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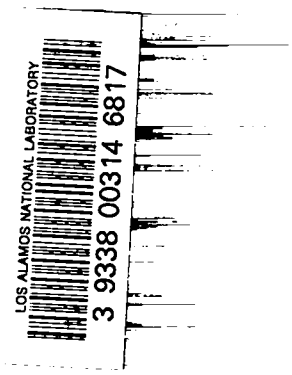
High-Temperature Environmental Testing of Liquid Plutonium Fuels



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by

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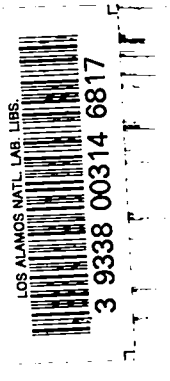
R. H. Perkins



HIGH-TEMPERATURE ENVIRONMENTAL TESTING OF LIQUID PLUTONIUM FUELS

R. L. Andelin*, L. D. Kirkbride**, and R. H. Perkins

ABSTRACT

Equipment for testing containers for liquid plutonium alloys at 900° to 1100°C has been developed and used. Uncarburized and carburized tantalum and Ta-5W capsules were tested with Pu, Pu-Fe, and Pu-Co-Ce. The Pu-Co-Ce alloys are less corrosive than Pu-Fe (10 at. % Fe), which in turn is less corrosive than plutonium. Carburization of tantalum and Ta-5W containers greatly improves their corrosion resistance to liquid plutonium alloys. Carburized Nb-10W and Nb-1Zr alloys are satisfactory containers for Pu-Co-Ce alloys containing 2 g Pu/cm^3.

INTRODUCTION

Liquid metal alloys as fuel in fast nuclear reactors possess several advantages over solid fuels. These include the elimination of fuel slump as a factor in criticality accidents, a large coefficient of thermal expansion, the release of the bulk of the volatile fission products, and the potential for simplified fuel handling and low fabrication costs.[1,2]

The Pu-Co-Ce system has been investigated as a possible fuel for a Liquid Metal Fast Breeder Reactor. The plutonium concentration in this system can be varied from 0 to 13 g/cm^3 without raising the melting point above 450°C. Satisfactory containment of this liquid fuel must be demonstrated, however, before advantage can be taken of its favorable properties.

Tantalum alloys, with and without carbide layers, offer considerable promise as containers for these liquid fuels. Carburized niobium alloys may also be satisfactory containers for Pu-Co-Ce alloys with low plutonium concentrations (1-2 g Pu/cm^3). The development and proof testing of these container materials may require many thousands of hours of corrosion testing because, at temperatures $\leq$ 750°C, fuel penetration through the walls of the containers is so slow that statistically valid corrosion data cannot be obtained in a shorter interval. No Pu-Co-Ce fuel penetration through the parent material has been observed in corrosion tests at $\leq$ 750°C for as long as 11,200 hours; welds in container materials are the only regions that have exhibited external surface contamination. Therefore, an accelerated corrosion testing technique was required to evaluate new container materials and to determine

the effects of additives to the fuel and container alloys.

Plutonium penetrates through tantalum alloys by diffusion along grain boundaries; the rate of penetration increases with increasing temperature according to the equation[3]

$$D = D_o e^{-Q/RT},$$

where D is the diffusion rate, D_o is the frequency factor, and Q is the activation energy. Therefore, plutonium penetration can be accelerated by increasing the testing temperature. The time required for plutonium penetration through a constant thickness of tantalum alloy is measured at two or more elevated temperatures, and the above equation allows the data to be extrapolated to lower temperatures suitable for the operation of a nuclear reactor.

EQUIPMENT

A sensitive method for detecting extremely small amounts of plutonium on the exterior surfaces of test elements was required to precisely determine the time for plutonium diffusion through capsule walls. Solid-state alpha-particle detectors are well suited for this purpose, but they must be operated at or below room temperature; consequently, they must be situated some distance from the elements being tested. Testing must be conducted in a vacuum so that the alpha particles possess sufficient range to reach the detectors.

Figure 1 shows the accelerated corrosion test (A.C.T.) equipment designed and built for the high-temperature testing of containers for liquid plutonium fuels.[4] A block diagram of this equipment is shown in Fig. 2.

Furnace and Quartz Tube Assembly

The test capsule is heated with a 14-in.-long x 3-in.-diameter hinged tube furnace containing three sets of platinum elements wired so that the top set is used for automatic temperature control, and the two bottom sets are run at an adjustable, preset voltage. The system allows several combinations of manual and controlled operation. The furnace is supported on ball bearings to facilitate opening by a motor drive for rapid cooling of the test capsule at the end of a run. The entire furnace assembly is inside a stainless steel enclosure which maintains a negative pressure of approximate 1/2 in. water.

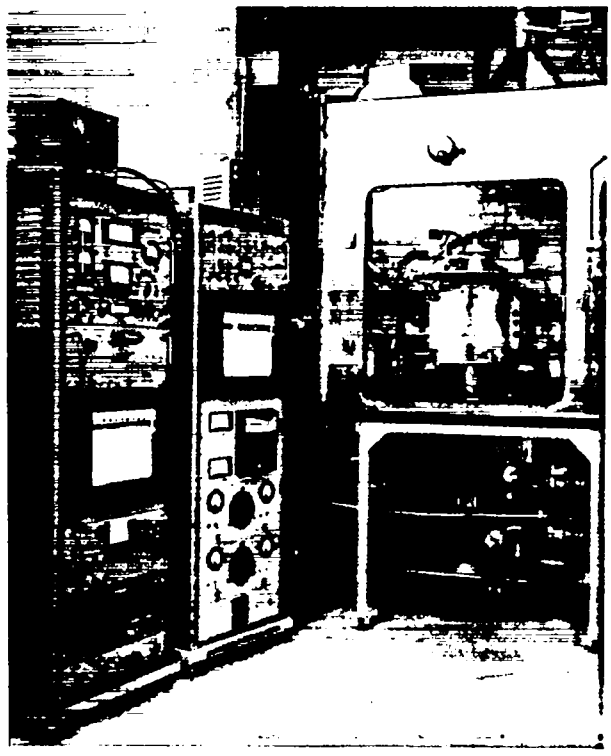


Fig. 1. Accelerated corrosion test (A.C.T.) station for high-temperature environmental testing of liquid plutonium fuels.

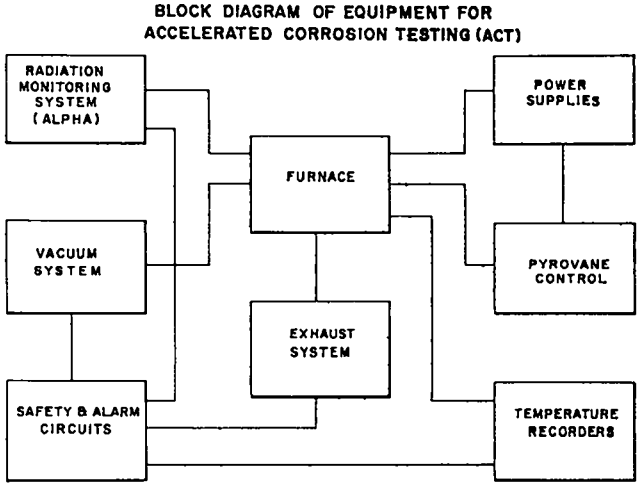


Fig. 2. Block diagram of A.C.T. equipment.

The quartz tube assembly which fits inside the furnace and mounts on the vacuum system is shown in Fig. 3. At the top and bottom are water-cooled (6°C water) aluminum assemblies, each of which

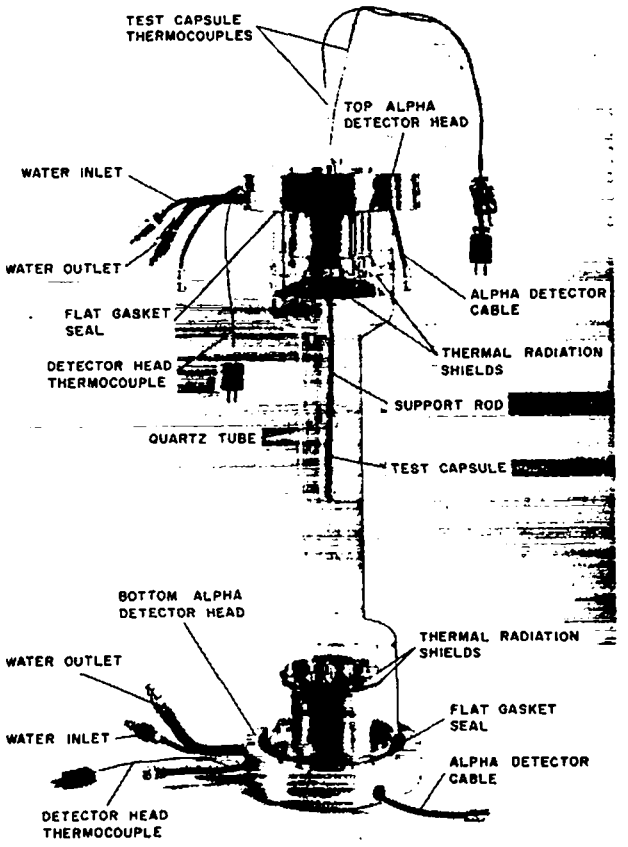


Fig. 3. Quartz tube assembly.

houses three solid-state alpha-particle detectors. The thermal radiation shields are tantalum. Two Type S tantalum-sheathed thermocouples are used to monitor the top and bottom capsule temperatures. A pair of iron-constantan thermocouples monitor the detector head temperatures. Viton gaskets seal both ends of the quartz tube, inside of which is a quartz liner. Most of the alpha activity is deposited on this quartz liner when plutonium diffuses to the exterior surfaces of a capsule. After test, a clean liner is installed and the old one is removed for decontamination.

