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THE DEVELOPMENT OF HIGH PURITY TANTALUM AND ALLOYS FOR LIQUID
PLUTONIUM CONTAINMENT IN LAMPRE I

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ABSTRACT

By combining arc casting and electron beam melting, spectroscopically pure tantalum and alloys, suitable for containment of molten Pu-Fe alloys, were produced. The 0.1% W alloy was used for the first LAMPRE loading. The effects of a large number of additives on the corrosion resistance of tantalum were tested. Additions of up to 10% tungsten gave increasing endurance. Specimens of tantalum irradiated with neutrons until 3% converted to tungsten were still satisfactory in mechanical properties for reactor use. Either tungsten or the traces of yttrium remaining after arc melting can raise the one-hour recrystallization temperature of tantalum by 400°C. Effects of internal strain, critical strain and precipitation hardening in tantalum alloys were studied. High-temperature annealed tantalum had superior corrosion resistance, while impact extruded and ironed material was better than deep-drawn metal. Mechanical tests on tantalum with added interstitial elements showed that their presence to the extent expected in LAMPRE would be unlikely to weaken the tantalum. Evidence was found that oxygen promotes plutonium attack on tantalum. Small amounts of hydrogen, nitrogen and carbon had no effect on corrosion.

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Introduction

The Los Alamos Molten Plutonium Reactor Experiment Number One (LAMPRE-I) is a 1 Mw materials testing fast reactor for the evaluation of plutonium alloys as reactor fuels, and for testing compatibilities of various combinations of fuel and container materials. As details of the reactor are described in accompanying papers,^{1, 2, 3} only the development of the fuel container metal will be covered here.

LAMPRE fuel is contained in 142 sealed capsules, 8 inches long and 0.430 inches in diameter. This report summarizes the metallurgical studies which led to the material used in making these capsules.

Choice of Containing Metal

Exploratory corrosion tests revealed only four pure metals: tungsten, tantalum, molybdenum and niobium, having reasonable resistance to corrosion by liquid plutonium.⁴ Although tungsten was the most resistant to solution attack, its brittleness at usual temperature makes it difficult to form and hazardous to use as a container. Tantalum, which seemed next best to tungsten, is easily worked when in its pure form. As many of the impurities in the tantalum available at the beginning of the LAMPRE project were substances attacked by plutonium, efforts were made at first toward improving corrosion resistance by the removal of impurities.

Approaches to Pure Tantalum

Most tantalum produced commercially in 1958 was made by rolling sintered powder, although arc-cast material was becoming available. Disregarding tungsten and niobium, which were never thought to be harmful in small concentrations, different lots of tantalum tried contained typically 1000 ppm of impurities. Individual specimens contained as much as 3500 ppm iron, 400 ppm titanium, 500 ppm nitrogen, 400 ppm oxygen or 300 ppm carbon. Later controlled experiments have shown that such impurity concentrations lead to hardening, difficult working, and decreased and erratic corrosion resistance.

Tantalum production by vacuum-casting methods was then, fortunately, being perfected by several metallurgical companies. These included arc-casting at National Research Corporation, Fansteel Metallurgical Corporation and Metallwerk Plansee A.G., and electron beam melting at Temescal Metallurgical Corporation. Concurrently, techniques of preparing and sintering tantalum powder were advancing to a point where purity comparable with that of arc-melted metal was finally obtained.

Vacuum arc-melting of tantalum⁵ is used for consolidation, alloying and rough removal of the more volatile impurities. Although the concentrations of all impurities except tungsten and niobium are brought below 100 ppm by this technique, this was not considered good enough for LAMPRE use. Electron beam melting⁶ is therefore used for further purification, in many cases resulting in metal spectroscopically pure (Fig. 1) except for interstitial impurities of the order of 20 ppm each. Table I compares the analyses of average grade arc-cast tantalum before and after subsequent electron-beam melting. Only elements reported both before and after melting are listed.

