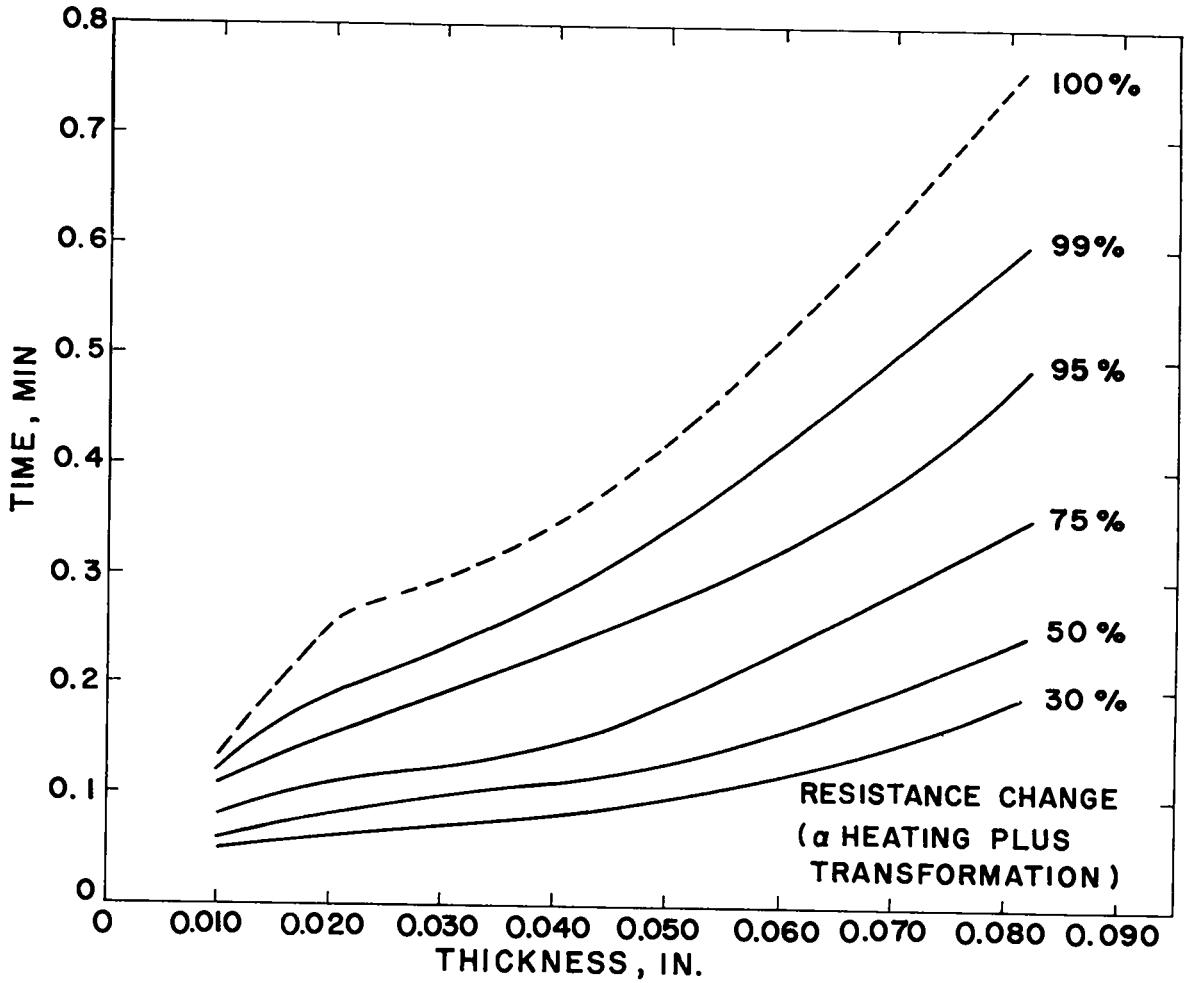

Fig. 11. Time for changes in resistance vs. thickness of high purity plutonium heated from ~30° to 165°C by immersion in silicone oil.

Figures 12 and 13 are similar to the previous two except that data for good quality plutonium are shown. Figure 12 shows the resistance change as a function of time for good purity plutonium of various thicknesses heated from ambient temperature to 165°C by immersion in silicone oil. The ring specimens, all 0.250 in. high, had thicknesses of 0.010, 0.020, 0.040 and 0.080 in. Again the thinner specimens transformed more rapidly.

Figure 13 gives the time for various resistance changes as a function of the thickness of the good purity plutonium.

There appears to be an anomaly in the result for the 0.020-in.-thick good purity plutonium specimen. Its resistance change up to 65% was indistinguishable from that of the 0.010-in.-thick sample. With the exception of this run, it is apparent that the high purity material transforms to the beta phase more rapidly than does good purity plutonium.

Figure 14 is a graph of the temperature and resistance change as a function of time for a 0.200-in.-diameter, 7.5-in.-long high purity plutonium rod heated from 30° to 165°C by immersion in a preheated silicone oil bath. The three temperatures shown were obtained from microthermocouples located on the surface of the rod, 0.050 in. beneath the surface of the rod and at the center. All three locations were ~2.38 in. from one end of the rod. The potential drop across a 2.75-in. length of unincumbered rod was converted to percentage resistance change.

Run No.	17	18	12	21
Piece No. J00-1341-	29	31	21	33
Thickness, in.	0.010	0.020	0.040	0.080
Height, in.	0.250	0.250	0.250	0.250
Current, amp	0.3	0.5	1.0	1.7
Initial potential drop, mv (6-in. length)	~51	~35	~34.5	~29
Initial temperature, °C	31	32	27	31

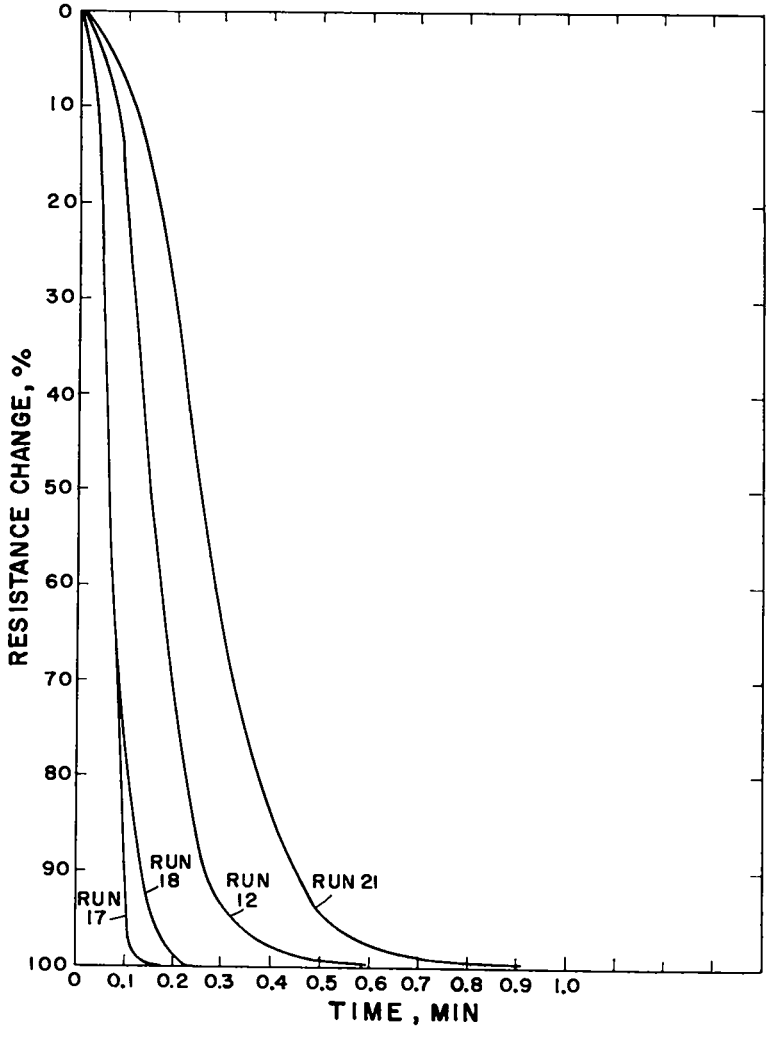

Fig. 12. Resistance change vs. time in bath (not at bath temperature) for good purity plutonium of various thicknesses heated from ~ 30° to 165°C by immersion in silicone oil (Run Nos. 17, 18, 12 and 21).