Alpha Detection System

A cutaway of the bottom water-cooled detector assembly is shown in Fig. 4. The aluminum parts are bonded together with Epon Adhesive No. 934 (Shell Oil Company).

Six nickel foils (four 20 μin. thick and two 50 μin. thick) between each alpha detector and the test specimen shield the detectors from thermal radiation. The foils also provide an energy

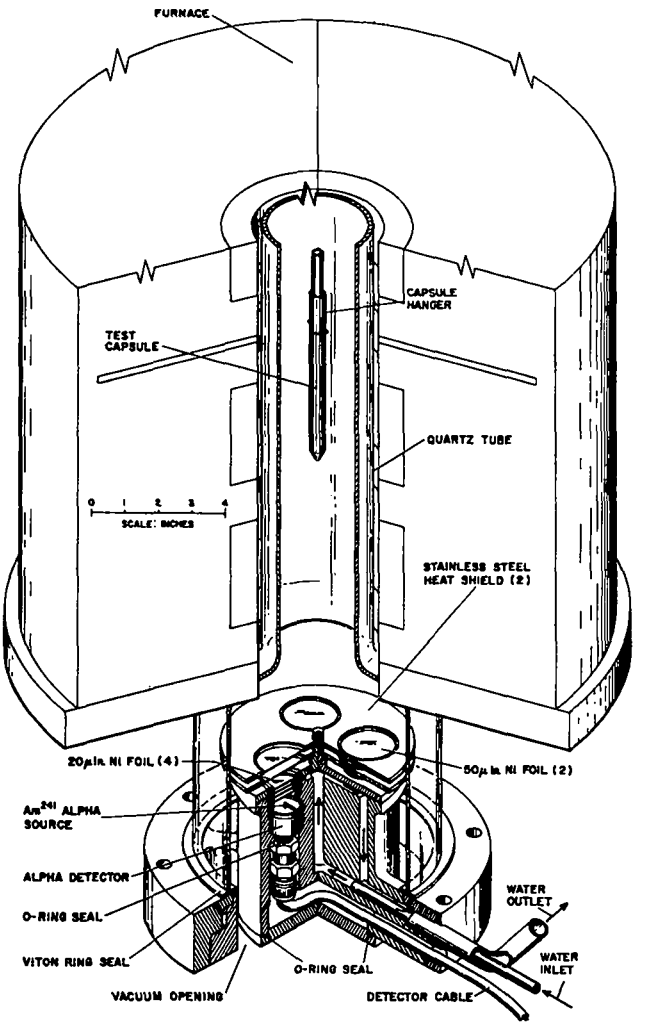


Fig. 4. Cutaway of bottom detector head.

separation between alpha particles from an ^{241}Am calibration source next to each detector and alpha particles from ^{239}Pu which appear on the exterior of a test capsule. Alpha particles from ^{239}Pu lose about 1 MeV of their approximate 5 MeV energy in traversing the foils.

A block diagram of the alpha detection system is shown in Fig. 5. The signals from the six detectors are combined in a mixer after passing through separate preamplifiers. The resultant signal is amplified and analyzed by two subsystems. One measures the plutonium alpha signal by a single-channel analyzer with a threshold at about 1.5 MeV and an upper level at about 4.5 MeV. The other subsystem has its discriminator set at about 4.5 MeV to provide an ^{241}Am calibration signal and a bias for subtraction of the background due to the calibration source. The subtraction circuit is set to give zero signal

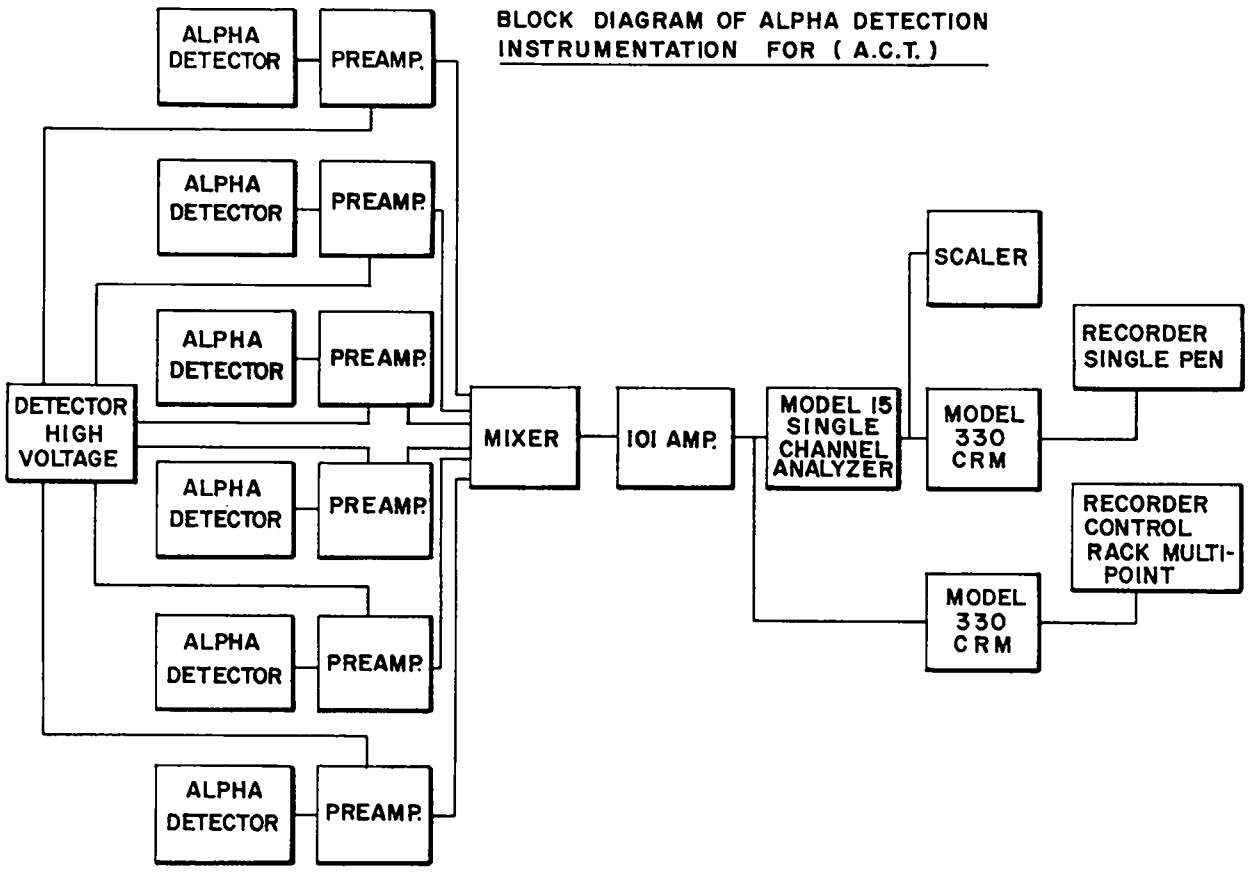


Fig. 5. Block diagram of alpha detection instrumentation.

when no plutonium contamination exists.

A dual input 400-channel analyzer is used to observe and monitor the signals from the A.C.T. stations. Segments consisting of 100 channels are used to observe the signals from each station. The proper operation of the equipment can be verified by counting the ^{241}Am signal, and the buildup of the plutonium on the external surfaces of a test capsule can be observed.

Vacuum System

Four-inch oil vapor diffusion pump systems with liquid nitrogen cold traps originally used to evacuate the A.C.T. stations required liquid nitrogen for the cold traps and could not be left unattended for long periods. Therefore, the diffusion pumps were replaced with 500 liter/sec ion pumps which can operate for long periods without maintenance. Sorption pumps are used for initial pumpdown and a motorized 6-in. gate valve may be closed to protect the ion pump if the pressure rises in the test chamber. Appropriate vacuum measuring instrumentation is used, principally during startup.

Safety and Alarm Circuits

Each A.C.T. station is equipped with safety and alarm instrumentation so that it can run unattended and be shut down automatically in the event of a malfunction or a high alpha signal. In an automatic shutdown the following events occur: (1) the timer clock stops, (2) the power to the furnace is shut off, (3) the furnace swings open to quench the fuel (approximately 15 min quench time from 1100°C), and (4) an exhaust duct damper opens for a timed interval to remove heat rapidly from the furnace enclosure.