TABLE I
Effect of Electron Beam Melting on Purity of Arc-Cast Tantalum
ppm Impurity^(a)

	<u>Arc-cast</u>	<u>Electron-beam Melted</u>
Ta	Balance	Balance
Al	60	< 10
Si	40	< 3
Ti	10	< 5
Cr	< 10	< 10
Fe	25	< 10
Ni	20	< 10
Cu	< 50	< 2
Nb	60	< 200
Mo	< 25	< 30
C	10	< 25
N	10	13
O	60	20

(a) The different sensitivities reported are due to the fact that the analyses were done at different laboratories.

Analyses of typical electron beam melted ingots are given in Table II.

Fig. 1. Spectroscopically pure electron beam melted tantalum.

TABLE II
Analyses of Electron Beam Melted Ingots: Parts Per Million^(a)

<u>Constituent</u>	<u>Ingot Number</u>	
	<u>K-454</u>	<u>K-556</u>
Ta	Balance	Balance
N	13	30
O	20	10

(a) The following constituents were reported as "not detected" in these specimens:
Be, B, Mg, Al, Si, P, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo,
Ag, Sn, W, Pb, Bi, C, H.

Besides the increased corrosion resistance associated with greater purity, the production of spectroscopically pure tantalum gave closer insight into the mechanism of intergranular attack. This had previously been ascribed to the leaching out of some foreign material rejected into the grain boundaries. In spectroscopically pure tantalum and the related alloys, carbon is the only impurity frequently present in excess of its solubility limit, and other experiments had shown that the presence of intergranular tantalum carbide in small quantity has no significant effect on corrosion. There is no evidence that intergranular attack of highly purified tantalum is associated with impurities in the grain boundaries.

Effects of Alloying Metals

After the production of very pure tantalum ingots had been perfected, further improvement of the corrosion resistance of the containers was sought through the addition of small amounts of alloying elements. Screening tests were run on some 80 different alloys based on 17 different elements.^{1,8} The effects of alloy additions are summarized in Table III.

TABLE III
Results of Screening Tests

<u>Additive</u>	<u>Weight Percent</u>	<u>Fabricability</u>	<u>Corrosion Resistance ^(a)</u>
Be	0.01	Fair	Similar
B	1	Not fabricable	
Al	<0.001 ^(b)	Good	Better
Y	<0.001	Excellent	Much better
Sc	<0.01	Good	Similar
La	<0.03	Fair	Better
Ce	<0.01	Fair	Similar
C	0.01	Fair	Similar
C	0.028	Fair	Worse
Si	1	Not fabricable	
Ti	0.01	Good	Better
Ti	0.03	Good	Better
Zr	0.03	Excellent	Similar
Zr	0.1	Excellent	Similar
Zr	0.5	Excellent	Worse
Zr	1.5	Excellent	Worse
Zr	2.9	Poor	Worse
Hf	0.1	Excellent	Similar
Hf	0.5	Excellent	Similar
Hf	1.5	Excellent	Worse
Hf	2.7	Excellent	Worse
Hf	3.0	Excellent	Similar
Hf	5.2	Poor	Much worse
Th	0.02	Excellent	Similar
Th	0.03	Excellent	Similar
Th	0.07	Excellent	Similar
Th	0.5	Poor	Worse
Th	1.5	Poor	Worse
Th	3.0	Poor	Worse
W	0.1	Excellent	Similar
W	1.0	Excellent	Similar
W	1.5	Excellent	Similar
W	1.7	Excellent	Better
W	2.9	Excellent	Better
W	5.8	Excellent	Better
W	10.4	Good	Much better
U	1.2	Good	Similar
Re	1.5	Excellent	Better
Re	3.0	Excellent	Better
Re	5.5	Poor	Better
Fe	<0.01	Fair	Similar
Fe	0.015	Fair	Similar

(a) Corrosion resistance compared to pure tantalum.

(b) Frequently most of the additive was unavoidably lost during arc-casting.