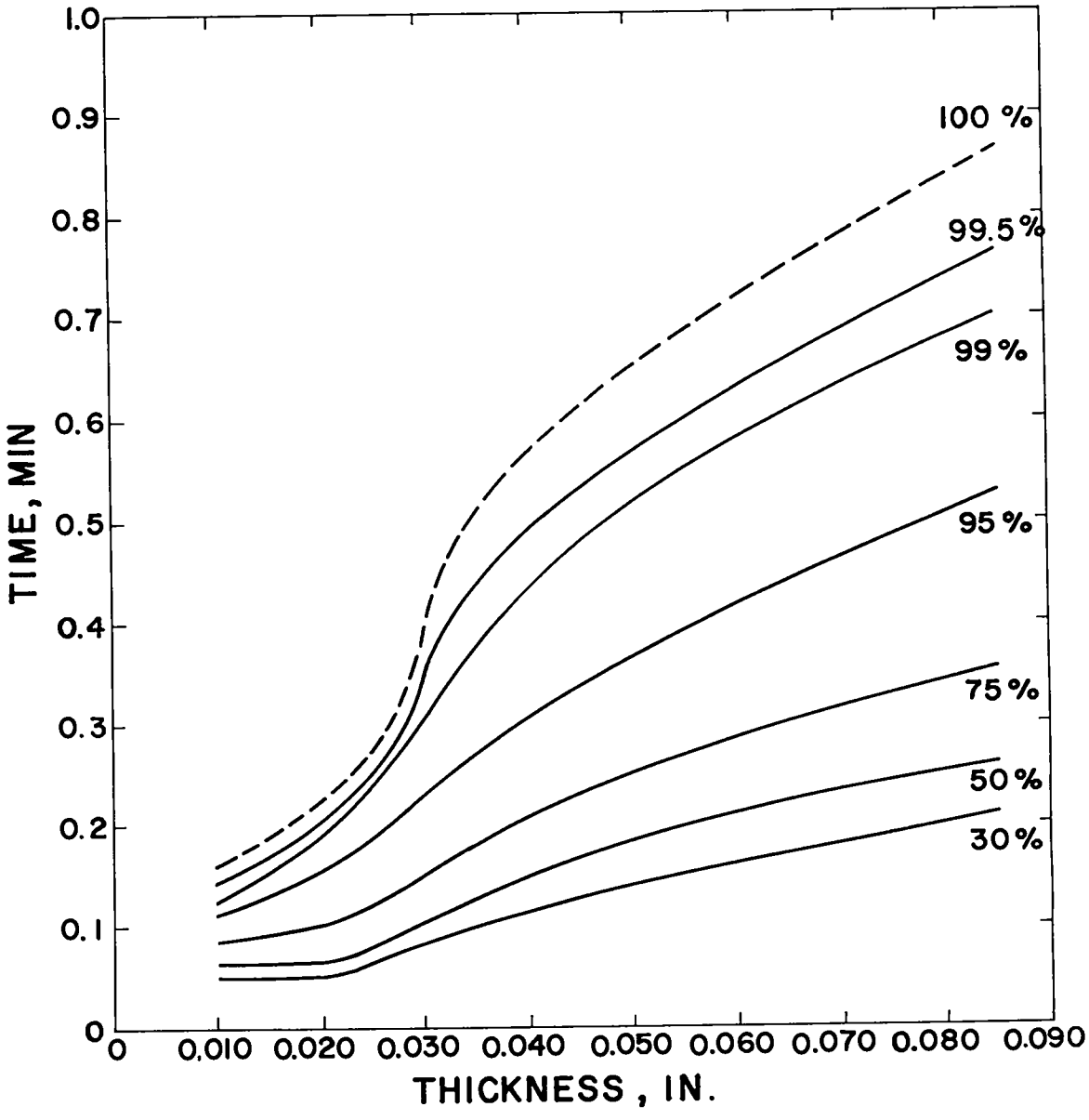

Fig. 13. Time for changes in resistance vs. thickness of good purity plutonium heated from ~30° to 165°C by immersion in silicone oil.

Piece No. H00-1100-1
Piece size: 0.200 in. diameter, 7.5 in. long
Current: 1.8 amp
Initial potential drop: ~9 mv at 30°C over 2.75-in. length
Thermocouple location:
No. 1. On surface, 2.25 in. from one end
No. 2. 0.050 in. deep, 2.375 in. from same end
No. 3. 0.100 in. deep, 2.5 in. from same end

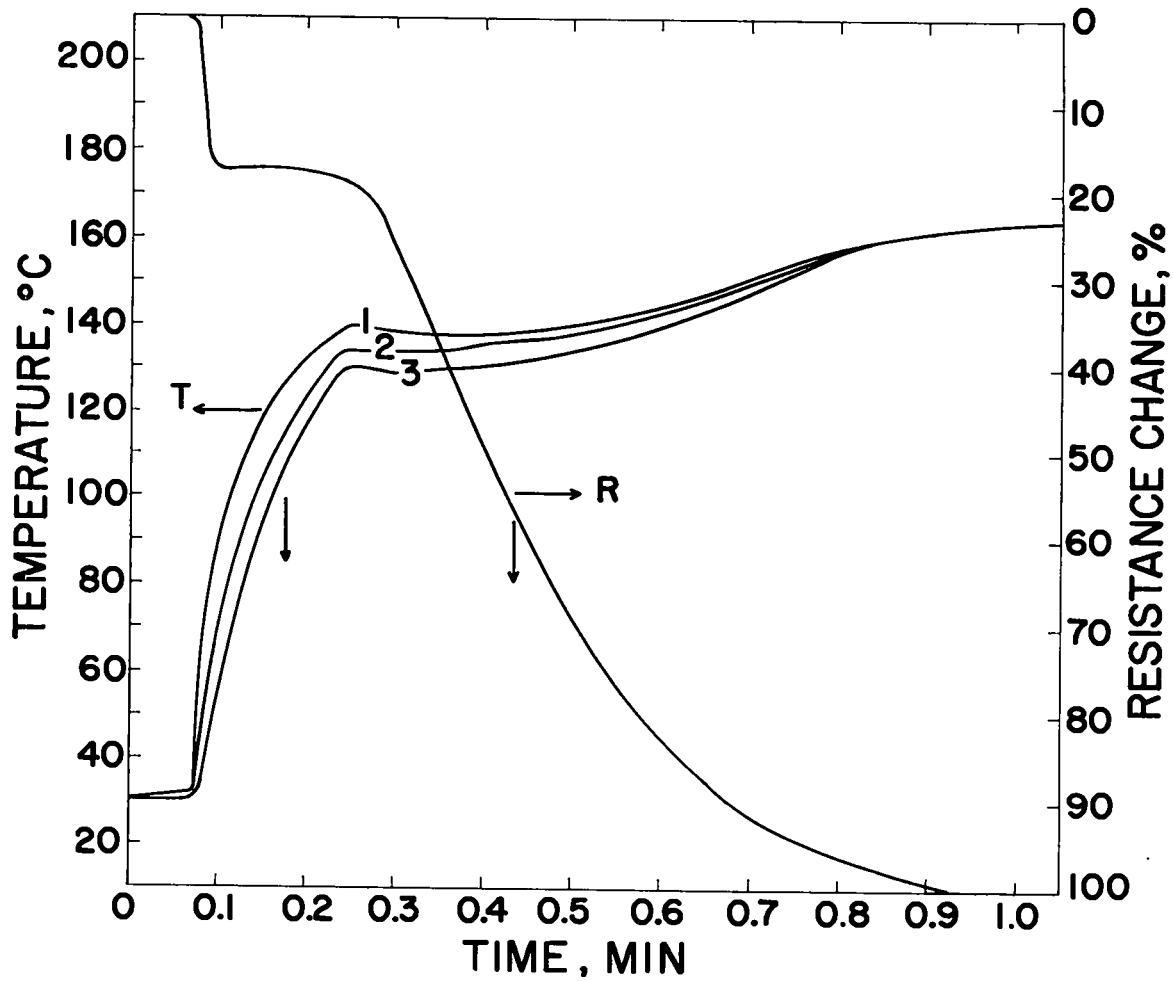

Fig. 14. Temperature and resistance change vs. time for a high purity plutonium rod heated from 30° to 165°C by immersion in silicone oil (Run No. 33).

The rod was immersed in the oil bath 0.08 min after an arbitrary zero time. The resistance change curve broke downward sharply and then flattened out for a period of about 0.15 min before decreasing again. This initial drop, amounting to 17%, is more pronounced than was observed for the ring type specimens. This amount indicates that some transformation to beta phase had occurred on the surface since it is in excess of that required for heating of the alpha-phase material.

The large temperature gradients in the specimen during heating are also to be noted.

A study of these data point out several of the limitations of trying to study the kinetics of the alpha-to-beta phase transformation using immersion heating techniques: Large temperature gradients are present and are constantly changing. There is no way of determining which part of the heating is causing the temperature of alpha-phase material to increase and which part is causing transformation to beta phase since, as indicated by the resistance change, both processes are taking place together. Some regions in the specimen are heated above the transformation temperature before the entire specimen has been transformed. Among other factors this may be related to stresses and strains caused by thermal gradients and the large volume change associated with the transformation, and previously existing micro-cracks and impurities.

