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$^{238}PuO_2$/Titanium Compatibility at 800°C and 1000°C

Dale R. Schaeffer and Paul E. Teaney

August 17, 1979

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Contract No. DE-AC04-76-DP00053

PRINTED IN THE UNITED STATES OF AMERICA

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5285 Port Royal Road
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Content

Abstract

The compatibility between $^{238}PuO_2$ and titanium was studied. Test specimens were heated at 800°C for 32 to 720 days and at 1000°C for 30 to 180 days. The results indicate reduction of the $^{238}PuO_2$ by the titanium caused solid solution hardening of the titanium, occasional intergranular attack by plutonium at 800°C, and intergranular and lattice diffusion by plutonium at 1000°C.

Introduction

The use of $^{238}PuO_2$ in Radioisotopic Thermoelectric Generators requires the assurance that the $^{238}PuO_2$ will remain contained during normal usage and during any possible abnormal occurrence. This compatibility study of $^{238}PuO_2$ with titanium is a part of the evaluation of possible containment materials.

Test specimens were heated at 800°C for 32 to 702 days and at 1000°C for 30 to 180 days (Table 1). The configuration of the compatibility specimen is shown in Figure 1. The specimen consisted of three capsules. The inner (titanium) capsule was gas-tungsten-arc welded after being loaded with $^{238}PuO_2$. The loaded titanium specimen was subsequently electron-beam welded in a tantalum capsule and an outer container of Hastelloy-X. The outer container provided oxidation resistance for the high-temperature heat treatment in air. The tantalum capsule protected the titanium liner from possible nitrogen diffusion through the Hastelloy-X during the extended high-temperature exposure. An interaction between the titanium and the tantalum capsules did occur; however, their interaction did not affect the results of the PuO_2/titanium compatibility.

Prior to assembly, the tantalum and titanium capsules were chemically cleaned in a 10 ml HF, 10 ml HNO_3, 30 ml lactic acid solution to minimize any oxide barrier which may exist on the surface of the specimens.

The impurity content of the fuel used for the tests is shown in Table 2. The fuel

Table 1 - Ti/PuO_2 COMPATIBILITY TEST MATEX

Temperature (°C)	Time (days)					
800	32	61	90[a]	180	361	720
1000	30	60	90[a]	180		

[a] Duplicate specimens and a blank were tested for 90 days at each temperature

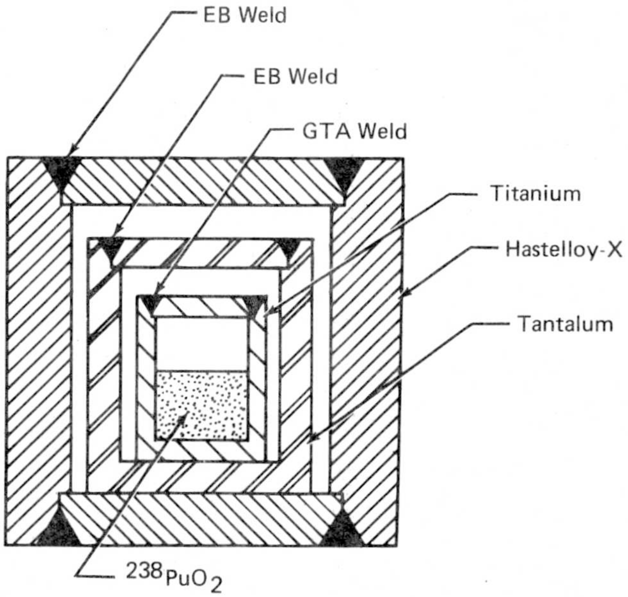

FIGURE 1 - Configuration of titanium/plutonium dioxide compatibility specimens.

Table 2 - IMPURITIES IN $^{238}PuO_2$

Impurity (wt %)	
Ni	0.05
Fe	0.36
Sn	trace
Al	0.11
Ca	0.07
B	0.04
Mn	0.06
Pb	0.23
Si	trace
Cr	0.41
Mo	<0.14
Cu	<0.04
Co	0.28
Mg	0.07
Zn	0.04
Na	trace
Total	<1.90%

contained less than 1.9 wt % total impurities.

800°C compatibility

PuO_2/titanium compatibility at 800°C is characterized by a slight surface reaction and the diffusion of plutonium and oxygen into the titanium. The surface reaction created an irregular edge when the PuO_2 was in direct contact with the titanium (Figures 2 and 3). The depth of the surface attack increased slowly with time as described in Table 3. The irregular edge appeared to be the result of the loss of pieces of the titanium substrate and the formation of a reaction product. Identification of the reaction product was not possible because it was not found in sufficient quantity to permit electron microprobe analysis.

Table 3 - DEPTHS OF ATTACK INTO THE TITANIUM AT 800°C

Time at 800°C (days)	Depth of Surface Attack (μm)	Depth of Intergranular Penetration (μm)
30	0	0
60	13	32
90	10 to 20	>280
180	13 to 25	No penetration observed
361	13 to 25	370
720	25 to 38	860

Plutonium diffusion into the titanium occurred when the PuO_2 was in direct contact with the titanium and occurred at a faster rate in the grain boundaries than through the grains. A visual comparison of the magnitudes of the intergranular and lattice diffusivities is shown in Figure 4 where the etchant has preferentially attacked the plutonium-bearing titanium. The depth of the grain boundary attack increased with time-at-temperature as described in Table 3. The reaction product that formed in the grain boundaries and occasionally intragranularly is indicated by arrows in Figure 5. Accurate analysis of this phase was impossible because of its small size; however, it was very rich in plutonium.

The voids observed in the titanium (Figures 3 and 5) are located primarily in the grain boundaries. Visual examination revealed that most voids were partially filled or appeared to have been previously filled with the plutonium-rich grain boundary phase; therefore, most of the voids are artifacts of metallographic preparation.

The presence of oxygen in the titanium was assumed because of the increase in hardness

FIGURE 2 - A typical portion of the titanium edge after being in contact with $^{238}PuO_2$ for 720 days at 800°C showing the irregular edge and subsurface reaction product (as polished, 125X).

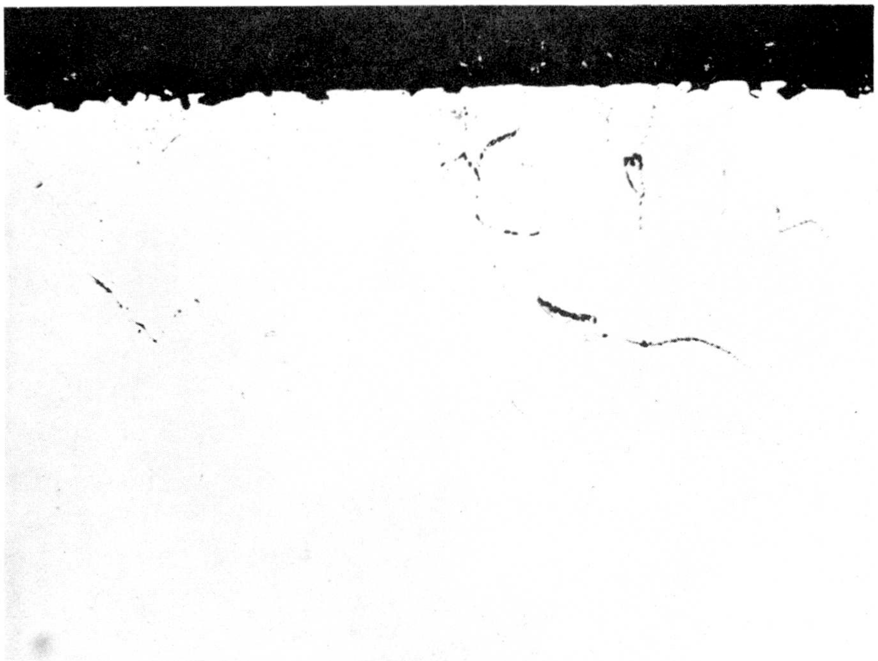

FIGURE 3 - The titanium edge after being in contact with $^{238}PuO_2$ for 720 days at 800°C (as polished, 62.5X). Note surface and intragranular attack.

