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**Plutonium-238 Dioxide/T-111
Compatibility Studies**

G. J. Jones, J. E. Selle and P. E. Teaney

September 19, 1975



Research and Development Report

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G. J. Jones,* J. E. Selle† and P. E. Teaney

Issued: September 19, 1975

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ABSTRACT

The tantalum-base alloy, T-111, is an ideal radioisotope encapsulant from the aspect of mechanical properties, but unfortunately undergoes severe oxygen embrittlement during long-term, high-temperature exposure to PuO_2 . The present study was undertaken in an effort to improve T-111/ PuO_2 compatibility by testing the hypothesis that reduction of fuel stoichiometry to the range $\text{PuO}_{1.75}$ to $\text{PuO}_{1.8}$ would suspend the embrittlement process by producing a state of thermodynamic equilibrium within the capsule. Reduction was to be accomplished in situ using yttrium metal. Test temperatures ranged from 773 K to 1373 K, with aging times of 60 days, 240 days, and 2 yr.

Initial results indicated the desired reaction did not proceed rapidly enough at the aging temperatures to stop T-111 embrittlement. However, efforts to force the reduction prior to aging by heating specimens to above 1573 K for 1 hr were successful. Such pretreated capsules showed no signs of embrittlement during aging, even after 2 yr at temperatures as high as 1173 K.

Test specimens employing pelletized fuel indicated the solid-state diffusion of oxygen from the fuel to the T-111 was the dominating transport process, although some vapor-phase transport was observed. The latter can only be attributed to volatile oxide impurities in the fuel.

Analysis of the oxygen absorption rates for nonpretreated capsules showed that oxygen diffusion in T-111 was the rate-controlling process. This result, coupled with known values for oxygen mobility in substoichiometric plutonia, indicates that "pretreatment" does result in the desired thermodynamic equilibrium at temperatures up to at least 1173 K.

INTRODUCTION

Radioisotopic thermoelectric generators (RTG's) are finding increasing use in applications where reliable, long-term, low-wattage power is required and access is difficult. In these devices, the heat generated by decay of a radioisotope is directly converted to electrical energy by means of thermoelectric materials.

Safety considerations necessitate complete containment of the radioactive fuel in these units in any credible accident environment. This requires encapsulation materials which have sufficient high-temperature toughness to survive such situations as fire or high-velocity impact and which are not degraded by prolonged exposure to the generator environment.

One of the most widely used radioisotopic fuels in such units is plutonium-238 dioxide. Since this isotope is an alpha-emitter, extensive radiological shielding is unnecessary, while its 87.4-yr half-life makes it ideal for long-term, higher-power sources. The dioxide form of this material has good thermal stability and high specific power.

As for encapsulation, tantalum-base materials possess the necessary toughness, as well as being formable and weldable. Unfortunately, these alloys become embrittled by prolonged high-temperature exposure to PuO_2 due to oxidation by the fuel.^{1,2} The present program was designed primarily to study this interaction in the 773-1373 K region with one such alloy, T-111, a solid-solution consisting of 90 wt % Ta, 8 wt % W, and 2 wt % Hf, originally developed for use in space power systems. It was also desired to evaluate a technique proposed to suppress the oxygen transport process in an attempt to reduce the embrittlement.

It has been suggested³ that, if the stoichiometry of the fuel can be reduced, a point will be reached where the oxygen partial pressure of the fuel is equal to, or less than, that of oxygen in tantalum. This would effectively stop the net transfer of oxygen to such encapsulating materials. (The effect of the presence of hafnium in T-111 on the desired equilibrium was not known.) In this work, the reduction technique chosen was to mix the plutonia with a reducing agent such as yttrium or hafnium in the heat source. If the oxygen "getter" was effective, the stoichiometry of the plutonia could be reduced before the encapsulants absorbed appreciable oxygen. The reducing agent used in these tests was yttrium, chosen mostly because of its ease of handling at room temperature, although its ability to entrap a wide number of volatile impurities was also a consideration.^{4,5}

PROCEDURE

The test specimens consisted of two T-111 layers with deep-drawn bodies and flat caps GTA (gas-tungsten arc) welded at one end. The liner cap and body were both 0.51 mm thick with approximately 2.7 cm³* occupied by

*This corresponds to approximately 6 W(thermal) or 15 g of PuO_2/Y mixture.

the fuel/yttrium mixture. The strength member, or second layer, employed a 1.02-mm-thick cup and a 1.53-mm-thick cap. A thin T-111 shim covered the fuel during closure to protect the weld from contamination. The actual configuration is shown in Figure 1. Typical T-111 analysis data are listed in Table 1, while the maximum allowable and average impurity levels for the inert gas atmosphere in the welding glovebox are listed in Table 2.

The fuel used was hydroxide-precipitated PuO_2 shards, from 53 to 500 μm in diameter; they received their final sintering at 1873 K for 2 to 4 hr (depending on the quantities present), during which time they also underwent oxygen-16 exchange. Table 3 lists the maximum and average impurity levels seen in the several fuel batches used. The yttrium was added to these specimens in the form of small machine turnings on the same size scale as the fuel. The analytical results for the yttrium are listed in Table 4. A single yttrium level was used, corresponding to reduction of plutonia to $\text{PuO}_{1.75}$.

Test temperatures varied from 773 K to 1373 K with times of 60 days to 2 yr; however, no single capsule type saw all test conditions. Because of the rather extreme temperatures, those capsules being heated to over 1173 K were secondarily encapsulated in 3.7-mm-thick Hastelloy-X, while those held at 1173 K or below used only a 0.51-mm Hastelloy-C clad. All heating was done in continuously monitored high-temperature ovens.

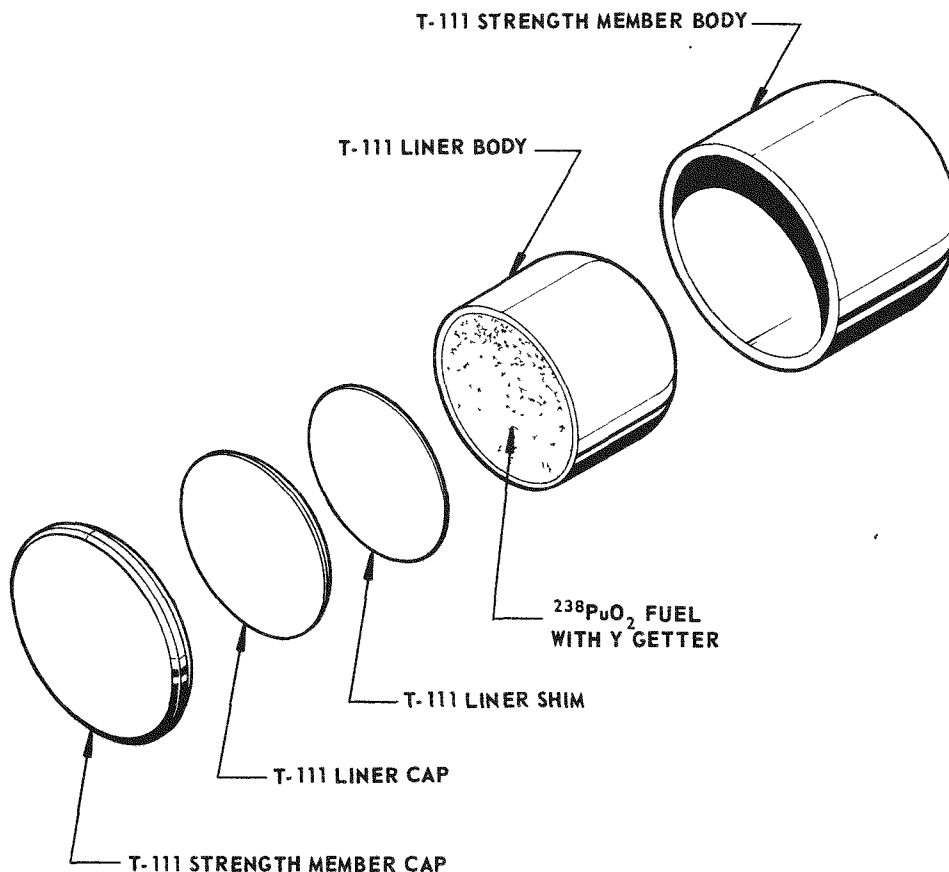


FIGURE 1 - Basic test capsule configuration.

Table 1

T-111 PURITY SPECIFICATION

<u>Element</u>	<u>Minimum</u>	<u>Maximum</u>
W	7.0	8.5 wt %
Hf	1.7	2.3 wt %
Nb		1000 ppm
Mo		200 ppm
Ni		50 ppm
Fe		50 ppm
Zr		1000 ppm
H		10 ppm
O		100 ppm
N		50 ppm
C		50 ppm
Total of All Other Impurities		300 ppm
Any Other Single Impurity		50 ppm

Table 2

WELDING ATMOSPHERE SPECIFICATION

<u>Component</u>	<u>Concentration</u>
He	75%
Ar	25%
O	<25 ppm
N	<160 ppm
H ₂ O	<60 ppm

Table 3

PLUTONIA PURITY SPECIFICATION^a

<u>Element</u>	<u>Average</u>	<u>Maximum</u>
Al	50	50
B	<10	-
Ba	<25	-
Ca	<250	-
Cd	ND ^b	-
Cr	75	120
Cu	<50	-
Fe	250	380
Mg	<20	-
Mn	<20	-
Na	ND	-
Ni	<50	80
Pb	ND	-
Si	<50	50
Sn	ND	-
Ta	ND	-
Zn	ND	-

^aValues in parts per million.

^bND - Not detected.

Table 4

YTTRIUM ANALYSIS RESULTS^a

<u>Element</u>	<u>Powder</u>	<u>Foil and Chips</u>
Al	20	12
Ca	ND ^b	55
Cr	-- ^c	1 ^c
Cu	20	-- ^c
Fe	100	90
Mn	5	<1
Ni	50	38
Si	50	80
Ta	>0.3% <1.0%	>0.3%
C	0.41%	0.11%
F	-- ^c	840
H	330	190
O	1.41%	2.16%
N	320	1.02%

^a Parts per million except where noted.

^bND - Not detected.

^cNot reported.

The majority of the specimens were bare capsules and these are designated by the F's in Table 5. In addition, several F-type units were encased in Min-K TE 1400 thermal insulation in a partial mockup of an actual generator and are designated by the M's. In order to obtain information on oxygen transport mechanisms, two special test capsules designated L-type were fabricated. These units employed fuel in the form of a vacuum hot-pressed, monolithic pellet, at approximately 85% of theoretical density. In one of these specimens the fuel pellet was held in contact with one segment of the capsule wall, while in the second the pellet was completely supported by iridium wire standoffs. A schematic representation of the configurations is shown in Figure 2. After 60 days at 1173 K these units were metallographically examined to obtain estimates of the relative importance of the two principal transport mechanisms: vapor-phase and solid-state surface.

Table 5
PuO₂/T-111 COMPATIBILITY TEST MATRIX

Time	Temperature (°K)				
	773	873	1073	1173	1373
60 days	M	MP	F	FPL	P
240 days	M	MP	F	FP	P
2 yr	M	MP	F	FP	

Key: F = Capsule with enough Y to produce PuO_{1.75}.
M = F capsule encased in thermal insulation (generator mock-up).
P = F capsule pretreated for 1 hr at 1623 K.
L = Oxygen transport study capsules.

Once specimens were removed from test they were sectioned and the fuel was set aside for later study. The capsule segments were mounted and metallographically examined. Microhardness traverses were obtained using a Leitz Miniload to make indentations at constant intervals* and a Leitz Classimet for evaluation.⁶ If a reaction product was noted, it was further examined by means of an electron microprobe. Oxygen and nitrogen determinations were also routinely made on each specimen. Finally, fuel stoichiometry determinations were attempted by x-ray diffraction, TGA weight gain, and neutron count calculations. The last, based on increased neutron emission from atmospheric-reoxidized, oxygen-exchanged fuel, proved the most satisfactory if the original neutron count values were available.

RESULTS

Yttrium Segregation

Initial metallographic work on the "M" and "F" type capsules indicated that there was no hardening of the strength members, but that irregular hardening of the liners occurred (hardness numbers for as-formed T-111 average about 250 VHN; readings above 300 VHN are usually indicative of

*The instrument calibration for the microhardness indenter was in mils, where 1 mil = 25.4 μm. For this reason all traverse distances will be denoted in mils.

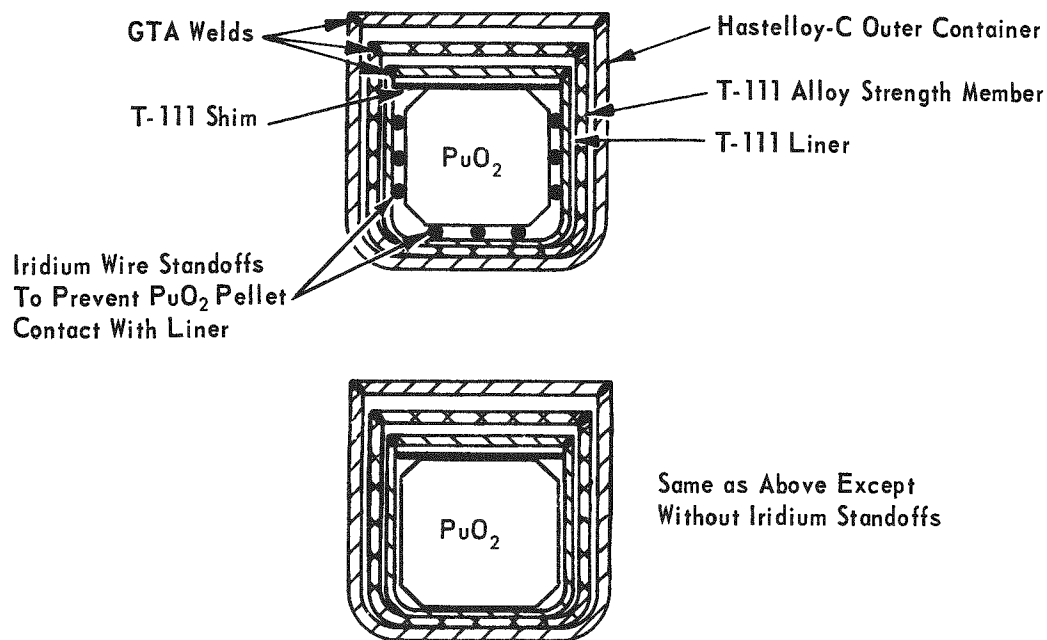


FIGURE 2 - L-type capsule design (for oxygen transport mechanism studies).

embrittled material). Parallel microhardness traverses across the side-wall of the liners gave values that varied by as much as several hundred Vickers hardness numbers. The reason for this became evident when a microhardness traverse was made down the sidewall of the specimen tested at 1173 K. The indentations were made at 0.127-mm intervals, 0.025 mm from the inside edge, beginning near the top and continuing to the bottom of the specimen. These data are shown in Figure 3. Note that the microhardness values are higher near the top and bottom and lower near the middle, indicating less oxygen entered the container wall in the latter area. This could occur if, due to fuel loading techniques, there were a higher concentration of yttrium in the middle of the capsule than at the top and the bottom. Examination of radiographs (Figure 4) of these capsules did show definite segregation of the yttrium, with the highest concentration approximately midway between the top and bottom of each specimen. The yttrium is indicated by the light bands in the figure. Following these observations the tests were repeated and care was taken to ensure a homogeneous distribution of yttrium in the capsules.

F-Type Capsules

Samples were run for 60 days, 240 days, and 2 yr at the various temperatures. The oxygen and nitrogen values are listed in Table 6 along with Vickers hardness numbers (VHN) for various capsules. Photomicrographs of the liners and microhardness traverses across the liners and strength members of the domes and sidewalls of the 2-yr 873 K, 1073 K and 1173 K specimens are given in Figures 5 through 7. (Note that 773 K data have not been included since they are essentially identical with 873 K data.) There was no indication of embrittlement or reactions in the specimen tested for 2 yr at 873 K or below. Embrittlement of the liners of the specimens tested at 1073 K and 1173 K is indicated by the microhardness

traverses in Figures 6 and 7. Microhardness gradients ranging from 240 VHN at the inside edge to approximately 275 VHN at the outside edge are indicated for the strength member dome and sidewall of the specimen tested at 1073 K. Electron microprobe analysis revealed no explanation for the gradients. However, they most probably are due to nitrogen diffusion through the Hastelloy-C clad. This probably also accounts for the high values obtained along the outside edge of the strength member dome of the specimen tested at 1173 K, shown in Figure 7.

It is evident from these results that the yttrium was not effective in reducing the plutonia at these temperatures. This may be due either to the failure of the yttrium protective oxide to completely disappear or

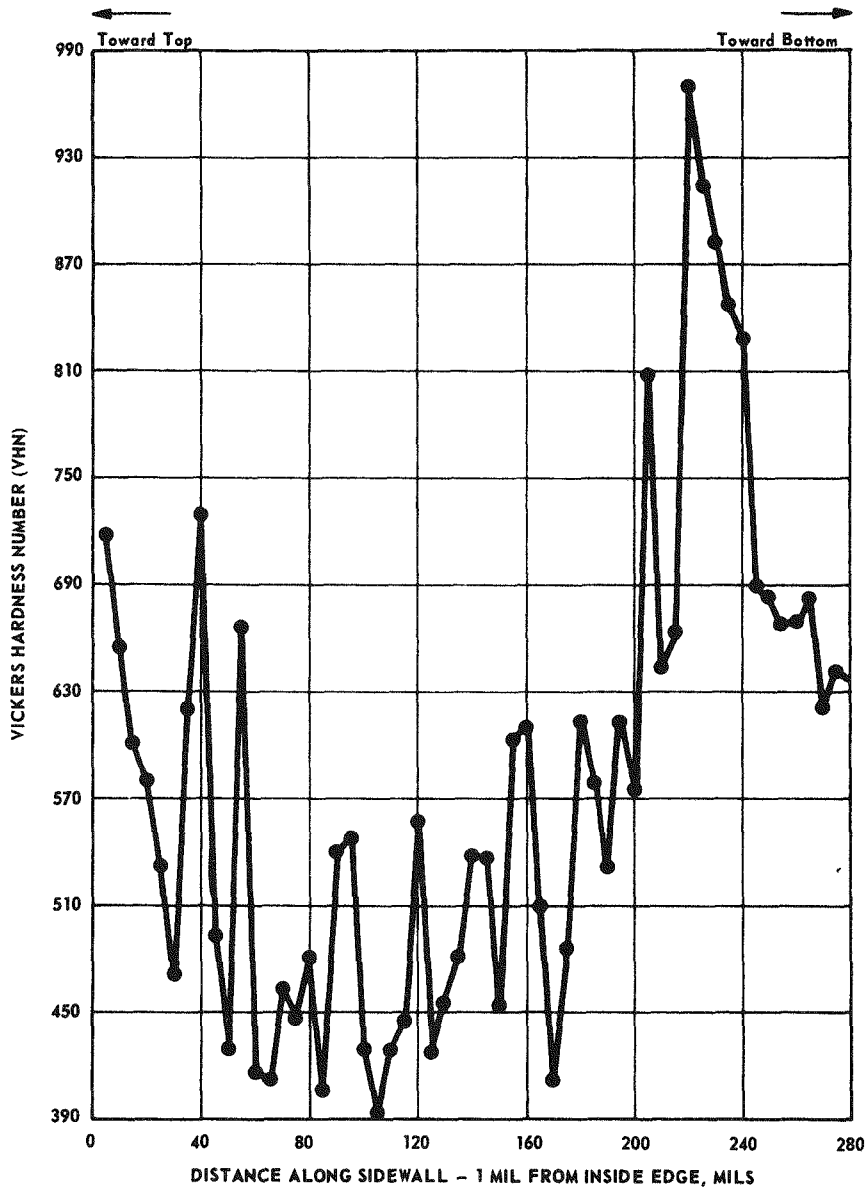


FIGURE 3 - Microhardness traverse of original 1173 K, 60-day F-type capsule.

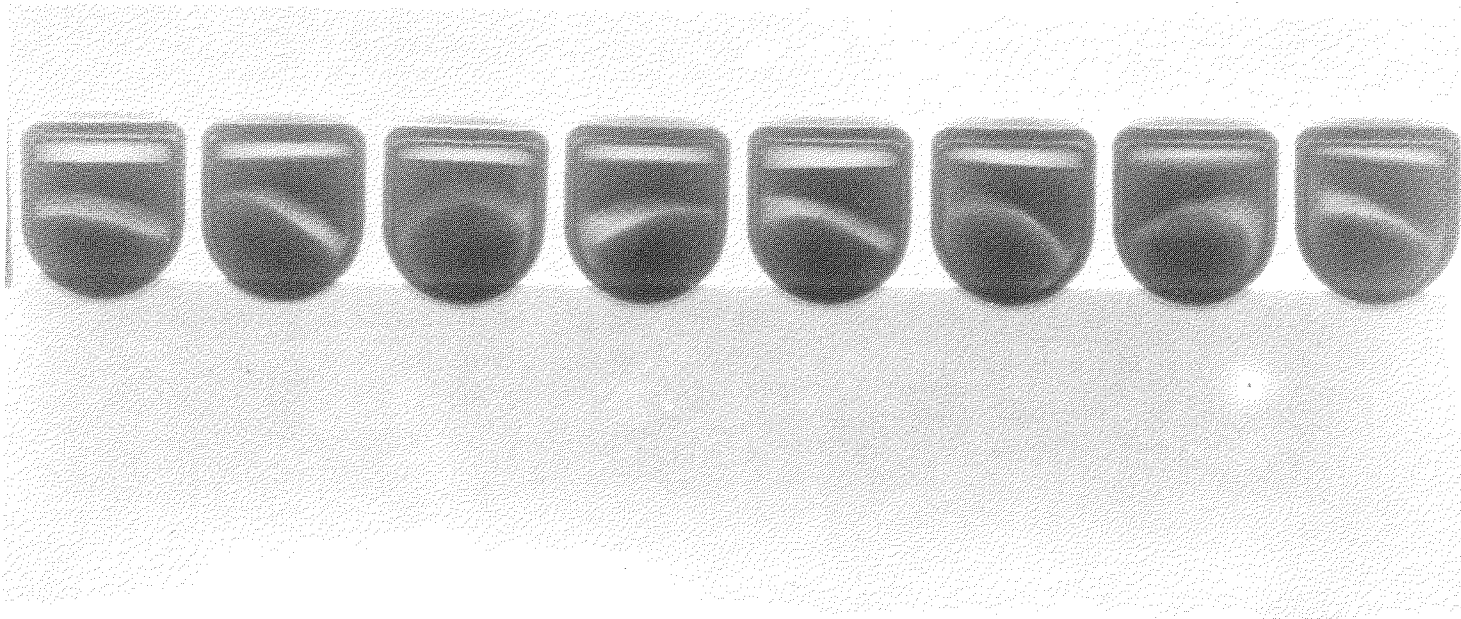


FIGURE 4 - Radiograph showing yttrium segregation as light band in fuel.