Beta-to-Alpha Phase Transformation

The beta-to-alpha phase transformation of plutonium was followed in the same way as the alpha-to-beta phase transformation using the same specimens. After the specimens had transformed to beta phase as a result of heating, they were cooled by quenching, usually in a silicone oil bath at ambient or higher temperatures. Most of the runs were made on specimens with initial temperatures of 130°, 165° and 200°C. Variables studied include specimen thickness, purity and cooling rate and starting and quenching temperature. The potential drop in the specimen was measured with time and referred back to the original ambient temperature value before the heating and cooling.

The electrical resistance of the specimen should return to its original ambient temperature value provided the beta-to-alpha phase transformation is as complete as the original material. There are, however, at least two complications resulting from cycling plutonium up into the beta-phase temperature region and back: microcracking and retained beta phase.

From previous work it is known that a single alpha-beta-alpha phase temperature cycle will result in a furnace-cooled, as-cast plutonium specimen with a density lower by 0.1 g/cc. High purity material shows this value a short time after the cycle. Good purity plutonium will have a lower density after the cycle, and its density will slowly rise to this limiting value over a period of several weeks. Similar data were obtained for the runs reported in Figs. 15, 16 and 17

The temperature and potential drop vs. time are shown in Fig. 15 for a ring specimen (cross section 0.040 by 0.250 in.) of good purity plutonium quenched from 130° to 32°C by immersion in silicone oil. The break in the temperature curve occurred at an indicated value of 64°C, at which time there had been a change of 8% in the potential-drop curve. Densities, in g/cc, of this specimen were as follows:

	After Alpha-Beta-Alpha Temperature Cycle		
Before Heating	2 hr	1 wk	2 wk
19.52	19.29	19.37	19.41

Figure 16 is the plot of the temperature and potential drop vs. time for a run similar to that shown in Fig. 15 in that a ring-type specimen of the same dimensions of good purity plutonium was used. The beginning temperature was 165° and the bath temperature was 34°C. The break in the temperature curve occurred at an indicated value of 48°C, at which time the potential drop change was 4.5%. Densities, in g/cc, of this specimen were as follows:

	After Alpha-Beta-Alpha Temperature Cycle		
Before Heating	2 hr	1 wk	2 wk
19.51	19.31	19.36	19.39

Figure 17 shows the temperature and potential drop vs. time for a run identical to that for Fig. 16 except that a high purity plutonium specimen was used. The sample was quenched from 165° to 27°C. The break in the temperature curve occurred at an indicated temperature of 67°C, at which time the change in the potential drop curve was 17%.

Piece No. J00-1341-23
Cross section: 0.040 by 0.250 in.
Current: 1 amp

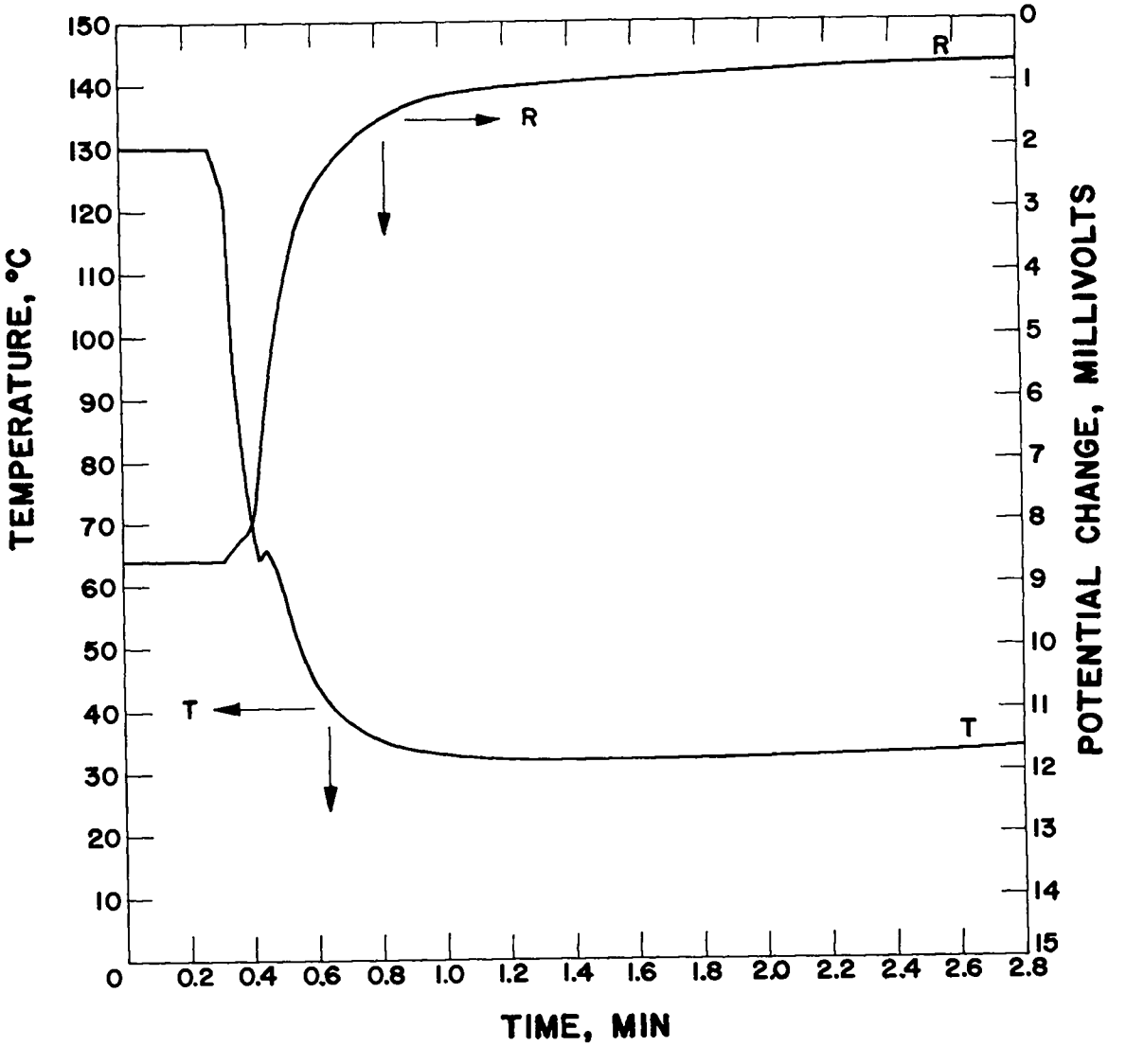

Fig. 15. Temperature and potential drop vs. time for good purity plutonium cooled from 130° to 34°C by quenching in silicone oil (Run No. 16).