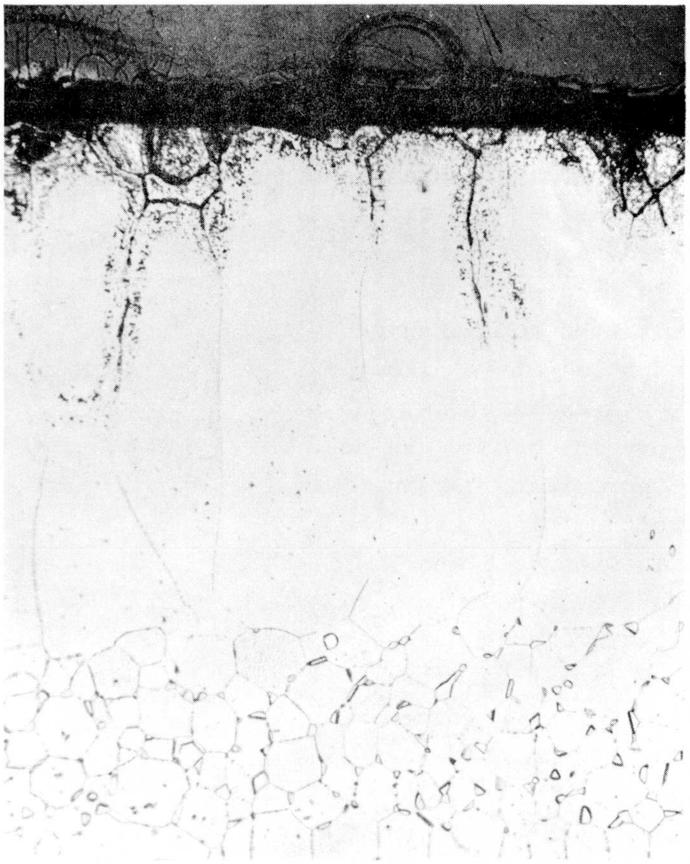

FIGURE 4 - Etched portion of the titanium after contact with $^{238}PuO_2$ for 720 days at 800°C revealing the relative magnitude of lattice and grain boundary diffusion of plutonium. Etchant: 5 to 7 ml Hf, 2 to 4 ml HNO_3, 100 ml H_2O (62.5).

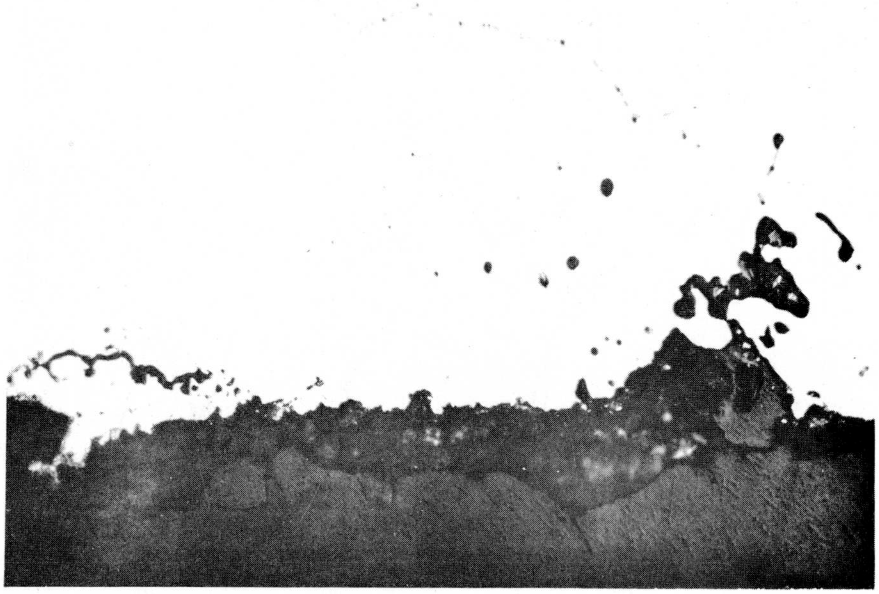

FIGURE 5 - Contact between $^{238}PuO_2$ and titanium at 800°C for 361 days resulted in intergranular attack. The arrows indicate the retained reaction product (250X, as polished).

of the titanium (Electron microprobe examination of the titanium did not find oxygen; however, the microprobe is insensitive to oxygen.) Microhardness traverses across samples heated at 800°C for 361 and 720 days are given in Figures 6 and 7. The increase in hardness is greater in the titanium in contact with the PuO_2 than in that portion of the capsule not in direct contact with the PuO_2. A correlation between hardness and oxygen content can be made [1,2], and thus approximate oxygen concentrations are included along with the microhardness values in Figures 6 and 7. A diffusion coefficient for oxygen in titanium can be determined from the hardness traverses by assuming a linear relationship between hardness and oxygen concentration, a semi-infinite specimen, and a constant surface composition (The relationship between hardness and oxygen in the range experienced in this test does deviate somewhat from linearity [1]; however, the data are sufficient to provide a calculation of approximate diffusion coefficients.) The solution of Fick's second law for these assumtions is:

$$\frac{H-H_o}{H_m-H_o} = \left[1 - \phi\left(\frac{x}{2\sqrt{Dt}}\right)\right]$$

where H = hardness at distance x from interface

H_o = initial hardness of titanium (assumed to be 340 VHN which was the hardness of the blank capsule)

H_m = maximum hardness of the titanium (a hardness of 1100 VHN was used [1])

ϕ = error function

t = time (sec)

D = diffusion coefficient (cm^2/sec)