A shutdown occurs if a signal is received to indicate: (1) loss or decreased flow of cooling water to the top or bottom detector heads, (2) pressure rise in the vacuum system (set for a chamber pressure greater than 10^{-4} torr), (3) maximum capsule temperature limit (usually set about 25°C above the operating temperature for a given run), (4) loss of exhaust from the furnace enclosure, and (5) a high alpha-particle count caused by plutonium. A power lockout relay is also provided. Any of the above signals, except No. 5, will sound an alarm.

EXPERIMENTAL PROCEDURE

At the start of each experiment, the test capsule is placed in the center section of the quartz chamber, as shown in Fig. 3. The system is then evacuated, first with the sorption pumps and finally with the ion pump. When the pressure in the test chamber falls below 10^{-6} torr, the furnace is turned on. It normally requires 1.8 to 2.0 hours to reach operating temperature (900°-1100°C). The equipment can then operate unattended until either an equipment malfunction occurs or a high alpha signal is received.

When plutonium diffuses to the exterior surfaces of a capsule, the alpha count increases as indicated on the plutonium count rate meter. The signal drives the recorder toward the shutdown trip point. A typical spectrum obtained on the 400-channel analyzer during a test is shown in Fig. 6. The ^{241}Am peak is at the far right. The dashed lines indicate the buildup of the plutonium peak.

The ultimate sensitivity of the A.C.T. system is about 0.1 μg of ^{239}Pu. In actual tests, the trip point is set at a higher value to avoid premature shutdown due to a fluctuation of the recorder. The trip point is set at 0.3 mV on the recorder, and the subtraction circuit is adjusted so that this setting corresponds to a needle deflection of approximately 1.5 cps on the plutonium count rate meter.

The time required to build up a sufficient signal to trip the shutdown mechanism is a function of the fuel being tested, the test temperature, and the location of the plutonium penetration. In general, the higher the temperature, the greater the rate of plutonium buildup on the exterior of the capsule. Also, the rate of alpha-signal increase is greater for plutonium than for Pu-Fe. Carburization of tantalum capsules also inhibits the rate of plutonium diffusion and signal buildup. The amount of plutonium on the exterior surfaces of a capsule required to provide a shutdown signal depends on its position on the capsule. Plutonium on the bottom tip acts as a point source and is readily seen by the three bottom detectors. The amount of plutonium in this position that will provide a signal strong enough to terminate the test is smaller than that required on the center of the capsule where the source is shielded from several of the detectors. The source strengths which have produced test terminations, as measured by other alpha counters after equipment shutdown, have ranged from 750 to > 20,000 cpm.

Among the items recorded for each test are the total clock time, the total heat-up time, and the approximate time from the appearance of alpha contamination to shutdown. From these numbers, the lifetime of the capsule at a given temperature is obtained. If a shutdown occurs before plutonium penetration takes place and the test is started up again, this heat-up time is also included. The time from appearance of alpha contamination to shutdown is determined as follows. A line is drawn on the recorder chart paper parallel to the time axis through the middle of the oscillations made by the pen before plutonium penetration occurs. The interval between the last time the pen touches this line and the time of trip is taken as the "time from appearance of alpha contamination to trip."

The time at test temperature is taken as the total clock time less the heat-up time. Any correction for plutonium penetration during heat-up is insignificant at total clock times of > 20 hours; even at 10 hours the correction is less than 5%, which is within experimental error. Consequently, a correction was not made for times $\geq$ 10 hours. If the total clock time is under 5 hours, a positive correction is made to the time at test temperature. The correction is estimated from the temperature dependence curve and the heat-up curve. This correction was necessary on only three capsules containing pure plutonium and tested at 1100°C.

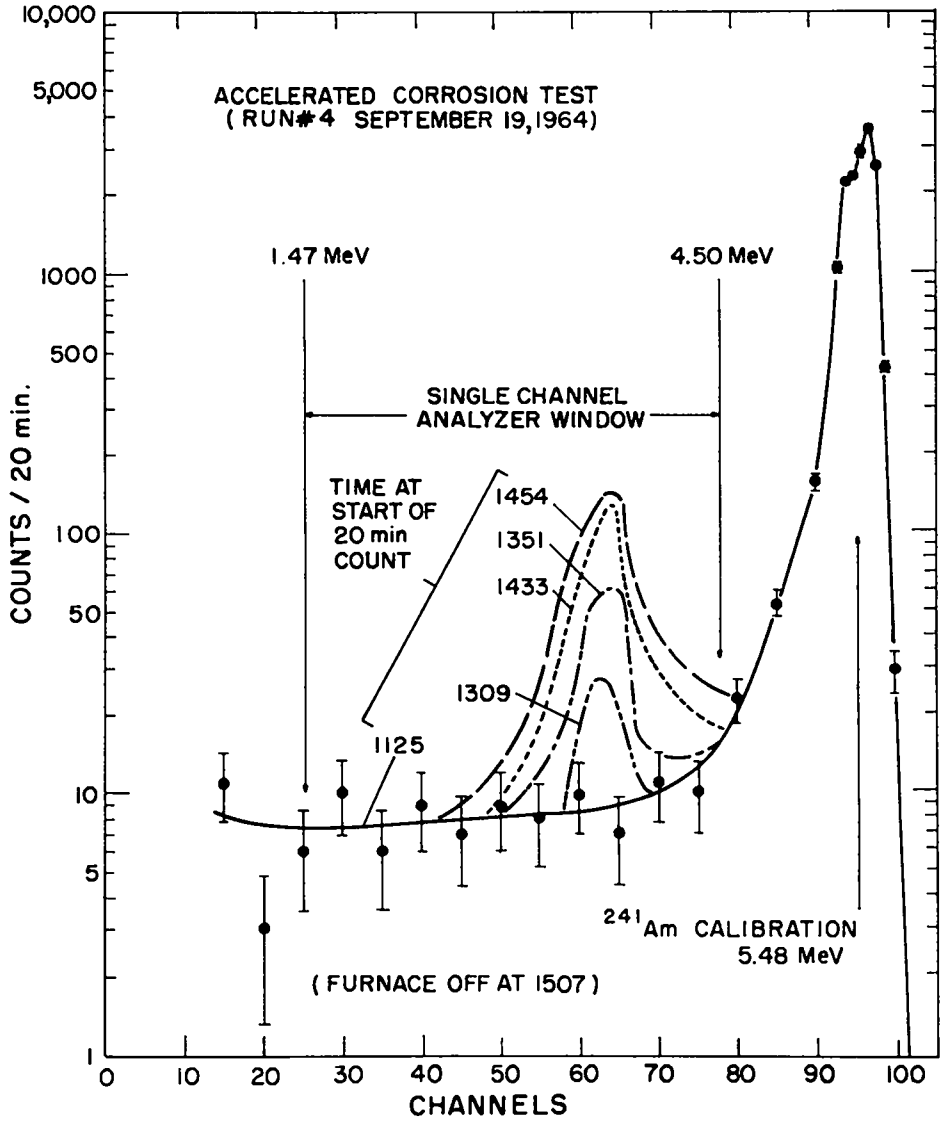


Fig. 6. Typical spectrum obtained during a high-temperature test showing plutonium peak buildup.

RESULTS AND CONCLUSIONS

The following fuel-container systems have been studied in A.C.T. apparatus:

1. Pu-Fe alloy (10 at. % Fe) in Ta capsules.
2. Pu in Ta capsules.
3. Pu-Co-Ce alloys (6.2 and 8 g Pu/cm^3) in Ta capsules.
4. Pu in carburized Ta capsules.
5. Pu in carburized Ta-5W capsules with carburized high-carbon (230 and 60 ppm) Ta end caps.
6. Pu-Co-Ce alloy (2 g Pu/cm^3) in carburized Nb-10W capsules.
7. Pu-Co-Ce alloy (2 g Pu/cm^3) in carburized Nb-1Zr capsules.

Experimental data are tabulated in the Appendices and are plotted in Fig. 7. Data obtained on Pu-Fe alloy up to 700°C in sodium loops are also plotted. The Pu-Fe curve extrapolates into data points from sodium loop testing.

The linear relationship obtained is strong evidence for a constant mechanism for the appearance of surface contamination over the temperature range studied and illustrates the validity of extrapolating short-term, high-temperature test data for this system to lower temperatures of interest for reactor operation. The data also imply no observable difference between high-purity sodium (< 1 ppm oxygen) and high vacuum ($\leq 1 \times 10^{-7}$ torr) as an external capsule environment during testing.