Table 6
 "F" TYPE SPECIMEN DATA

Specimen	Sample Origin	O ₂ (ppm)	N ₂ (ppm)	Average Hardness (VHN)
Fueled Control (No Heat Treatment)	Liner Side	107	7	235
	Liner Dome	151	7	254
	Strength Member Side	143	2	238
	Strength Member Dome	147	53	248
60 days @ 1073 K	Liner Dome	37	49	250
	Liner Side	321	80	260
	Strength Member Dome	74	31	255
	Strength Member Side	10	50	251
60 days @ 1173 K	Liner Dome	1070	100	252
	Liner Side	1883	110	328
	Strength Member Dome	29	72	263
	Strength Member Side	23	45	255
240 days @ 873 K	Liner Side	72	2	291
	Liner Bottom	220	11	262
	Strength Member Side	52	20	253
	Strength Member Bottom	56	11	238
240 days @ 1073 K	Liner Side	1184	3	541
	Liner Bottom	452	1	581
	Strength Member Side	91	20	247
	Strength Member Bottom	53	20	229
240 days @ 1173 K	Liner Side	1330	6	816
	Liner Bottom	>2000	11	728
	Strength Member Side	69	49	243
	Strength Member Bottom	79	59	240
2 yr @ 873 K	Liner Sidewall	156	18	249
	Liner Dome	158	16	260
	Strength Member Sidewall	48	<5	252
	Strength Member Dome	45	6	260
2 yr @ 1073 K	Liner Sidewall	1630	42	634
	Liner Dome	2010	10	621
	Strength Member Sidewall	60	30	256
	Strength Member Dome	284	36	260
2 yr @ 1173 K	Liner Sidewall	2543	96	717
	Liner Dome	3667	40	834
	Strength Member Sidewall	61	44	265
	Strength Member Dome	106	102	296

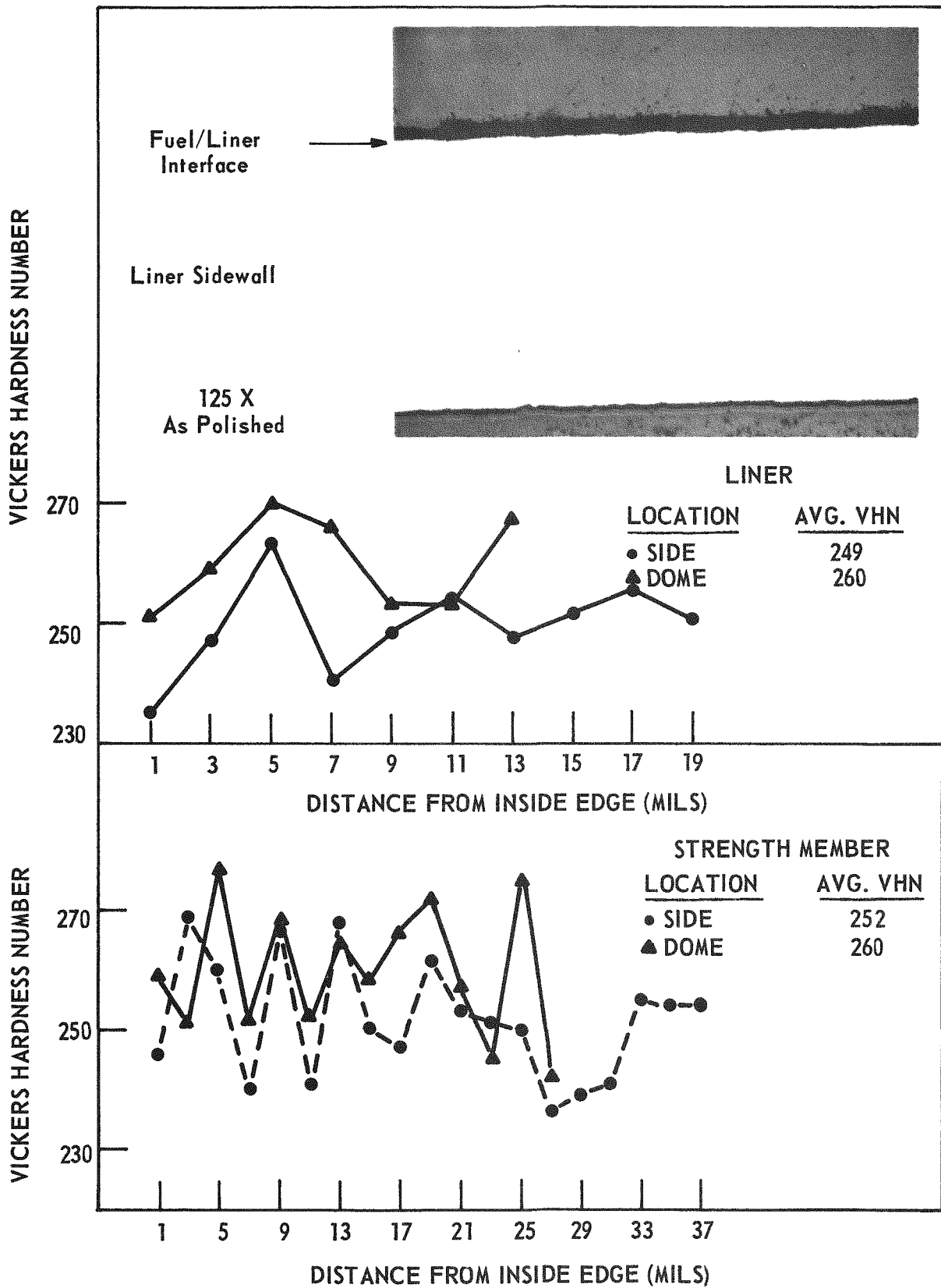


FIGURE 5 - Photomicrograph and microhardness traverses for 873 K, 2-yr F-type capsule.

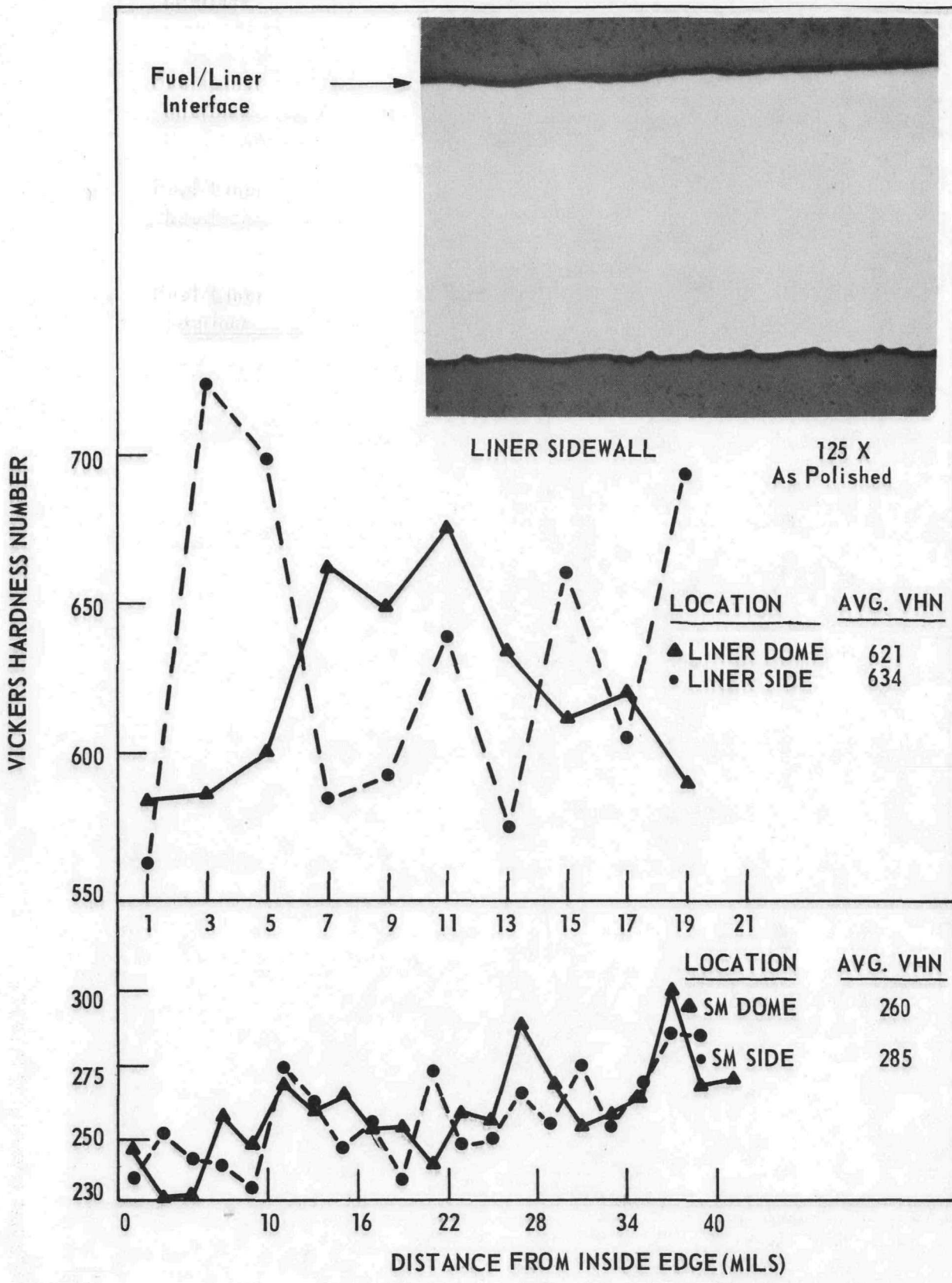


FIGURE 6 - Photomicrograph and microhardness traverses for 1073 K, 2-yr F-type capsule.

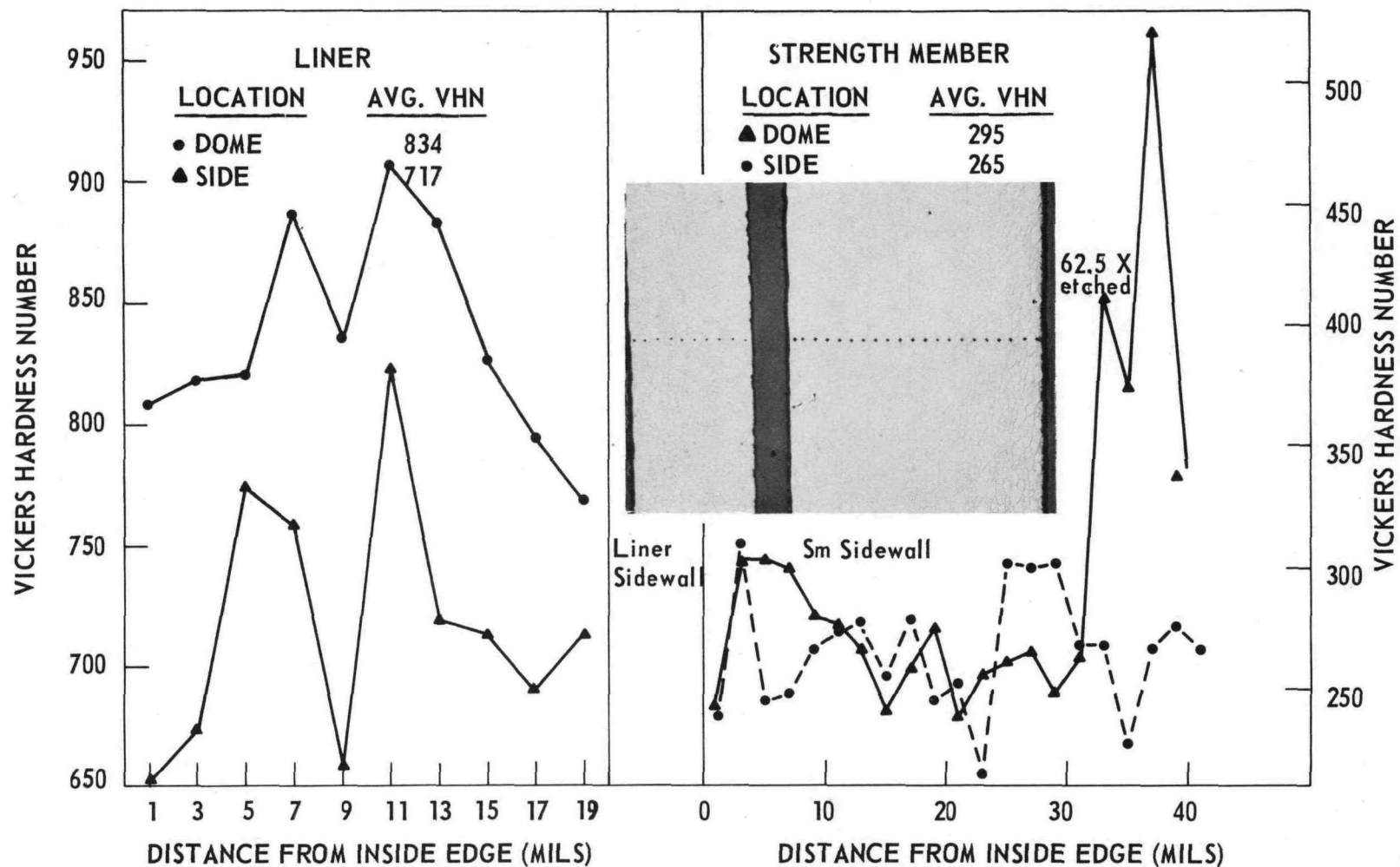


FIGURE 7 - Photomicrograph and microhardness traverses for 1173 K, 2-yr F-type capsule.

to the predominance of solid-state oxygen transport under these conditions. The results of the inhomogeneous capsules tend to support the latter hypothesis, although there is also independent evidence of the former.⁷

Further insight was gained when the original 1073 K, 60-day capsule was examined. Apparently the fuel/yttrium mixture was close to the weld during closure, since some of this material was found melted near the weld. Although this capsule had to be replaced, the data obtained were significant because the T-111 in the vicinity of the melted material was significantly more ductile than anywhere else on the liner. This effect was attributed to the reduction of the fuel when the PuO₂/Y material was heated to an elevated temperature; therefore it was decided to try to use this technique to force the reduction process.

Pretreatment Studies

Three F-type capsules were heated to temperatures of 1573 K, 1673 K, and 1723 K, respectively, for 1 hr, then placed on test at 1173 K for 60 days. A fourth specimen was "pretreated" at 1673 K for 1 hr and then examined without any aging.

Microhardness traverses were made across the liner and strength member of each specimen. Plots of the values obtained from each specimen are given in Figures 8 through 11. Also, the average hardness values for the domes and sides of the liners are listed in Table 7 along with oxygen and nitrogen analysis results.

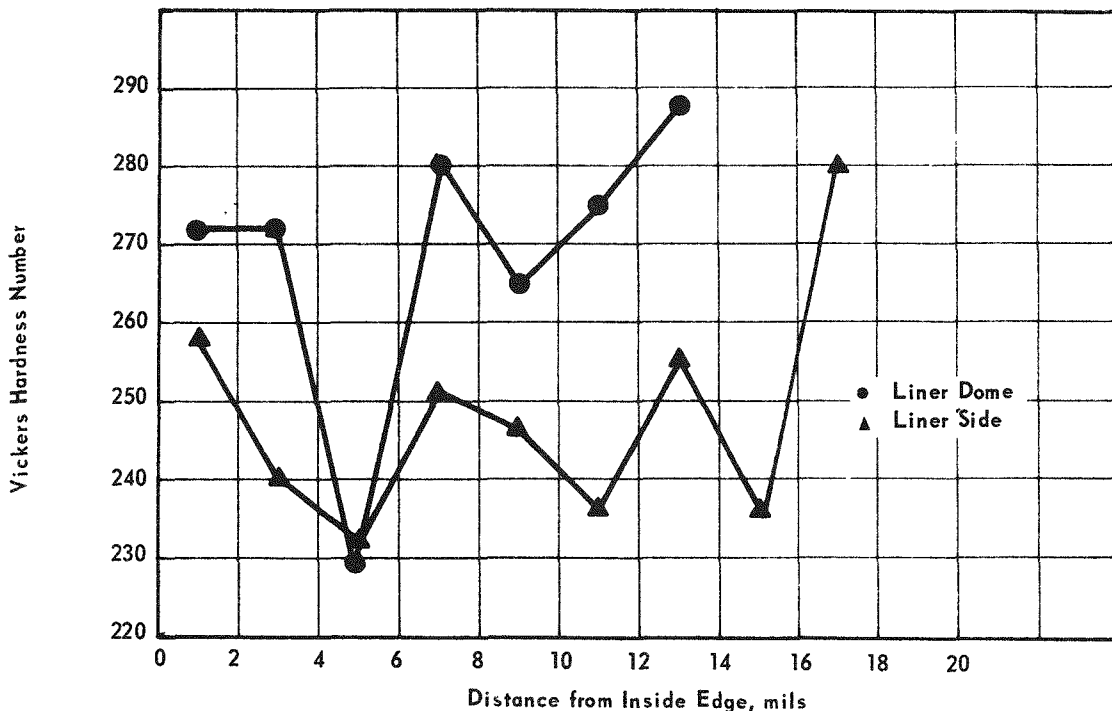


FIGURE 8 - Microhardness traverses for pretreated capsule (1 hr @ 1573 K) aged at 1173 K for 60 days.

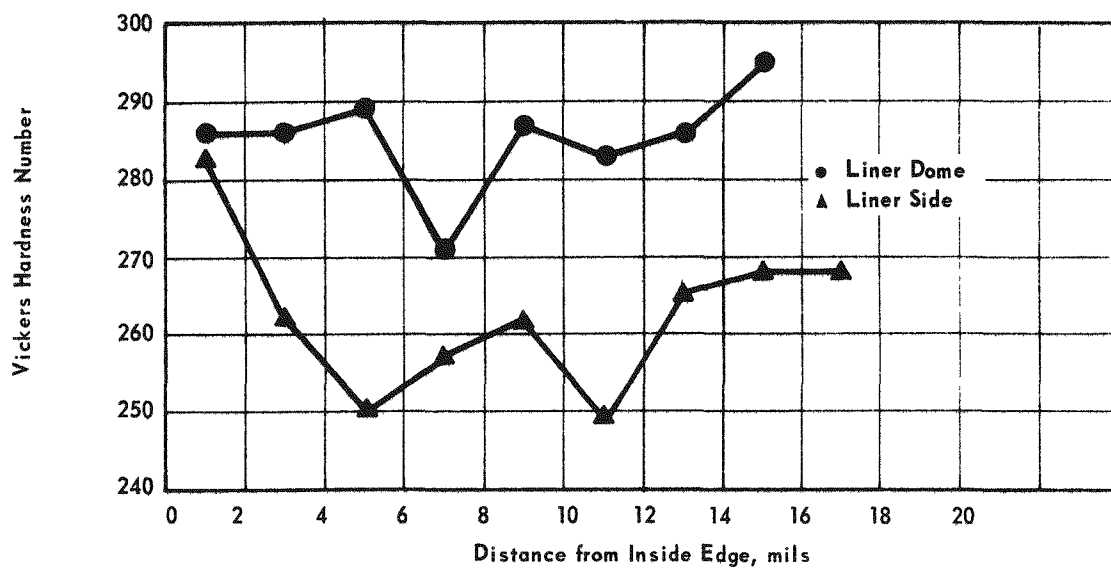


FIGURE 9 - Microhardness traverses for pretreated capsule (1 hr @ 1673 K) aged at 1173 K for 60 days.

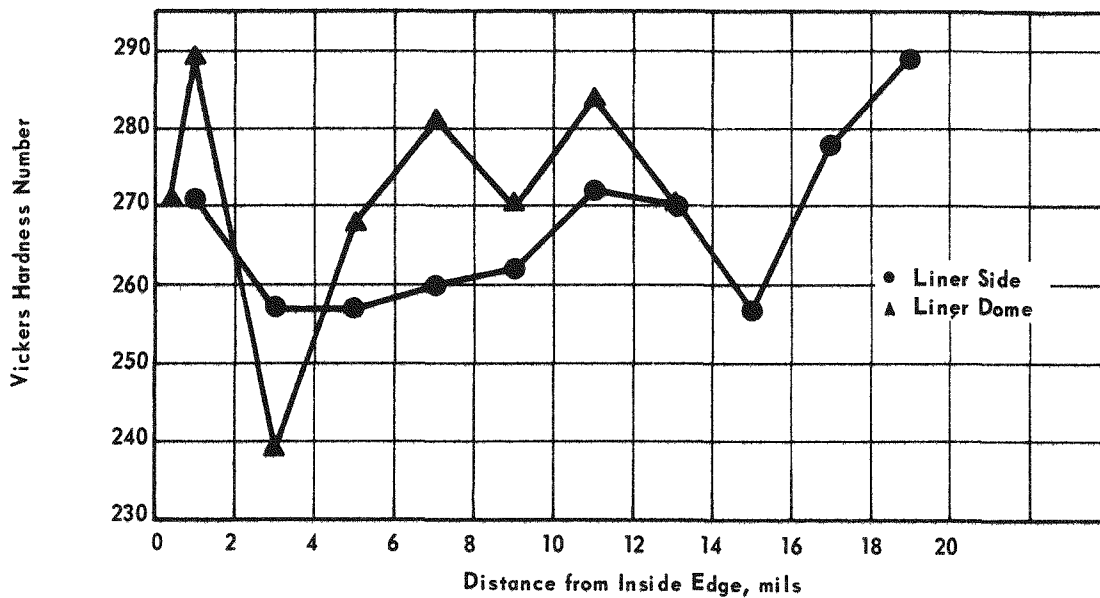


FIGURE 10 - Microhardness traverses for pretreated capsule (1 hr @ 1673 K) - no aging.