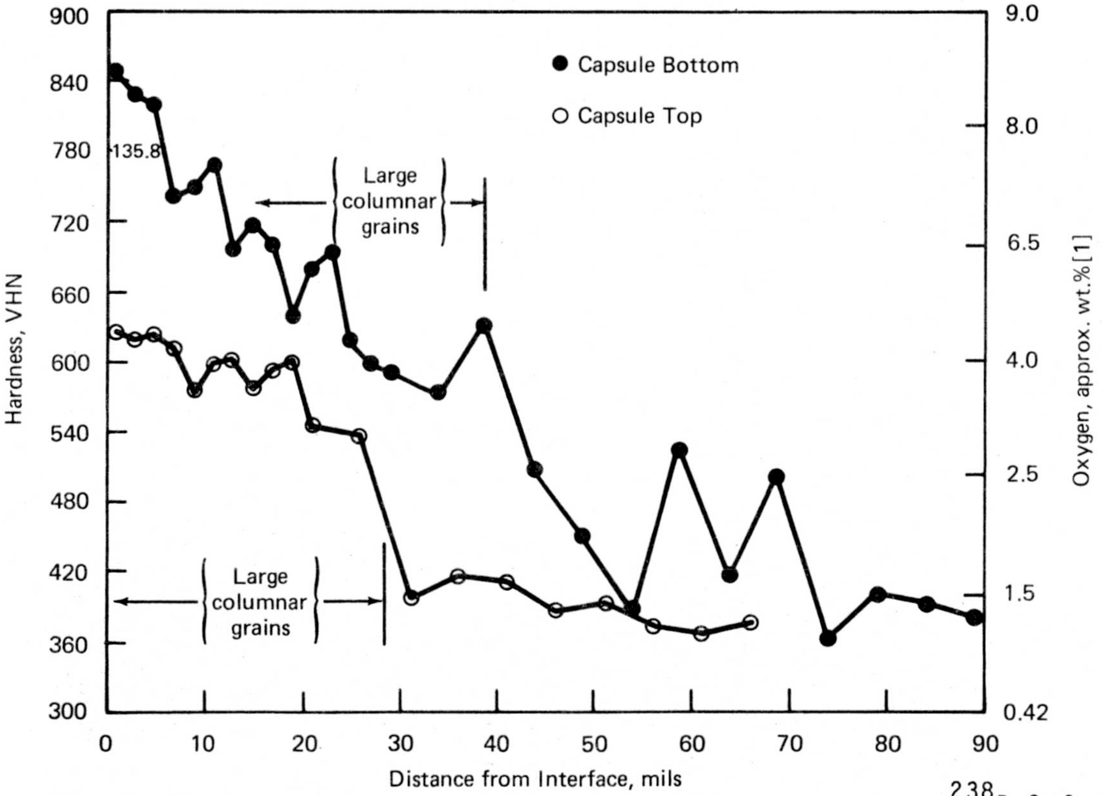

FIGURE 6 - Microhardness traverse across titanium after contact with ^{238}PuO for 361 days at 800°C. The capsule bottom was in direct contact with the $^{238}PuO_2$. The capsule top was in the same closed system but not in direct contact with the $^{238}PuO_2$.

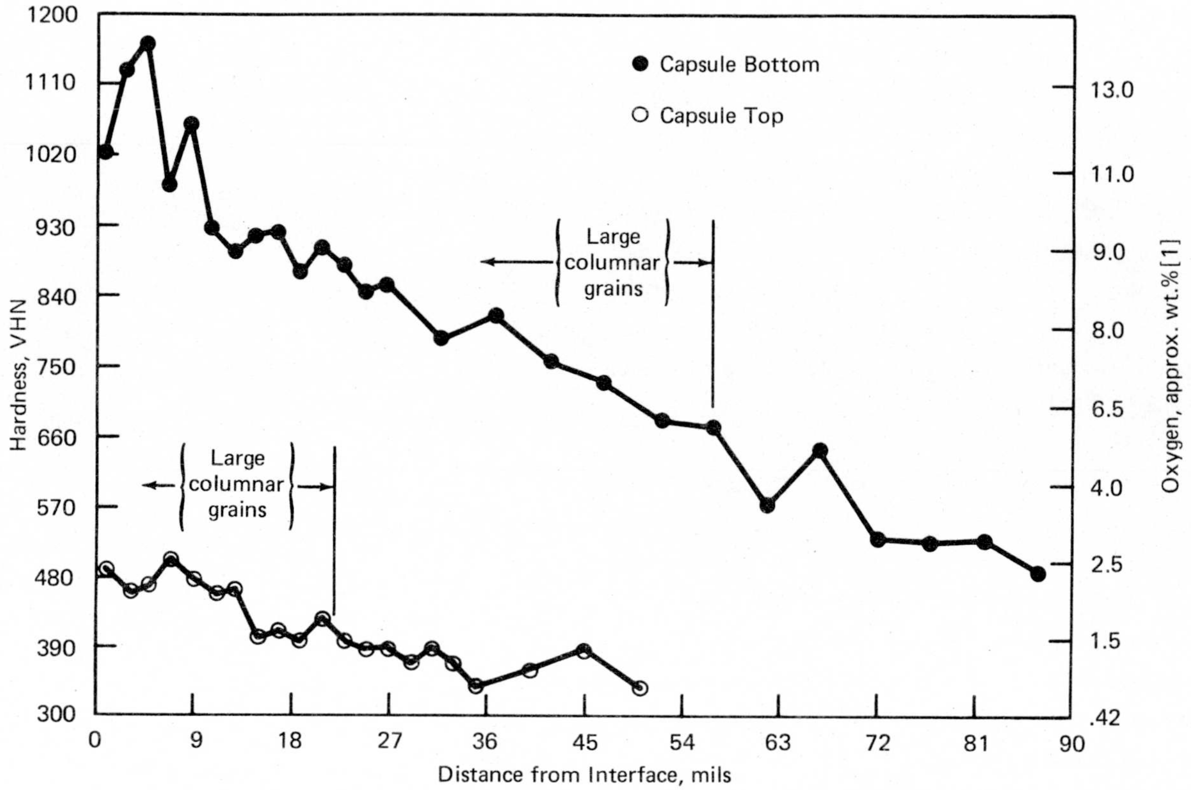

FIGURE 7 - Contact between $^{238}PuO_2$ and titanium at 800°C for 720 days resulted in intergranular attack. The arrows indicate the retained reaction product (250X, as polished).

Calculated values of the diffusion coefficient were between 1.2 and 2.7 x 10^{-10} cm^2/sec. This compares favorably with published values for the diffusion of oxygen in titanium, [3,4,5] substantiating the conclusion that the hardening is caused by oxygen.

Rough estimates of the amount of oxygen absorbed by the titanium can be made knowing the distribution of oxygen in the titanium and the surface area of the capsule. This estimate suggests the reduction of PuO_2 to stoichiometry of Pu_2O_3 or less which reinforces the thermodynamically feasible reduction of PuO_2 by titanium ($\Delta G°$ for the reaction $Ti + 4PuO_2 \rightarrow TiO_2 + 2Pu_2O_3$ at 800°C is -29.2 kcal.)

Lattice diffusion of oxygen appeared to affect the grain structure of the titanium (Figure 4). The columnar growth of the edge grains was a relatively close function of the square root of the aging time which is in agreement with the equation given previously for oxygen penetration into the titanium. Correlating the hardness determinations with the grain structure in the area of the capsule in direct contact with PuO_2 suggests an oxygen content of roughly 4 wt % at the boundary between the large columnar and smaller equiaxed grains. Columnar grain growth in the titanium not in direct contact with the PuO_2 appeared associated with oxygen concentrations of 3 wt % or lower.

1000°C compatibility

The compatibility of titanium with $^{238}PuO_2$ at 1000°C can be described by the formation of a porous surface layer and solid solution hardening by oxygen. Typical photomicrographs of the surface layer and accompanying incursions into the substrate are given in Figures 8 through 12. The intergranular incursions were not uniformly distributed but appeared to coincide with the more highly stressed areas of the capsule. The penetrations extended entirely through the 80-mil thick titanium at one site in the 90-day specimen and at four locations in the 181-day sample. In the as-polished condition the layer and accompanying incursions appeared to contain two phases (Figures 9, 11, and 12). An electron microprobe trace analysis of the two-phased region indicated in Figure 12 is displayed in Figure 13. The microprobe analysis determined that the two phases vary in plutonium and titanium content. Examination of the plutonium/titanium phase diagram (Figure 14) suggested that either sufficient plutonium has diffused into the titanium to cause the eutectoid transformation to occur, or that the phase precipitated as a result of decreasing solubility (The Pu/Ti phase diagram requires about 18 wt % plutonium to permit the eutectoid transformation to occur; however, this does not take into consideration the effect caused by any oxygen present in the layer). Etching revealed the acicular structure characteristic of the transformation product of beta titanium (Figures 8, 10, and 15) giving evidence that the concentration of beta-stabilizing plutonium is high enough to neutralize the alpha-stabilizing effect of the oxygen which is also present in the layer. Comparison of the etched structure with the microprobe trace indicated that the plutonium-rich phase is in the grain boundries of the acicular alpha.