Most of the additions tried caused no significant change in the properties of the tantalum. Only tungsten and yttrium alloys showed significantly greater corrosion resistance, while zirconium, hafnium, thorium and carbon were distinctly harmful in the higher concentrations tested. Alloys with boron, silicon and over 280 ppm carbon could not be rolled, and were therefore not investigated further. Tungsten seemed the most promising additive, as it was itself very resistant to plutonium corrosion, and was known to strengthen tantalum when present in solid solution.⁹ It would, furthermore, inevitably be present as a result of the transmutation of the tantalum. Tests on electron beam and arc melted alloys showed no appreciable change in corrosion resistance with up to 1.5% tungsten, but 3% to 10% alloys showed superior resistance. Tungsten also raised the annealing temperature and refined the grain structure (Fig. 2), but made the alloy much more difficult to form into capsules. It seems, however, that the presence of 10% tungsten so reduces the corrosion-promoting effects of welding, described later, that it may become possible to use capsules of the 10% alloy seam-welded directly from sheet. Coupon tests on tantalum containing 3 to 10% tungsten showed little or no attack in 500 hours at 750°C, while 10% tungsten welded capsules have shown no leakage in 1400 hours at 625°C.

Specimens of tantalum were irradiated at Battelle until 1.5% and 3% transmuted to tungsten,¹⁰ the latter corresponding to 37% plutonium burnup. The ultimate strength, yield strength, elongation and hardness of each specimen were compared with those of alloys of the same composition made by conventional alloying procedures. The change in each mechanical property for a given tungsten content was found much greater for the irradiated specimen. It was therefore concluded that for up to 3% transmutation, fast neutron damage to the tantalum structure had a much more powerful effect on properties than the concurrent growth of tungsten. The changes in mechanical properties during the irradiation were not great enough to make the metal unsuitable for reactor use.

The possibility that increased corrosion may result from fission recoil bombardment has been studied. Although it seems probable that this effect will be small, the answer must await examination of capsules actually irradiated at temperature in LAMPRE.

Metals more active than tantalum were added to it to promote the removal of oxygen as monoxides during vacuum casting, and to hinder the absorption of impurities during fabrication. It was hoped that the use of metallic "sacrificial deoxidants" would result in lower final content of interstitial impurities than the conventional addition of carbon. This advantage has not been realized; the alloys show no difference in ranges of oxygen and carbon content.

Fig. 2. Tantalum-0.1% tungsten electron beam melted ingot used for first core loading of LAMPRE.

Yttrium, although it failed to reduce interstitial impurities to the very low levels anticipated, was found to have other beneficial effects on tantalum which are not easy to explain. During the arc melting process, almost all the yttrium distills out, either as YO or as the metal. Arc melting with 0.2% yttrium takes several times as long as with pure tantalum, because of the time needed for the vaporized metal to diffuse out of the confined space between the ingot and the electrode. At the end of the run, the yttrium content is found to be below 40 ppm,* the limit of spectroscopic detection.

Despite this depletion, the yttrium has a profound effect on the properties of the tantalum produced. Although cooling must be slow in a retarded melting process, the product shows a refined grain structure. The recrystallization temperature is increased by 400°C or more, and the metal is more difficult to work.

No convincing explanation has been found for the change in properties of tantalum associated with these very small concentrations of yttrium. Efforts were made to obtain some measure of the changes by examining two specimens of tantalum-0.1% tungsten alloy sheet, arc-cast in the same way from the same starting stock, except that one was melted with an added 0.2 a/o yttrium. When these specimens were compared, using both X-ray spectrography and X-ray diffraction, no significant differences were observed in either the compositions or in the residual stress concentrations.¹¹

Since corrosion seems to be associated with recrystallization, as will be explained below, and the presence of traces of yttrium greatly decreases the recrystallization rate, there is possible correlation with the increased corrosion resistance. Yttrium-alloyed tantalum, with tungsten, has therefore been specified for the second loading of LAMPRE.