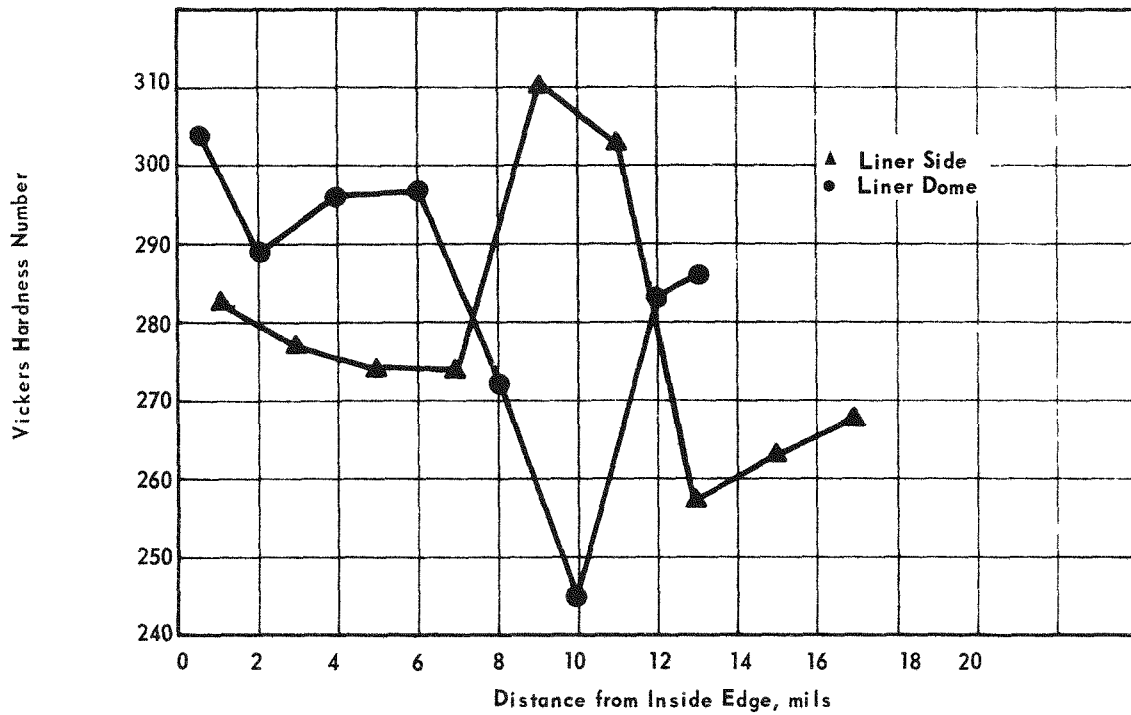


FIGURE 11 - Microhardness traverses for pretreated capsule (1 hr @ 1723 K) aged at 1173 K for 60 days.

Table 7

INITIAL PRETREATMENT STUDY RESULTS

Conditions	Sample Origin	O ₂ (ppm)	N ₂ (ppm)	Average Hardness (VHN)
Pretreated at 1573 K followed by 60 days at 1173 K	Liner Side	187	14	248
	Liner Bottom	134	14	269
	Strength Member Side	101	20	
	Strength Member Dome	155	332	
Pretreated at 1673 K followed by 60 days at 1173 K	Liner Side	286	21	263
	Liner Bottom	151	12	285
	Strength Member Side	131	64	
	Strength Member Bottom	203	29	
Pretreated at 1723 K followed by 60 days at 1173 K	Liner Side	547	35	279
	Liner Bottom	429	45	284
	Strength Member Side	145	11	
	Strength Member Bottom	157	12	
Pretreated at 1673 K; no follow-up heat treatment	Liner Side	327	24	267
	Liner Bottom	220	14	272
	Strength Member Side	133	14	
	Strength Member Bottom	123	13	

In general, the hardness of T-111 liners increases with increasing pretreatment temperature; however, the values are low, indicating that the liners are ductile and contain an insignificant level of effective interstitial contamination. The oxygen can be considered to be associated with the overaged hafnia precipitates and, therefore, has essentially no effect on mechanical properties.^{8,9} Most important, however, the data indicate that, after pretreatment, no additional oxygen was introduced into the liner during the 60 days at 1173 K. This cannot be said of the equivalent F-type capsule (Figure 3).

Based on these results, a compromise temperature of 1623 K was chosen for further study. Before aging studies were begun, however, it was decided to run a series of tests to investigate the effect of the form of the yttrium, the mechanical integrity of pretreated plutonia, and the effect of pretreatment of a capsule without yttrium. The specific tests are listed in Table 8. Data for the specimen that contained PuO₂ and no getter (specimen E) are shown in Figure 12. Without yttrium, embrittlement of the capsule occurred between 6 and 8 mils (152 to 203 μm) into the specimen from the fuel/metal interface. No reaction products were observed in the specimen; however, the inside edge of the specimen was much smoother and more even than the outside edge, indicating a slight general reaction at the inside surface.

Table 8

SPECIAL COMPATIBILITY SPECIMENS

<u>Sample Identification</u>	<u>Description^a</u>	<u>Purpose of Test</u>
A	PuO _{1.75} (2.56 g PuO ₂ + 0.140 g Y chips)	Determine if yttrium homogeneity is critical for pretreatment.
B	2.8 g PuO ₂ + 0.295 g Y foil liner } Y foil liner only (0.290 g) } 2.89 g PuO ₂ + 0.300 g Y foil liner }	Evaluate effectiveness and condition of yttrium foil liner.
C		
D		
E	2.8 g PuO ₂	Pretreatment reference capsule.
F	PuO _{1.75} (2.8 g PuO ₂ + 0.153 g Y powder) } PuO _{1.75} (2.8 g PuO ₂ + 0.153 g Y powder) }	Fines analysis of fuel before and after pretreatment.
G		

^aAll encapsulated in T-111 and pretreated for 1 hr at 1623 K.

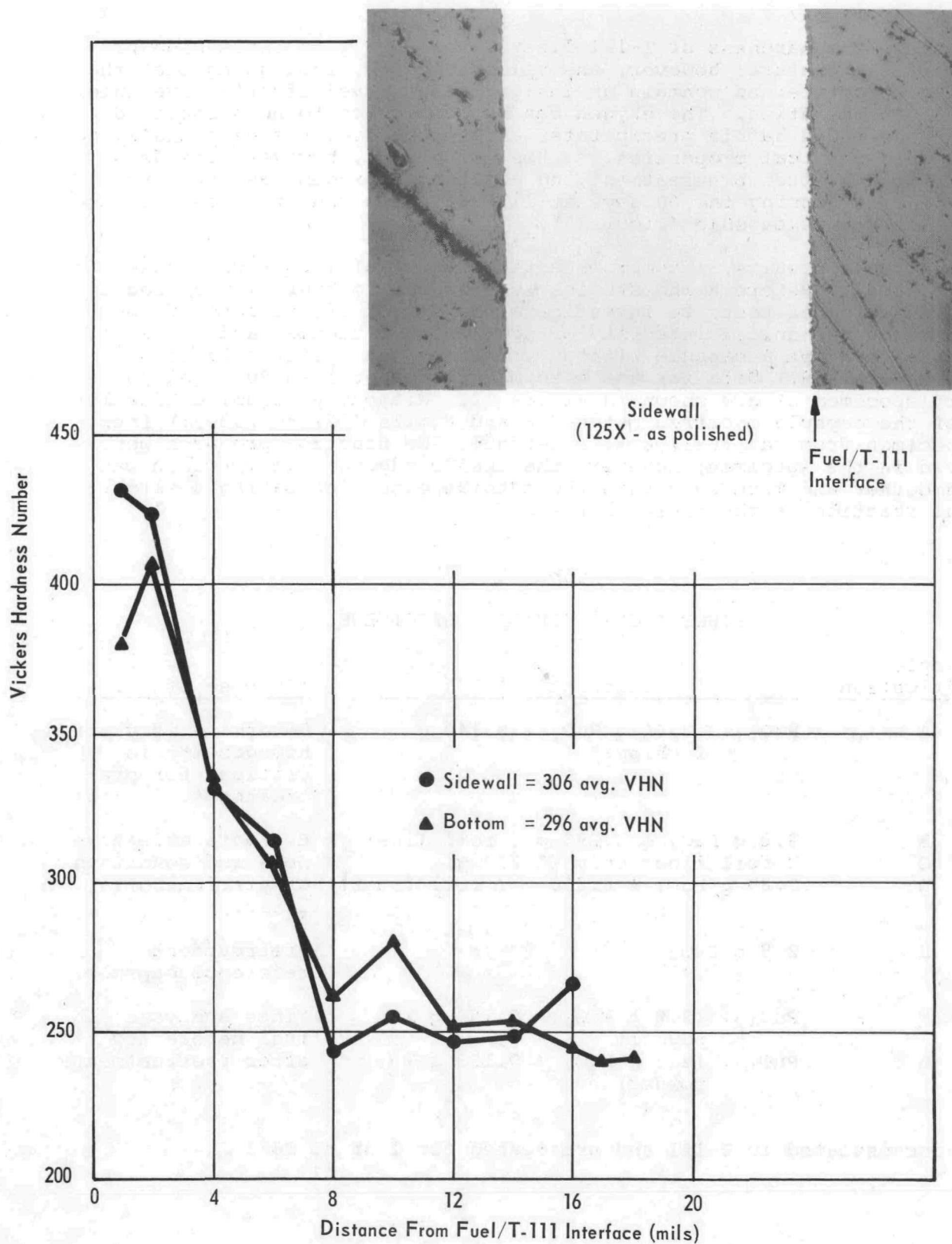


FIGURE 12 - Micrograph and microhardness traverses for Specimen E (reference capsule - PuO_2 , no γ - pretreated 1 hr at 1623 K).

Data for the duplicate fines generation specimens F and G, which were loaded with PuO₂ and yttrium powder, are shown in Figures 13 and 14, respectively. When a comparison is made to the data for the specimen loaded with PuO₂ only, the effectiveness of the yttrium powder is evident. Uptake of oxygen by the T-111 liner is nearly eliminated. Metallographic examination of the liners of the specimens revealed no evidence of reaction except for the presence of a thin (<5- μ m) white phase at spots along the fuel/metal interface of one specimen, as shown in Figure 15. This has recently been related to hafnium depletion of the T-111 at the interface and has no detrimental effect on the liner. Fines analyses of these specimens indicated no measurable increase in particles smaller than 5 μ m as a result of pretreatment.

Metallographic and microhardness data for specimen A, loaded with yttrium foil chips (0.254 mm thick x 3 mm square), appear to indicate that the chips are just as effective as the powder for getting the oxygen from the PuO₂ during pretreatment. The data are shown in Figure 15. Microhardness values were very similar to those obtained for the specimens that contained yttrium powder. The results of this test also imply that yttrium powder homogeneity would not be as critical in specimens if they were pretreated after fabrication.

Data obtained from the specimens that were lined with yttrium foil were not as favorable as for the specimens loaded with yttrium powder or chips. The exact reason for this is not known at this time, but appears to be related to the passivity of the large sheet surface as compared with the turnings or high-curvature corners of the chips. Data for the specimen that contained yttrium foil only (specimen C) are shown in Figure 16. As expected, the microhardness values are low. However, metallographic examination of the specimen revealed reaction zones between the yttrium foil and the T-111 liner in various areas of the specimen. The reaction products can be seen in the high-magnification photomicrograph in Figure 16. Metallographic examination of subsequent specimens revealed more of this eutectic reaction at the T-111/yttrium interfaces and the interfaces between the yttrium chips. Electron microprobe analysis showed the eutectic to be composed of high-silicon-bearing dendrites in a matrix high in yttrium. The silicon-yttrium phase diagram shows a eutectic at 1533 K with 13 at.% silicon. The yttrium foil in this specimen was very friable after the test. As such, particles of yttrium fell out during polishing, which gouged and scratched the polished surface of the T-111 liner, resulting in a rather-poor-quality micrograph.

Data for duplicate specimens B and D, which were lined with yttrium foil and contained PuO₂, are shown in Figures 17 and 18, respectively. Microhardness values across the sidewalls of the specimens indicate no oxygen contamination of the T-111. However, microhardness values across the domes of the specimens indicated embrittlement of the liner at the inside edge of the T-111. This is most probably related to the presence of the PuO₂, since it was not observed in Specimen C. It was subsequently found in other pretreated specimens, especially those using chips, but was much more prominent and serious in those using foil as a getter.

P-Type Capsules

As shown in Table 5, capsules pretreated for 1 hr at 1623 K were placed on test at 873 K, 1173 K, and 1373 K for times of 60 days, 240 days, and 2 yr. In the case of the 60-day specimen, microhardness traverses were conducted across the cap, sidewall, and dome of the liners and strength members of

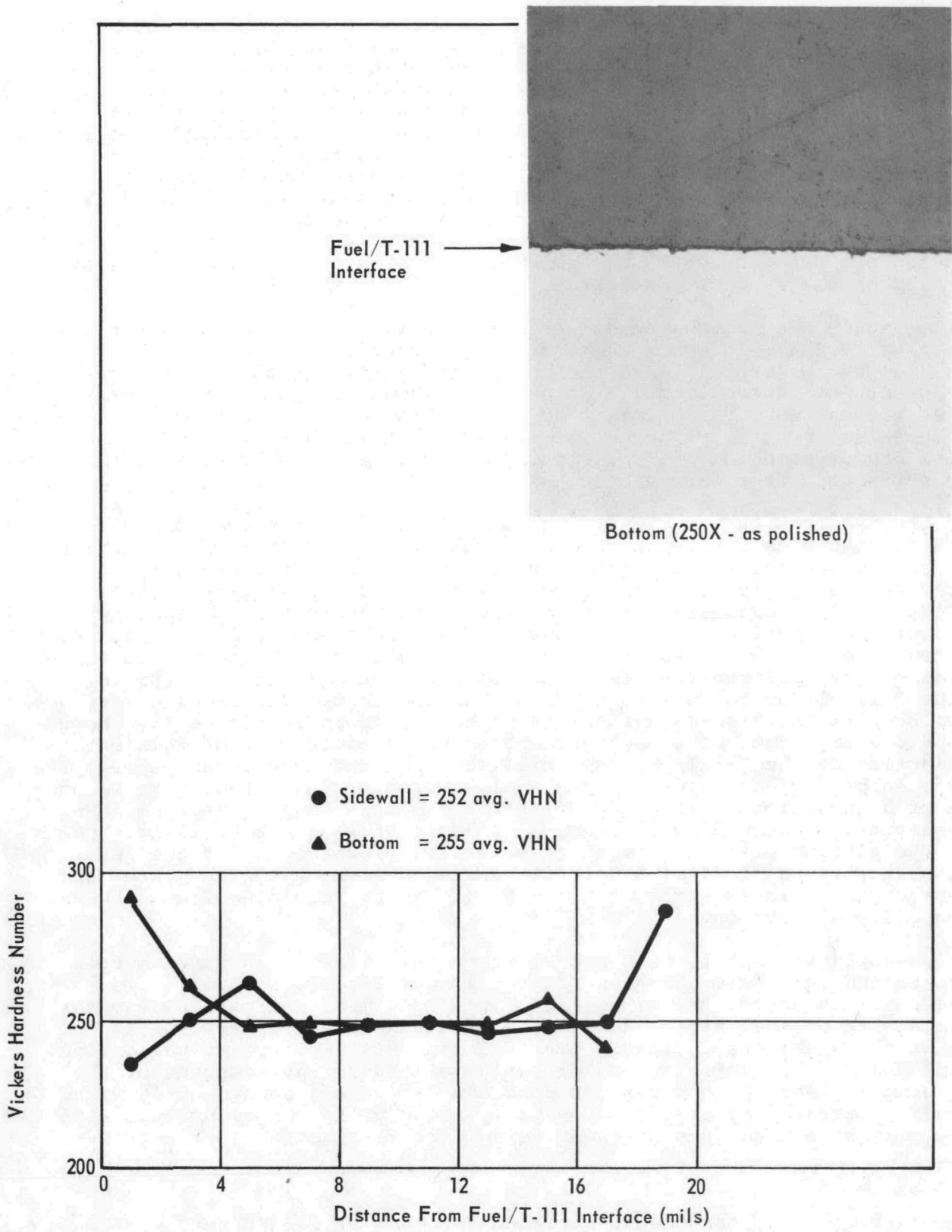


FIGURE 13 - Micrograph and microhardness traverses for specimen F ($\text{PuO}_2 + \text{Y}$ powder - for fines analysis - pretreated 1 hr at 1623 K).

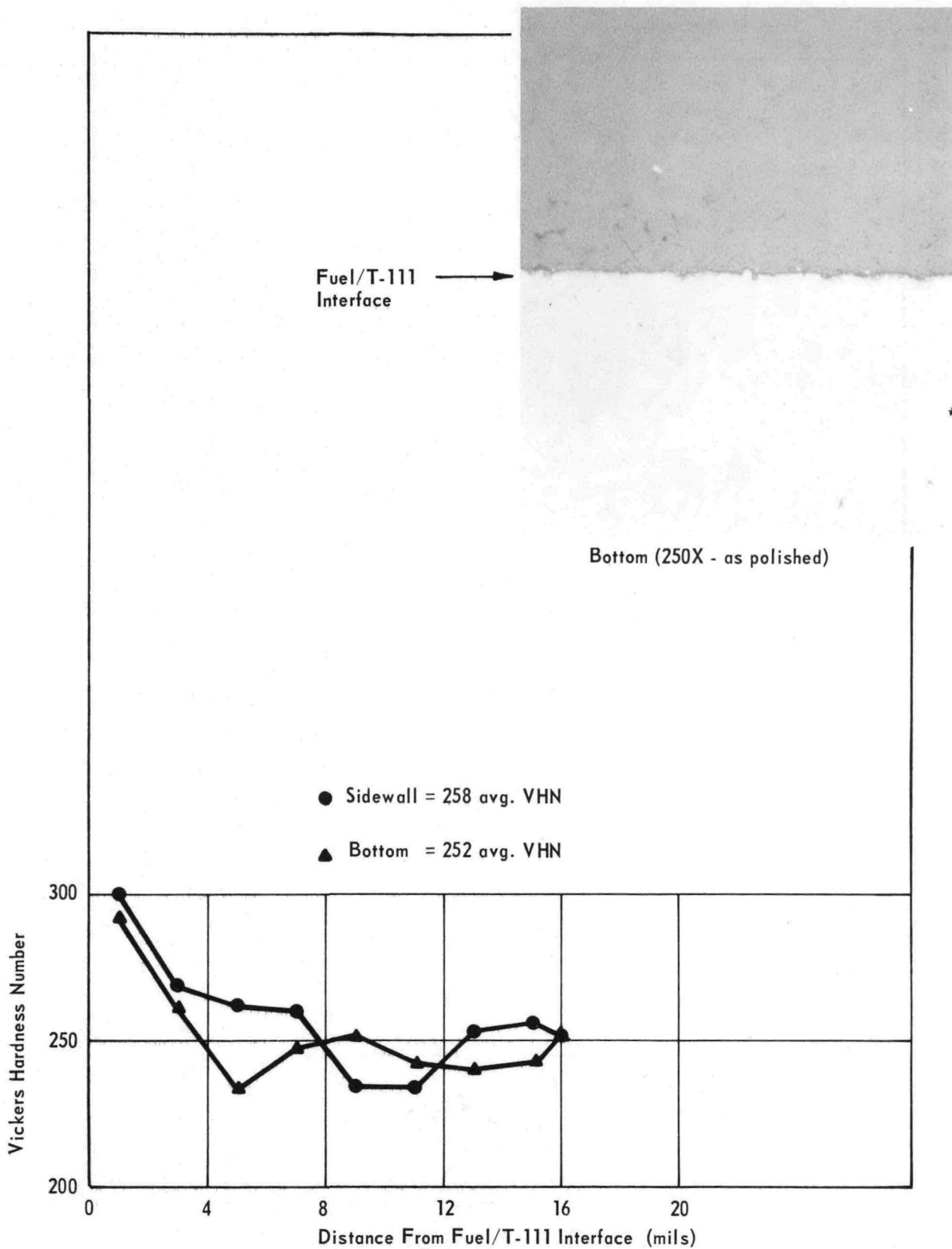


FIGURE 14 - Micrograph and microhardness traverses for specimen G ($\text{PuO}_2 + \text{Y}$ powder - duplicate fines analysis capsule - pretreated 1 hr at 1623 K).

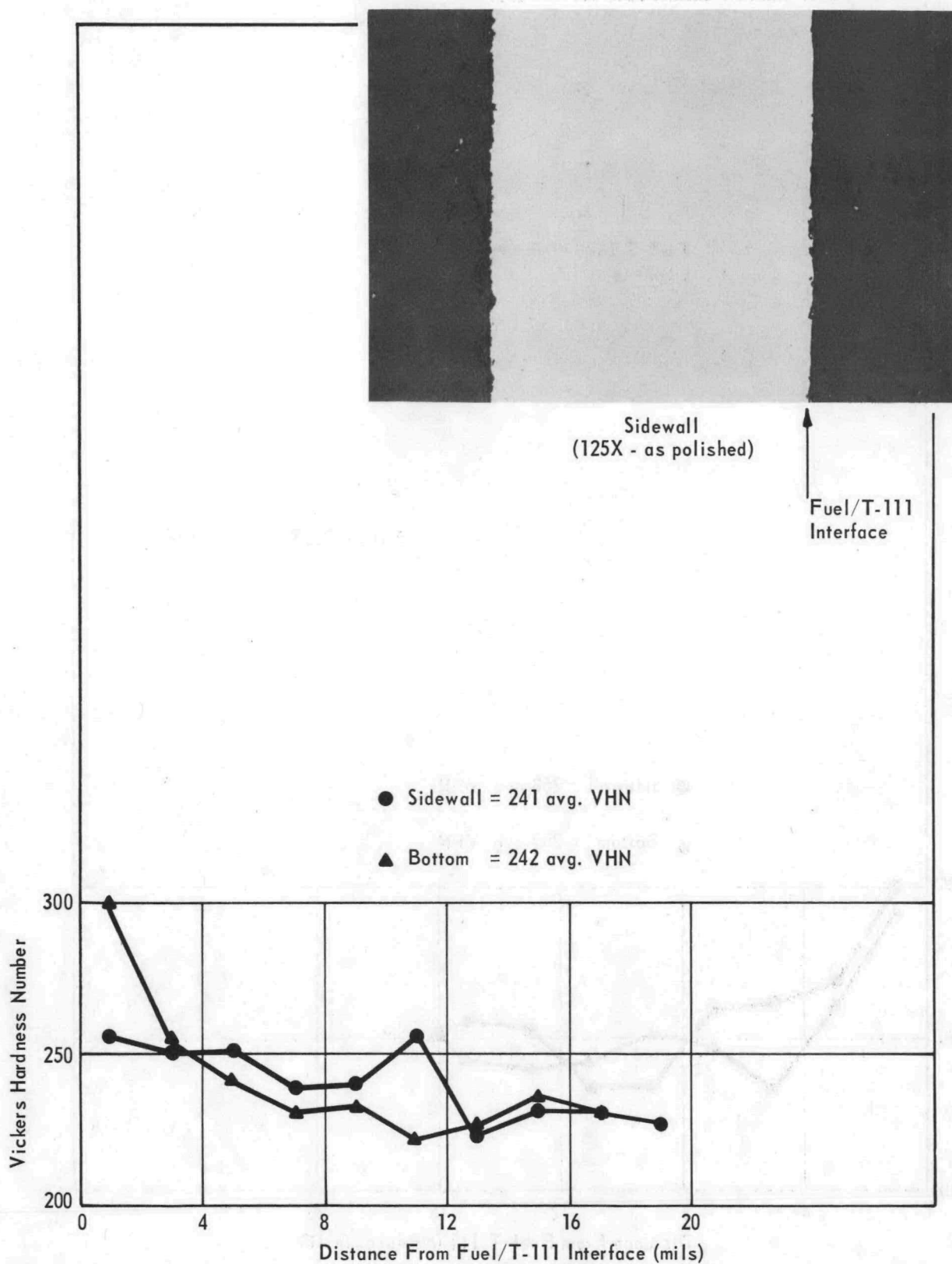


FIGURE 15 - Micrograph and microhardness traverses for specimen A ($\text{PuO}_2 + \text{Y}$ chips - pretreated 1 hr at 1623 K).