Piece No. J00-1341-21
Cross section: 0.040 by 0.250 in.
Current: 1 amp

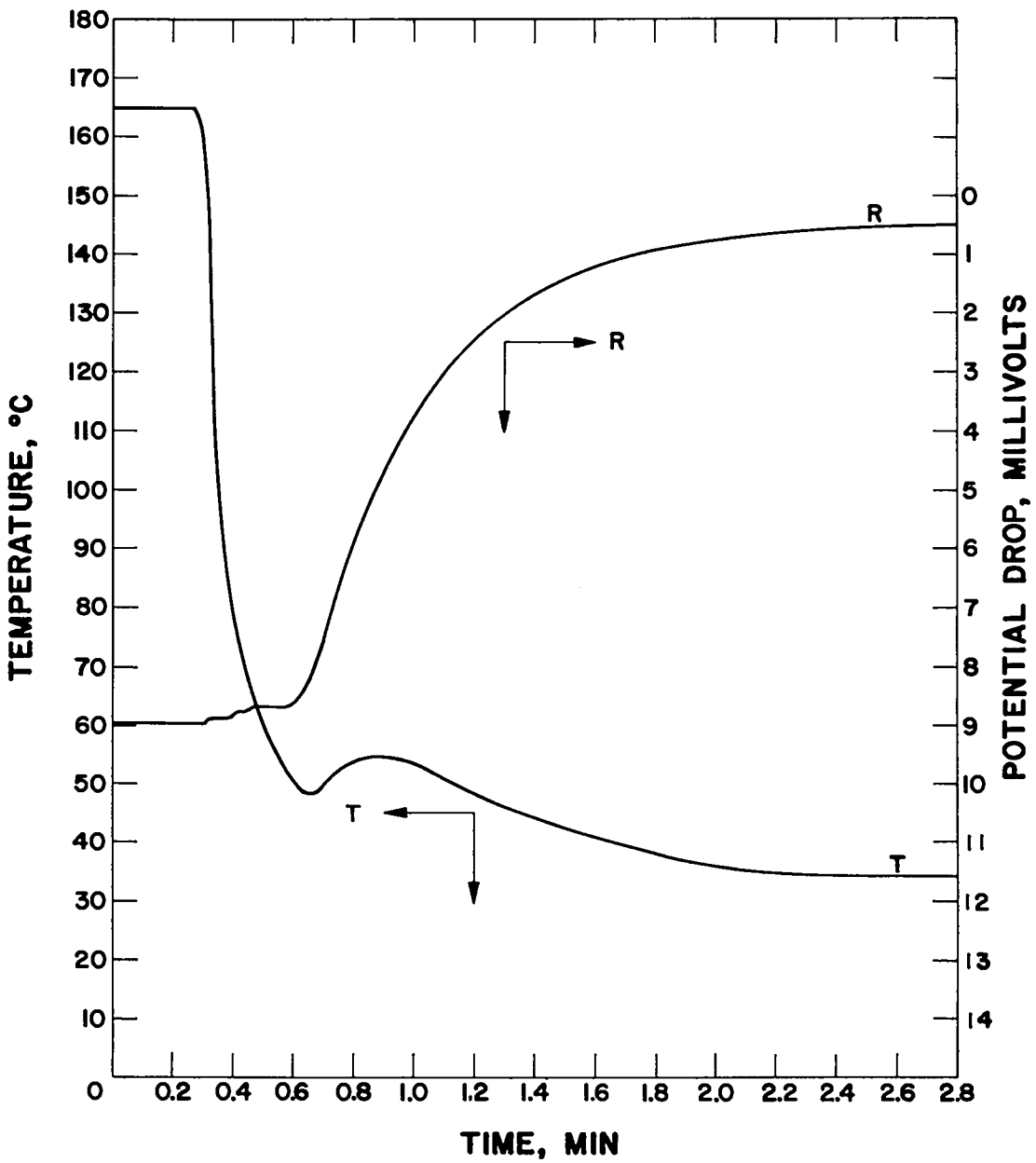

Fig. 16. Temperature and potential drop vs. time for good purity plutonium cooled from 165° to 34°C by quenching in silicone oil (Run No. 12).

Piece No. H00-1198-7
Cross section: 0.040 by 0.250 in.
Current: 1 amp

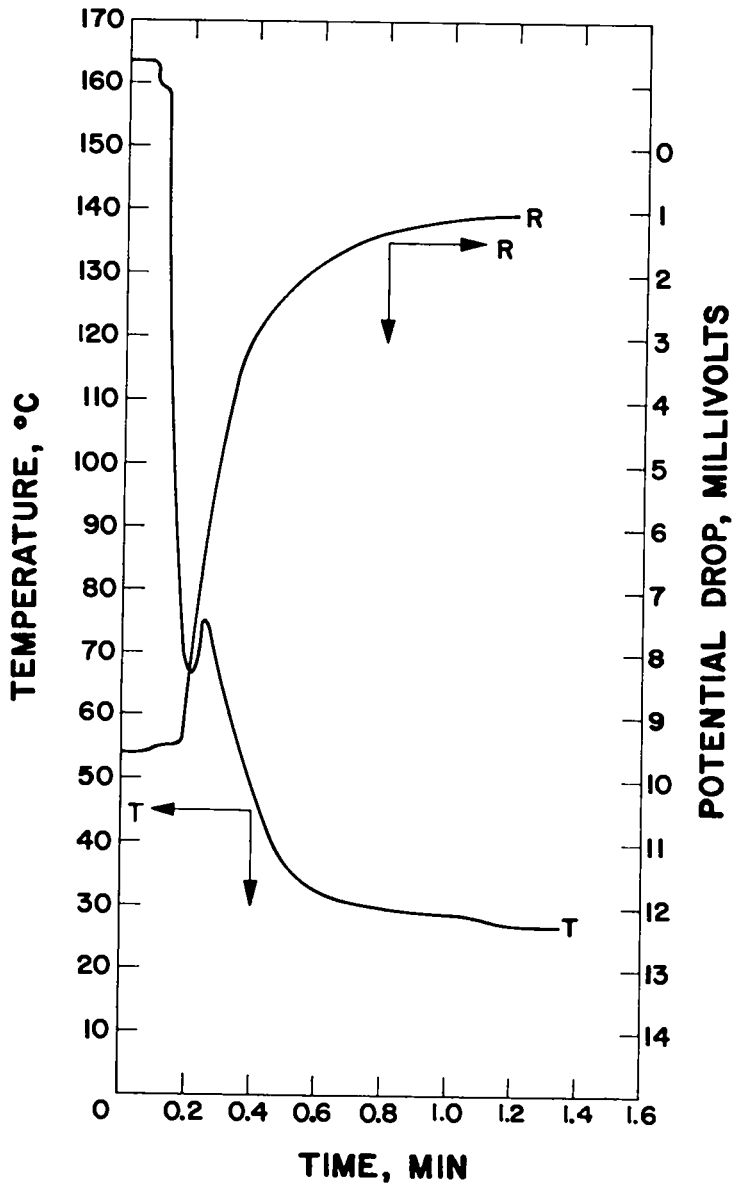

Fig. 17. Temperature and potential drop vs. time for high purity plutonium cooled from 165° to 27°C by quenching in silicone oil (Run No. 4).

Densities, in g/cc, of this specimen were as follows:

	After Alpha-Beta-Alpha Temperature Cycle		
Before Heating	2 hr	1 wk	2 wk
19.62	19.49	19.51	19.50

The temperature and potential drop as a function of time are shown in Fig. 18 for a high purity plutonium specimen quenched from 165°C in liquid nitrogen. This ring-type specimen had the same dimensions as the three previously described. The break in the temperature curve occurred at an indicated value of 12°C at which time the potential drop had changed by 28%. (Note that the time scale in this figure is expanded over the previous three.)

The resistance values are only valid for the early part of the run since an initial value was not obtained at -196°C. The zero point on the curve represents the ambient temperature value. Unfortunately, the potential drop circuit opened after 0.15 min, probably because of solidification of silicone oil on the surface of the specimen.

Other than in the preceding experiment pre-heated specimens of plutonium were not immersed in baths at temperatures below ambient. Aside from the thermal gradient, the cooling rate of a specimen is dependent on its thermal conductivity and the thermal coefficient of the "film" between the coolant bath and the specimen. The usual fluids, such as water, trichloroethylene, ethanol and liquid nitrogen, used for sub-zero baths boil at temperatures below the plutonium beta-phase