The thickness of the plutonium-bearing surface layer and the depth of plutonium lattice diffusion into the titanium (including the surface layer) are listed in Table 4 as a function of aging time.

Table 4 - PLUTONIUM DIFFUSION IN TITANIUM AT 1000°C

Time (days)	Thickness of Surface Layer (μm)	Depth of Pu Lattice Diffusion (μm)
30	50	325
60	120-150	550
90	135-300	675
90	225	710
181	300	755

Plots of the square of the distances as a function of aging time are given in Figures 16 and 17. The thickness of the surface layer (Figure 16) followed a parabolic time dependence which suggests that the rate determining step is a diffusion process. Except for the 181-day sample, the plutonium lattice diffusion also followed a parabolic dependence of the aging time (Figure 17). The apparent change in behavior might be due to the anisotropic nature of alpha titanium, or perhaps the other determinations were artificially high due to grain boundary diffusion.

There were protrusions extending from the surface layer (Figures 8 through 11) which are not characteristic of the original interface. These protrusions along with the voids in the surface layer imply growth of the layer into the PuO_2.

Globular precipitates were found occasionally in the surface layer (indicated by arrows in Figure 18) in the samples aged at 1000°C for 90 days or less. Electron microprobe analysis found only plutonium (The electron microprobe analysis did not find oxygen; however, the microprobe is insensitive to oxygen).

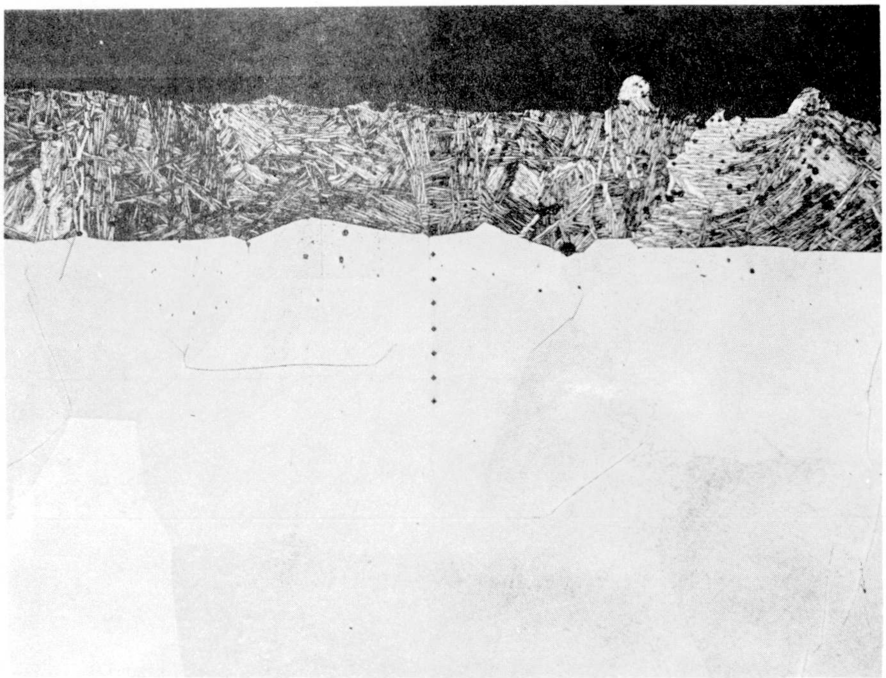

FIGURE 8 - Typical portion of the titanium edge after contact with $^{238}PuO_2$ for 181 days at 1000°C. Note acicular structure of surface layer with primary alpha below. Etchant: 5 to 7 ml Hf, 2 to 4 ml HNO_3, 100 ml H_2O (62.5X).

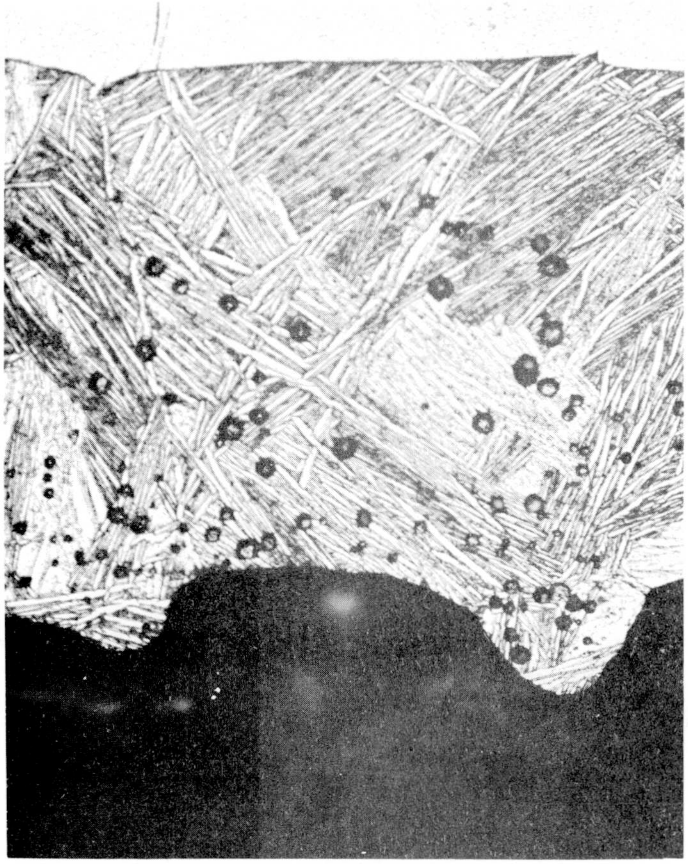

FIGURE 9 - A typical portion of the two phase surface layer which formed on the titanium after 181 days at 1000°C (as polished, 250X).

FIGURE 10 - Same as Figure 2 but etched to reveal acicular structure. Etchant: 5 to 7 ml Hf, 2 to 4 ml HNO_3, 100 ml H_2O (250X).

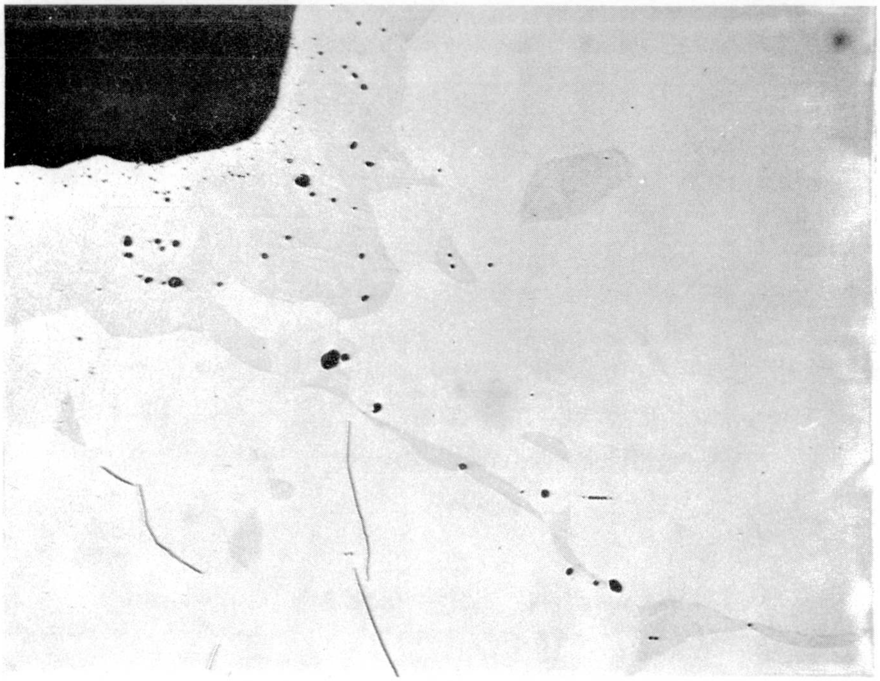

FIGURE 11 - The two phase surface layer occasionally penetrated the titanium intergranularly as shown in this sample heated for 90 days at 1000°C (as polished, 62.5X).