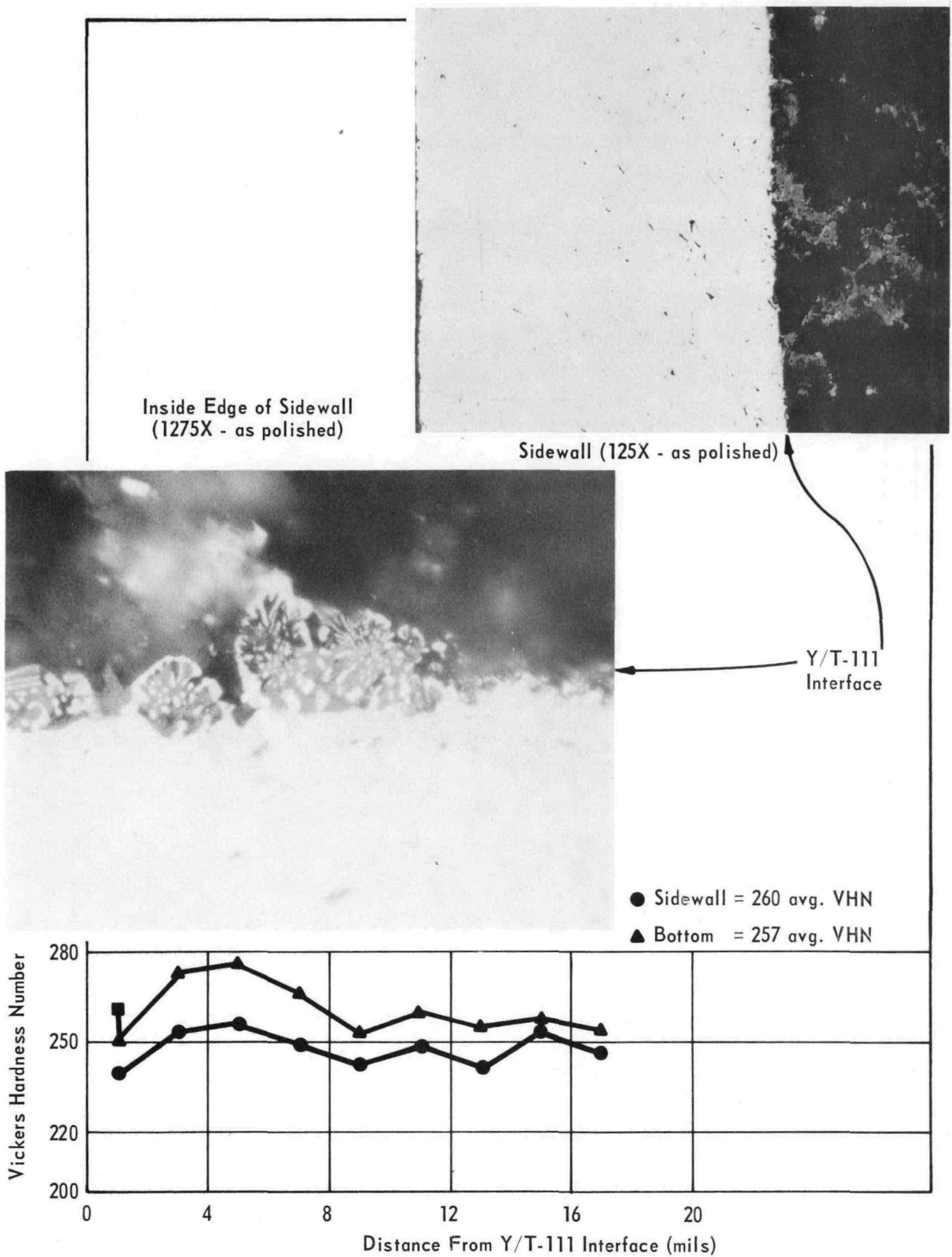


FIGURE 16 - Micrographs showing reaction zone and microhardness traverses for specimen C (Y foil liner only - pretreated 1 hr at 1623 K).

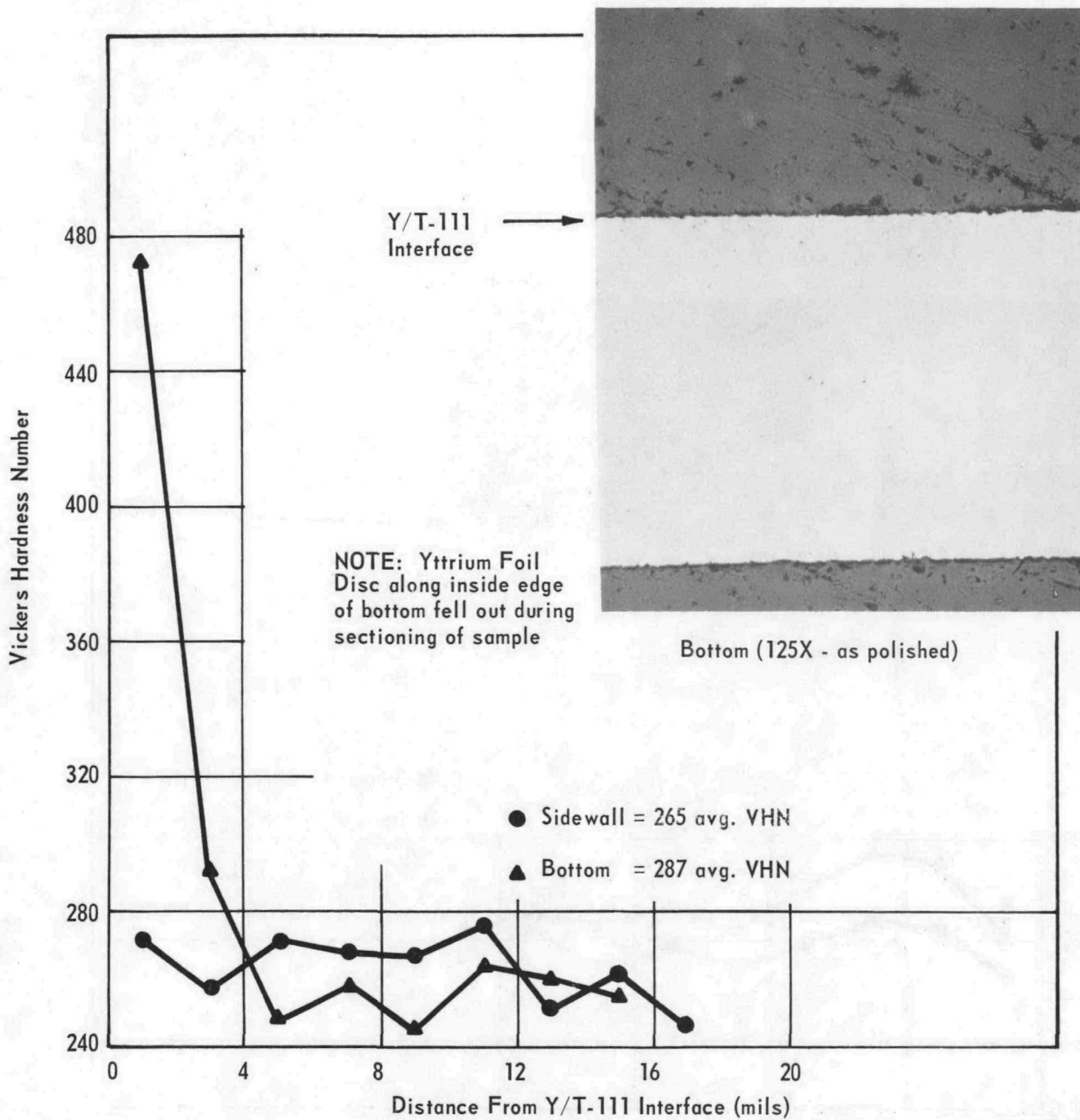


FIGURE 17 - Micrograph and microhardness traverses for specimen B (PuO_2 + Y foil liner - pretreated 1 hr at 1623 K).

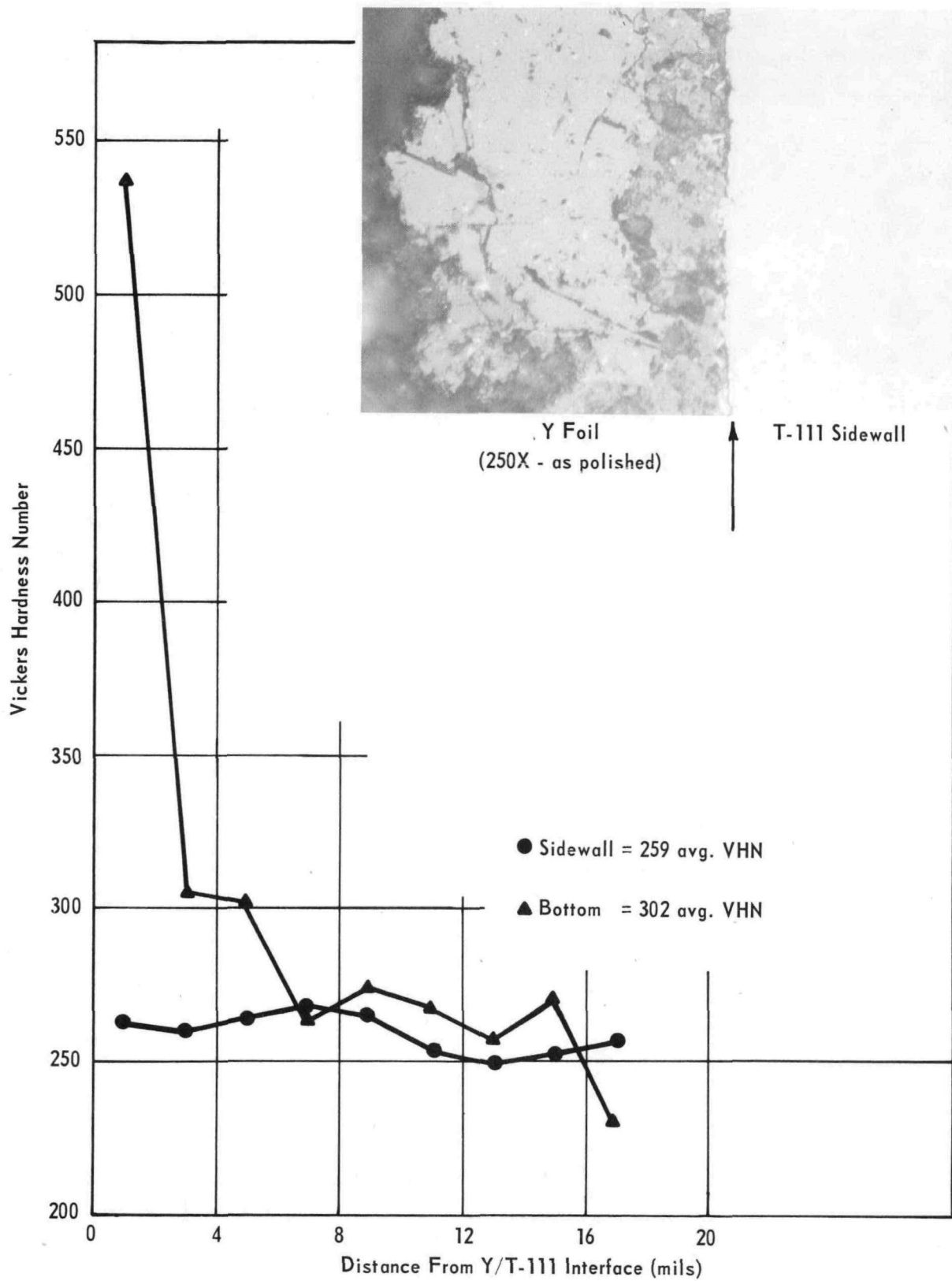


FIGURE 18 - Micrograph showing reaction zone and microhardness traverses for specimen D (PuO_2 + Y foil liner - pretreated 1 hr at 1623 K).

the specimens. The results for the specimens tested at 873 K and 1173 K are shown in Figures 19 and 20. There were no indications of embrittlement of the liners and strength members of either capsule. A very slight microhardness gradient is indicated on the outside edge of the strength member of the specimen tested at 1173 K (Figure 20), suggesting the possibility of either diffusion of components from the Hastelloy-C

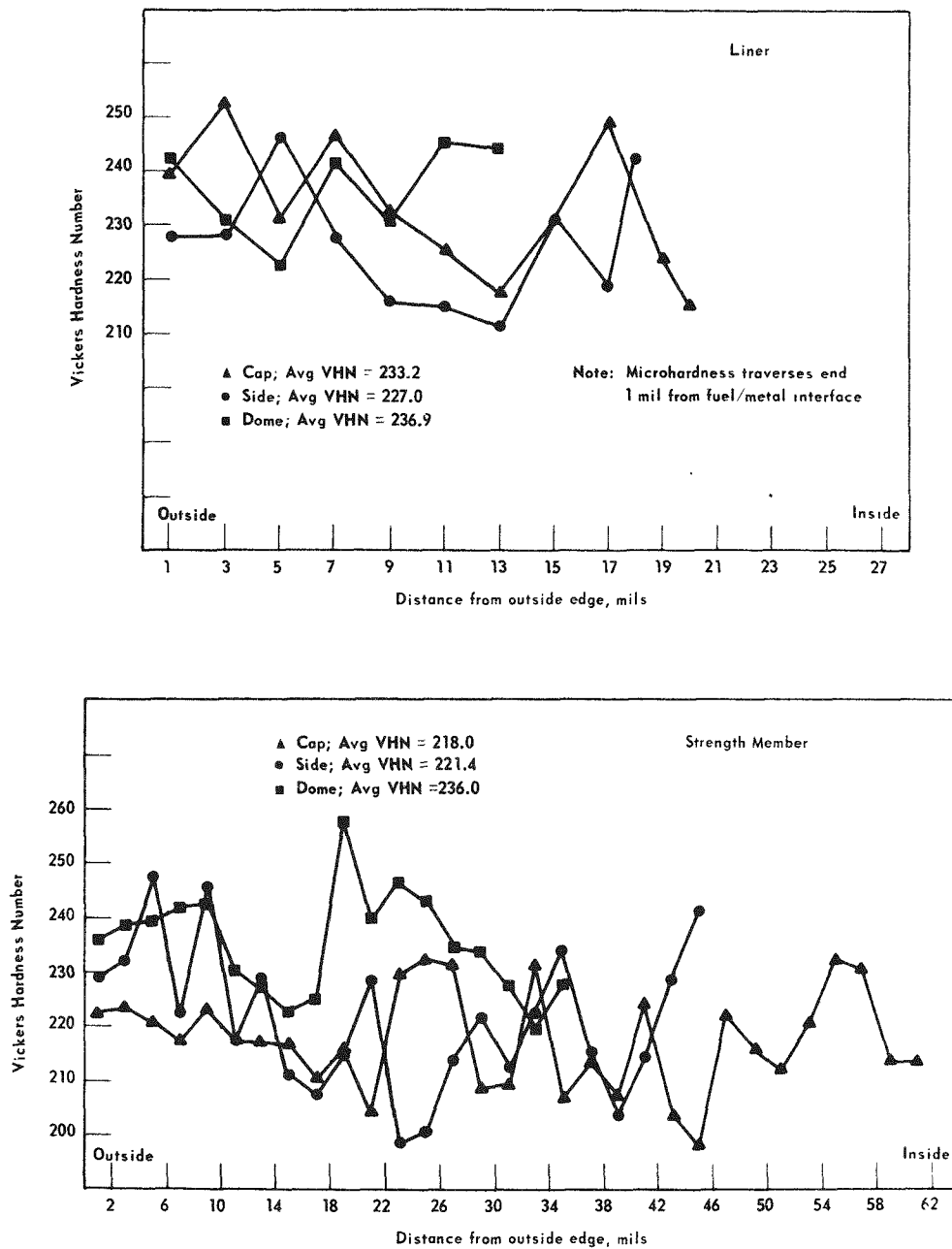


FIGURE 19 - Microhardness traverses for 873 K, 60-day P-type capsule.

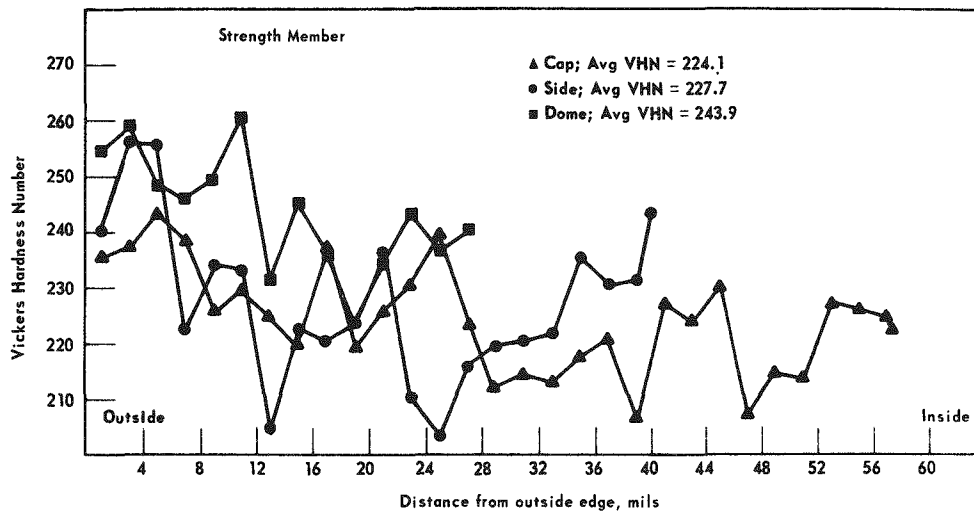
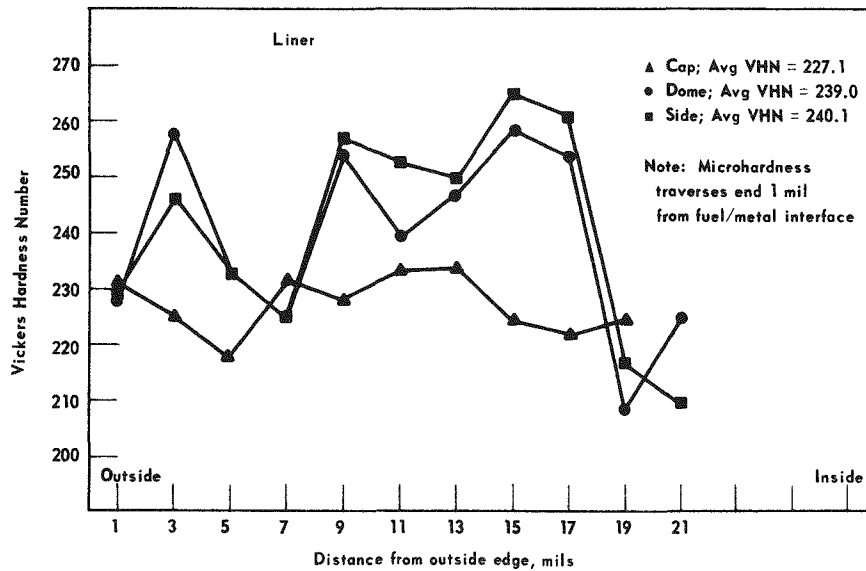
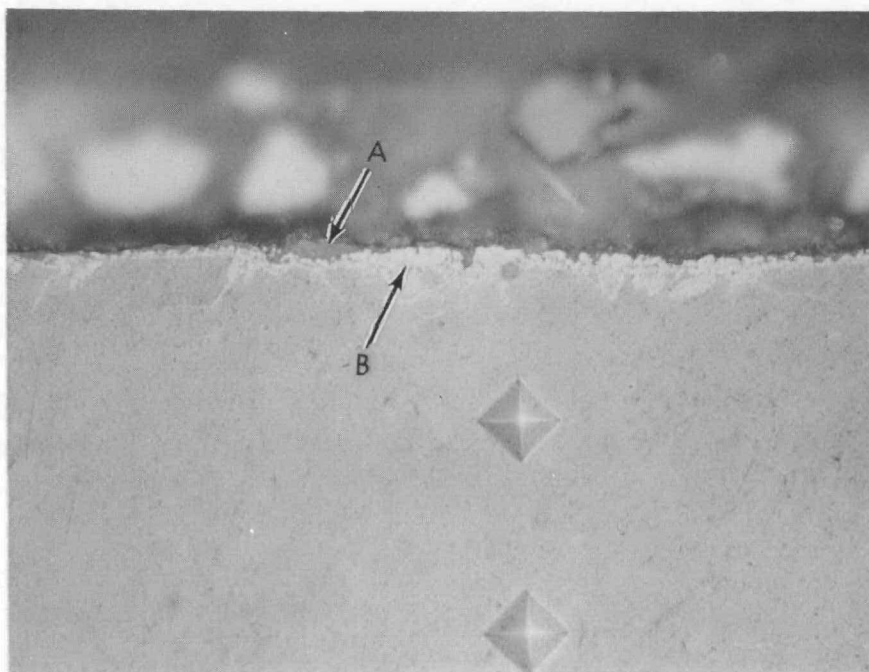


FIGURE 20 - Microhardness traverse for 1173 K, 60-day P-type capsule.

clad, or of nitrogen through the clad, to a depth of approximately 6 mils into the strength member. Metallographic examination of these specimens in the as-polished condition revealed no evidence of detrimental reaction. The aforementioned white-appearing phase was observed along the fuel/metal interface of the specimens penetrating up to 5 μ m into the T-111 liner. Also very small gray deposits, such as shown in Figure 21, were seen randomly located along the fuel/metal interface. This same phenomenon was observed in the original pretreated specimens and has been identified as yttrium adhering to the T-111 surface. Microhardness traverses across the liner and strength member of the specimen tested for 60 days at 1373 K are shown in Figure 22. The liner shows obvious evidence of embrittlement,



600X - as-polished condition

FIGURE 21 - Photomicrograph of T-111 liner showing gray surface deposit (A), and white-appearing phase (B).

particularly in the dome region, while the gradient from the outside of the strength member indicates the clad was not completely effective at this temperature.