Pu-Fe in Ta Capsules

The first fuel system tested in A.C.T. equipment was Pu - 10 at. % Fe alloy in high-purity (<200 ppm total impurities) tantalum containers that had been annealed for 1 hour at 1450°C. These capsules had been prepared by deep drawing; the only welds were the final closure welds in the gas space. This type of capsule was used in the LAMPRE reactor, and considerable low temperature (600°-700°C) corrosion data are available from sodium loop tests. The main objectives of the first tests were to compare test environments (sodium and high vacuum) and to determine if high-temperature data could be extrapolated to lower temperatures more suitable for reactor operation. The Pu-Fe eutectic alloy is not as satisfactory as Pu-Co-Ce alloys for use in a large fast reactor because of its high, fixed plutonium concentration.

Three capsules were tested at 1160°C. Plutonium diffused through the walls of the capsules in the gas space and below the liquid level in times varying from 12.1 to 15 hours. None of the weld regions exhibited plutonium penetration.

Eleven of these capsules were tested at 1100°C from 16.4 to 47.9 hours (25.5 hour average). This wide spread in data is typical of corrosion experiments. Plutonium penetration occurred in the gas space and below the liquid level. None of the closure welds were contaminated.

Eight capsules were tested at 1000°C; the results were somewhat scattered and difficult to interpret. One capsule exhibited surface contamination in the closure weld after 18.2 hours. Three capsules were penetrated by plutonium in the gas space and below the fuel level in times ranging from 48.0 to 51.6 hours. These times are interpreted as the normal times required for plutonium penetration at this temperature.

One capsule ran for 206.9 hours before plutonium diffused through the capsule walls. Visual and metallographic examination of this capsule revealed that it had picked up sufficient carbon (presumably from backstreaming diffusion pump oil) to give the external surfaces of the capsule the gold color typical of $TaC_{\geq 0.95}$. Carbon had diffused intergranularly, and carbides were observed in the grain boundaries throughout the capsule. This intergranular diffusion of carbon retarded intergranular penetration of plutonium and improved the corrosion performance of the tantalum by a factor of 4.

To test the hypothesis that plutonium penetration of tantalum was inhibited by intergranular carbon diffusion from backstreaming pump oil, one capsule containing Pu-Fe fuel was tested at 1000°C in a system with no liquid nitrogen in the cold trap. This capsule was tested for 660 hours and 3 melt-freeze cycles without exhibiting external plutonium contamination. This capsule was also gold-colored on the external surfaces, presumably due to formation of TaC.

Four runs were made with Pu-Fe alloy in Ta containers at 950°C in a system equipped with oil-vapor diffusion pump. Two of the tests were terminated at 171 and 207 hours without external plutonium contamination. A molecular sieve trap was then inserted into one of the A.C.T. stations in an attempt to

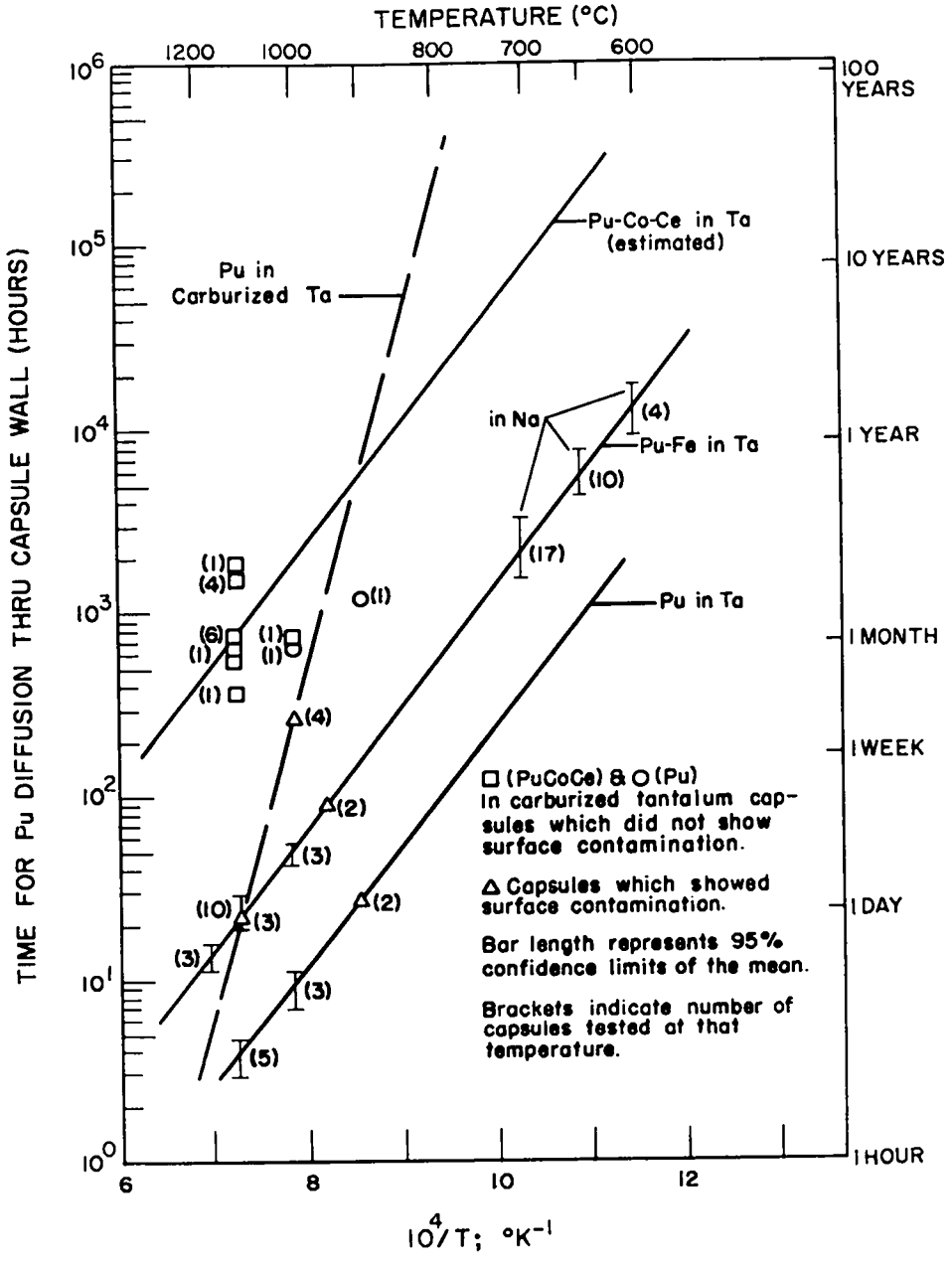


Fig. 7. Temperature dependence of capsule lifetime.

eliminate backstreaming of diffusion pump oil. The next two capsules tested exhibited external plutonium contamination after 249 and 295 hours; one capsule had been penetrated at the top weld and the other was contaminated at the liquid level. Both had been carburized during testing, although the amount of carburization was less than that occurring before introduction of the molecular sieve trap.

Eight tests of the Ta/Pu-Fe system were conducted at 900°C. Only one capsule exhibited plutonium contamination which occurred after 721 hours of testing. External carburization was observed on all of the test capsules.

Metallography was performed on capsules tested at 1100°C, 1000°C, and 900°C. Photomicrographs and autoradiomicrographs of capsule 2128 (tested at 1100°C for 34.6 hours) are shown in Figs. 8 and 9. Two areas of plutonium penetration were detected in the gas phase below the cap weld on the same circumference and about 180° apart. The autoradiomicrograph of the section through these two areas (Fig. 8a) shows two general regions of grain boundary penetration separated by regions of no penetration. The metallographic section (Fig. 8b) shows the normal structure of tantalum.

Four sections were examined through the fuel phase. Typical microstructures of these sections are shown in Fig. 9. A reaction layer was observed on or adjacent to the tantalum wall in all sections. The large particles attached to the reaction layer were identified by microprobe analysis as pure tantalum surrounded by a thin layer of Ta-Fe alloy, and the fine bright particles in the fuel were identified as a Ta-Fe alloy. Tantalum was not detected in the fuel other than in these particles, but the detectability limit of tantalum in plutonium is estimated to be between 0.1 and 1.0 per cent.

Pu in Ta Capsules

Plutonium is much more corrosive than either Pu-Fe or Pu-Co-Ce fuels and its substitution for these alloys is one way to accelerate corrosion testing. Annealed tantalum capsules were loaded with plutonium and tested at 1100°C, 1000°C, and 900°C. Five capsules tested at 1100°C exhibited plutonium penetration in times ranging from 3.41 to 4.6 hours. In each case, the parent material,

Fig. 8a. Autoradiomicrograph of tantalum capsule 2128 showing plutonium penetration in gas space.

Fig. 8b. Cross section of capsule 2128 in gas space. Etched.

Fig. 9a. Ta-Fe reaction layer on wall and in fuel near bottom tip of Ta capsule 2128. Unetched, 150X

Fig. 9b. Ta-Fe reaction layer on wall and in fuel near top of fuel phase in capsule 2128. Large particles are tantalum. Unetched, 100X.

rather than the weld, was contaminated. The three capsules tested at 1000°C were penetrated by plutonium after 8.2 to 10.1 hours. Again, all plutonium penetration was below the liquid level.