Piece No. H00-1198-10
Cross section: 0.040 by 0.250 in.
Current: 1 amp

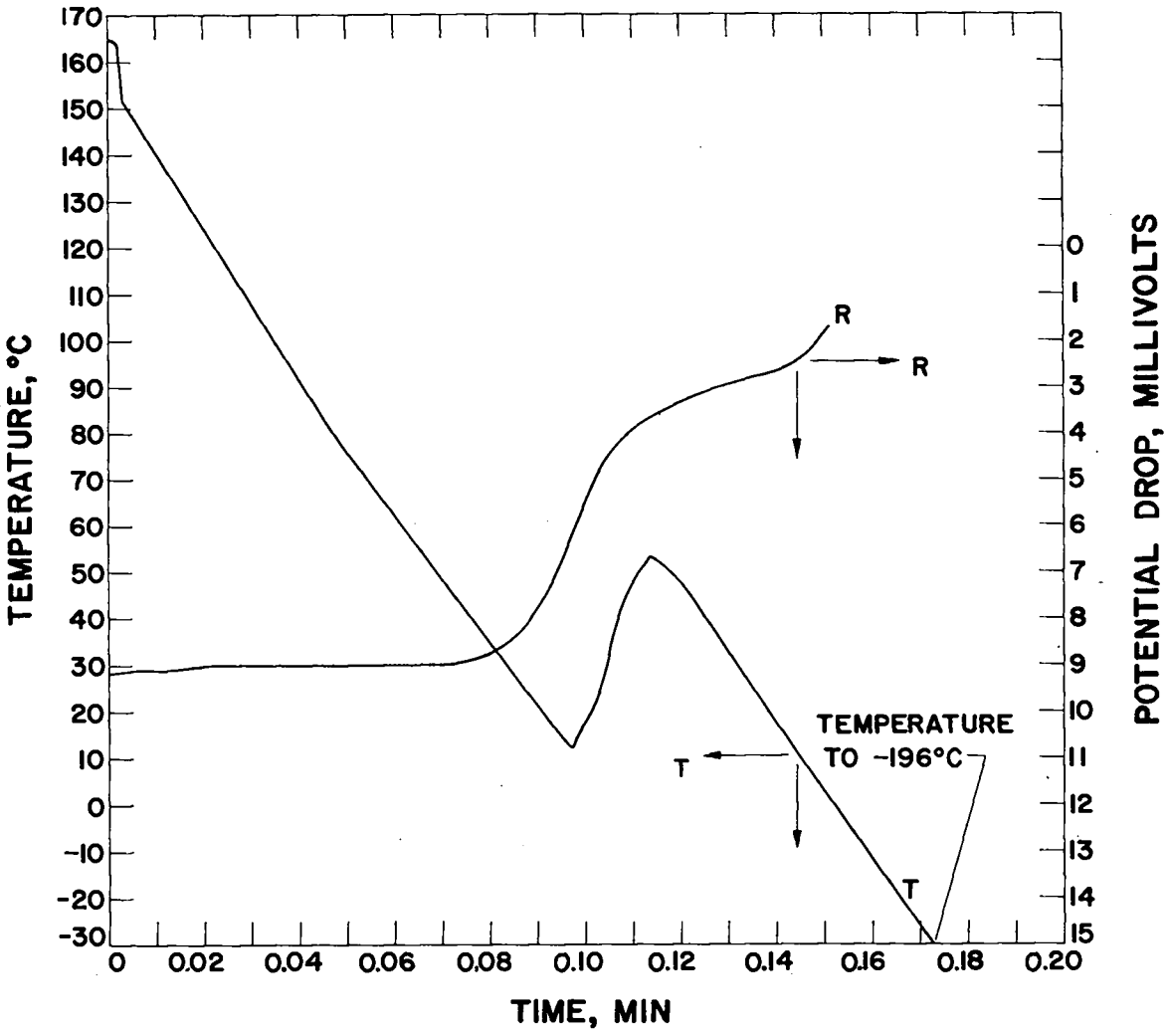

Fig. 18. Temperature and potential drop vs. time for high purity plutonium cooled from 165° to -196°C by quenching in liquid nitrogen (Run No. 24).

minimum temperature. Thus, the immersion of specimens of beta-phase plutonium into these baths immediately causes boiling of the fluid in contact with the plutonium and results in a large film coefficient. Therefore, the cooling rate of the specimen is not as rapid as might be expected.

To verify this concept two cylinders (0.5 in. in diameter, 0.5 in. long) of highly polished stainless steel were prepared with a microthermocouple located at the center. These specimens were heated in a constant temperature oven to the same oven and specimen temperature of about 205°C. The specimens were removed from the oven and each placed as rapidly as possible into one of four cold temperature baths. These were ice water, trichloroethylene-dry ice, ethanol-dry ice and liquid nitrogen. The indicated specimen temperature was recorded as a function of time. The experiment was repeated using two baths at a time until each type of bath had been used three times.

The data from the above are shown in Fig. 19. The ice water cools the specimen more rapidly than trichloroethylene-dry ice, which in turn cools more rapidly than ethanol-dry ice, which is faster than liquid nitrogen.

The resistance change and specimen temperature as a function of time for high purity and good purity plutonium cooled from 165° to ~35°C by quenching in silicone oil are shown in Fig. 20. The ring specimens had cross sections of 0.040 by 0.250 in. The temperature of the high

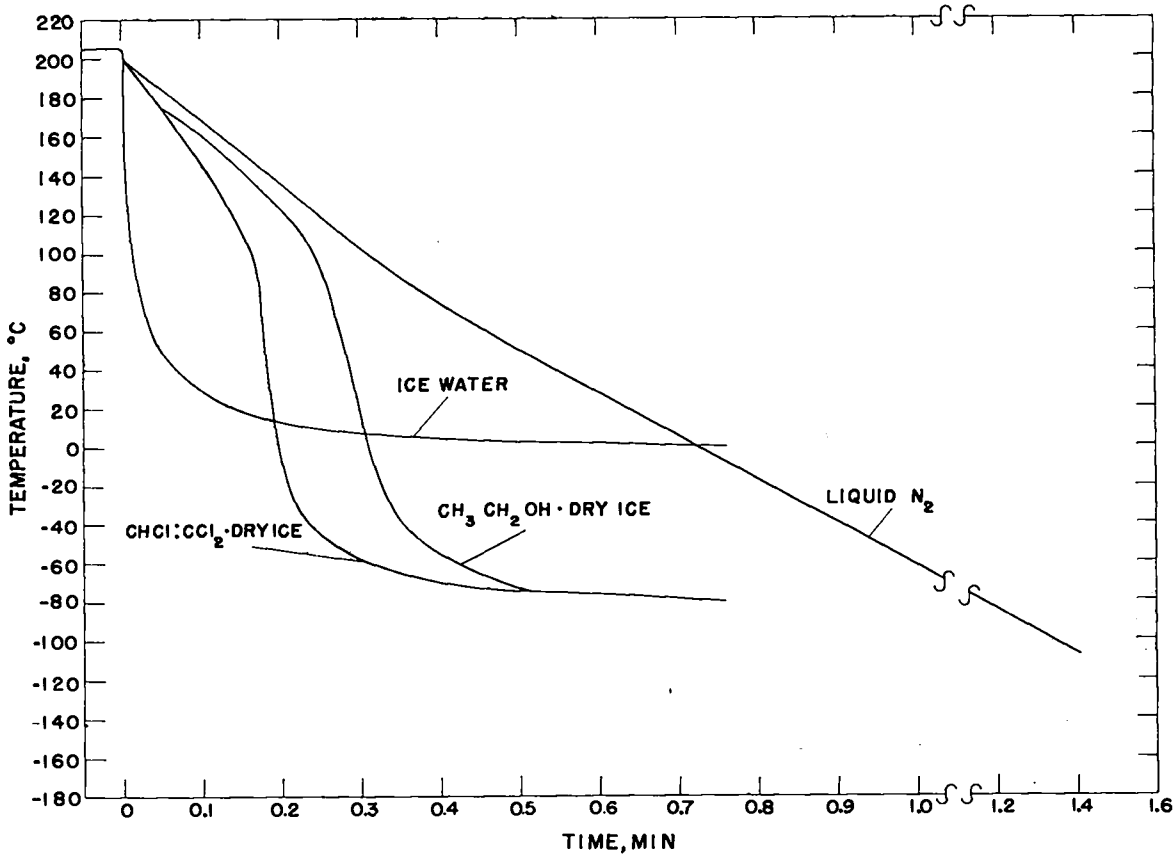

Fig. 19. Temperature vs. time for 0.5-in.-diameter, 0.5-in.-long stainless steel rods cooled from ~205° to 0°, -80° and -196°C by quenching in ice water, trichloroethylene-dry ice, ethanol-dry ice and liquid nitrogen.

Run No.	11	12
Plutonium purity	High	Good
Piece No.	H00-1198-11	J00-1341-21
Thickness, in.	0.040	0.040
Height, in.	0.250	0.250
Current, amp	1.0	1.0