Heat Treatment

Recrystallization. Recrystallization behavior was investigated for high purity tantalum and various alloys with tungsten and yttrium, in the form of 90% cold reduced strip and/or finished fuel capsules. The amounts of strain hardening thus achieved are shown in Table IV, which shows that for a given reduction some alloys strain hardened more rapidly than others.

* Forty ppm is the limit of sensitivity of the spectroscopic technique used at Los Alamos. Battelle regularly reports tantalum melted with yttrium as containing less than 10 ppm yttrium. A specially prepared sample in which they measured 10 ppm yttrium showed a distinct segregated phase.

TABLE IV

Proportionate Increase in Microhardness Due to Straining by Cold Reduction

Sample	Diamond Pyramid Hardness		% Increase in Hardness Due to Working
	Annealed	As Worked	
0.1% W + Y capsule	107	184	72
0.1% W capsule	89	200	124
Ta strip	80	197	101
0.1% W + Y strip	107	152	42
1.6% W strip	131	290	121
4% W strip	155	291	88
6% W strip	219	394	80

Figure 3 shows the time for complete recrystallization plotted against vacuum annealing temperature.

From examination of these data, we can state the following:

1. Unalloyed, electron beam melted tantalum can be recrystallized at 800°C in 20 to 48 hours and at 1200° in 30 minutes.
2. Additions of tungsten in amounts of 0.1% to 1.6% can increase recrystallization temperature by 300 to 400°.
3. The retarding effect of tungsten additions can be reduced or nullified if the amount of strain hardening is sufficient.
4. Small additions of yttrium to either tantalum or tantalum-tungsten raise the temperature necessary to recrystallize in one hour by 400 to 750° and this effect is not appreciably reduced by high amounts of prior strain.

Critical Strain

The amount of strain at which large grain growth occurs during annealing is called the critical strain and is of interest because it affects surface finish and produces variations in deformation characteristics. This behavior was investigated for unalloyed tantalum and various tantalum-tungsten alloys.

The experimental procedure involved prior annealing, in vacuum, of strip at the minimum temperature required to effect complete recrystallization, cold rolling at various increments from 0 to 90%, and evaluation by quantitative metallography and measurement of observed grain size. Results are summarized in Table V.

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Fig. 3. Time for complete recrystallization vs. annealing temperature for tantalum and its alloys with tungsten and yttrium.

TABLE V

Material	Annealing Temperature °C	Critical Strain %	Size of Large Grains, Microns	% of Large Grains	Size of Initial Grains, Microns
Unalloyed Ta	1100	18	580	30	50
Ta-0.1% W	1200	13	400	13	50
Ta-1.0% W	1500	3 and 22	400 and 280	55 and 85	50
Ta-3.0% W	1600	19.5	200	60	75

A sample of the type of curve obtained from this investigation is shown in Figure 4 for Ta-0.1% W alloy, where it can be seen that grain growth occurs at a very rapid rate at 13% strain. Similar curves were obtained for the other alloys except Ta-1.0% W which showed a double peak.

Recovery

Under suitable kinetic conditions, the mechanical and physical properties of a cold worked metal return to what they were when the metal was in the unworked or annealed state. Using the traditional definition of recovery, i. e., the restoration of these properties without observable structural changes, the recovery of initial hardness for electron beam melted tantalum was investigated. Figure 5 shows the changes in microhardness which took place when specimens were heated in vacuum at temperatures up to 1900°.

The figure indicates that restoration of microhardness was not complete until 95% recrystallization was achieved; and at the onset of recrystallization, microhardness had recovered about 67%. The hump in the curve at 1450° is attributed to a hardening reaction which is discussed in the next section.

Precipitation Hardening

When tantalum or its alloys with tungsten and/or yttrium contain carbon as an impurity in the amounts of 25 to 60 ppm, it can be made to undergo a precipitation hardening reaction by heating in vacuum in the temperature range of 1100 to 1900°C. Figures 6 and 7 show the data obtained by heating various alloys in the form of cold rolled strip, in the temperature range mentioned above. The specimens were heated for 1 hour in vacuum, then helium quenched to retain the microstructures. Data from the figures indicate that all the materials except one, Ta-1% W-Y capsule, attained a peak hardness after heating at 1450°. The peak hardness for this alloy occurred after heating at 1600°. The steep downward slope of capsule alloys Ta-1% W-Y and Ta-0.1% W-Y is attributable to delayed recovery and recrystallization. For all materials, the

Fig. 4. Critical strain data. Grain size and percent of field occupied by large grains vs. percent cold reduction.