Six tantalum capsules were tested at 900°C. One experiment was terminated by rupture of the capsule due to a melt-freeze cycle. Three other capsules exhibited plutonium penetration of the closure welds after test times of 20.0 to 26.1 hours. The test times for the two remaining capsules were 41.9 and 43.7 hours, and plutonium contamination was observed below the liquid level.

Metallography was performed on capsule 2192 (tested for 10.1 hours at 1000°C). External autoradiography showed that the areas of plutonium penetration in this capsule were just below the liquid level and near the bottom of the capsule. Three sections were taken: one longitudinal section through the liquid level, and transverse sections through each of the two contaminated areas below the liquid level. Autoradiomicrographs of these sections did not reveal penetration through the tantalum wall. Photomicrographs of these sections (Figs. 10 and 11) indicate that the plutonium attacked the tantalum at grain boundaries as well as along the surface by dissolving around small, fairly uniform areas of the grains. This latter effect may be associated with plutonium penetration along subboundaries of the tantalum.

The effect of annealing temperature on the corrosion resistance of tantalum was examined. Capsules annealed for 1 hour at 1650°C, 1850°C, and 2050°C were loaded with plutonium and tested at 1000°C. The experimental results are plotted in Fig. 12.

Plutonium diffusion through the tantalum annealed at 2050°C was very rapid. This rate is similar to the rapid diffusion of plutonium that occurs in tantalum welds, which also consist of large grains. The poor corrosion resistance of large-grain tantalum is probably due to the increased solubility of carbon at the annealing or welding temperatures. This carbon goes into solution in the metal matrix during the annealing treatment, and rapid cooling after annealing prevents it from segregating to the grain boundaries.

Fig. 10a. Dissolution of wall of Ta capsule 2192 just above liquid level. Unetched, 300X.

Fig. 11a. Grain boundary and possible subgrain boundary attack just below fuel level in capsule 2192. Unetched, 600X.

Fig. 10b. Dissolution of wall of capsule 2192 at liquid level. Unetched, 600X.

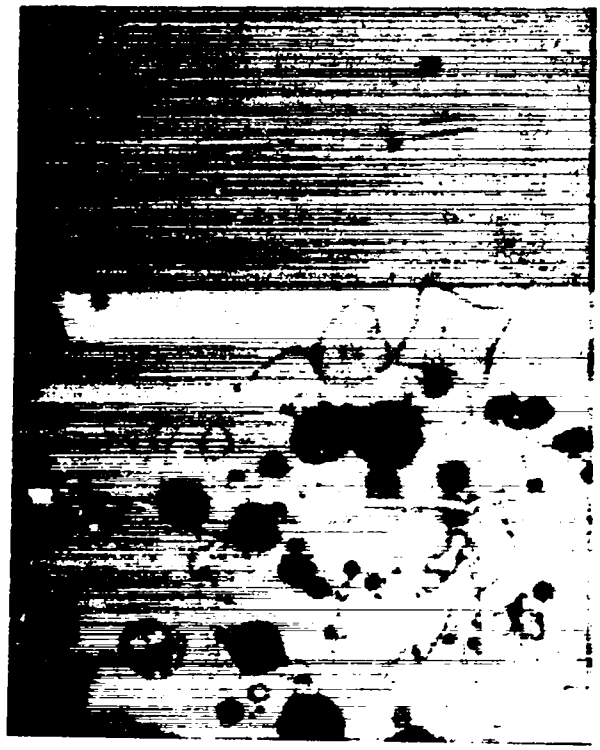


Fig. 11b. Tantalum crystals at surface of fuel in capsule 2192. Unetched, 300X.

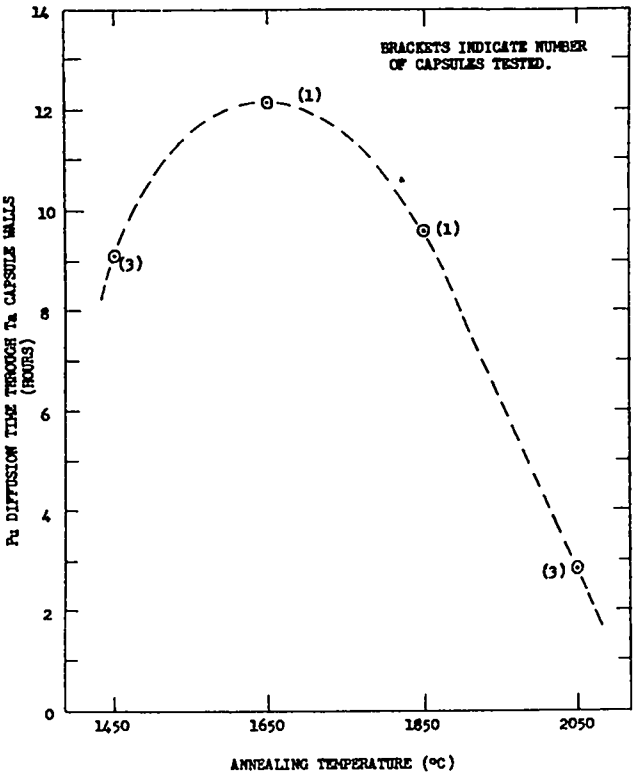


Fig. 12. The effect of annealing temperature on rate of plutonium diffusion through tantalum capsule walls at 1000°C.

Pu-Co-Ce Alloys in Ta Capsules

Eight tantalum capsules containing Pu-Co-Ce alloys (6.2 and 8.0 g Pu/cm^3) were tested in A.C.T. equipment. Seven were run at 1100°C and one at 1000°C. Run times varied from 326 hours to 1760 hours, and the experiments usually included several melt-freeze cycles. Because no external plutonium contamination was observed in any of these experiments, no estimate of the average lifetime of tantalum capsules containing Pu-Co-Ce alloys can be made. However, since five capsules were tested for times greater than 1400 hours at 1100°C, it is evident that the average lifetime is in excess of this figure. Four capsules were tested in an A.C.T. station utilizing a 500 liter/sec ion pump, and no carburization of these capsules occurred during test.

Metallography was performed on the single capsule (2138, with 8.0 g Pu/cm^3) tested in an oil-vapor diffusion pumped system for 660 hours at 1000°C. Three sections were taken from the capsule for examination: a transverse section above the liquid level, a longitudinal section through the liquid level, and a transverse section through the bottom of the capsule. Autoradiomicrography revealed no evidence of penetration of plutonium into the tantalum. Photomicrographs of these sections are shown in Figs. 13 and 14.

Fig. 13a. Reaction layer on tantalum wall above fuel level in capsule 2138. Unetched, oblique light, 600X.

Fig. 13b. Reaction layer and grain boundary precipitate below liquid level in capsule 2138. Unetched, oblique light, 600X.

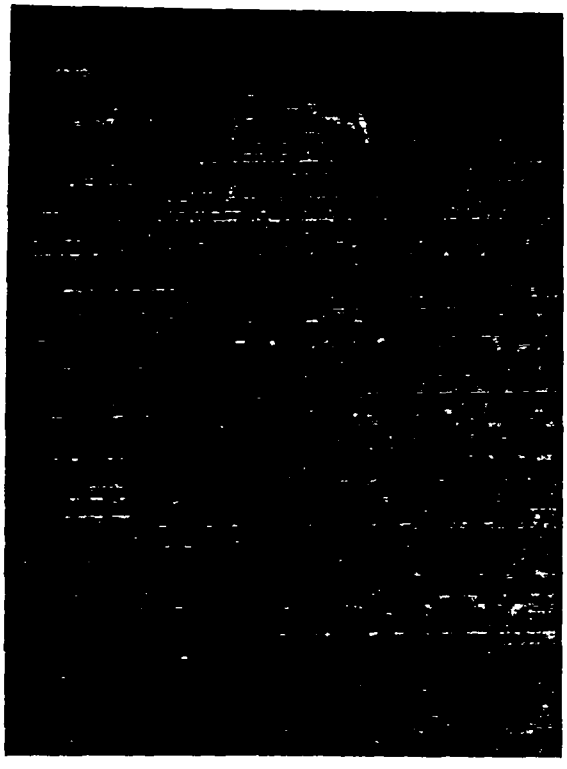


Fig. 14a. Outer surface of capsule 2138, showing carbides in grain boundaries. Etched, 600X.