Oxygen, nitrogen, and average hardness numbers for all three capsules are summarized in Table 9. If oxygen numbers are compared with those of the F-type capsules, it is evident that pretreatment greatly restricts oxidation, since the 1173 K F-type specimen is actually more embrittled than the corresponding 1373 K P-type specimen.

The 240-day tests showed little change from the 60-day results as far as oxygen embrittlement of the liners at or below 1173 K is concerned. Except for the usual localized spots revealed along the fuel/liner interface of the specimens by etching, there is no indication of reaction in, or embrittlement of, the liner or strength member of the specimen tested at 873 K (Figure 23).

Data for the specimen that was tested for 240 days at 1173 K are shown in Figure 24. Except for two slightly higher values (approximately 300 VHN) near the middle of the liner sidewall, the liner of the specimen showed no evidence of embrittlement. A microhardness gradient increasing toward the outside edge is indicated for the sidewall and dome of the strength member of the specimen tested at 1173 K, suggesting nitrogen diffusion through the clad into the strength member.

Table 9

OXYGEN, NITROGEN AND AVERAGE MICROHARDNESS
DATA FOR 60-DAY P-TYPE SPECIMENS

Sample Temperature (°K)	Location	O ₂ (ppm)	N ₂ (ppm)	Average VHN
873	Liner Wall	183	14	227
	Liner Dome	156	16	237
	Strength Member Wall	83	37	221
	Strength Member Dome	82	34	236
1173	Liner Wall	266	26	240
	Liner Dome	164	8	239
	Strength Member Wall	188	78	228
	Strength Member Dome	96	52	244
1373	Liner Wall	1006	27	346
	Liner Dome	1000	42	340
	Strength Member Wall	113	134	231
	Strength Member Dome	837	213	238

Photomicrographs and microhardness traverses of the liner and strength member of the specimen tested for 240 days at 1373 K are shown in Figures 25 and 26. Slight embrittlement of the sidewall of the liner of the specimen is indicated by an average VHN of 323. However, microhardness values across the liner dome are low. A photomicrograph of the outside edge of the strength member of the 1373 K specimen is shown in Figure 26 along with microhardness traverses across the strength member. The high microhardness values at the outside edge of the strength member are in the white phase reaction area shown in the photomicrograph. This reaction layer exists around the entire outer surface of the strength member of the specimen. Electron microprobe analysis shows it consists predominantly of components from the Hastelloy-C clad. Chromium, iron, nickel, tantalum, and tungsten were found, with a phase structure quite similar to that reported for Hastelloy-X/tantalum interaction.¹⁰

Oxygen, nitrogen, and average VHN values for liners and strength members of the 240-day pretreated specimens are shown in Table 10. Except for the slightly higher nitrogen values for the strength member of the 1173 K specimen, data for the specimens tested for 240 days at 873 K and 1173 K are very similar. The higher nitrogen value for the strength member of the 1173 K specimen correlates with the microhardness gradient near its outside edge, described previously. Increased nitrogen diffusion through the clad into the strength member with increased temperature also accounts for the higher nitrogen values for the strength member of the specimen tested at 1373 K. Considerable oxygen contamination of the liner occurred in the 1373 K specimen. The strength member also shows some slight oxygen pickup. However, the microhardness values are much lower than would be expected for T-111 containing this much oxygen. This could result if the 240-day, 1373 K heat treatment overaged the T-111 alloy and incoherent HfO₂ precipitates formed. This material would then be in a more ductile condition.

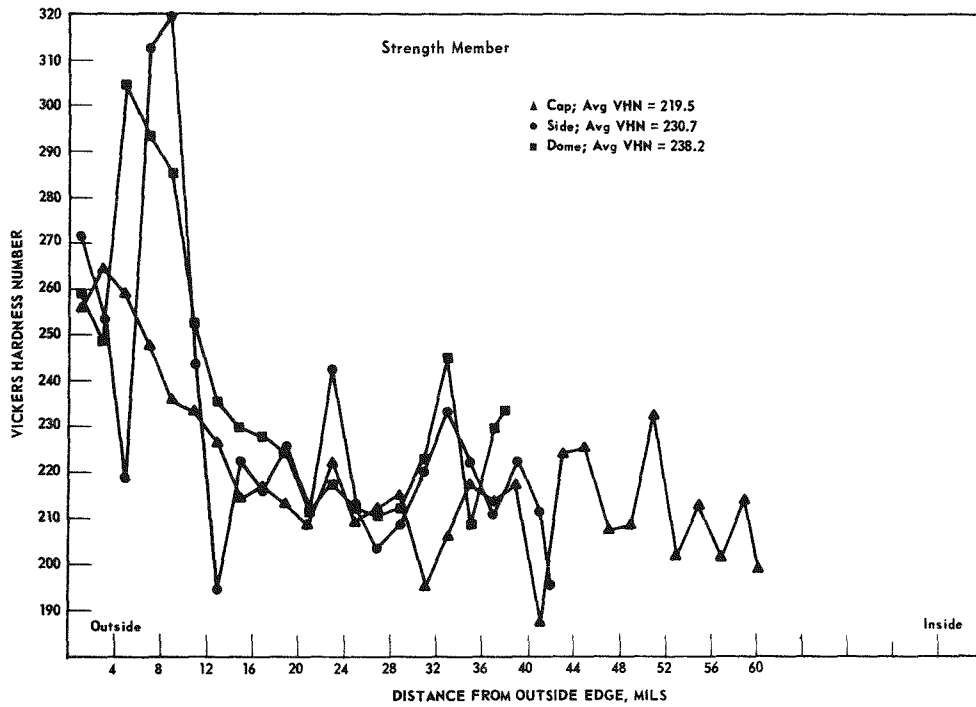
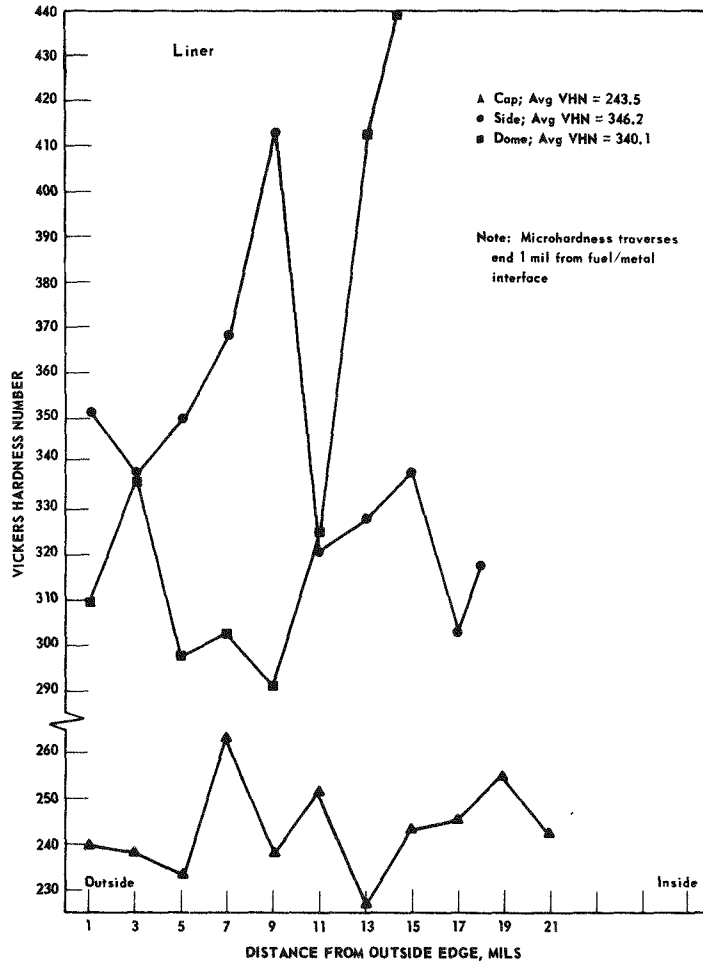


FIGURE 22 - Microhardness traverses for 1373 K, 60-day P-type capsule.

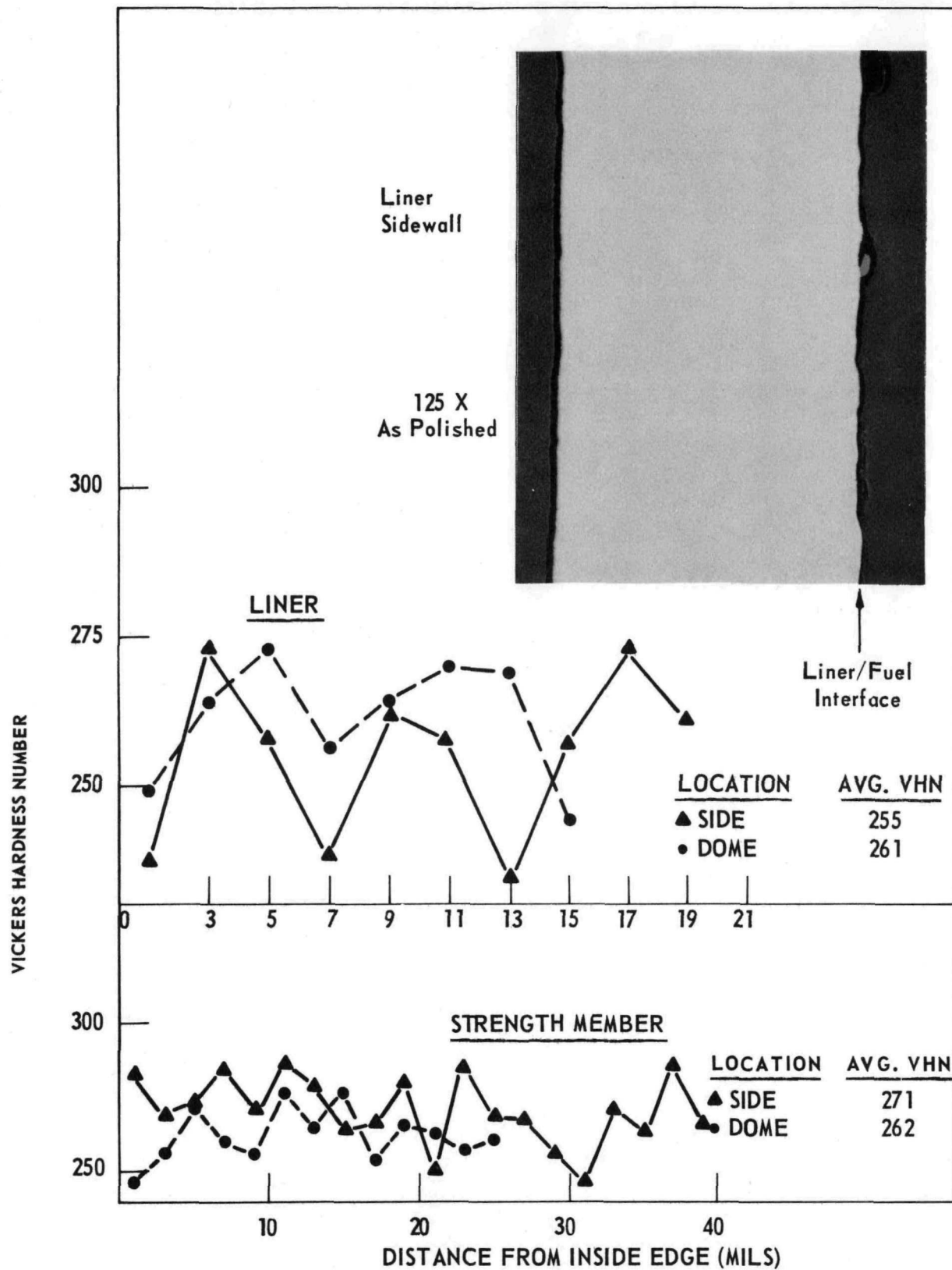


FIGURE 23 - Photomicrograph and microhardness traverses for 873 K, 240-day P-type capsule.

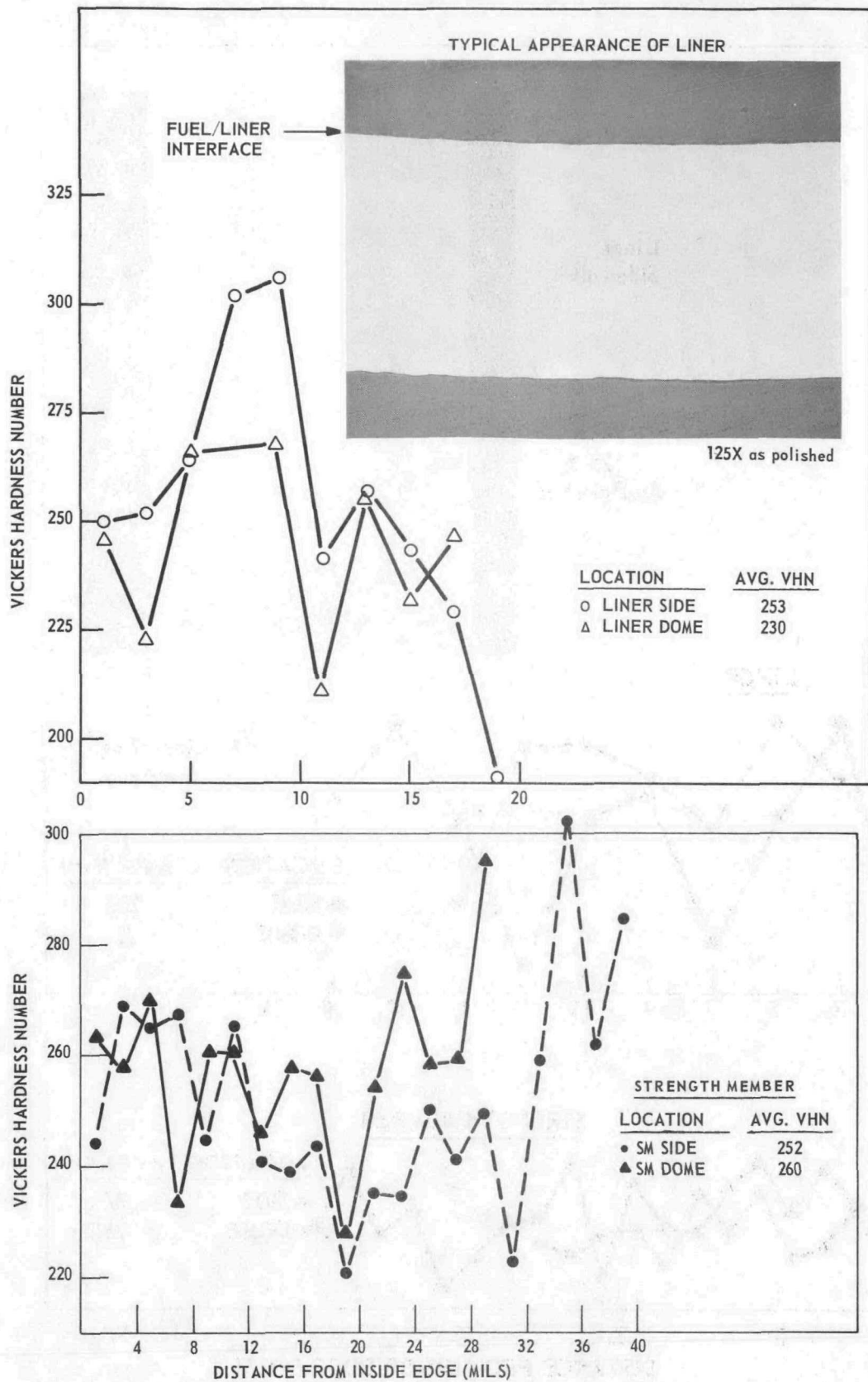


FIGURE 24 - Photomicrograph and microhardness traverses for 1173 K, 240-day P-type capsule.

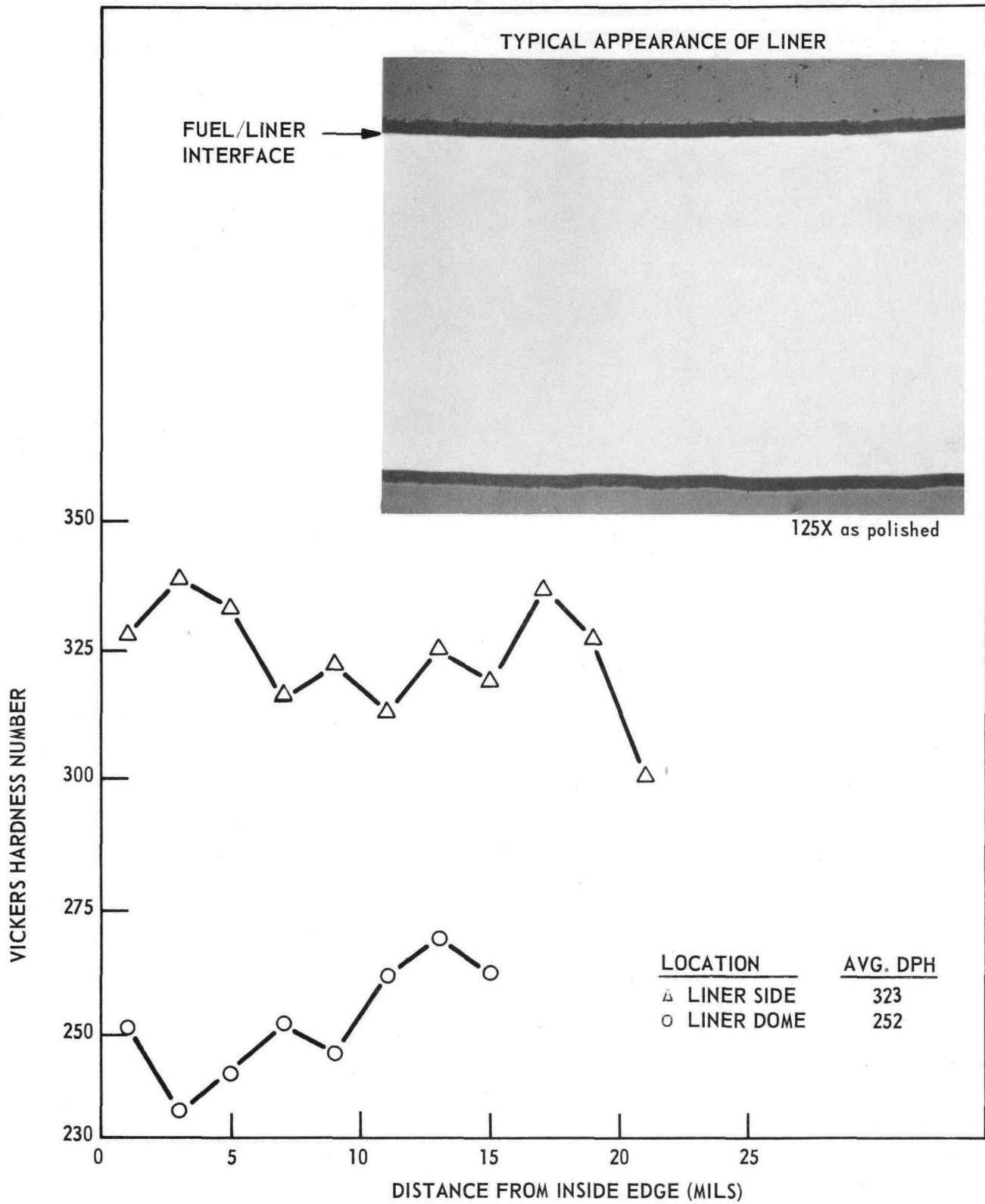


FIGURE 25 - Photomicrograph and microhardness traverses for 1373 K, 240-day P-type capsule liner.

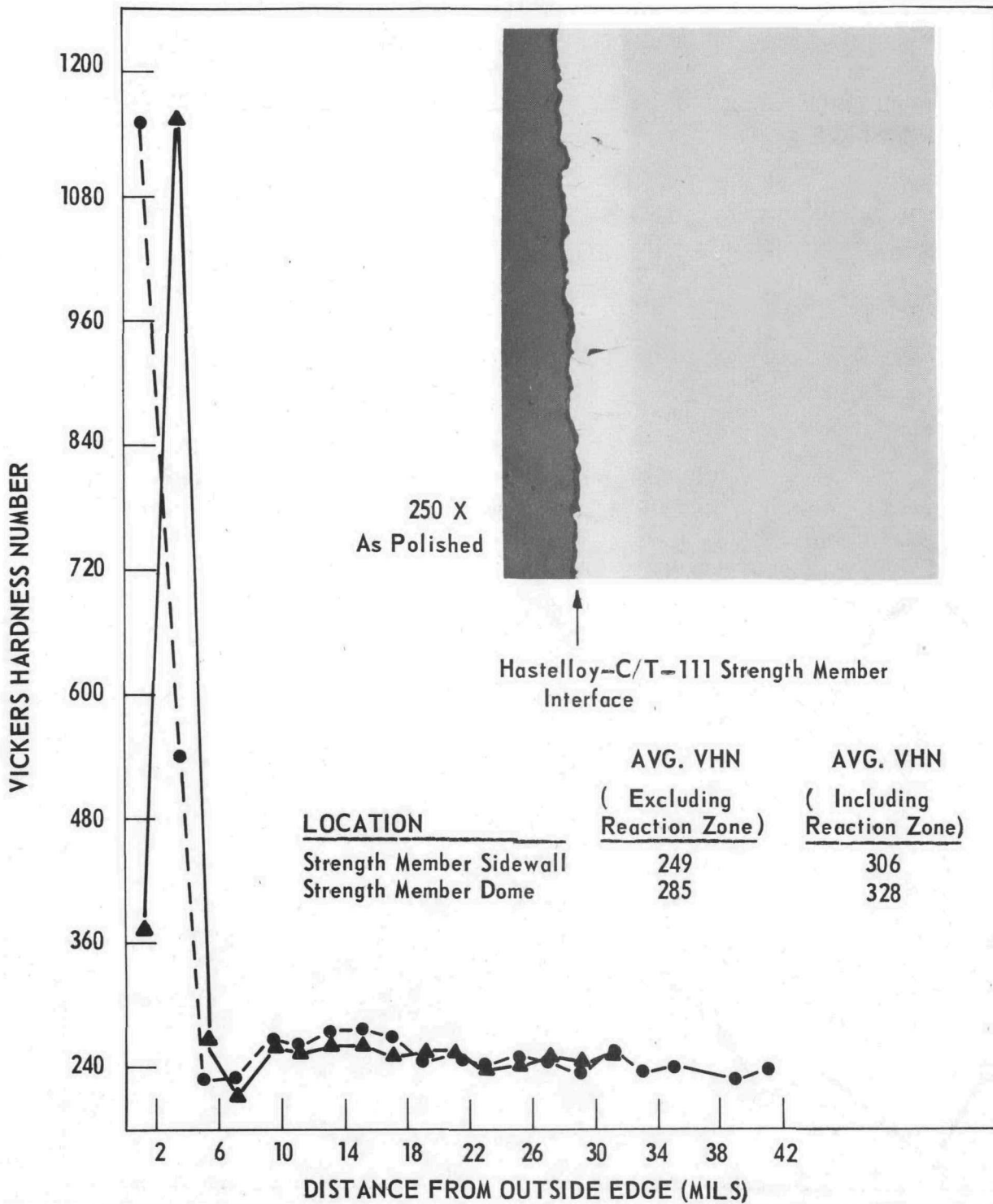


FIGURE 26 - Photomicrograph and microhardness traverses for 1373 K, 240-day P-type capsule strength member.