Fig. 5. Recrystallization. Recovery of hardness in one-hour anneal at different temperatures.

Fig. 6. Precipitation hardening. Hardness resulting from annealing various tantalum alloys at different temperatures.

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Fig. 7. Precipitation hardening. Hardness resulting from annealing yttrium-treated alloys at different temperatures.

initial portion of the curves, i. e., up to the peak hardness, was characterized by the appearance of a coarse precipitate phase, similar in mode of occurrence and appearance, to that identified by Battelle¹² as Ta_2C . At higher temperatures than that giving the peak hardness, this precipitate was apparently dissolved. Although significant changes of the precipitate were not observed during the climb to peak hardness, it is believed that the hardening is associated with changes in the character of some precipitate which may not be visible to the microscope, and that subsequent softening is a result of the precipitate being dissolved. Figures 8 through 10 illustrate the changes in microstructure which take place during heating at the various temperatures. The activation energy, approximately 40 kcal., observed for the precipitation hardening suggests that the hardening reaction occurring is controlled by diffusion of either carbon or nitrogen in the tantalum lattice.

Effects of Tantalum Structure on Corrosion

Very good corrosion resistance was observed in some early capsules from Metallwerk Plansee A. G., in which the fine, heavily worked structure had the form of platelets oriented parallel to the surfaces (Fig. 11). This is a microstructure characteristic of ironed material. It was postulated that this structure presented a minimum of grain boundary area to the fuel and created a tortuous path of penetration through the wall (Fig. 12). In deep-drawn capsules the platelets were oriented radially, and the rapid penetration by plutonium was ascribed to the direct paths existing through the material (Fig. 13). The ratio between penetrations in the radial and longitudinal directions, respectively, was actually observed to be proportional to the number of grain boundaries of those orientations originally present in the tantalum. These conclusions led to the early specification of impact extrusion and ironing instead of deep drawing.

Ironed capsules, however, still exhibited a point of weakness at the juncture between the worked structure and the heat-affected zone associated with the weld at the cap. Fuel alloys showed a tendency to penetrate at this point, then creeping downward through the worked structure. The advancing plutonium caused recrystallization of the tantalum, presumably through dissolution of strained crystals and precipitation of unstrained tantalum, as this recrystallization in the presence of fuel occurs of the order of hundreds of times faster than recrystallization of intact metal, and is complete within a few hours at 700°C. Figure 14 shows a specimen penetrated by fuel alloy and recrystallized, while a small area still unaffected shows the unaltered heavily ironed tantalum structure.

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Fig. 8. Tantalum-0.1% tungsten, as rolled. Spotty distribution of tantalum carbide. (X 750)

Note: All magnifications are quoted on the basis of eventual reduction to a length of 4-1/2 inches when printed.

Fig. 9. Tantalum-0.1% tungsten, completely annealed at 1100°C. Carbide visible between and inside grains. (X 750)

Fig. 10. Tantalum-0.1% tungsten, annealed at 1450°C. Carbide is completely dissolved, corresponding to maximum hardening. (X 750)

Fig. 11. As-ironed tantalum alloy microstructure. (X 350)

Fig. 12. Ironed high-purity tantalum, showing mode of plutonium penetration. (X 110)

Fig. 13. Deep-drawn high-purity tantalum, showing mode of plutonium penetration. (X 110)

There is evidence that penetration at the heat-affected zone may result either from internal energy differences between the general worked structure and the annealed structure near the weld, or from diffusion of copper from the chill block in which the capsule is clamped during welding. Diffusion of some such deleterious substance as thorium from the welding electrode into the heat-affected zone has also been suggested. The results of independent studies of the effects of carbon and nitrogen, and the practice of purging and thorough blanketing with helium and argon of selected purities before welding, seem to have eliminated interstitial elements as primary causes.