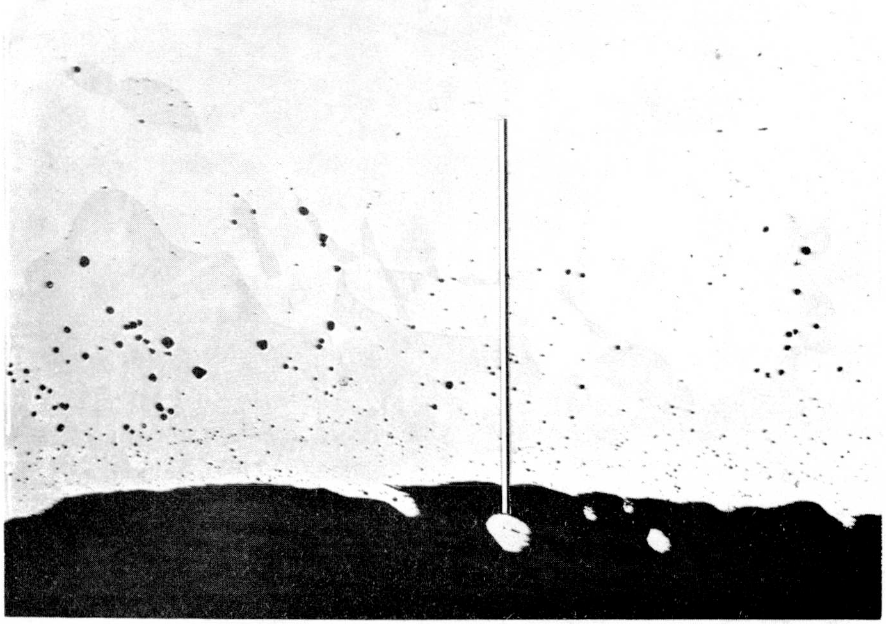

FIGURE 12 - A portion of the titanium edge after contact with $^{238}PuO_2$ for 90 days at 1000°C. The line indicates position of electron microprobe trace displayed in Figure 5. (as polished, 62.5X).

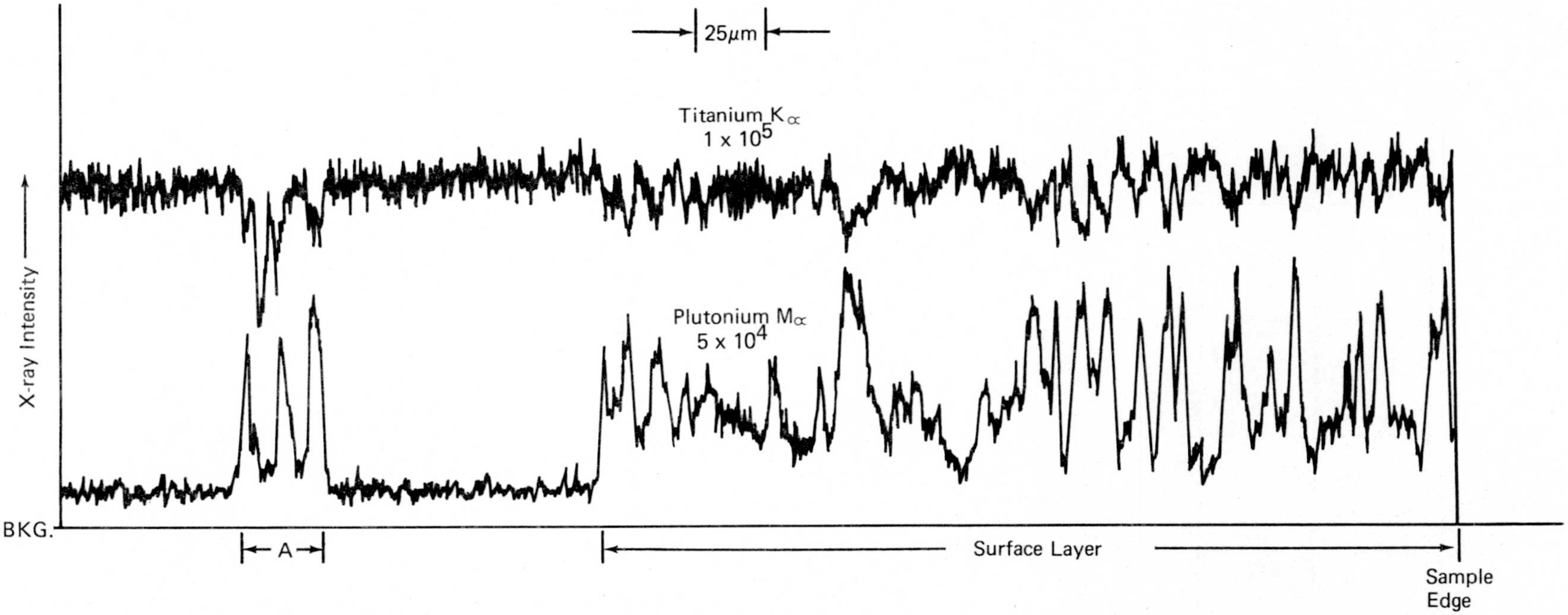

FIGURE 13 - A reproduction of the electron microprobe trace of the titanium edge after contact with $^{238}PuO_2$ for 90 days at 1000°C. A photomicrograph of the area analyzed is seen in Figure 4. Note the concentrations of plutonium in the surface layer.