Table 10

OXYGEN, NITROGEN, AND AVERAGE MICROHARDNESS
DATA FOR 240-DAY P-TYPE SPECIMENS

Sample Temperature (°K)	Location	O ₂ (ppm)	N ₂ (ppm)	Average (VHN)
873	Liner Sidewall	268	18	255
	Liner Dome	395	35	261
	Strength Member Sidewall	47	0	271
	Strength Member Dome	90	15	262
1173	Liner Sidewall	319	21	253
	Liner Dome	249	20	230
	Strength Member Sidewall	68	44	252
	Strength Member Dome	118	77	260
1373	Liner Sidewall	2509	66	323
	Liner Dome	3345	10	252
	Strength Member Sidewall	125	150	249 ^a
	Strength Member Dome	250	197	285 ^a

^aAverage does not include vapor-deposited Hastelloy-C layer on outside surface of sample.

The data obtained from the two P-type capsules aged for 2 yr add further support to the pretreatment concept. Except for the usual localized oxygen-enriched zones along the fuel/liner interface formed during pretreatment, there was no evidence of fuel/liner reaction, or of embrittlement of the liners by the fuel as a result of aging in either specimen.

Microhardness data and typical microstructures for the liner and strength member of the 873 K specimen are shown in Figures 27 and 28, respectively. In the liner, hardness values are quite low except at the typical oxygen-enriched zones at the fuel/liner interface mentioned above. The 304 VHN value shown in Figure 27 coincides with such a spot. The strength member shows a hardness gradient near the outside edge of the sidewall. Electron microprobe analysis revealed no evidence of diffusion of components from Hastelloy-C, so the gradients most likely are due to nitrogen permeation through the Hastelloy-C clad.

The metallographic data obtained from the 1173 K specimen liner and strength member are shown in Figures 29 and 30. Again the liner microhardness data are generally quite low, except at isolated spots throughout the thickness. (The cause of this effect will be discussed below.) The strength member showed a much more pronounced hardness gradient than did the 873 K capsule, as would be expected. Again, no Hastelloy-C constituents could be found, indicating that the observed effect was most probably due to nitrogen permeation through the clad.

Oxygen, nitrogen and average Vickers hardness data are summarized in Table 11. The nitrogen values for the strength members tend to confirm the hypothesized cause of the observed hardness gradients. Most striking, however, is the very high oxygen content of the 1173 K liner in

LINER SIDEWALL (125X)

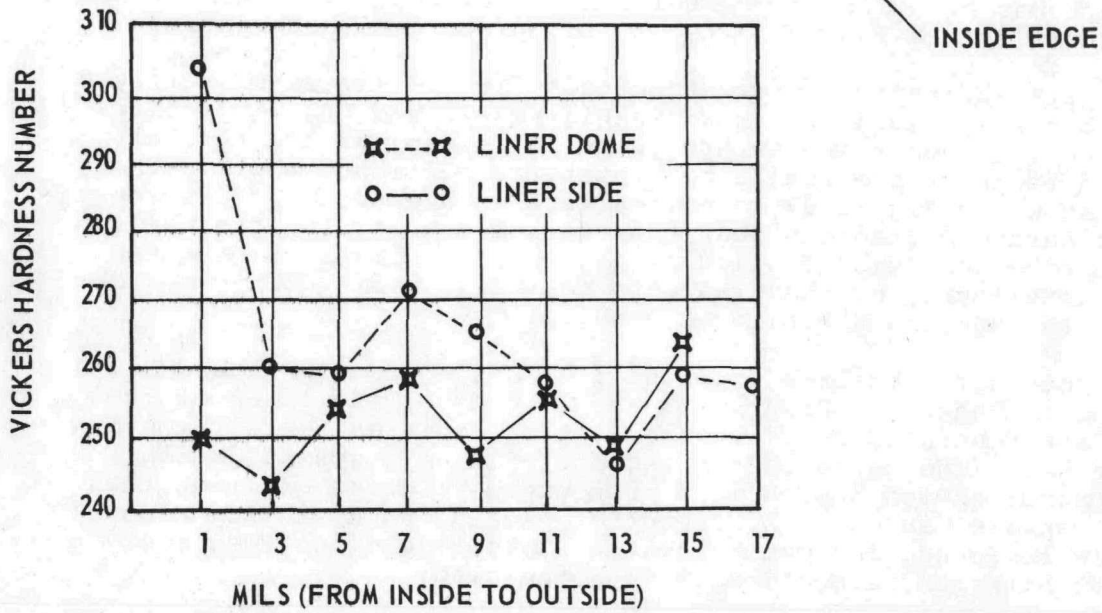
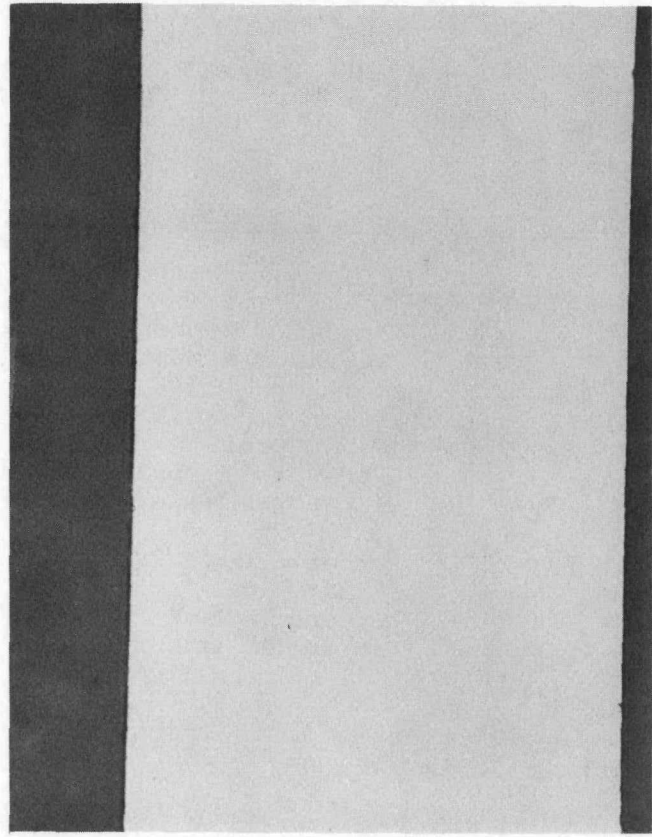
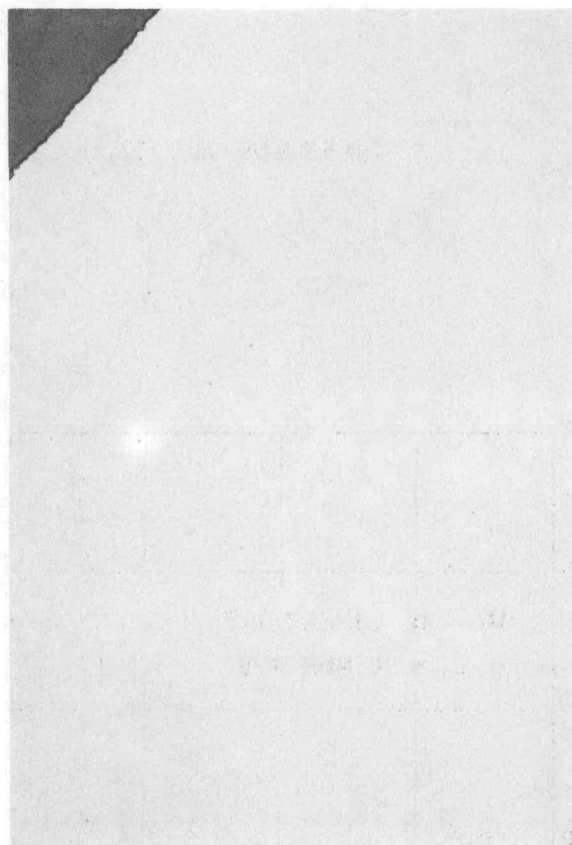


FIGURE 27 - Microhardness traverses and photomicrograph for P-type liner (2 yr at 873 K).

INSIDE EDGE →



STRENGTH MEMBER SIDEWALL (125X)

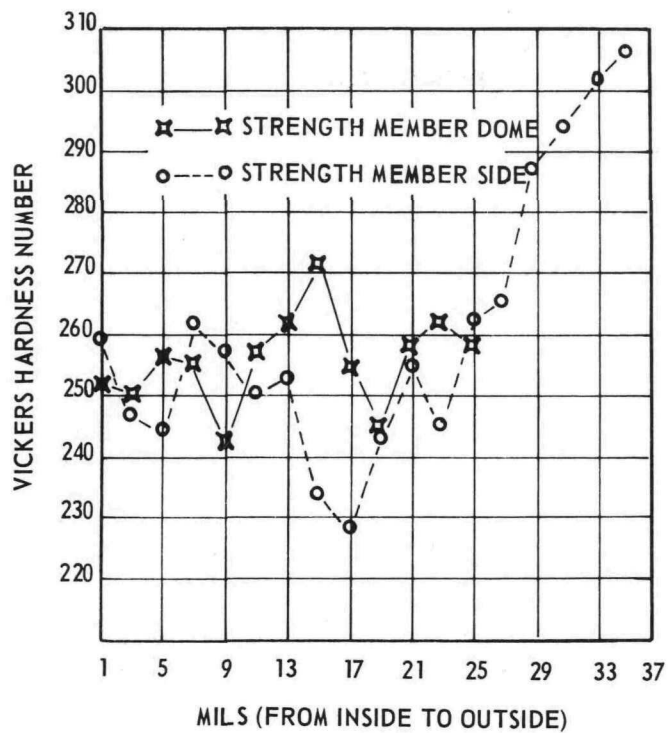


FIGURE 28 - Microhardness traverses and photomicrograph for P-type strength member (2 yr at 873 K).

LINER SIDEWALL (125X)

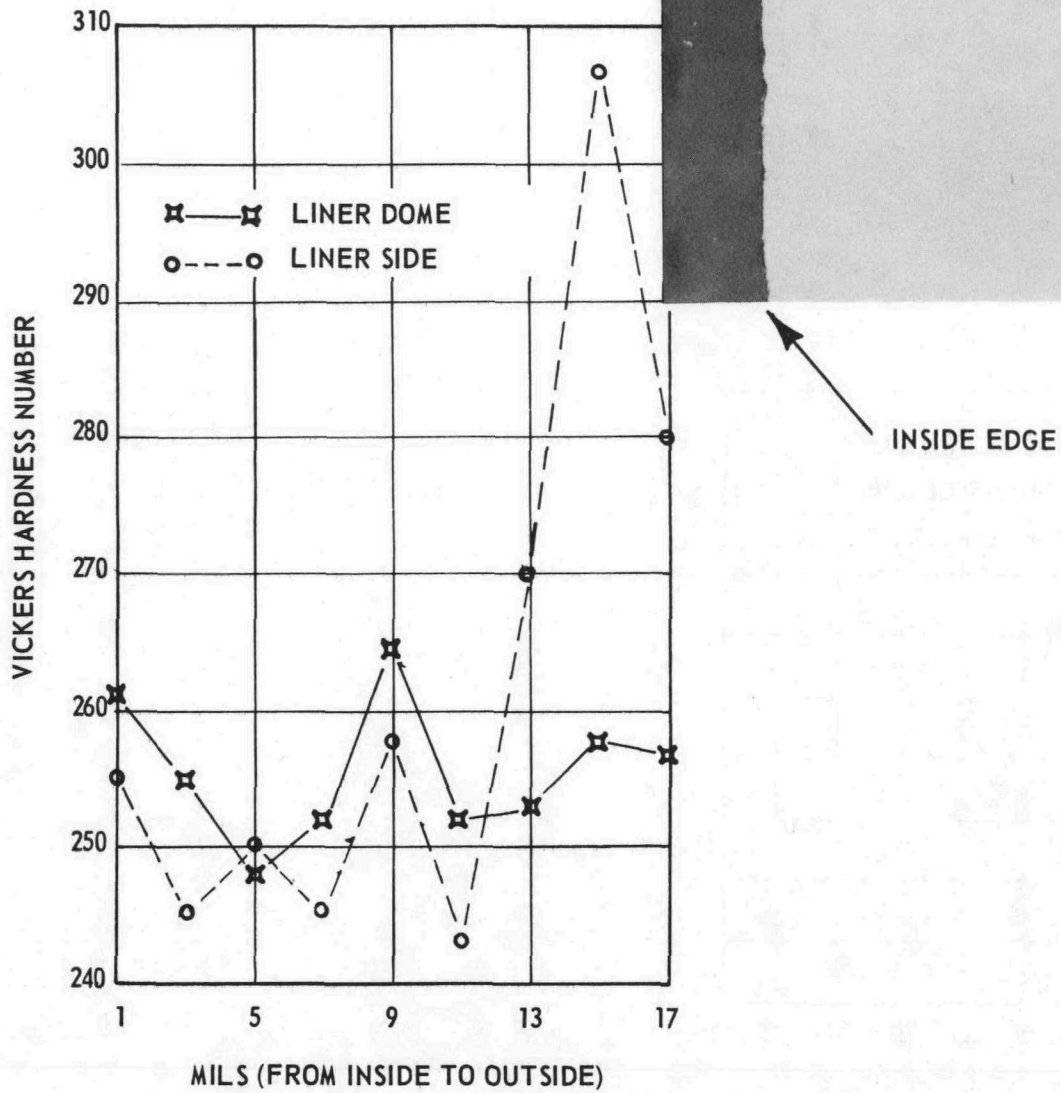
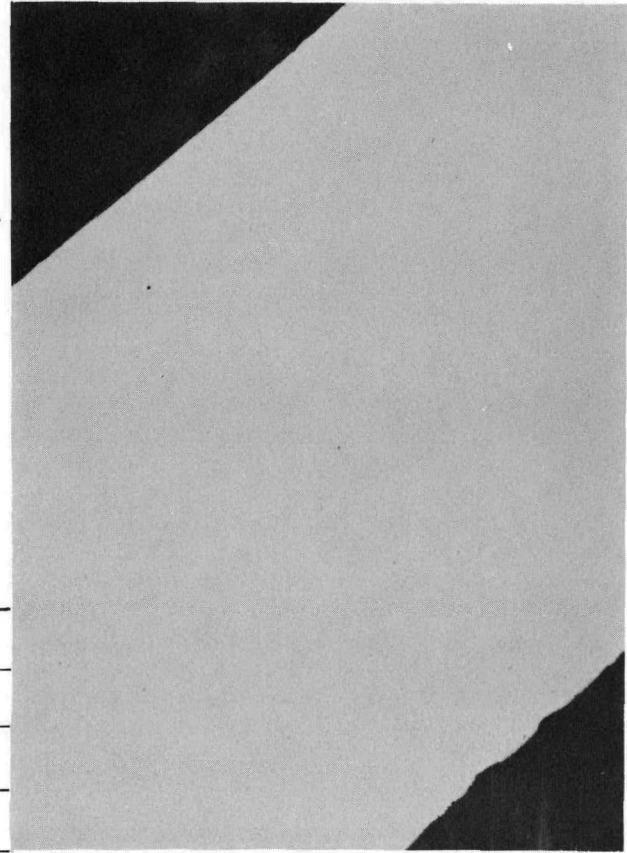


FIGURE 29 - Microhardness traverses and photomicrograph for P-type liner (2 yr at 1173 K).

INSIDE EDGE →



STRENGTH MEMBER
DOME (125X)

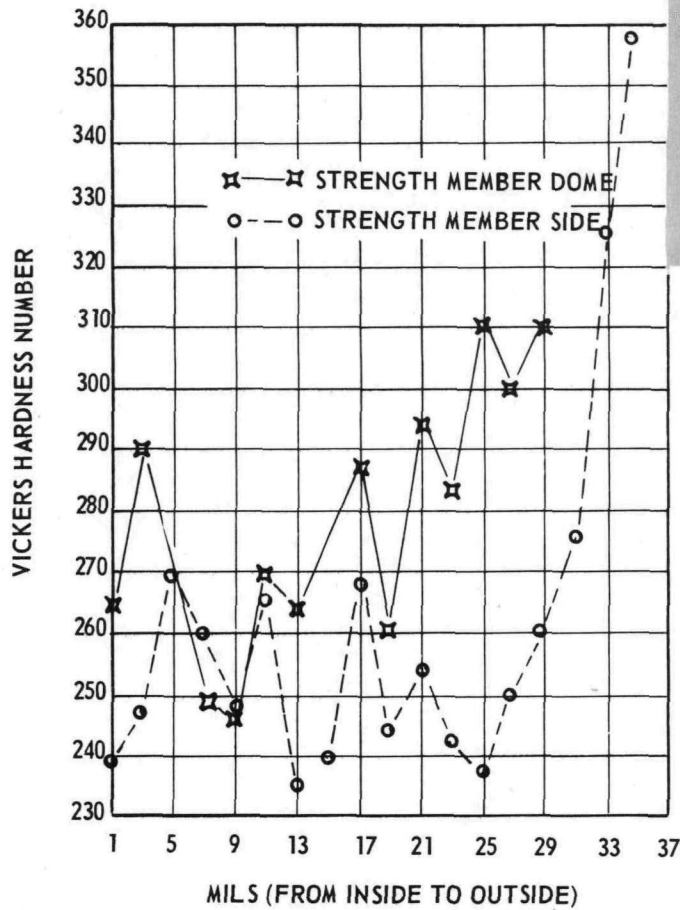


FIGURE 30 - Microhardness traverses and photomicrograph for P-type strength member (2 yr at 1173 K).

Table 11

P-TYPE CAPSULE DATA

<u>Sample</u>	<u>Location</u>	<u>O₂</u> <u>(ppm)</u>	<u>N₂</u> <u>(ppm)</u>	<u>Average</u> <u>VHN</u>
2 yr @ 873 K	Liner Sidewall	315	10	264
	Liner Dome	95	0	253
	Strength Member Sidewall	88	10	261
	Strength Member Dome	132	10	256
2 yr @ 1173 K	Liner Sidewall	1215	27	261
	Liner Dome	932	14	256
	Strength Member Sidewall	69	41	262
	Strength Member Dome	74	44	279

light of the low hardness values. Both sets of results were rechecked numerous times with every effort made to assure that no plutonia was adhering to the liner, but no reasons could be found to doubt either hardness or oxygen data. Such results would be expected of material which has undergone extensive oxygen contamination followed by long-term, high-temperature aging. It does not seem possible that such aging could occur at 1173 K, and it was definitely not observed in the equivalent F-type capsule which contained nearly three times as much oxygen. While a short-term high-temperature excursion near the end of the aging period could explain these results, the furnace control system should preclude this and it would have also led to overaging of the nitrogen-contaminated strength member. Therefore the only hypothesis that appears consistent with all observations is that the liner material was contaminated prior to testing - probably during rolling. Based on the liner microhardness data, experience with other capsules and a knowledge of the properties of overaged, contaminated T-111, it appears that little of the observed oxygen could have been absorbed during aging.

(Unfortunately, during the earlier capsule fabrication when these specimens were made the only T-111 available had indeed been contaminated during rolling. It was thought at that time that most material with high oxygen content had been eliminated. This apparently was not the case.)

Comparison of the 60-day and 240-day P-type capsule results indicates that no measurable embrittlement takes place at or below 1173 K. Even at 1373 K, while oxygen uptake by the liner is severe, microhardness values indicate the liner remains rather ductile.

Retreatment Studies

With the effectiveness of the pretreatment process established, efforts were directed to determining the feasibility of treating previously fabricated capsules to force the yttrium/PuO₂ reaction. Two specimens which had been fabricated more than 1 yr earlier were returned to Mound from Sandia. Neither of the capsules had seen temperatures in excess of 673 K and they spent most of their time below 400 K. The clad was removed from one of the sources and the specimen was heated for 1 hr at 1623 K. This specimen is referred to as the "retreated" capsule. The remaining sample was sectioned and examined without heat treatment for comparison.

Metallographic examination of both specimens in the as-polished condition revealed no evidence of reaction. Microhardness traverses were made across the liners and the strength members of the specimens. The results are shown in Figure 31 for the comparison capsule and in Figure 32 for the "retreated" capsule. No embrittlement of either specimen is indicated by the data.