The hypothesis of an internal energy difference as the cause of attack at the heat-affected zone is strengthened by the fact that capsules annealed before loading and welding have better corrosion resistance than those with any worked structure. Treatment at the minimum annealing conditions of one hour at 1050°C doubled the time required for plutonium penetration.

Annealing at higher temperatures leads naturally to the growth of larger and more symmetrical crystals. It would seem reasonable that this further growth past a visually complete anneal should involve minor changes in internal energy, probably having no effect on corrosion. The experimental fact is, however, that at least up to 1450°C, higher annealing temperatures result in progressively improved corrosion resistance, as shown in Table VI.

TABLE VI
Percent of Ta-0.1% W Test Capsules Failing as a Function of Annealing
Temperature and Exposure Time

Annealing Temperature	<u>Cumulative percent failing in given time</u>			
	<u>700 hr.</u>	<u>1400 hr.</u>	<u>2100 hr.</u>	<u>2800 hr.</u>
1050°C	100	---	---	---
1200	50	100	---	---
1350	0	25	75	---
1450	0	0	0	0

Experiments are now in progress on capsules annealed at temperatures as high as 2200°C to determine how far the improvement from high temperature annealing may go. It may, in this way, be possible to correlate the improved corrosion behavior with other phenomena, such as the precipitation hardening discussed above.

The alloy selected for the first core loading of LAMPRE was an electron beam melted alloy of tantalum with 0.1% tungsten, annealed after fabrication (Fig. 15). This

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Fig. 15. Microstructure of electron beam melted annealed tantalum-0.1% tungsten alloy used for first core loading of LAMPRE. Inclusions are carbide. (X 550)

alloy has no detectable impurities except about 80 ppm interstitial elements. The precipitate of tantalum carbide both between and inside the grains seems to have no bad effects. Although later investigation demonstrated that 0.1% tungsten has a significant effect only in grain refinement, not in increasing corrosion resistance; the development work, and especially the long-period certification tests, on more improved alloys had not been completed when it was necessary to choose a proven satisfactory composition for the first loading. Specifications for succeeding loadings include melting from a starting stock containing 0.2% yttrium and 0.75% or more tungsten. The superior resistance of these higher tungsten alloys and of alloys made with yttrium has been demonstrated. Further development is to concentrate on heat treatment and the perfection of methods for fabrication of harder alloys. It is possible that the salutary effects of high temperature annealing, described above, will cause a return to pure tantalum, which recrystallizes at much lower temperatures than its alloys.

Interstitial Solutes in Tantalum Alloys

The elements known to be present in interstitial solution in the alloys used in LAMPRE are oxygen, nitrogen, hydrogen and carbon. The effect of each on the corrosion behavior and mechanical properties of tantalum, and the transport behavior of each, were studied.

A standard method for measuring the distributions of interstitial solutes on a microscopic scale was set up by Perkins,¹³ who determined the microhardnesses of a large number of specimens containing known additions of oxygen, nitrogen, and hydrogen respectively.

A screening corrosion test was run,⁸ comparing degassed tantalum with specimens containing 5 a/o oxygen, 5 a/o nitrogen and 7 a/o hydrogen respectively. All these concentrations were far in excess of anything expected in a reactor, and resulted in both inter- and intra-granular precipitates. At the end of the test, the hydrogen had escaped to the plutonium phase without damage to the tantalum, the nitrogen remained, causing no observable change in corrosion rate, while the oxygen diffused out, leaving a severely corroded specimen. This is in agreement with the mechanism for attack proposed by C. S. Smith,¹⁴ who postulated a wetted film of oxide formed by oxygen diffusing out of the individual tantalum grains. This mechanism is supported by the fact that oxygen in the fuel, where it is most stable, is innocuous.