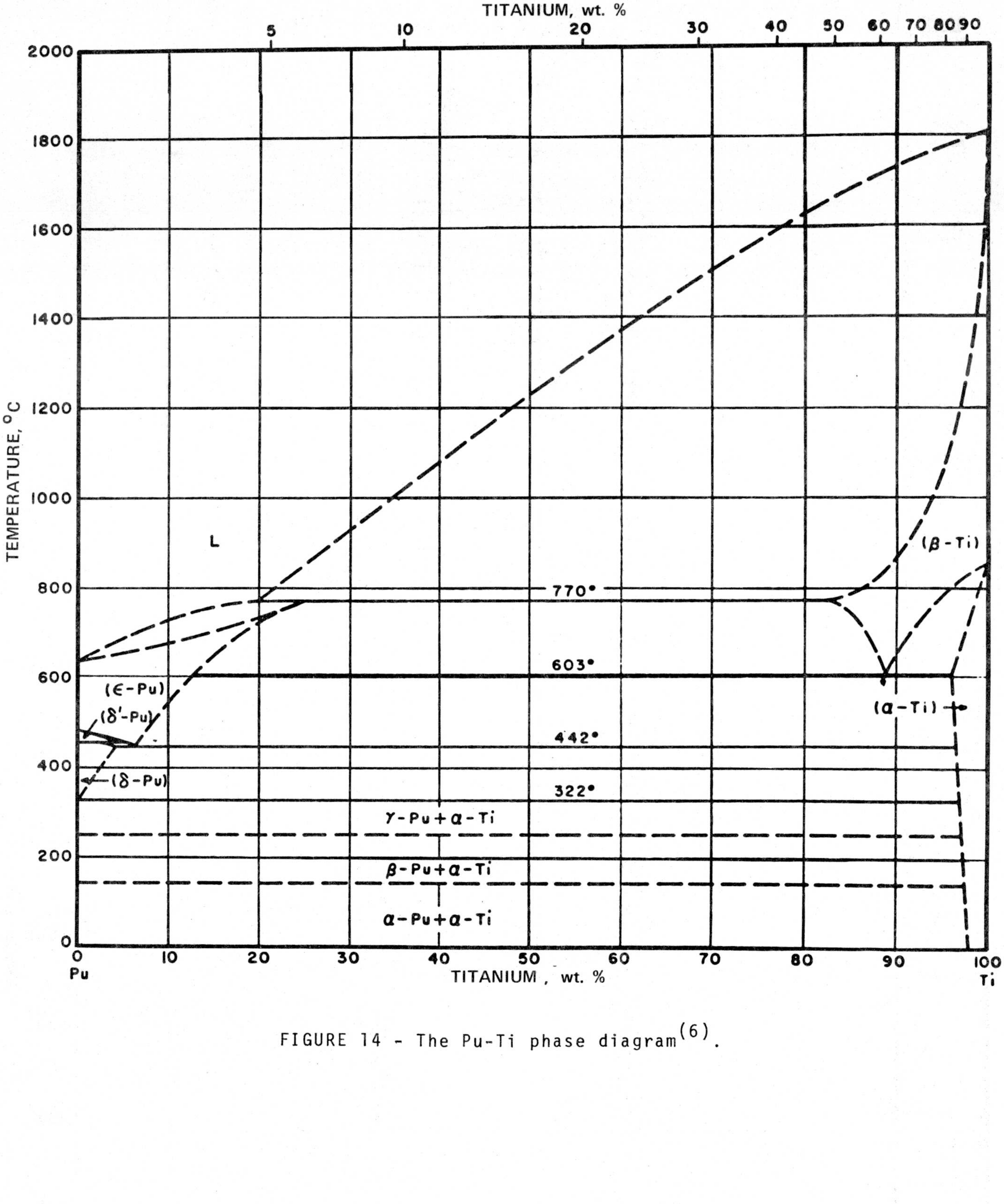

FIGURE 14 - The Pu-Ti phase diagram(6).

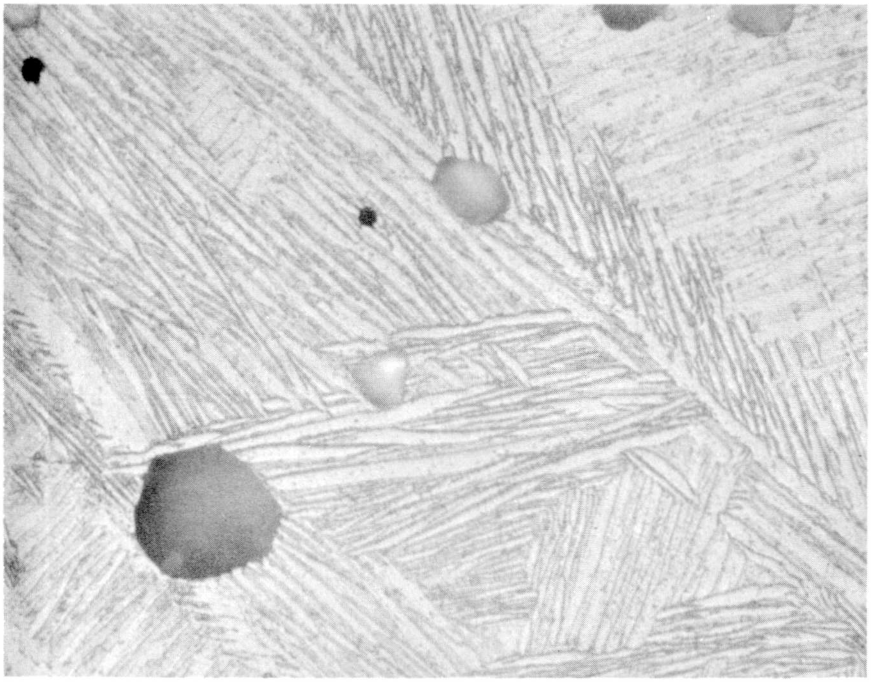

FIGURE 15 - A typical portion of the surface layer formed on the titanium showing the acicular structure common to transformed beta. Etchant: 5 to 7 ml Hf, 2 to 4 ml HNO_3 100 ml H_2O (720X).

Absence of these precipitates in the 181-day samples suggests that a more even distribution of the plutonium occurs with increasing time at temperature.

Diffusion of oxygen into the titanium is assumed from microhardness determinations and from the structure of the base metal. A microhardness traverse of a 90-day sample is seen in Figure 19. The relationship between hardness and oxygen content discussed previously indicates that the titanium below the plutonium-bearing surface layer had an oxygen content of roughly 5 to 8 wt % resulting in the primary alpha structure seen in Figure 8. This is in agreement with the Ti/O phase diagram (Figure 20).

The titanium that was not in direct contact with the PuO_2 was also solid solution hardened by oxygen. Hardness values indicated that the titanium contained about 6 wt % oxygen at the edge and roughly 1.5 wt % in the substrate below. The Ti/O phase diagram (Figure 20) indicates that at 1000°C the alpha transus is at about 0.5 to 1 wt % oxygen, and the beta transus requires roughly 2 wt % oxygen. The structure of this titanium that was not in direct contact with the PuO_2 was a mixture of primary and acicular alpha below a surface layer of primary alpha. This is in agreement with the phase diagram and verifies the hardness-to-oxygen relationship.

Cracks were observed in the titanium aged for 60 days or more (Figures 8, 9, and 11). The cracks did not occur in the transformed beta surface layer and thus indicate the inability of the solid-solution-hardened, alpha titanium to deform under the pressures experienced during the test.