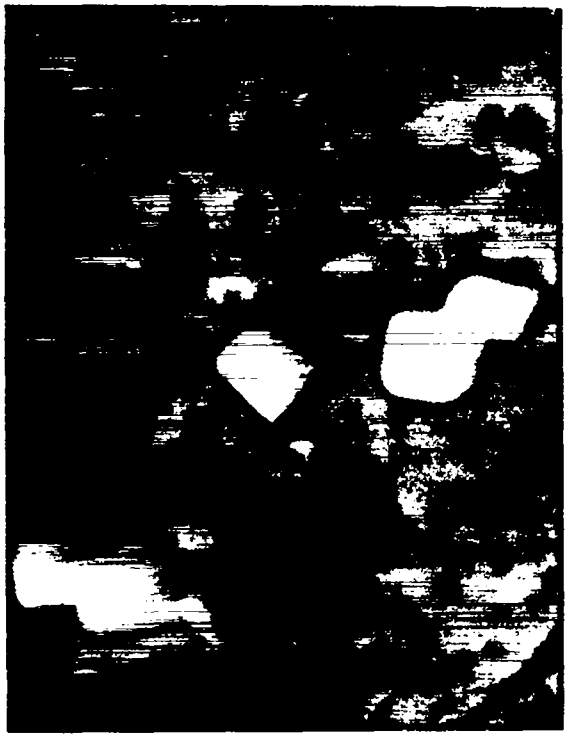


Fig. 14b. Crystals in fuel at bottom of capsule 2138. Unetched, oblique light, 600X.

A thin reaction layer was present on the outside walls and in the grain boundaries of capsule 2138. Microprobe examination revealed that the layer is TaC, formed by reaction between tantalum and backstreaming diffusion pump oil.

If an average lifetime of 1500 hours at 1100°C is assumed for tantalum capsules containing Pu-Co-Ce fuel, and a curve is drawn parallel to the Pu-Fe and Pu curves, an average containment lifetime of 20 years at 700°C is predicted. Of course, the slope of the curve for Pu-Co-Ce penetration may be different from that found for Pu and Pu-Fe alloy. However, it seems reasonable to assume that the slopes will be the same since plutonium is the diffusing species in each case. The selected average lifetime (1500 hours at 1100°C) is probably conservative, and the true lifetime may be considerably longer.

Pu in Carburized Ta Capsules

Since inadvertent carburization of tantalum capsules during long-term tests considerably improved their corrosion resistance, it was decided to deliberately carburize capsules before loading them with fuel. The capsules were carburized by heating them to 950°C for 100 hours in a vacuum in which diffusion pump oil was allowed to backstream (no liquid nitrogen in the cold trap). The capsules were then loaded with plutonium, and the final closure welds were made. These welds were externally carburized by a similar technique, utilizing an induction furnace to obtain localized heating.

The time required for external carburization using backstreaming oil-vapor is too long for use as a production technique. Therefore, an internal carburization technique was developed consisting of the following steps:

1. The tube to be carburized is packed with outgassed activated carbon granules.
2. The tube is heated under vacuum to 1700°C, and held at that temperature for about two minutes to drive off any helium still contained in the carbon (the carbon is cooled under helium after outgassing).
3. The tube is back-filled with hydrogen and held for five minutes.
4. The hydrogen is pumped out, and the tube is back-filled with helium and cooled to room temperature.

This procedure produces a duplex carbide layer of TaC and Ta_2C approximately 3 microns thick, and carbon diffuses into the parent material along the grain boundaries to a depth of approximately 0.008 in.[5]

Capsules carburized by the two techniques were corrosion tested with plutonium at 900°C, 1000°C, and 1100°C. When internal pack carburization was used, the final closure weld was not carburized, and plutonium penetration occurred through this weld. Attempts to carburize this weld externally were not always successful. End caps of a Ta-C alloy (230 ppm C) were used to prevent this weld penetration. These caps are discussed in more detail in the following section.

The following discussion is limited to capsules exhibiting penetration through the parent material and not through the welds. In these cases plutonium was detected on external surfaces below the liquid levels. The three carburized tantalum capsules tested at 1100°C lasted 11.7, 19.9, and 24.6 hours (18.7 hours average). This duration differs considerably from the average lifetime for uncarburized tantalum of 3.5 hours. The four capsules tested at 1000°C lasted 95.8, 112.8, 239.6, and 617.8 hours (266 hours average), an improvement by a factor of 9 over uncarburized tantalum containers. The one 900°C test of a carburized capsule containing plutonium was terminated after 1100 hours, with no evidence of plutonium penetration.

An internally carburized tantalum capsule with high carbon (230 ppm) end caps was tested for 24.6 hours at 1100°C and later sectioned for metallographic studies. Three samples were taken from this capsule (capsule 2264): a longitudinal section through the top weld, a longitudinal section through the area of plutonium penetration just below the liquid level, and a transverse section through the fuel near the bottom of the capsule. Photomicrographs of the carbide layer above and below the fuel level are shown in Fig. 15. The layer above the fuel level was quite uniform, but the surface of the tantalum was uneven.

The carbide layer below the fuel level was no longer uniform, varying in thickness from 1 to 13 microns. Adjacent to the carbide layer was a brownish-gray layer which electron microprobe examination showed to contain plutonium and a light

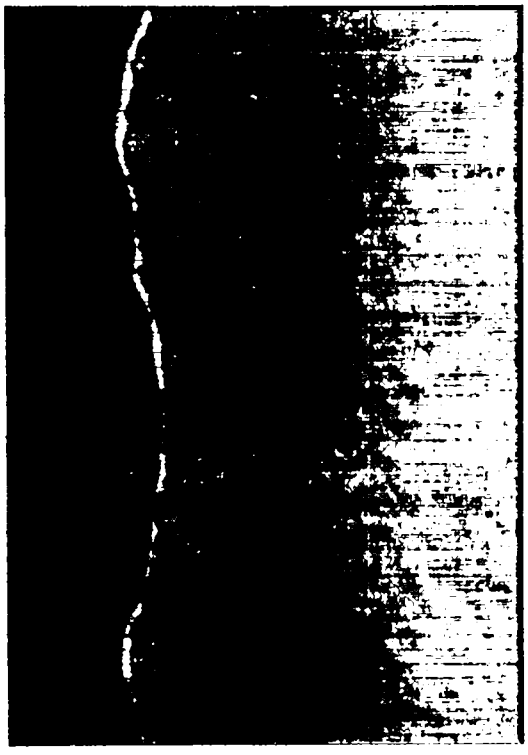


Fig. 15a. Carbide layer on tantalum wall above fuel level in capsule 2264. Unetched, 600X.

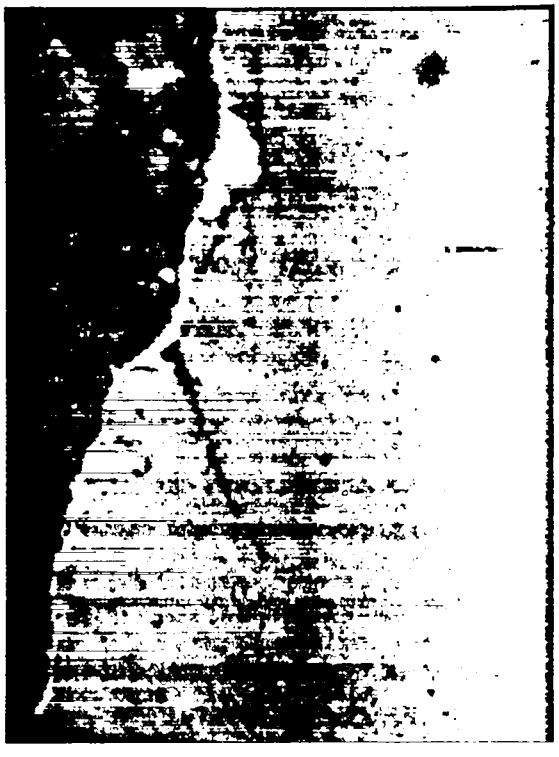


Fig. 15b. Capsule wall below fuel level in capsule 2264, showing brownish-gray phase adjacent to tantalum wall and nonuniform carbide layer on wall. Unetched, 600X.

element. A gray phase was present in the tantalum grain boundaries along with the white tantalum carbide precipitate.

The corrosion data obtained on internally carburized tantalum capsules containing plutonium are plotted in Fig. 7. The slope of the curve for carburized tantalum is different from the slope obtained with the uncarburized material. Extrapolation to 700°C gives an expected average lifetime of 20 years. Although the slope of the lifetime versus temperature curve has not been determined with high precision, it is apparent that carburization of tantalum vastly improves its resistance to corrosion by plutonium.

The activation energy for plutonium penetration through carburized tantalum is in excess of 70 kcal. This activation energy no doubt varies with the thickness of the carbide layer and the depth of carbide penetration in the grain boundaries. The carbide layer and/or carbides in grain boundaries slow plutonium diffusion through the container walls. The mechanism of this inhibition of plutonium diffusion is not now known, but it will receive additional study.

Pu in Carburized Ta-5W with Ta-C Alloy End Caps

Moderate tungsten additions to tantalum greatly increase its ultimate and yield strengths with only moderate lowering of its percentage of elongation.[6] Since container strength is important for withstanding large thermal and pressure stresses and preventing capsule distortion during fuel freezing, a Ta-W alloy is preferred to unalloyed tantalum. A Ta-5W alloy was selected as having the best combination of mechanical properties for use as a container for liquid plutonium alloys.

Capsules of this alloy were fabricated and carburized for A.C.T. studies utilizing the following procedure:

1. Carburize 4-in. lengths of Ta-5W tubing and Ta-C alloy (60 and 230 ppm C) end caps.
2. Weld bottom end caps in place.
3. Load capsules with plutonium.
4. Make final closure welds.