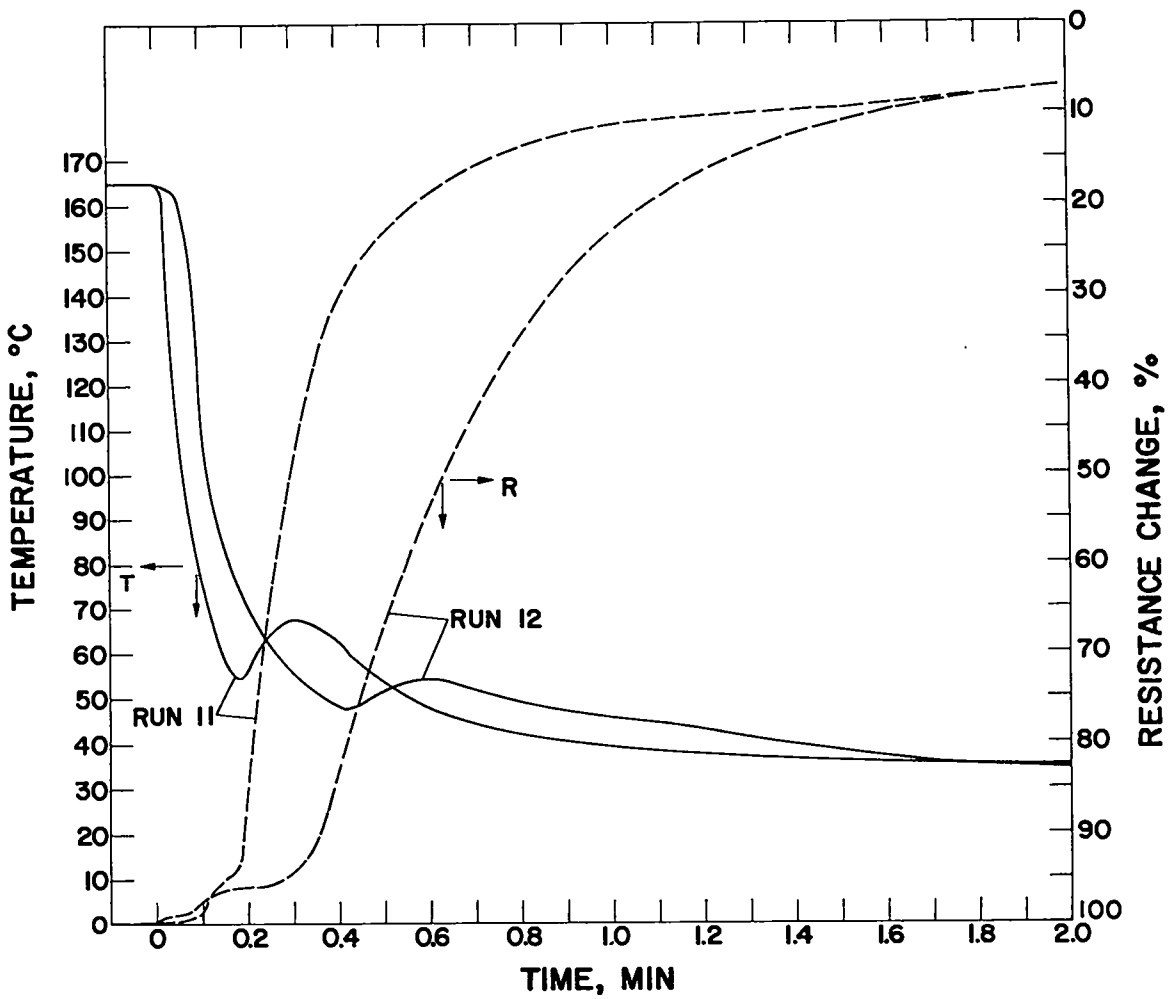

Fig. 20. Temperature and resistance change vs. time for high purity and good purity plutonium cooled from 165° to ~35°C by quenching in silicone oil (Run Nos. 11 and 12).

purity material fell more rapidly and had a break at 55°C. The temperature of the good purity sample broke at 48°C. Just prior to the break the resistance change of the high purity specimen was 5% and 20% for the good purity.

Figure 21 shows the resistance change vs. time for high purity plutonium specimens cooled from 130°, 165° and 200°C to ambient temperature by quenching in silicone oil and from 165° to -196°C by quenching in liquid nitrogen. The ring-type samples had cross sections of 0.040 by 0.250 in. The lower the initial temperature of the specimen, the more rapidly the resistance changed, suggesting heat flow limitations. The sharp response of the resistance change curve for the specimen quenched in liquid nitrogen also shows the effect of heat flow.

A high purity ring specimen (cross section 0.040 by 0.250 in.) was cooled from 165° to 86°C by quenching in silicone oil. The sample was held in the bath for about 115 min and then quenched to 37°C. The specimen temperature and potential drop as a function of time are shown in Fig. 22. It is evident that there was a 3% change in resistance as the specimen cooled from 165° to 120°C.

Figure 23 shows the resistance change vs. time for good purity plutonium specimens of various thickness cooled from 165°C to ambient temperature. The ring-type samples had thicknesses of 0.010, 0.020, 0.040 and 0.080 in. and heights of 0.250 in. The run using the specimen with a thickness of 0.020 in. was terminated after the initial 25% change

Run No.	15	4	8	24
Piece No. H00-1198-	9	7	5	10
Thickness, in.	0.040	0.040	0.040	0.040
Height, in.	0.250	0.250	0.250	0.250
Current, amp	1.0	1.0	1.0	1.0
Initial temperature, °C	200	165	130	165
Bath temperature, °C	35	27	25	-196

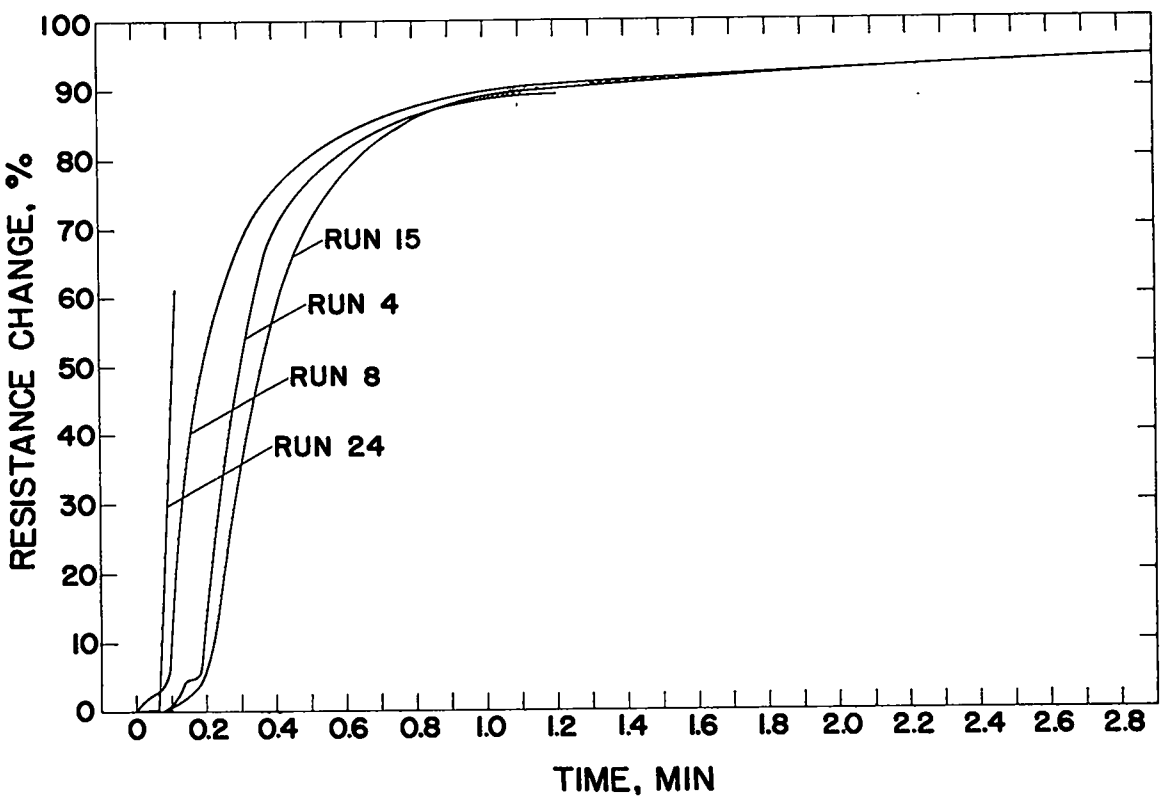

Fig. 21. Resistance change vs. time for high purity plutonium specimens separately cooled from 130°, 165° and 200°C to ambient temperature by quenching in silicone oil and from 165° to -196°C by quenching in liquid nitrogen (Run Nos. 15, 4, 8 and 24).

Piece No. H00-1198-12
Cross section: 0.040 by 0.250 in.
Current: 1 amp

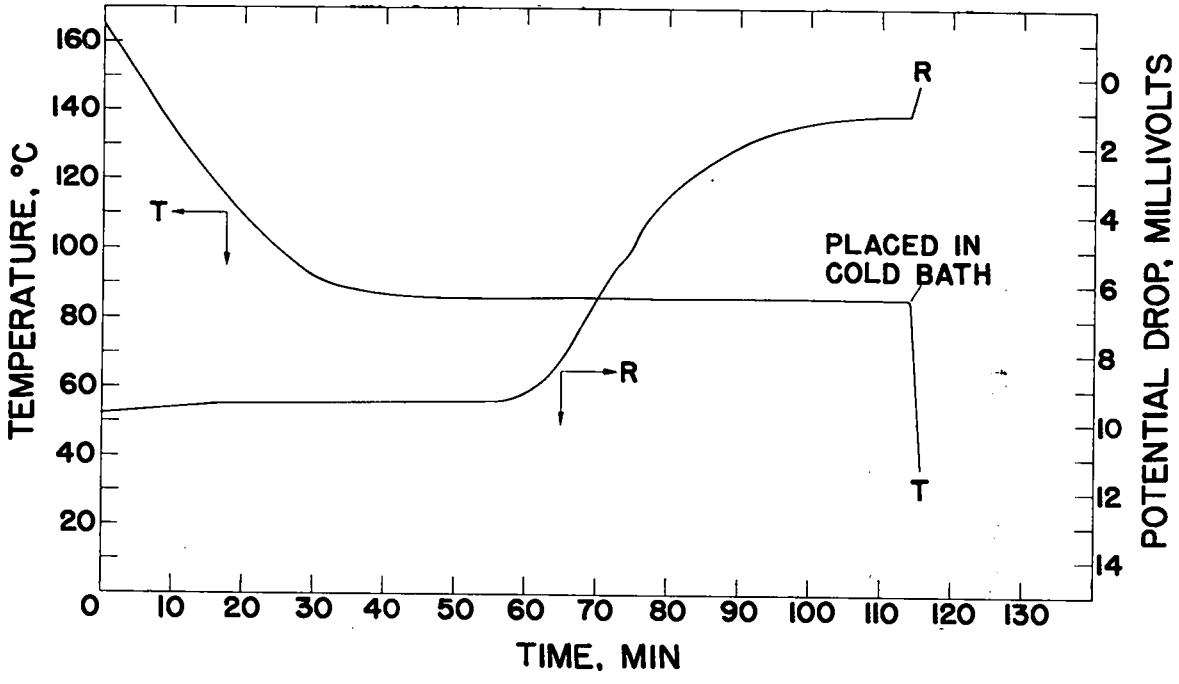

Fig. 22. Temperature and potential drop vs. time for high purity plutonium cooled from 165° to 86°C by quenching in silicone oil (Run No. 27).