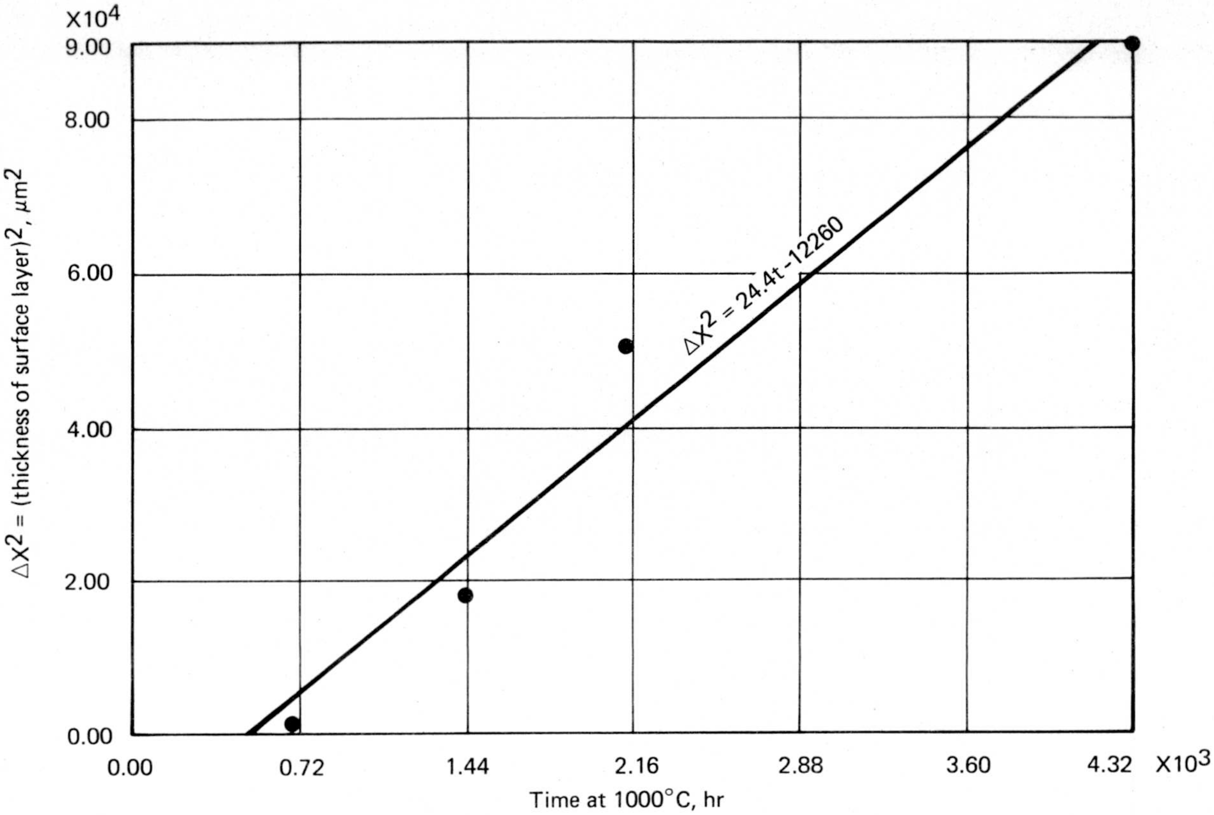

FIGURE 16 - Plot of the square of the plutonium bearing, surface layer as a function of aging time at 1000°C.

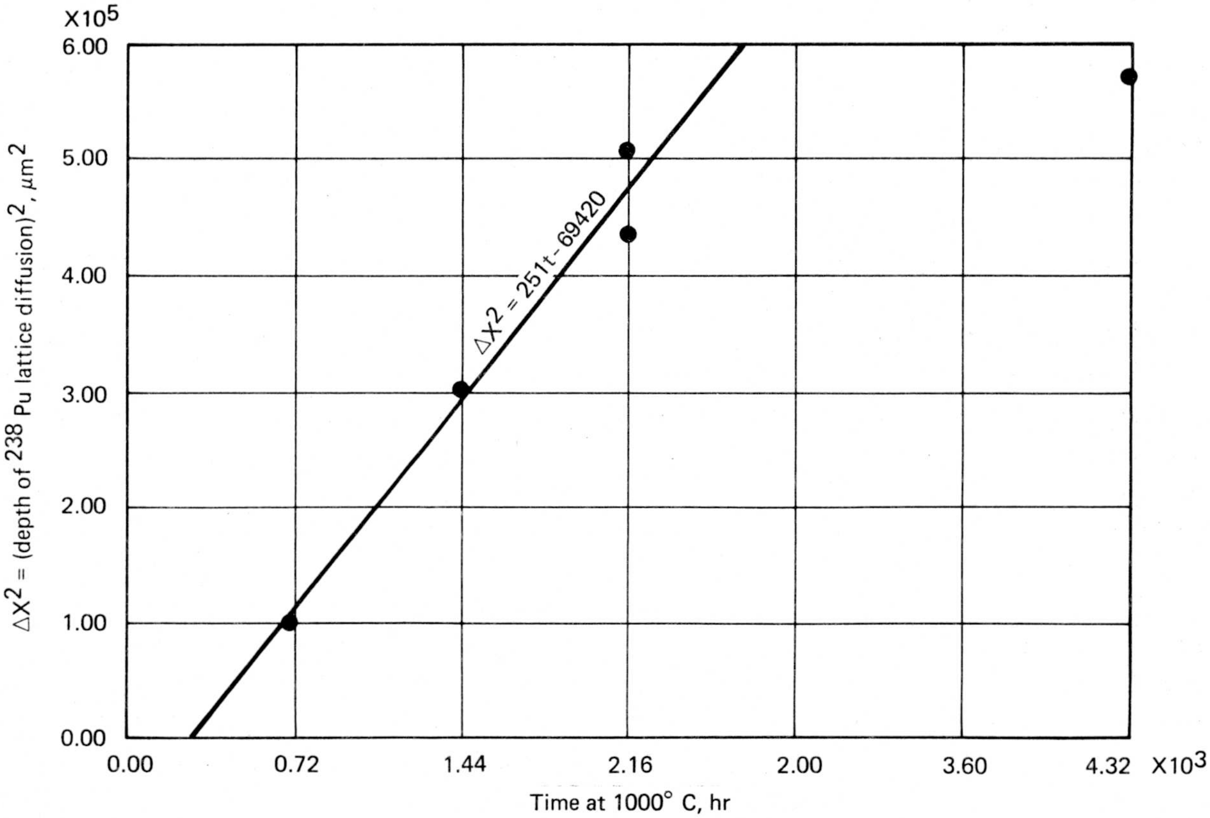

FIGURE 17 - Plot of the square of the depth of plutonium lattice diffusion as a function of aging time at 1000°C.

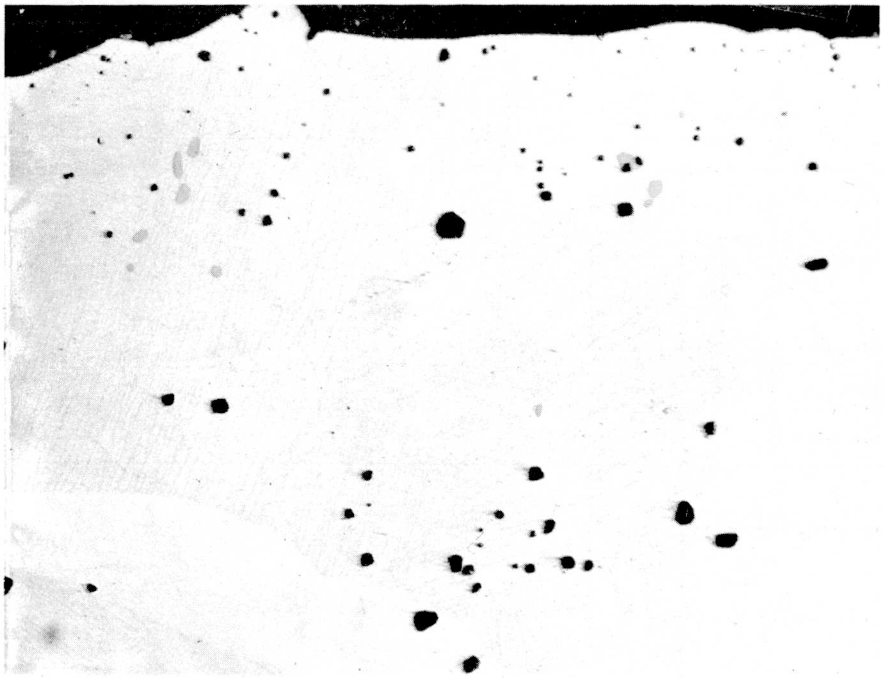

FIGURE 18 - Arrows indicate larger plutonium-rich precipitates which formed in the surface layer in the samples heated at 1000°C for 90 days or less (as polished, 250X).