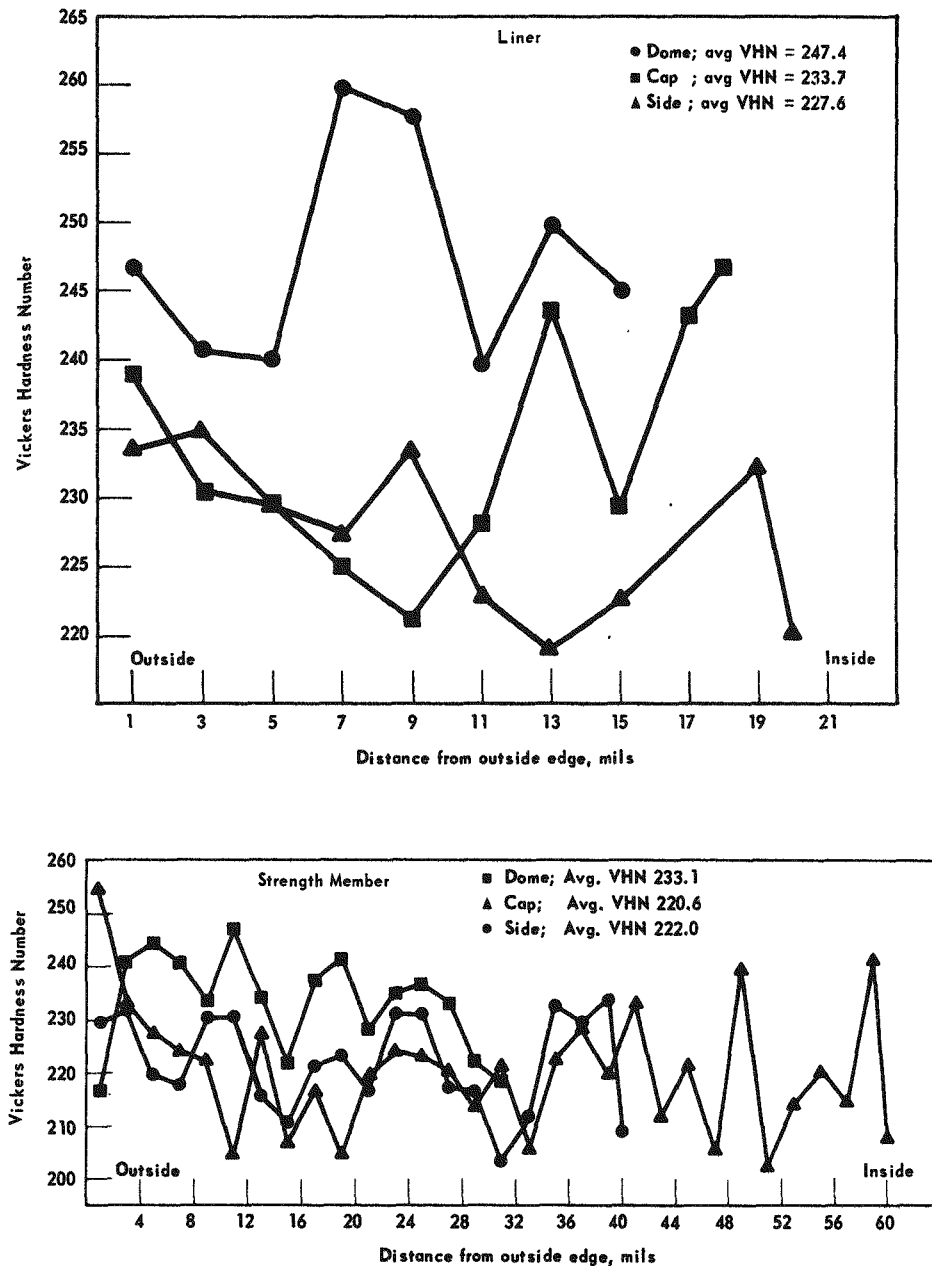


FIGURE 31 - Microhardness traverses for nonretreated capsule.

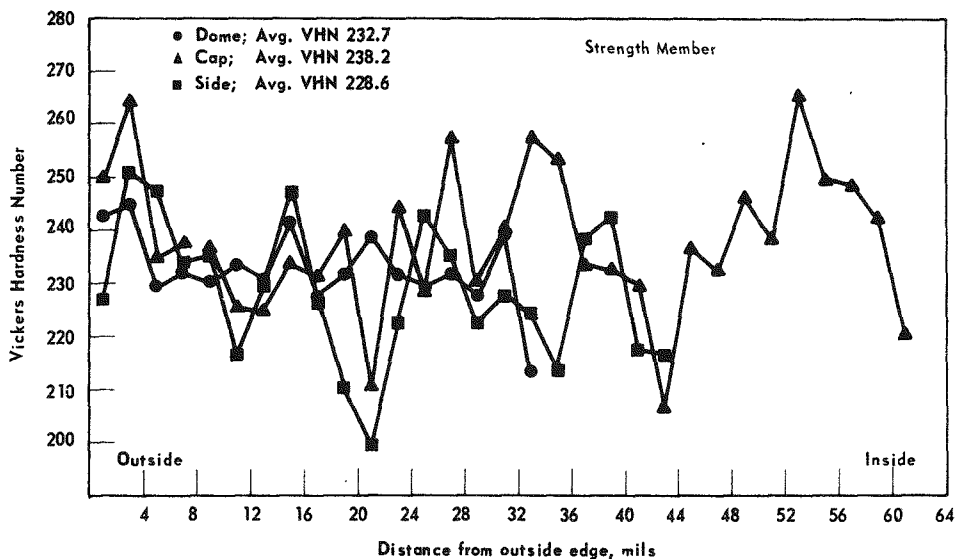
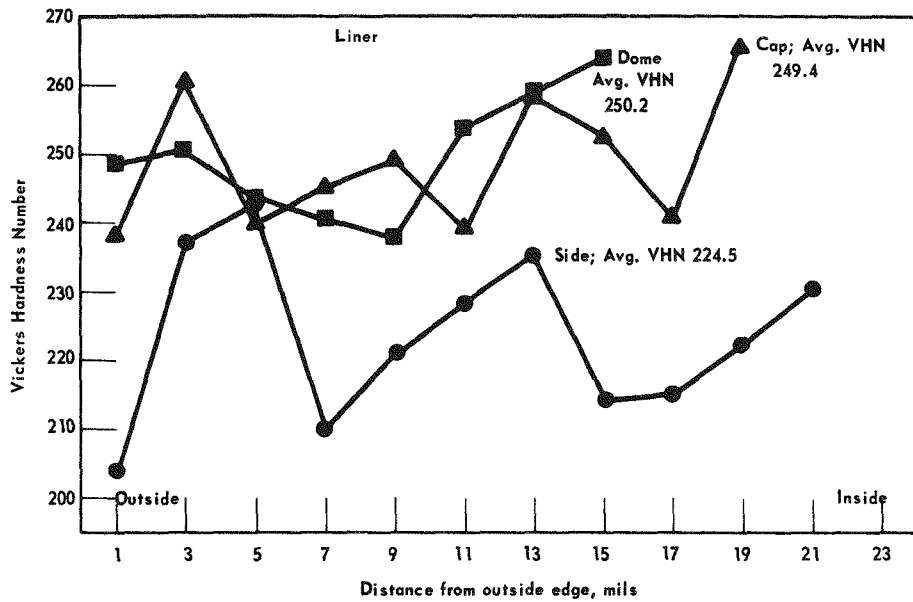


FIGURE 32 - Microhardness traverses for retreated capsules.

Samples from the liners and the strength members of the specimens were analyzed for oxygen and nitrogen. The values obtained are shown in Table 12. There is very little difference between the values obtained from the "retreated" and comparison capsules, except for two unexplainably high nitrogen values for the strength member and liner walls of the comparison capsule.

During analysis of the "retreated" capsules, one of the microhardness traverses yielded a series of anomalously high values (374 VHN maximum), near the inside edge of the liner, much like the pretreated foil specimen. Etching revealed the embrittled spot shown in Figure 33. In addition to

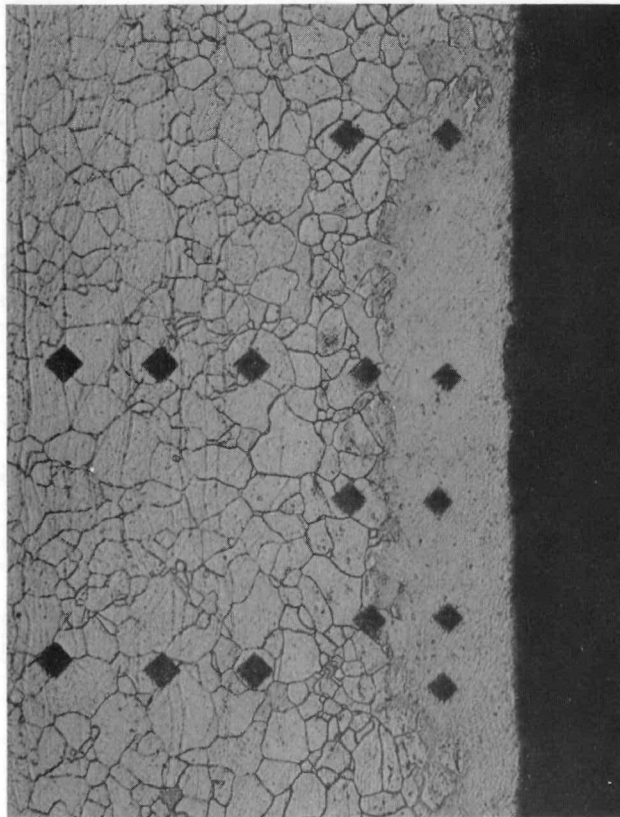


FIGURE 33 - Photomicrograph showing embrittled spot located along fuel/T-111 interface of retreated specimen (250X etched).

Table 12

OXYGEN AND NITROGEN DATA FOR "RETREATED"
AND "NONRETREATED" CAPSULES

<u>Sample Description</u>	<u>Sample Origin</u>	O ₂ (ppm)	N ₂ (ppm)
Retreated (1 hr @ 1623 K)	Liner Wall	198	24
	Liner Dome	96	22
	Strength Member Wall	40	24
	Strength Member Dome	98	54
Comparison Capsule (Nonretreated)	Liner Wall	209	82
	Liner Dome	168	42
	Strength Member Wall	91	123
	Strength Member Dome	55	24

this spot, several other similar appearing but smaller areas were revealed along the liner edge. Etching of previous capsules also revealed similar microstructures. Repeated attempts to determine the nature of this region by electron microprobe analysis were unsuccessful. No difference could be found between the composition of the spots and the composition of the parent material. It was, therefore, hypothesized that these were most likely regions of localized oxygen enrichment. The sensitivity of the electron microprobe for this element is poor, and up to 8 wt % could be present without being detected. Verification of the oxygen was finally obtained by use of an ion microanalyzer. The somewhat higher hardness values are indicative of T-111 containing overaged hafnia particles.^{8,9} As long as the hafnia particles are overaged, or large, they do not degrade the mechanical properties of the liner and hence are of little consequence.

Neutron emission rates of the fuel removed from the specimens were compared to neutron emission rates obtained when the specimens were fabricated. Assuming any change in the neutron emission rate was due to re-oxidation of the fuel after sectioning with oxygen of natural isotopic abundance, fuel stoichiometries of $\text{PuO}_{2.01 \pm 0.01}$ and $\text{PuO}_{1.80 \pm 0.02}$ were indicated for the comparison capsule and "retreated" capsule, respectively. This indicates that no oxygen was gettered by yttrium and that no oxygen from the fuel reacted with the liner during the approximately 1 yr of self-heating of the capsule. Nearly complete reaction between the PuO_2 and the yttrium is indicated in the "retreated" capsule.

Pellet Pretreatment Tests

The last pretreatment test involved a capsule designed for a pellet fuel form of the geometry shown in Figure 34. The capsule was pretreated at

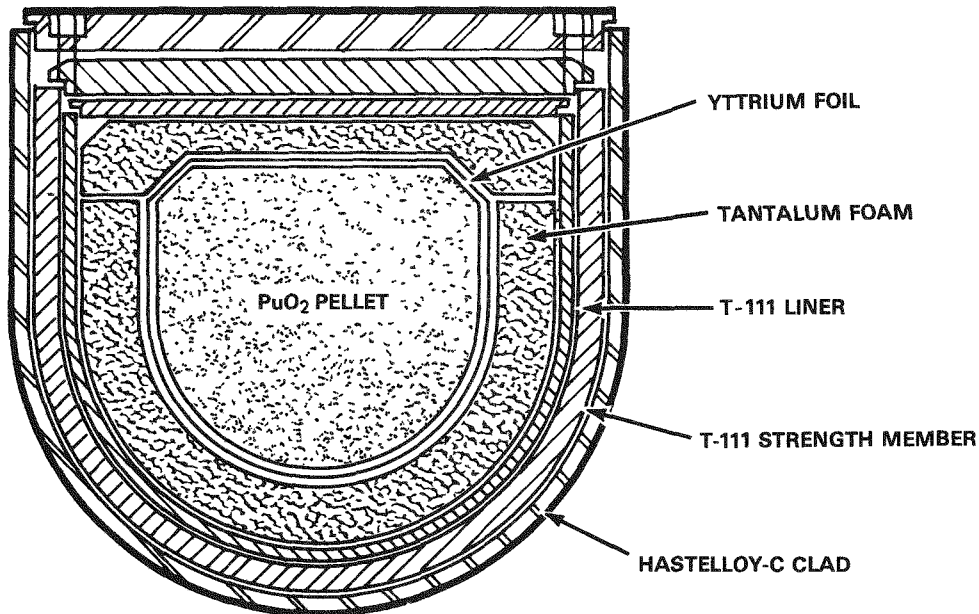


FIGURE 34 - Pellet pretreatment capsule geometry.

1623 K for 1 hr, sectioned, and evaluated. Metallographic examination of the liner and the strength member of the specimen in the as-polished condition revealed no evidence of reaction.

Metallographic examination of the tantalum foam revealed no obvious evidence of reaction, except for the random location of small gray deposits (apparently at points of contact) along the tantalum-yttrium interface. Electron microprobe analysis indicated that these were deposits of yttrium oxide. Attempts were made to locate oxygen gradients in the tantalum foam, but none were detected. When the specimen was sectioned, the yttrium foil surrounding the pellet was observed to be fairly ductile, suggesting that very little oxidation of the foil occurred during the pretreatment. This was confirmed by metallographic examination of the foil. Photomicrographs of the foil from the specimen were compared to photomicrographs of yttrium in the "oxidized" and "as-received" condition. Only slight oxidation of the foil from the specimen was indicated. These observations together with the oxygen and nitrogen data in Table 13 suggest that most of the oxygen given up by the fuel was taken by the tantalum foam support.

Table 13

OXYGEN AND NITROGEN DATA FOR THE
PRETREATED PLUTONIA PELLET CAPSULE

<u>Specimen</u>	<u>Sample Location</u>	<u>O₂ (ppm)</u>	<u>N₂ (ppm)</u>
Ta Foam/Y Foil/PuO ₂ Pellet Design Capsule (Pretreated for 1 hr @ 1623 K)	Tantalum Foam	1775	54
	Yttrium Foil	1618	171
	Liner Dome	126	18
	Liner Wall	161	17
	Strength Member Dome	106	12
	Strength Member Wall	28	12
Ta Foam (As Received)		682	24

Microhardness traverses were conducted across the lid, sidewall, and dome of the liner and the strength member of the specimen. The values obtained are shown in Figure 35. No interstitial contamination of the T-111 alloy is indicated by the data.

The fuel pellet was removed from the specimen and submitted for neutron counting. Comparison of the values obtained before and after pretreatment indicated essentially no change in the stoichiometry of the ²³⁸PuO₂ pellet. The lack of reduction in stoichiometry of the pellet further verifies the limited oxidation of the yttrium foil. Apparently the density and reduced surface area of the pellet as compared with the shards results in greatly reduced oxygen transport at the pretreatment temperature.

Oxygen Transport Studies

Because of the difference between the P-type and F-type capsules and the observed hardness gradients, much discussion has centered about the actual mechanism by which oxygen is transported to a T-111 liner in a heat source capsule. Two mechanisms are possible: (1) transport through

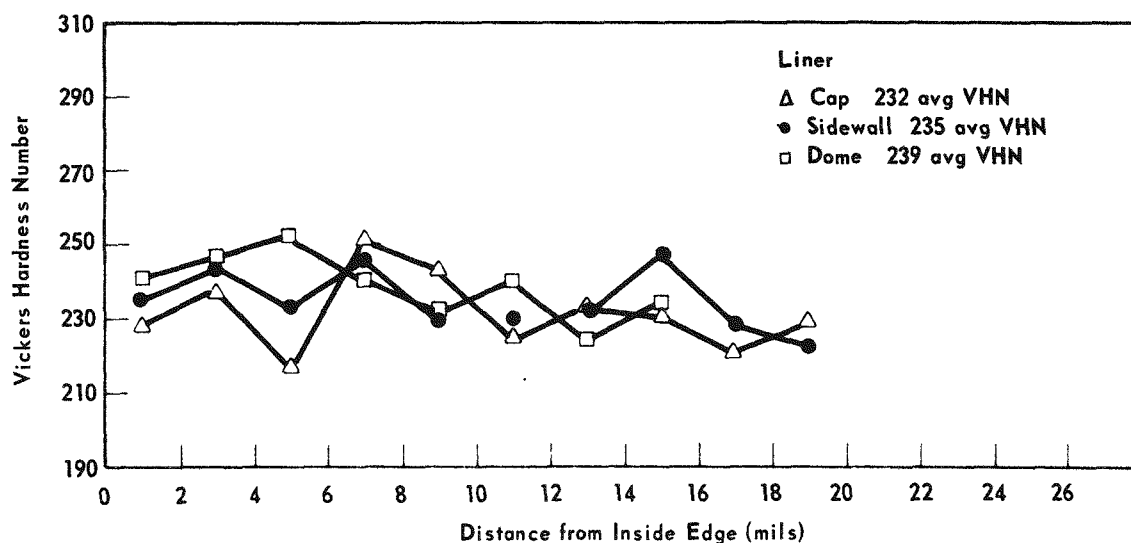
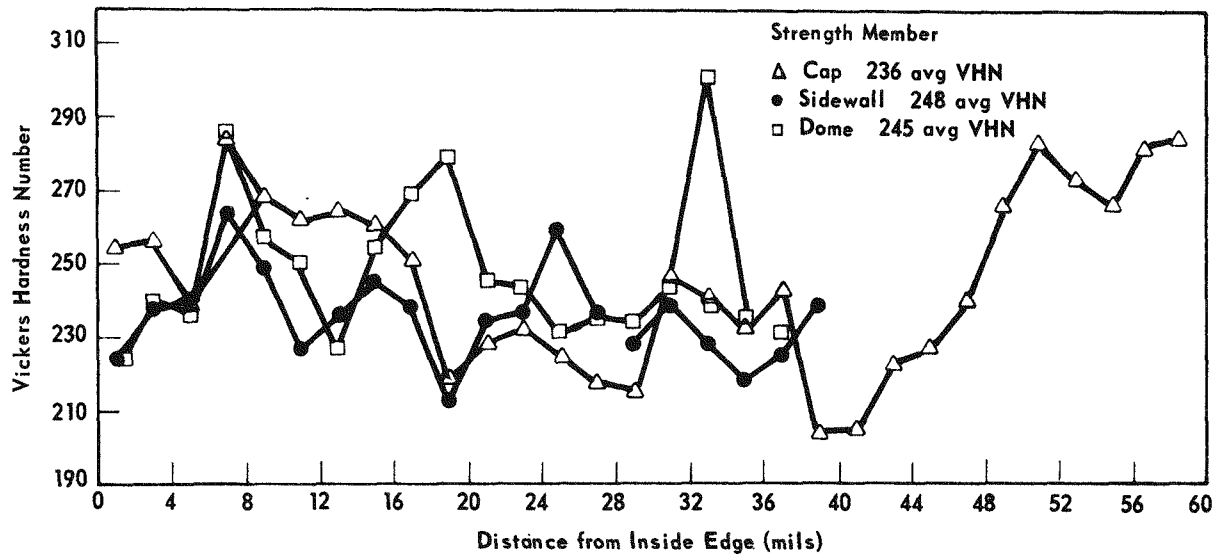


FIGURE 35 - Microhardness traverses for pretreated plutonia pellet capsule.

the vapor phase; or (2) solid-state diffusion across the fuel-liner interface. Although it was expected that solid-state diffusion across the fuel-liner interface was the primary mechanism, the contribution of the vapor-phase transport was not known. In order to establish the importance of each mechanism to the total oxygen uptake a simple set of experiments was conducted.

Two capsules were loaded with fuel pellets in the configurations shown in Figure 2. Both capsules utilized standard hardware with 6-W plutonia pellets. The pellet in one capsule was wrapped several times with 0.51-mm iridium wire to provide a standoff so that the fuel could not touch the liner. The pellet in the second capsule was placed in direct contact

with the liner bottom. After welding, the capsules were radiographed to verify internal geometry and then placed on test for 60 days at 1173 K. After removal from the furnace the capsules were cross-sectioned and examined. Microhardness measurements were made at various locations around the capsules and samples were selected for oxygen and nitrogen analyses.

A summary of the oxygen and nitrogen analyses and microhardness traverses is given in Table 14. From this table, it is apparent that oxygen transfer occurs by solid-state contact much more readily than by the vapor-phase mechanism. For the capsule with the standoff pellet, the oxygen analyses indicated identical values at the dome and the sidewall. However, for the direct-contact pellet, there was considerable difference between the dome of the capsule where the pellet was in direct contact and the sidewall where it was not.

Table 14
OXYGEN, NITROGEN, AND AVERAGE HARDNESS DATA FOR
OXIDATION MECHANISM TESTS (1173 K, 60 DAYS)

<u>Specimen</u>	<u>Location</u>	<u>O₂ (ppm)</u>	<u>N₂ (ppm)</u>	<u>Average VHN</u>
Direct Contact Pellet Capsule	Liner Sidewall	828	60	404
	Liner Bottom	2402	54	858
	Strength Member Sidewall	174	50	225
	Strength Member Bottom	227	44	250
Standoff Pellet Capsule	Liner Sidewall	694	38	444
	Liner Bottom	694	54	422
	Strength Member Sidewall	138	86	228
	Strength Member Bottom	227	58	252

Microhardness traverses for each liner are shown in Figures 36 and 37. Differences in average hardness values for equivalent locations could be related to the relative position of the pellet with respect to the liner, with higher average values due to closer proximity of the pellet at that point. In the case of the standoff pellet capsule, the liner sidewall is slightly harder than the dome while the corners are softer. This is probably due to a higher dislocation density in these regions as a result of the fabrication technique.

If the reaction kinetics in the vapor transport case are described by the Langmuir equation, as stated by Inouye,¹¹ the actual oxygen pressure must be at least 10^6 times the amount over pure plutonia¹² at 1173 K. This would be possible if transport were dominated by oxygen-bearing impurities within the fuel, which could either volatilize stoichiometrically or release oxygen to the atmosphere.