Some effort was made to correlate corrosion with tantalum/fuel/tantalum inter-crystalline angles, following the principles of Smith,¹⁵ who pointed out that small inter-granular dihedral angles correspond to intergranular penetration.

Plutonium-10 a/o iron alloy was successfully melted into a sintered tantalum frit¹⁶ (Fig. 16). It is seen that the unaffected tantalum structure has the angles near 120° characteristic of equilibrium, but that the gray plutonium phase contacts the tantalum interfaces with the small angles associated with intergranular penetration. This was expected from the known high oxygen content of the tantalum.

Further fundamental study of intergranular angles could not be justified after it became possible to produce routinely tantalum alloys of satisfactory corrosion resistance.

There is a great deal of evidence that oxygen is active in promoting corrosion. Greater susceptibility of many capsules to attack above the liquid level leads to the idea that this might result from the slower loss of oxygen from the Ta into a thin film of plutonium than into a mass of it. The solubility of oxygen in plutonium is of the order of only 30 ppm at its melting point. The same effect is observed at parts of the tantalum surface originally covered by gas bubbles (Fig. 17). Recent high purity tantalum containing an average of 20 ppm oxygen has been more corrosion resistant than earlier tantalum which contained typically over 150 ppm. The wide variation in oxygen concentration, from 20 to 200 ppm being found frequently in a single capsule, may correlate with the random spotty failure found in apparently similar capsules.

Controlled tests on the oxygen content of tantalum are difficult, because the comparatively rapid diffusion of oxygen at test temperatures assures that almost all of it will diffuse from tantalum into plutonium in a few hours. Any analysis after a test gives little or no information about initial oxygen distribution.

The evidence that oxygen is involved in intergranular attack is strong enough to cause the specification of low oxygen content for reactor capsules.

As Gebhardt and Preisendanz¹⁷ had already studied the effect of oxygen on the mechanical properties of tantalum, their work was not repeated. They showed that up to 1.4 a/o of oxygen does not weaken tantalum. The buildup of this much oxygen in the tantalum while in the reactor is highly unlikely, as the thermodynamic relations and the high diffusion rate of oxygen in tantalum ensure that its residence in the metal will be only transitory when in the presence of liquid plutonium.

Although corrosion tests had shown no effect resulting from large concentrations of nitrogen and hydrogen, there remained the possibility of their causing severe embrittlement.

Rings of standard length were cut from fabricated tantalum capsules and heated in atmospheres of nitrogen or hydrogen until they contained the desired quantity of gas. They were then held at temperature long enough to ensure homogeneous distribution.

Fig. 16. Etched microstructure of tantalum frit containing plutonium. Typically large angles between tantalum grains, with small angles enclosing invading liquid plutonium. (X 110)

Fig. 17. Intergranular attack originating at an area initially occupied by a helium bubble below the plutonium surface. Penetration from a thin plutonium film. (X 110)

The specimens were crushed transversely in a universal testing machine, a technique chosen because it was easily adaptable to the testing of sections cut from capsules tested with plutonium, with little danger of the spread of activity.

In all cases, failure occurred in tension. The transition from ductile to brittle fracture occurred between 1.8 and 3.4 a/o nitrogen, while samples containing as much as 6.6 a/o hydrogen still failed in a ductile manner.

The addition of nitrogen or hydrogen caused small increases in the strength of the tantalum. The strength remained at least equal to the strength of pure tantalum as long as the metal remained in a ductile state, that is, at least up to 3.4 a/o nitrogen or 6.6 a/o hydrogen.

As hydrogen in the reactor would be continuously flowing from the sodium through the tantalum to the plutonium, there remained the possibility of cumulative damage from repeated hydriding and dehydriding of the metal. Samples of tantalum which had been repeatedly gassed with hydrogen and degassed broke in the same ductile manner as tantalum which had not been gassed.