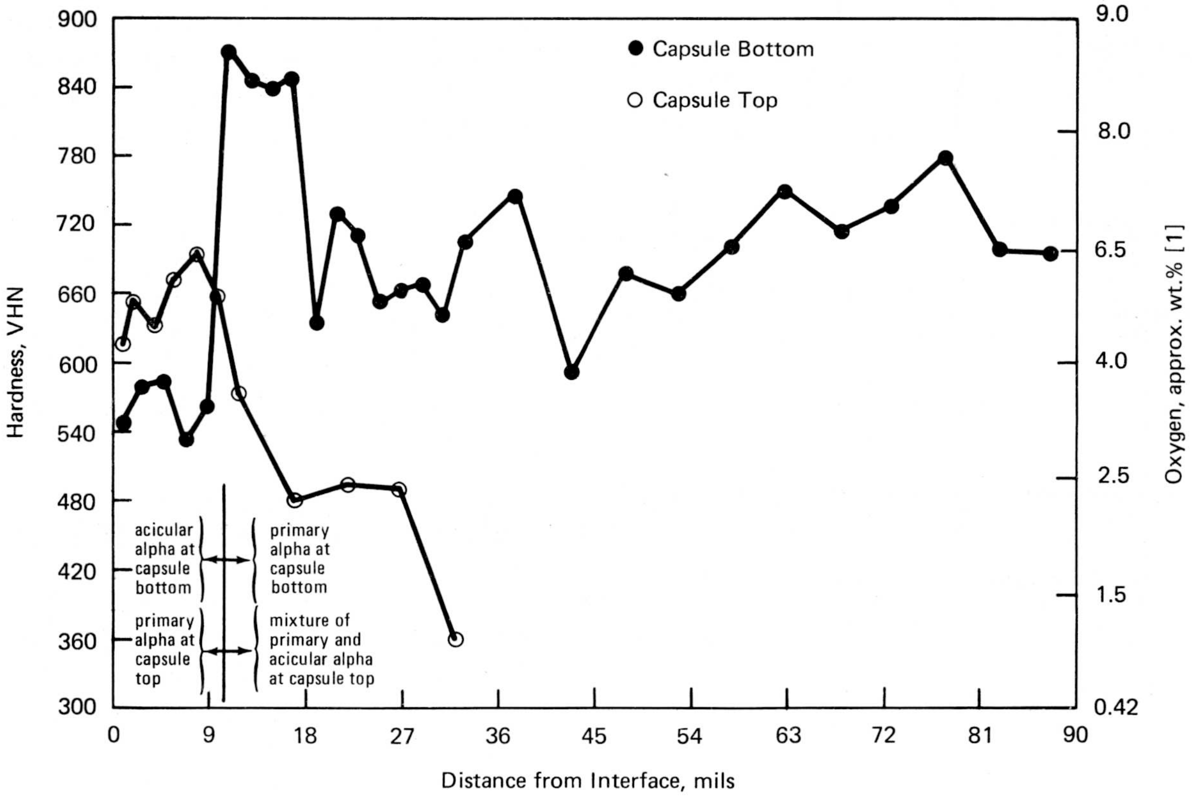

FIGURE 19 - Microhardness traverse of titanium after contact with $^{238}PuO_2$ for 181 days at 1000°C. The capsule bottom was in direct contact with the $^{238}PuO_2$. The capsule top was in the same closed system but not in direct contact with the $^{238}PuO_2$.

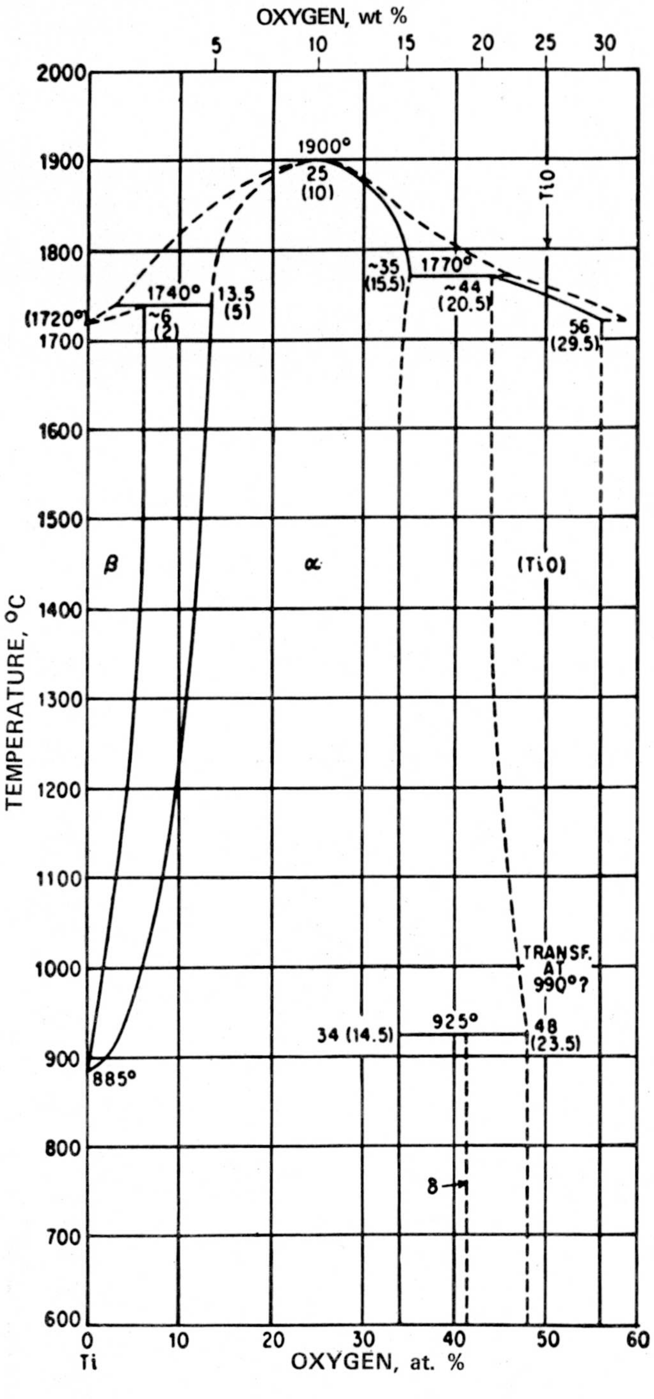

FIGURE 20 - The Ti/O phase diagram (1).

Summary and conclusions

Observations in the PuO_2/titanium compatibility couple after aging at 800°C include diffusion of plutonium and oxygen into the titanium. Lattice diffusion of plutonium is slow and causes little effect; however, grain-boundary diffusion is relatively rapid causing preciptitation of a second phase in the grain boundaries. The lattice diffusion of oxygen is faster than the grain-boundary diffusion of plutonium and causes extensive solid solution hardening.

At 1000°C oxygen diffused into the titanium causing extensive solid solution hardening and stabilizing the alpha structure of the titanium. Plutonium diffused into the edge of the titanium and overcame the alpha stabilizing effect of oxygen resulting in a surface layer and occasional grain-boundary penetrations of beta titanium. The amount of plutonium in the beta titanium was sufficient to cause the formation of a plutonium-rich phase in the grain boundaries of the transformed beta structure.

These tests show, conclusively, that titanium is not a suitable container for $^{238}PuO_2$ at 800°C or 1000°C. The ability of the capsule to retain its integrity during impact would be doubtful because of solid solution hardening of oxygen and intergranular attack by plutonium.

Acknowledgement

The authors would like to express their gratitude to D. L. Roesch for the electron microprobe analyses and to A. R. Kiefer for the metallographic support.

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