These capsules were tested to determine if carburized Ta-5W is as corrosion resistant as carburized tantalum, and to establish the carbon content in the end caps required to protect the welds. The bottom weld was in direct contact with plutonium, so that the susceptibility of the weld to plutonium penetration was measured directly, with no lag time due to plutonium climbing up the walls of the capsules.

Four capsules with 60 ppm C end caps were tested at 1100°C; one exhibited contamination before reaching operating temperature, and the others lasted 25.2, 37.1, and 39.1 hours (33.8 hours average). The bottom end caps of all capsules were penetrated. One capsule with 230 ppm C end caps lasted for 460 hours at 1000°C. Plutonium was detected on the external surfaces of the capsule approximately 100 hours before the signal was strong enough to terminate the experiment. The plutonium diffused through the center of the bottom cap. Three capsules with tantalum end caps containing 60 ppm C lasted 73.5, 288, and 465 hours at 1000°C. Again the buildup of the plutonium signal was very slow. The capsules exhibited contaminated bottom welds after test.

Because several capsules with 60 ppm C end caps were penetrated through the bottom welds, it is doubtful that this amount of carbon is sufficient to cause carbon segregation to the grain boundaries of the welds during the welding operation, thus protecting them from plutonium penetration. On the other hand, some evidence has accumulated during sodium loop tests that the material containing 230 ppm C has poor corrosion resistance. Therefore, a carbon content between 230 ppm and 60 ppm (perhaps 120 ppm) may be optimum.

The average lifetimes of these carburized Ta-5W capsules with carburized high carbon end caps were 322 hours at 1000°C and 33.8 hours at 1100°C. These average lifetimes are slightly longer than those of carburized tantalum capsules containing plutonium. Since no penetration of the carburized Ta-5W walls was observed, it is apparent that carburized Ta-5W has at least as good corrosion resistance to plutonium as does carburized tantalum.

Pu-Co-Ce Alloy (2 g Pu/cm^3) in Carburized Nb-10W and Nb-1Zr Capsules

The effective fast neutron absorption cross section of tantalum is approximately four times that of niobium. Therefore, it is desirable to use a niobium alloy in place of tantalum as a container material for liquid Pu-Co-Ce fuel. The use of

niobium allows the plutonium concentration in the fuel to be lowered to 1 to 2 g/cm^3, instead of 6 to 8 g Pu/cm^3 required in a system utilizing tantalum as a container.

Two carburized Nb-10W capsules were tested with Pu-Co-Ce alloy containing 2 g Pu/cm^3. The capsules were pack-carburized at 1550°C for 10 minutes. The resulting NbC + Nb_2C layer was approximately 6 microns thick, and carbides were present in the grain boundaries to a depth of approximately 0.007 in.[5]

One capsule was tested at 1000°C for 725 hours without showing external plutonium contamination. The capsule was withdrawn from test for metallographic studies. Sectioning and examination showed that the carbide layer was penetrated in many places by the fuel. The maximum depth of plutonium penetration along the niobium grain boundaries was approximately 0.010 in., near the fuel/gas interface. The depth of plutonium diffusion at other sites was approximately 0.002 in. Limited dissolution of the niobium base alloy occurred, and chemical analysis of the fuel revealed that it contained > 2.5 wt % niobium. Another carburized Nb-10W capsule containing 2 g Pu/cm^3 Pu-Co-Ce was tested at 1100°C for 1110 hours and 6 melt-freeze cycles without exhibiting external plutonium contamination.

A carburized Nb-1Zr capsule containing 2 g Pu/cm^3 Pu-Co-Ce alloy was tested for 873 hours at 1100°C without indications of plutonium penetration. The fuel was frozen 4 times during this test period. Since no carburized Nb-10W and Nb-1Zr capsule failed during test, no comparison between the two alloys as containers for Pu-Co-Ce fuels can be made.

SUMMARY

Accelerated corrosion test (A.C.T.) equipment has been developed to test containers for liquid plutonium alloys at temperatures of 900°-1100°C. Experiments lasting in excess of 1000 hours were routinely carried out in this equipment.

Uncarburized and carburized tantalum capsules have been corrosion tested with Pu, Pu-Fe, and Pu-Co-Ce alloys, and carburized Nb-10W and Nb-1Zr containers have been tested with 2 g Pu/cm^3 Pu-Co-Ce alloys. The following conclusions were reached:

1. Plutonium is more corrosive than Pu-Fe (10 at. % Fe), which in turn is more corrosive than Pu-Co-Ce alloys.
2. Plutonium penetration through Ta and Ta-W alloys is by grain boundary diffusion, rather than by solution attack.
3. The activation energy for plutonium diffusion through tantalum is approximately 30.4 kcal.
4. The activation energy for plutonium diffusion through carburized tantalum is in excess of 70 kcal.
5. High annealing temperatures for tantalum (> 1650°C), with accompanying grain growth, increase the rate of plutonium diffusion.
6. No plutonium contamination was detected on the exterior surfaces of tantalum capsules containing Pu-Co-Ce alloys that were tested for times up to 1760 hours at 1100°C.
7. Carburization of tantalum greatly improves its corrosion resistance to liquid plutonium alloys.
8. Liquid plutonium and plutonium alloys can be contained in carburized tantalum containers for several years at 700°C.
9. High carbon tantalum alloys appear to be satisfactory for end caps. Welds are protected by the precipitation of carbides in the grain boundaries.
10. Carburized Ta-5W alloy has corrosion resistance comparable to carburized tantalum.
11. Carburized niobium alloys are promising container materials for Pu-Co-Ce alloys with low plutonium concentrations.

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APPENDIX A

A.C.T. Capsule Test Data, Pu-Fe Fuel in Ta Capsules

Run No.	Capsule No.	Time at Temp (h)	Number of Freezes Before Test End	Major Area of Contamination	Activity (cpm)
			Tests at 1160°C		
1-25	2174	13.5	0	Gas phase below weld	15,000
1-26	2175	12.13	0	Gas phase and ∿ 3" from bottom	20,000
1-27	2176	14.98	0	Gas phase below weld	20,000
			Tests at 1100°C		
1-1	2128	34.55	0	Gas phase below weld	15,000
1-2	2129	20.12	4	Bottom tip	2,500
1-3	2130	16.40	0	Gas phase below weld	750
1-4	2131	16.87	1	Bottom tip	10,000
1-5	2132	31.60	0	Gas phase below weld	5,000
1-6	2133	27.25	0	Bottom tip	2,500
1-7	2134	47.90	0	Bottom tip	1,200
1-8	2135	21.70	0	Gas phase below weld	1,500
1-9	2136	23.62	1	Below fuel level ∿ 1" from bottom	2,500
1-10	2137	23.00	0	Gas phase below weld	1,500
1-15	2165	18.0	0	Gas phase below weld	5,000
			Tests at 1000°C		
1-12	2159	48.0	0	Gas phase below weld and ∿ 1" below fuel level	20,000
1-17	2168	48.4	0	Gas phase below weld	8,000
1-19	2170	51.6	0	Gas phase below weld, and ∿ 2" from bottom	20,000
1-42*	2102	18.2	0	Weld	> 20,000
			Tests at 950°C		
1-32	2090	32.3	0	Weld	20,000
1-46**	2272	22.3	2	Gas phase and ∿ 1" below fuel	15,000
1-47**	2273	79.0	2	Gas phase below weld	> 20,000
1-48**	2274	28.0	0	Weld	> 20,000
1-49**	2275	27.5	0	Weld	> 20,000
1-50**	2277	27.6	0	Weld	> 20,000
1-45**	2105****	26.5	2	Weld and center of top cap	> 20,000
1-52**	2276***	105.6	1	∿ 1-1/2" below fuel level	20,000
2-9	2088	7.6	0	No penetration; top head developed leak; did not restart	

*Molecular sieve trap on pumping system.
**VacIon pumping system.
***Weld carburized in vacuum.
****Weld carburized with a carbon arc at 30 A.