Run No.	17	18	19	12	21
Piece No. J00-1341-	29	31	31	21	33
Thickness, in.	0.010	0.020	0.020	0.040	0.080
Height, in.	0.250	0.250	0.250	0.250	0.250
Current, amp	0.3	0.5	0.5	1.0	1.7
Bath temperature, °C	26	--	37	34	22

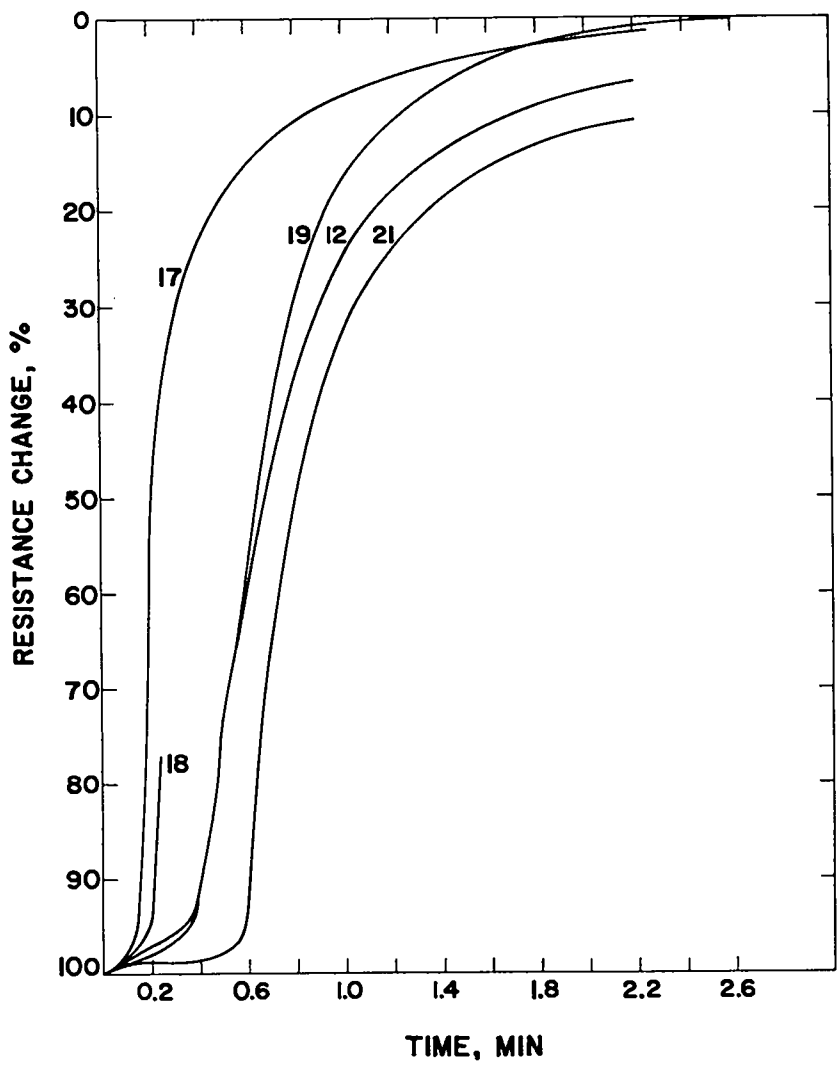

Fig. 23. Resistance change vs. time for good purity plutonium specimens of various thicknesses cooled from 165°C to ambient temperature by quenching in silicone oil (Run Nos. 17, 18, 19, 12 and 21).

in resistance occurred because the recording equipment failed. The specimen was reheated to 165°C and quenched. This repeated run caused the resistance change curve to be shifted to the right, which is consistent with other multiple heating and cooling cycles on the same specimen. The thin specimens (0.010 and 0.020 in.) were essentially transformed to alpha phase in less than 3 min.

The data shown in Fig. 24 are similar to those presented in Fig. 23 except that high purity plutonium was studied. The ring specimens, all 0.250 in. high, were 0.020, 0.040 and 0.080 in. thick. The resistance change for the 0.020-in.-thick specimen became the original value in about 0.5 min and then exceeded that value. The thickest specimen behaved similarly after 24 min.

Figure 25 is a plot of the temperature and resistance change vs. time for a high purity, 0.200-in.-diameter, 7.5-in.-long plutonium rod which was quenched from 165° to 32°C by immersion in silicone oil. Three microthermocouples, located ~2.38 in. from one end, were positioned on the surface, 0.050 in. below the surface and in the center of the rod.

The initial resistance change shows some beta-to-alpha phase transformation on the surface. There is essentially no further transformation until the indicated temperatures range from 63° to 67°C, at which time all thermocouples show a temperature spike and rapid transformation occurs. The rod initially cooled with an indicated 15°C

Run No.	35	11	39
Piece No. H00-	1411-51	1198-11	1411-50
Thickness, in.	0.020	0.040	0.080
Height, in.	0.250	0.250	0.250
Current, amp	0.5	1.0	1.7
Bath temperature, °C	26	36	30

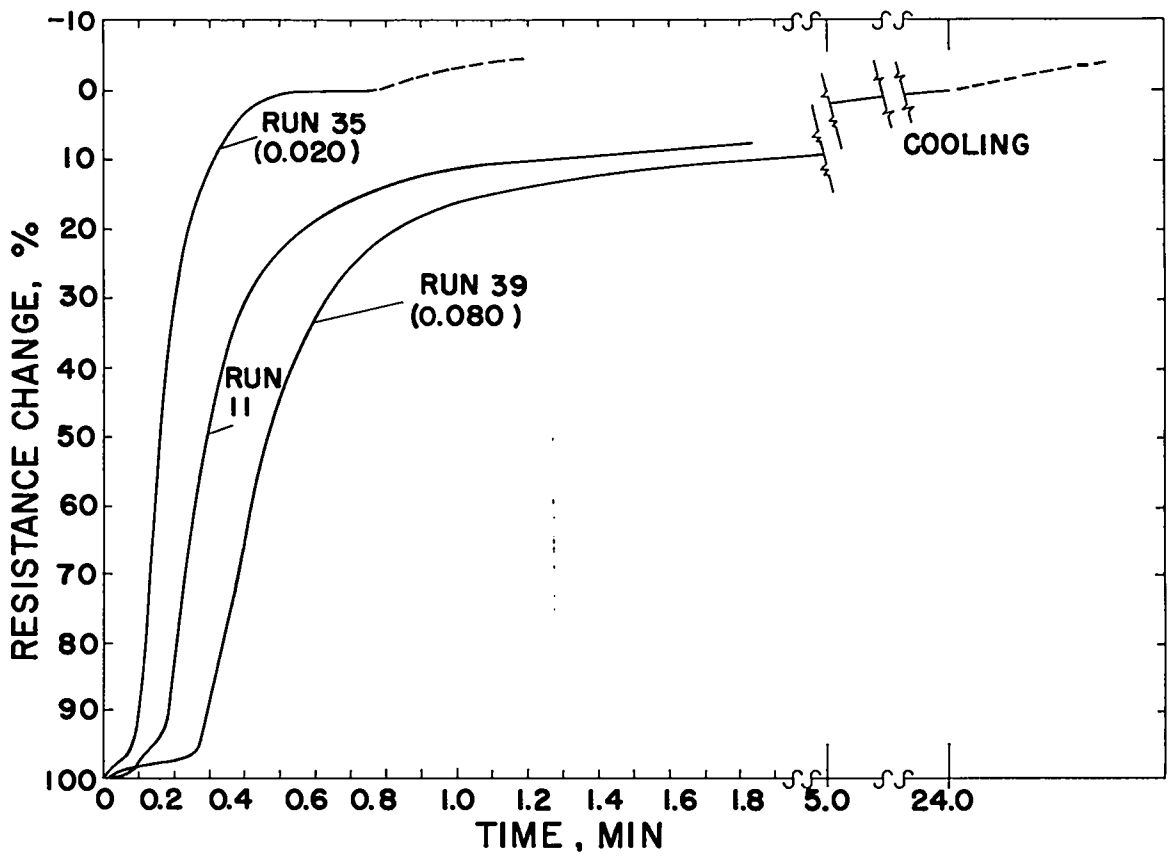

Fig. 24. Resistance change vs. time for high purity plutonium specimens of various thicknesses cooled from 165°C to ambient temperature by quenching in silicone oil (Run Nos. 35, 11 and 39).