DISCUSSION

The only microstructural change in the liner which could be related to the pretreatment process was the occurrence of the isolated spots of high hardness mentioned earlier. Although these regions, characterized by their high oxygen concentration in the form of overaged hafnia precipitates,

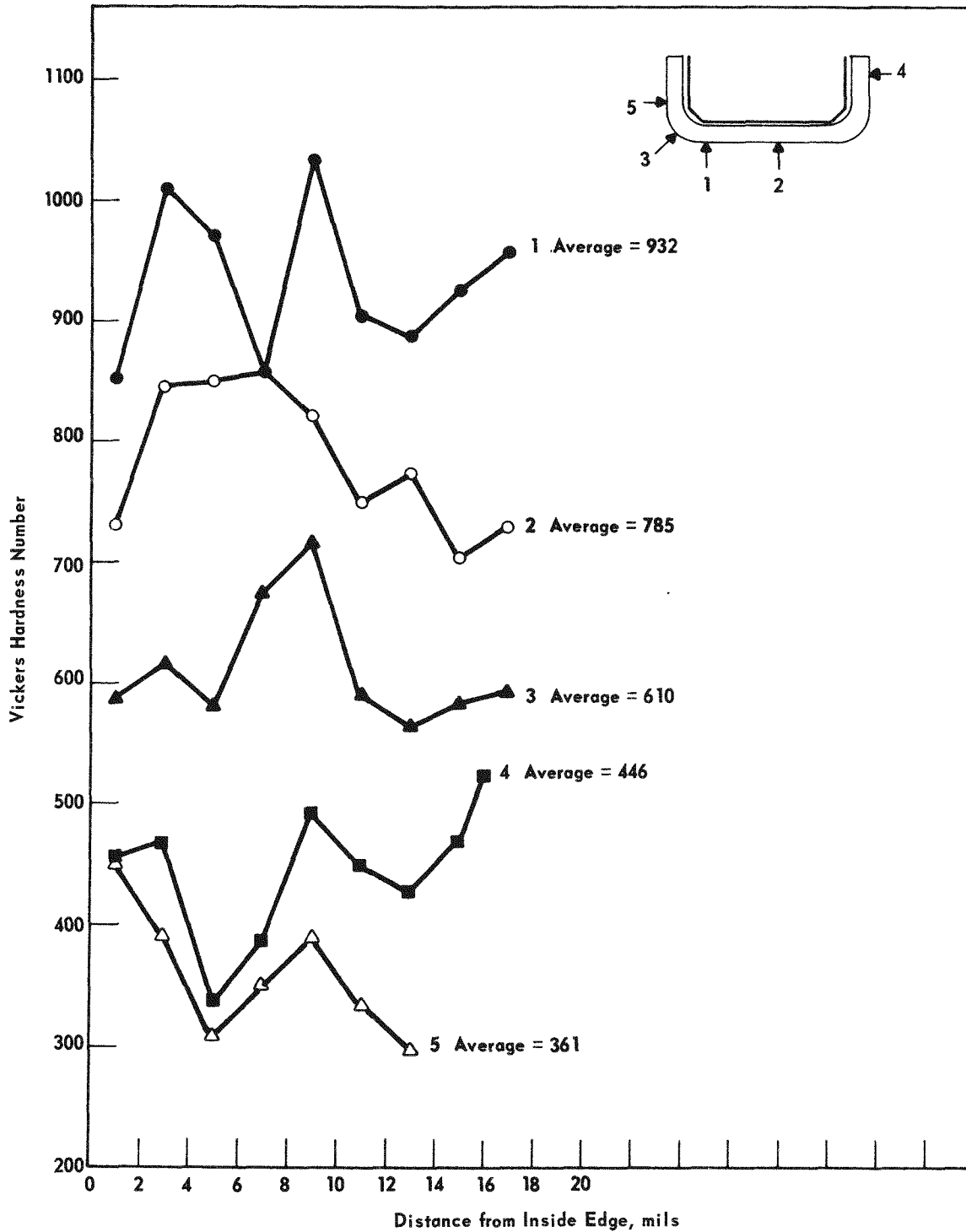


FIGURE 36 - Microhardness traverses on liner of direct-contact pellet capsule (1173 K, 60 days).

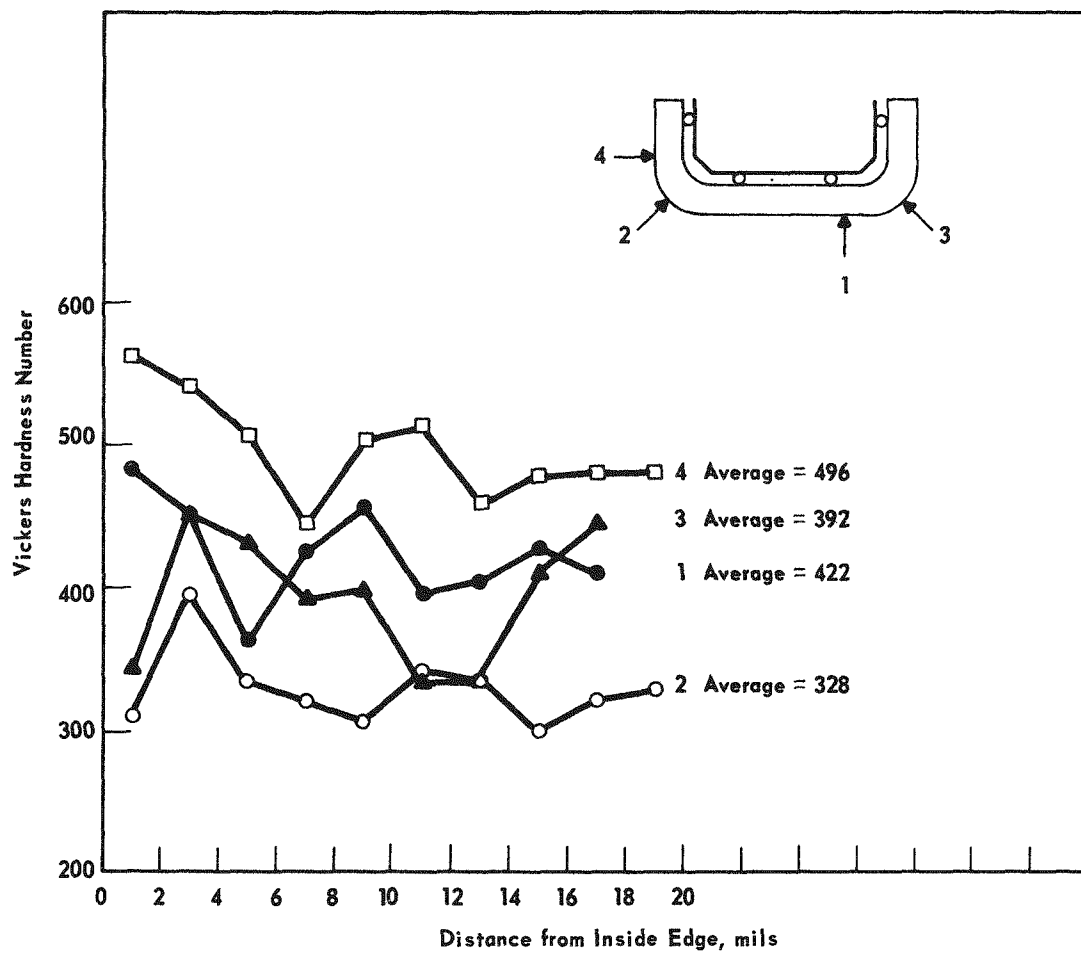


FIGURE 37 - Microhardness traverses on liner of standoff pellet capsule (1173 K, 60 days).

do not affect the mechanical properties of the liner, they are of some interest. The maximum depths of these spots as a function of capsule treatment are listed in Table 15. From this it is apparent that they do not increase with time, and as such are solely related to the pretreatment process. However, the use of yttrium powder leads to shallower zones than with the chips, indicating a correlation between the form and/or number of yttrium particles and the depth of the spots. For this reason further tests are planned to evaluate the effect of yttrium particle size, shape, and amount on the occurrence of the hardened regions.

Table 15

SUMMARY OF METALLOGRAPHIC DATA ON SMALL
REACTION ZONES IN PRETREATED CAPSULES

<u>Sample</u>	<u>Pretreatment</u>	<u>Heat Treatment</u>	<u>Zone Depth (mils)</u>
Blank	1 hr @ 1623 K	--	None
PuO ₂ Only	1 hr @ 1623 K	--	12 (max)
PuO ₂ + Y Chips	1 hr @ 1623 K	--	6.9
PuO ₂ + Y Chips	1 hr @ 1623 K	--	6.0
PuO ₂ + Y Chips	1 hr @ 1623 K	--	5.4
PuO ₂ + Y Chips	1 hr @ 1623 K	---	5.0
PuO ₂ + Y Powder	1 hr @ 1673 K	60 days @ 1173 K	4.9
PuO ₂ + Y Powder	1 hr @ 1673 K	--	4.6
PuO ₂ + Y Powder	1 hr @ 1623 K	240 days @ 873 K	3.9
PuO ₂ + Y Powder	1 hr @ 1623 K	60 days @ 1373 K	3.4
PuO ₂ + Y Powder	1 hr @ 1623 K	60 days @ 873 K	3.1
PuO ₂ + Y Powder	1 hr @ 1723 K	60 days @ 1173 K	2.7
PuO ₂ + Y Powder	1 hr @ 1573 K	60 days @ 1173 K	2.4

To underscore the effectiveness of the pretreatment process, oxygen, nitrogen, and average microhardness values for the liners of the P- and F-type capsules aged at 1173 K are compared in Table 16. The advantages of the pretreatment operation are evidenced by the lower oxygen and hardness values of the P-type specimen liners. Although some initial oxygen uptake by the liner occurs during pretreatment, very little if any additional oxygen pickup or embrittlement occurs with time in the pretreated specimen. However, the F-type specimens show increasing oxygen uptake and embrittlement of the liner with time.

Assuming the oxygen uptake of the liner in the F-type capsules is thermally activated, the controlling activation energy can be determined from the slope of log (r) versus 1/T, where r is the rate of oxygen absorption. The value of r can be obtained from the relation

$$r = \frac{C_t - C_0}{t}$$

Table 16

COMPARISON OF P- AND F-TYPE 1173 K LINER DATA

<u>Time</u>	<u>Capsule Type</u>	<u>Location</u>	<u>O₂ (ppm)</u>	<u>N₂ (ppm)</u>	<u>Average VHN</u>
60 Days	P	Sidewall	266	26	240
		Dome	164	8	239
	F	Sidewall	1883	110	291
		Dome	1070	100	252
240 Days	P	Sidewall	319	21	253
		Dome	249	20	230
	F	Sidewall	1330	6	816
		Dome	>2000	11	728
2 Years	P	Sidewall	1215	27	261
		Dome	932	14	256
	F	Sidewall	2543	96	717
		Dome	3667	40	834

where C_t is the concentration at time t , and C_0 is the initial concentration. For purposes of discussion, the average oxygen content for the strength members of the aged capsules in Table 6 was used to obtain $C_0 = 71$ ppm. The values* of r obtained by this method are plotted versus $1/T$ in Figure 38, with the indicated least-squares line corresponding to an activation energy of 94.6 kJ/mole (22.6 kcal/mole). Considering the difficulties involved, this value is quite close to the 95.8 to 114.3 kJ/mole (22.9 to 27.3 kcal/mole) reported for oxygen diffusion in tantalum.¹³ That this is the controlling process is further supported by the microhardness gradients observed in the 1173 K, 60-day specimen, such as shown in Figure 39. These gradients can occur only if the rate of oxygen supply to the fuel/T-111 interface is greater than the diffusion rate in the alloy. The fact that the activation energy obtained from these data is on the lower end of the reported energy range, even though T-111 is an alloy, may be related to the presence of pipe, or dislocation-enhanced, diffusion in the T-111. This would also explain why the oxygen content was highest in areas of high residual strain and well-defined dislocation network structure. This is graphically indicated in Figure 37, where the highest strain area of the sidewall is also the hardest region, although all points were equidistant from the fuel.

*Due to the anomalously high oxygen content and near-background microhardness values for the 1173 K, 60-day capsule, these results were not used. The problem with these data could be due to several things, but most likely is that either fuel was adhering to the liner segments analyzed or the fuel was excessively heated during closure due to insufficient clearance.

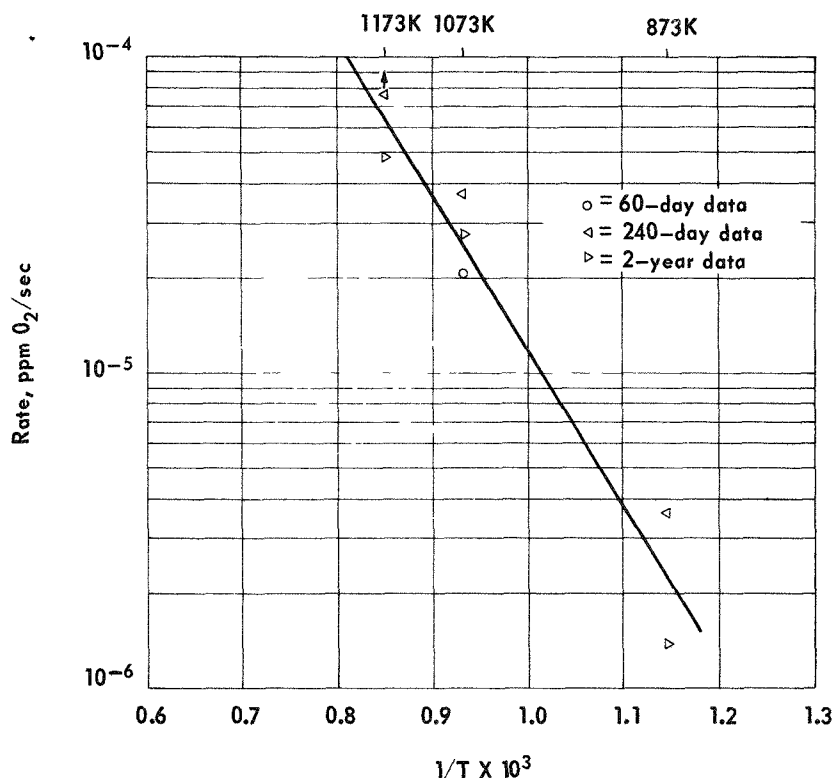


FIGURE 38 - Plot of $\log (r)$ versus $1/T$ used for activation energy determination for F-type capsules.

From these results it is readily apparent that pretreatment must simply stop the supply of oxygen to the liner at lower (≤ 1173 K) temperatures. Since for the P-type capsules oxygen pickup during aging did occur only in the 1373 K specimen, it is not possible to determine an activation energy which could then be used to identify the controlling transport process. However, it is possible to form some conclusions based on other facts and known plutonia properties.

Analysis of data obtained from the L-type specimens indicated that volatile oxide impurities in the fuel controlled at least the vapor transport in the F-type capsules. However, one of the most obvious results of pretreatment should be the reduction of the low-energy oxides, at least to the point where they are in equilibrium with $\text{PuO}_{1.75-1.80}$. Therefore, they no longer need to be considered separately and the discussion can be restricted to the properties of pure substoichiometric plutonia.

Chereau and Wadier¹⁴ calculated the diffusion coefficient for oxygen in substoichiometric plutonia at 1353 K and found it to be about 8×10^{-5} cm²/sec. Their resistivity measurements on the same material indicated that the ionic mobility was fairly insensitive to temperature and that, for $\text{PuO}_{1.772}$, the activation energy is only 6.5 kcal/mole. This would indicate that oxygen transport in the fuel is not the rate-controlling process. One must therefore conclude that the oxygen is available to the liner and simply does not react. The only possible explanation for

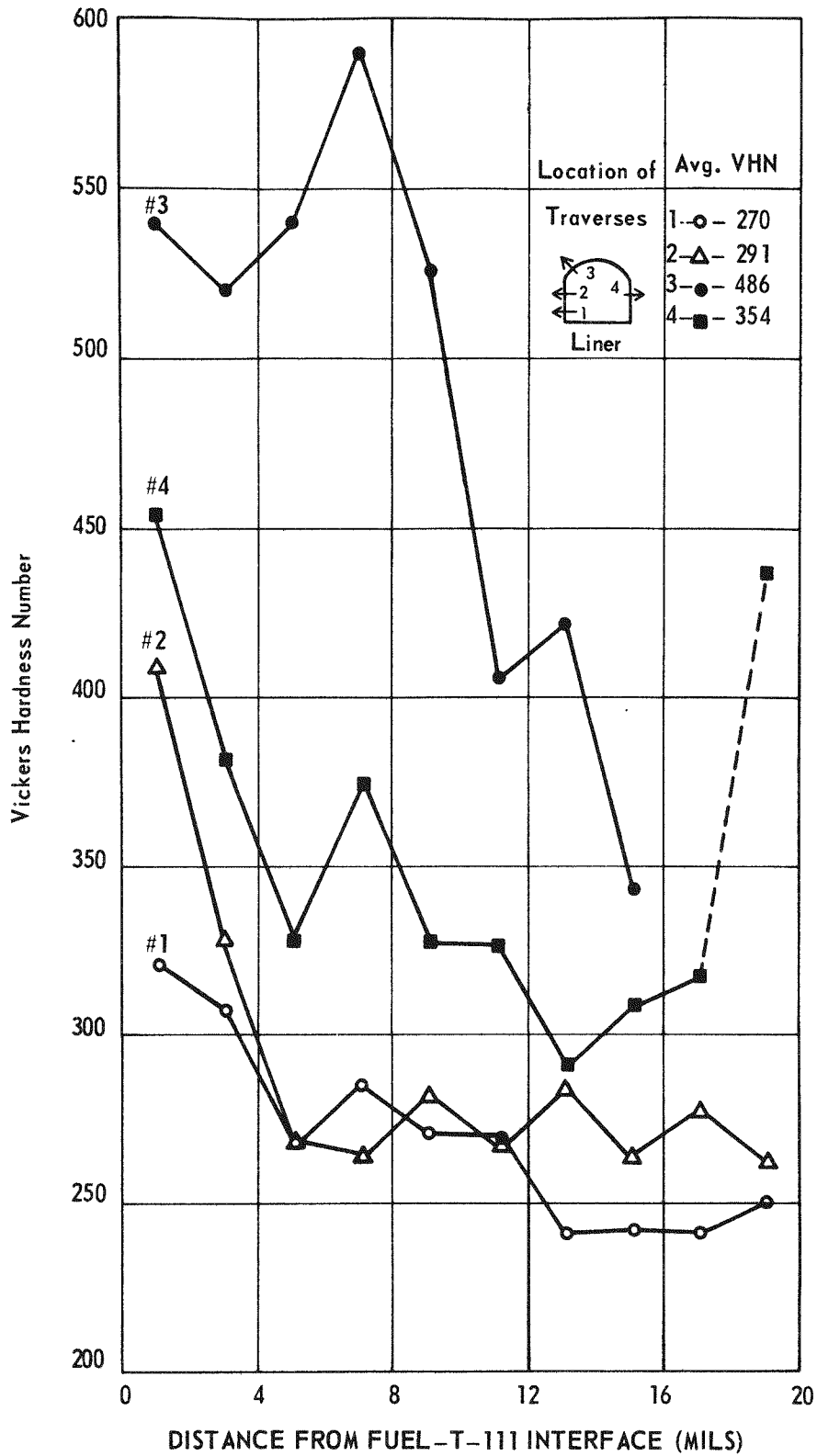


FIGURE 39 - Microhardness traverses showing oxygen gradient in 1173 K, 60-day F-type capsules.

this phenomenon is that at, and below, 1173 K it is energetically unfavorable for the fuel to give up oxygen to the liner, while at 1373 K the situation is reversed.

If one extends the free-energy data of Ackermann, Faircloth and Rand¹² to the temperatures of interest, it is obvious that it is energetically unfavorable for oxygen to go to the liner to form Ta_2O_5 .¹⁵ However, the free energy of formation of hafnia from bulk hafnium¹⁵ is approximately equal to that for $PuO_{1.75}$. Considering that the hafnium is in solution in the alloy and hence this free-energy value is probably shifted, it is quite likely that the observed behavior is due to the relative free energies of formation of hafnia in T-111 and $PuO_{1.75}$. Therefore, it seems reasonable to describe the pretreatment process as a reduction of the stoichiometry of the fuel to a point where, at or below 1173 K, it is unfavorable for hafnium in the liner to further reduce it. In this temperature range the system is essentially nonreactive and the components can be considered to be chemically inert. Above this temperature, as at 1373 K, this equilibrium is disturbed and the hafnium in the T-111 is able to further reduce the fuel. This process should proceed until the hafnium is exhausted or the fuel is reduced to the point where equilibrium is once more established. It is hoped that this hypothesis can be verified in future tests in which lower oxygen-to-plutonium ratios will be sought.

CONCLUSIONS

This study was undertaken in an effort to develop techniques for improving the long-term high-temperature compatibility between plutonium-238 dioxide and the tantalum-base alloy, T-111. This alloy possesses almost ideal mechanical properties for use as a primary encapsulant for this radioisotope, especially with regard to accident survival requirements. However, as most other tantalum-base materials, it suffers severe oxygen embrittlement during prolonged high-temperature exposure to the plutonium-238 dioxide. The present tests were designed specifically to evaluate the hypothesis³ that reduction of fuel stoichiometry to the range $PuO_{1.75}$ to $PuO_{1.80}$ would suspend this embrittlement process, producing a state of thermodynamic equilibrium within the capsule. Reduction was to be achieved in situ by mixing yttrium metal with the PuO_2 just prior to capsule closure. Test temperatures ranged from 773 K to 1373 K, while aging times of 60 days, 240 days, and 2 yr were used.

Initial results indicated the fuel was not reduced by the yttrium except at the highest test temperature, even though the T-111 was embrittled in capsules held as low as 1073 K. The lack of Y_2O_3 formation was attributed to the presence of a protective oxide on the yttrium. Based on this assumption, T-111 oxidation kinetics,^{8,9} and the lack of embrittlement of some welds which had accidentally been contaminated with the PuO_2/Y mixture, it was decided to try to force the reaction. Capsules were heated to above 1573 K for 1 hr and then examined. It was found that the fuel had been reduced to the desired stoichiometry with only negligible effects to the T-111. Subsequent aging of such "pretreated" capsules indicated that no embrittlement of the T-111 was observed, even after 2 yr, for temperatures as high as 1173 K. Nonpretreated specimens showed severe embrittlement for the same test conditions.

In order to help in the understanding of these results, the dominant oxygen transport process within the capsules was determined, using two

specimens containing hot-pressed plutonia pellets. In one, the pellet was allowed to touch the capsule walls, while in the other it was held off by iridium wire. Solid-state transport was found to be the dominant mechanism, but some vapor transport was observed. Analyses of these results indicated that the vapor-phase contribution must be governed by the presence of volatile oxide impurities within the fuel.

Analysis of the oxygen absorption rate of the T-111 for nonpretreated capsules indicated that the rate-controlling mechanism was the diffusion of oxygen in the T-111. This result, coupled with the known oxygen mobility data for substoichiometric plutonia,¹⁴ was used to show that pretreatment did indeed seem to produce the hypothesized thermodynamic equilibrium between the plutonia and the T-111, at temperatures up to at least 1173 K.

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