APPENDIX B

A.C.T. Capsule Test Data, Pu Fuel in Ta Capsules

Run No.	Capsule No.	Time at Temp (h)	Number of Freezes Before Test End	Major Area of Contamination	Activity (cpm)
			Tests at 1100°C		
2-1	2188	3.56	0	Several contaminated areas below fuel level	> 20,000
2-2	2189	3.41	0	Same	15,000
2-3	2190	3.46	0	Same	2,500
1-23	2214	4.6	0	Gas phase below weld	20,000
1-24	2215	4.22	0	Same	20,000
			Tests at 1000°C		
2-4	2191	8.8	0	Several contaminated areas below fuel level	13,000
2-5	2192	10.1	0	Same	6,000
1-34	2204	8.2	0	Same	20,000
1-58	2319 (1650°C anneal)	12.2	0	Same	> 20,000
1-59	2321 (2050°C anneal)	0.7	0	Same	> 20,000
1-60	2328 (1850°C anneal)	9.6	0	Same	> 20,000
2-33	2224 (2000°C anneal)	6.65	0	Above fuel level	> 20,000
2-34	2232A (2000°C anneal)	1.1	0	Below fuel level	> 20,000
			Tests at 900°C		
2-12	2206	20.0	0	Weld	20,000
2-13	2207	26.1	0	Weld	20,000
2-14	2208	26.1	0	Weld	20,000
2-24	2230	43.7	0	Fuel level	20,000
2-25	2240	41.9	0	At and below fuel level	20,000
1-35	2205	14.4	1	Capsule rupture due to volume expansion of fuel after melt-freeze cycle	-

APPENDIX C

A.C.T. Capsule Test Data, Pu-Fe Fuel in Ta Capsules, External Carburization Effect Observed

Run No.	Capsule No.	Time at Temp (h)	Number of Melt-Freezes	Remarks
			Tests at 1100°C	
1-38	2098	76.2	1	Lost pressure at 19.9 hours and capsule carburized; run terminated; no contamination
2-15	2172	376.8	1	Ran 218 hours at 900°C; lost liquid nitrogen at 140 hours; run terminated
			Tests at 1000°C	
1-14	2163	206.9	2	Pu contamination at bottom tip and ∿ 1" below fuel level (∿ 1000 cpm)
1-16	2167	96.0	0	Shut down because of mechanical pump failure; did not restart
1-18	2169	11.0	0	Lost liquid nitrogen at 11 hours; did not restart
2-6	2162	660.0	3	Run terminated after 660.0 hours; no liquid nitrogen used in system
			Tests at 950°C	
1-37	2097	207.3	0	Run terminated
1-40	2100	171.4	0	Ti getter at both ends of furnace; run terminated
1-41	2101	248.9	0	Molecular sieve trap on pumping system; Pu contamination at fuel level, ∿ 10,000 cpm
1-44	2104	294.6	0	Weld carburized with a carbon arc at 30 A; molecular sieve trap on pumping system; Pu penetration through the weld, ∿ 6000 cpm
			Tests at 900°C	
1-31	2164	291.4	0	Run terminated
2-7	2172	218.0	1	Lost liquid nitrogen at 140 hours; capsule carburized
2-8	2177	357.8	0	Run terminated
2-10	2094	19.5	1	Liquid nitrogen probe resistor burned out causing loss of liquid nitrogen
1-53	2278	146.0	1	Noise shutdown; run terminated
2-11	2095	316.3	4	Run terminated
1-33	2091	335 at 900°C 11 at 1100°C	0	Capsule exhibited Pu contamination below fuel level; ∿ 20,000 cpm
1-36	2096	250.3 at 900°C 13.3 at 1100°C	0	Capsule exhibited Pu contamination at weld and below fuel level; ∿ 20,000 cpm
1-13	2161	720.9	0	Capsule exhibited Pu contamination in the gas phase below the weld; ∿ 2500 cpm

APPENDIX D

A.C.T. Capsule Test Data, Pu Fuel, Carburized Ta and Ta - 5 W Capsules

Run No.	Capsule No.	Capsule Material	Time at Temp. (h)	Number of Freezes Before Test End	Major Area of Contamination	Approximate Activity (cpm)
			Tests at 1100°C			
1-20	2219	Ta; internally pack carburized	2.4	0	Weld	20,000
1-21	2220	Ta; internally pack carburized	10.58	0	Weld	20,000
1-22	2221	Ta; internally pack carburized	11.6	0	Weld	20,000
1-28	2222	Ta; capsule inverted; internally pack carburized. Externally carburized for 1.75 hrs	14.8	0	Weld	15,000
1-29	2223	same	9.4	0	Weld	5,000
2-16	2211	Ta; internally pack carburized; weld carburized with a carbon arc at 30 amps	32.83	0	Weld	10,000
2-17	2209	Ta; internally pack carburized; weld carburized with a carbon arc at 25 amps	10.47	0	Weld	20,000
2-18	2210	Ta; internally pack carburized; weld carburized with a carbon arc at 20 and 35 amps	13.73	0	Weld	20,000
2-28	2263	Ta; internally pack carburized; high carbon caps (230 ppm)	18.4	0	Below fuel level	> 20,000
2-29	2264	same	24.6	0	Below fuel level	> 20,000
2-30	2265	same	19.9	0	Below fuel level	> 20,000
2-31	2150	Ta; externally carburized; plug top	11.7	0	Below fuel level	> 20,000
1-64	1226	Ta-5W; internally pack carburized; high C (60 ppm) Ta end caps	37.1	0	Bottom end cap	> 20,000
1-65	1215	same	39.1	0	Bottom end cap	> 20,000
1-66	1217	same	Capsule exhibited Pu contamination before reaching operating temperature.			
1-67	1218	same	25.3	0	Bottom end cap	> 20,000
			Test at 1000°C			
1-55	2198	Ta; internally pack carburized; high carbon caps (230 ppm C)	95.8	0	Below fuel level	15,000
1-56	2201	Ta; internally pack carburized; high carbon caps (230 ppm C)	112.8	0	Below fuel level	15,000
2-27	2307	Ta; externally carburized	63.8	0	Below weld	> 20,000
1-57	2202	Ta; internally carburized; high carbon caps (230 ppm C)	239.6	0	Below fuel level	> 20,000
1-62	1224	Ta-5W; internally carburized; high carbon caps (60 ppm C)	465	0	Bottom weld	10,000
2-32	2199	Ta; internally carburized; high carbon caps (230 ppm C)	617.8	0	Below fuel level	17,000
2-35	D1214	Ta-5W; internally carburized; high carbon caps (230 ppm C)	460.2	0	Center bottom end cap	20,000
1-63	1225	Ta-5W; internally carburized; high carbon caps (60 ppm C)	288	0	Bottom weld	10,000
1-68	1219	Ta-5W; internally carburized; high carbon caps (60 ppm C)	73.5	0	Bottom weld	> 20,000
			Tests at 900°C			
1-54	2266	Ta; externally pack carburized; high carbon caps (230 ppm C)	1100	0	Test terminated. No Pu signal	

APPENDIX E

A.C.T. Capsule Test Data, Pu-Co-Ce (6.2 and 8.0 g Pu/cc) Fuel
(No Contamination Observed)

Run No.	Capsule No.	Fuel (g Pu/cc)	Time at Temp. (h)	Number of Melt-Freezes	Remarks
			Tests at 1100°C		
2-20	2139	8.0	326.1	2	Furnace element burned out; run terminated
2-23	2140	8.0	675.4	1	Lost liquid nitrogen at 678.4 hours; run terminated
2-26	2141	8.0	1760.0	4	Lost liquid nitrogen at 1600 hours; run terminated at 1770 hours
1-51	2142	8.0	500	2	Furnace element burned out; quartz tube collapsed; run terminated
1-61	2322	6.2	1411	4	Quartz tube collapsed; run terminated
1-61	2324	6.2	1411	4	Same
1-61	2325	6.2	1411	4	Same
1-61	2326	6.2	1411	4	Same
2-38	2317	6.2	790	2	Run terminated
2-38	2318	6.2	790	2	Same
2-38	2320	6.2	790	2	Same
2-38	2323	6.2	790	2	Same
			Tests at 1000°C		
1-11	2138	8.0	660.7	2	Test terminated

APPENDIX F

A.C.T. Capsule Test Data, Miscellaneous Tests

Run No.	Capsule No.	Conditions	Time at Temp. (h)	Number of Melt-Freezes	Major Area of Contamination	Activity (cpm)
			Tests at 1100°C			
1-30	2216	Inverted Ta capsule; Pu fuel	4.5	0	Weld	> 20,000
2-19	D-551	Ta+33 ppm Y; capsule had longitudinal weld; Pu fuel	Capsule ruptured at 0.5 hr due to volume expansion of fuel slug		Massive failure below fuel level	
2-21	D-550	same	1.08	0	Below fuel level on longitudinal weld; Pu visible	> 20,000
2-37	1188	Carburized Nb-10W capsule; Pu-Co-Ce (2 g Pu/cc) fuel	1110	6	Test terminated; no contamination	
1-71	1138	Carburized Nb-1Zr capsule; Pu-Co-Ce (2 g Pu/cc) fuel	873	4	Same	
			Tests at 1000°C			
2-22	D-526	Ta+72 ppm Y; capsule had longitudinal weld; Pu fuel	3.52	0	Below fuel level on longitudinal weld; Pu visible	-
1-39	2099	Ta capsule; Ti getter at center of both ends of quartz tube; Pu-Fe fuel	13.6		Weld Capsule had surface coating of Ti after test.	> 20,000
2-36	E-1180	Carburized Nb-10W capsule; Pu-Co-Ce (2 g Pu/cc) fuel	460	2	No Pu penetration. Test terminated.	
			Tests at 975°C			
1-43	2103	Ta capsule; molecular sieve trap on pumping system; Pu-Fe fuel	28.6	0	Weld	> 20,000