Piece No. H00-1100-1
Piece size: 0.200 in. diameter, 7.5 in. long
Current: 1.8 amp
Thermocouple location:
No. 1: On surface, 2.25 in. from one end
No. 2: 0.050 in. deep, 2.375 in. from same end
No. 3: 0.100 in. deep, 2.5 in. from same end

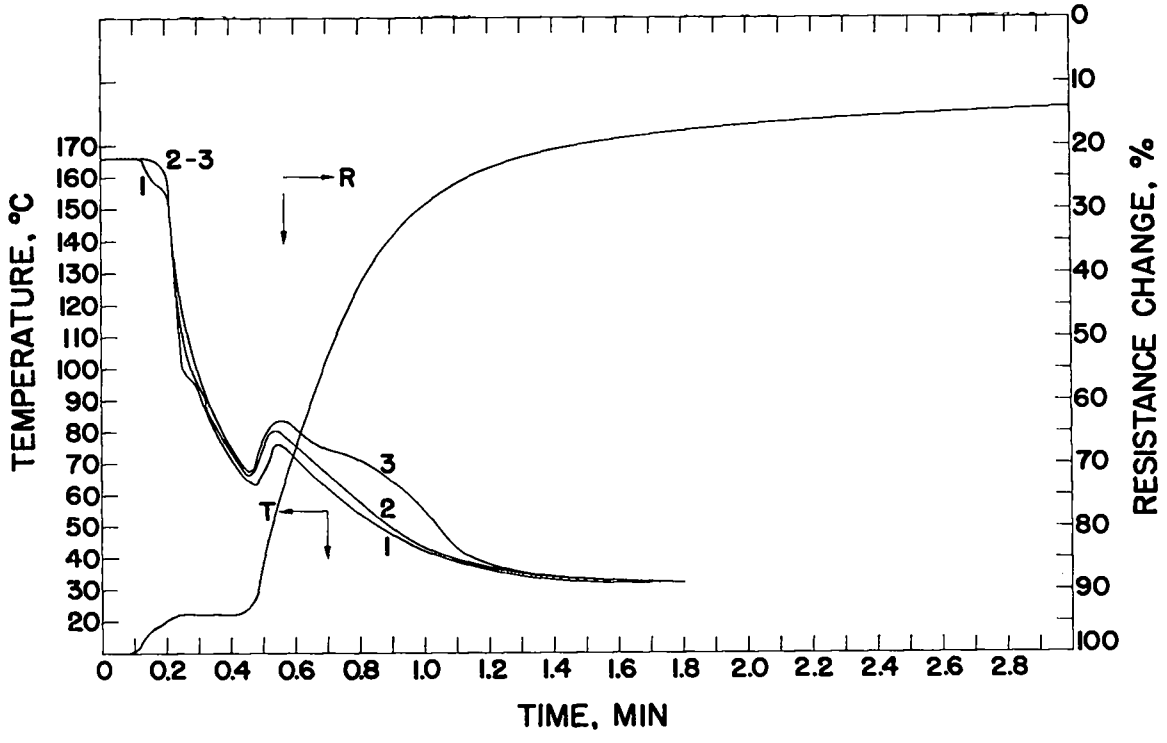

Fig. 25. Temperature and resistance change vs. time for a high purity plutonium rod cooled from 165° to 32°C by quenching in silicone oil (Run No. 33).

temperature gradient, but at the spike, this gradient was reduced to only 4°C. Subsequently, it developed to 15°C again and remained until the resistance change was 75%.

These data suggest some rapid surface transformation followed by very little if any transformation until the temperature spike occurred.

The temperature spike in this and in the previous runs is not directly related to the start of transformation; it represents a time when heat flow in the specimen is reversed.

CONCLUSIONS

The alpha-to-beta and beta-to-alpha phase transformations of plutonium appear to be very rapid, and the rate is primarily related to the rate at which energy can be supplied or removed. The time required for these transformations increases with specimen thickness and decreases as the specimen becomes more nearly pure, with respect to usual impurities.

Using electrical resistivity as a criterion, the beta-to-alpha transformation for thin, high purity plutonium goes essentially to completion in a few minutes upon being quenched from beta-phase to ambient temperature. The alpha-to-beta phase transformation appears to go to completion at a rate limited by the rate of energy deposition.

The use of microthermocouples imbedded in specimens and of electrical resistance is a technique by which transformation curves may be defined for a particular plutonium specimen. However, a study of the

kinetics of the alpha-to-beta and beta-to-alpha phase transformations by immersion methods is not ideal for several reasons: There exist large and continually changing thermal gradients in specimens, leading to athermal conditions. The thermal gradients can be sufficiently large as to cause transformation on the surface while the central specimen temperature is below that required for transformation. There is the problem of the film coefficient.

The initial heating or cooling rate of specimens is faster for higher density materials, which leads to faster initial transformation. In repeated runs on the same specimen the initial transformation is slower, which may be related to density or to the problems of microcracking or retained beta phase. Specific impurities may cause retention of beta-phase material and/or compound formation.

REFERENCES

1. R. D. Nelson, "Transformation Kinetics of Plutonium. Part I - A Study of the Beta to Alpha and Alpha to Beta Transformations", HW-55778 (1958).

2. R. D. Nelson, "Transformation Kinetics of Plutonium. Part II - A Study of the Beta to Alpha and Alpha to Beta Transformations", HW-56843 (1958).

3. R. D. Nelson and I. D. Thomas, "Transformation Kinetics of Plutonium", Proc. Sec. UN Int. Conf. Peaceful Uses of Atomic Energy, 6, 170-173, Geneva (1958).

4. M. B. Waldron, et al, "The Physical Metallurgy of Plutonium", Proc. Sec. UN Int. Conf. Peaceful Uses of Atomic Energy, 6, 162-169, Geneva (1958).

5. R. G. Loasby and J. N. Lowe, "Kinetics of the β - α Transformation in Plutonium", Plutonium 1960 ed. E. Grison, W. B. H. Lord and R. D. Fowler, 3-16, Cleaver-Hume Press, London (1961).

6. R. D. Nelson, "Transformation Kinetics of Plutonium. Part III", HW-70859 (1961).

7. Plutonium 1960, ed. E. Grison, W. B. H. Lord and R. D. Fowler, 30, Cleaver-Hume Press, London (1961).

8. L. J. Mullins, J. A. Leary and C. W. Bjorklund, "Large Scale Preparation of High Purity Plutonium Metal by Electrorefining (Preliminary Report)", LAMS-2441 (1960).

9. W. N. Miner, et al., "Plutonium", Rare Metals Handbook, 2nd Ed., ed. C. A. Hampel, 347, Reinhold Publishing Co., New York (1961).

10. Ibid, 354.

11. J. A. Lee and R. O. A. Hall, "Preliminary Measurements on the Thermoelectric Power of Plutonium Metal", AERE M/R 2800 (1959).

12. F. W. Schonfeld, private communication.

13. L. J. Mullins, J. A. Leary, A. N. Morgan and W. J. Maraman, "Plutonium Electrorefining", I & E C Proc Des Dev, 2, 20-24 (1963).

14. A. N. Morgan, et al., "The Los Alamos Plant for the Remotely Controlled Production of Plutonium Metal", Proc. Sec. UN Int. Conf. Peaceful Uses of Atomic Energy, 17, 537-554, Geneva (1958).

15. J. W. Anderson and W. J. Maraman, "Plutonium Foundry Practices", Trans AFS, 70, 1057-1072, (1963).

APPENDIX

The electrical resistivity of plutonium as a function of temperature was shown in Fig. 1. A comparison of these data with an experiment is as follows:

Run No. 12: good purity plutonium
Specimen cross section: 0.040 by 0.250 in.
Distance between potential pickup contacts: 6 in.
Direct current: 1 amp
Potential drop at 27°C: 34.5 mv

$$\rho = \frac{V}{I} \times \frac{A}{\ell}$$

$$\rho = \frac{34.5 \times 10^{-3}}{1} \times \frac{0.040 \times 0.250}{6} \times 2.54$$

$$\rho = 1.46 \times 10^{-4}\ \Omega\text{-cm}$$

($\rho = 1.45 \times 10^{-4}\ \Omega$-cm from Fig. 1)

Potential drop at 165°C: 25.5 mv

$$\rho = \frac{25.5 \times 10^{-3}}{1} \times \frac{0.040 \times 0.250}{6} \times 2.54 \times 1.03^{(a)}$$

$$\rho = 1.11 \times 10^{-4}\ \Omega\text{-cm}$$

($\rho = 1.08 \times 10^{-4}\ \Omega$-cm from Fig. 1)

where: ρ = electrical resistivity, Ω-cm
V = potential, volts
I = current, amp
A = cross-sectional area, cm^2
ℓ = length, cm

(a) Correction for thermal expansion and volume change on transformation.