The effects of the diverse diffusion behaviors of the different interstitials on the tantalum have been evaluated. Most of the fundamental data required were found in the literature.¹⁸⁻²⁰ Oxygen at 700°C flows across the thickness of a capsule in a few hours. On the other hand it requires hundreds of hours for appreciable flow across distances of a few centimeters, as from a weld to the fuel surface.

Hydrogen diffuses so rapidly in tantalum that its distribution will be essentially homogeneous, or in steady state, after a few hours. Calculations based on the work of Mulford and Sturdy²¹ showed that the concentration of hydrogen in contact with liquid plutonium at 650°C would not exceed 1.1 a/o, corresponding to equilibrium with a saturated solution of PuH₂ in liquid plutonium (Table VII).

TABLE VII
Calculated Hydrogen Concentrations in Equilibrium with PuH₂ in Pu-
10 a/o Fe at Reactor Temperatures

Temp °C	450°	650°
p (H ₂), mm Hg.	0.05	15
at. % H		
in Pu	1.9	4.0
in Ta	0.3	1.1
in Na	0.03	1.2

Hydrogen in the reactor was thereby judged not to harm the tantalum. It is most likely to cause trouble by precipitating the plutonium.

It seems probable that there will always be nitrogen coming into the sodium system of the reactor, either through leaks or through diffusion. Up to 200 grams per year are expected to enter by diffusion through the outer walls. If not picked up by the cold traps, this nitrogen will be deposited on tantalum surfaces. Because of its low diffusion rate, it will remain concentrated in the outer layers, and might conceivably lead to precipitation, embrittlement or progressive cracking. The small positive volume change resulting from the dissolution of nitrogen and the formation of nitrides has, however, the effect of counteracting the thermal stresses in the tantalum and thus minimizing the danger of cracking.

No significant tendency toward enhanced grain-boundary diffusion of nitrogen was found. In particular, evidence for possible nitrogen embrittlement along grain boundaries was sought. Nitrogen was allowed to diffuse into cylinders of tantalum and tantalum-tungsten alloys which had large grains and well-defined grain boundaries. Hardness traverses revealed no deviations at the grain boundaries from the theoretical distribution for diffusion into a cylinder. Application of a complete range of reasonable assumed grain boundary widths and diffusion coefficients to the approximate equation of Fisher²² showed that no measurable effect due to the grain boundaries should be expected. This technique gives, however, no idea of the absolute concentrations of nitrogen in the grain boundaries themselves, where it may at equilibrium be several times that of the concentration in the crystal lattices. The grain boundaries are so thin that concentrations existing only in the boundaries themselves would not be detected by the microhardness tester.

Diffusion coefficients of limited accuracy were obtained incidentally in this and other experiments. The presence of up to 10% tungsten had no significant effect on the diffusion rate of nitrogen in tantalum at 1000°C. This is in contrast to the behavior of oxygen, whose diffusion coefficient in tantalum at 700°C was diminished by about 50% in the 10% tungsten alloy.

The effects of small quantities of carbon in tantalum are difficult to evaluate, as carbon in concentrations close to saturation is present in all specimens. The average amount present is probably about 60 ppm, and it seldom falls below 20 ppm. Deposits of carbide are normally present both inside and between the grains. No ill effects can be attributed to carbides until the carbon concentration is over 200 ppm, when severe embrittlement results from the continuous intergranular layers of carbide formed. Under these conditions, failure could be due in part to mechanical effects from differential expansion.

Extended heating of tantalum samples above 1000°C permits greater diffusion of carbon through the metal and allows it to reach its most stable location, in the grain boundaries, thus favoring intergranular over intragranular carbide deposition. This has no overt deleterious effect in tantalum containing the usual concentrations of below 100 ppm of carbon.

Summary

The principal investigations concerned in the development of satisfactory container metal for molten plutonium fuels in nuclear reactors have been outlined. The studies to this time have resulted in the containers for the first core loading, made of ultra-pure tantalum alloyed with 0.1% tungsten, and annealed after fabrication. Problems still to be solved have been discussed. Development is continuing toward even better alloys for plutonium containment.

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