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RESUME OF URANIUM ALLOY DATA—XI

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February 1, 1956

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Bettis Plant

Pittsburgh, Pa.

Operated for the U.S. Atomic Energy Commission by
Westinghouse Electric Corporation

INTRODUCTION

The principal developments in the PWR uranium fuel program since the last panel meeting follow:

1. Irradiation-Induced Transformation in U-Mo and U-Nb Alloys

X-ray diffraction patterns obtained at Hanford on thermally transformed and irradiated U-9 w/o Mo indicate conclusively that the alpha plus epsilon phases are transformed to gamma during irradiation. No alpha could be detected in the patterns obtained, although it is possible that one-third of the original alpha could escape detection because of background activity. Line broadening measurements indicated that irradiation essentially eliminated alloy concentration gradients which existed prior to irradiation. Thus, the lamellar microstructure which persists in the irradiated samples can not be explained on the basis of a molybdenum concentration gradient. Another unexplained effect is the poorer corrosion resistance of the irradiated samples compared to gamma-quenched samples. This has been found to be true both for the thermally transformed and irradiated U-Mo and U-Nb alloys and may be related to the apparent lack of irradiation-induced structural changes. Note however that the corrosion behavior of the transformed samples improved upon irradiation. The panel's attention is directed to this for discussion and comment.

2. Aluminum-Base Alloys as Barrier Layers for U₃Si Fuel Elements

The first group of fuel elements prepared by brazing extruded U₃Si rods to Zircaloy-2 tubes with a 0.030 in. thick barrier of Al-6 w/o Cu failed after exposures of 56 to 77 days in 650°F water. None of the elements examined after failure showed evidence of bondline attack at the core-barrier interface. Failures were attributed to lack of clad-barrier bonding due to poor brazing technique or to build-up of oxide at the base of the 0.040 in. diam. defect. The latter caused bulging of the cladding and peeling at the core-barrier interdiffusion zone, thus exposing more fuel to the water. Despite exposure of relatively large areas of fuel by this mechanism, the fuel did not disintegrate, as happens with gamma phase alloys, but remained in one piece and corroded gradually at the exposed surface. These encouraging results have prompted fabrication and testing of additional fuel elements prepared by an improved brazing technique which ensures good clad-to-barrier and barrier-to-core bonds, thinner barrier layers of Al-base alloys, and less reaction of barrier and core alloys. It is planned to investigate, also, the use of thinner Zircaloy-2 cladding in an effort to localize bulging to the defect area and prevent peeling at the barrier-core interface.

3. Corrosion of Bare U-3.8 w/o Si Alloys

Additional data on cast samples of epsilonized U-3.8 w/o Si alloys confirm the previous findings concerning the adverse effects of carbon contamination. When the carbon content is above about 0.130 w/o it is not possible to epsilonize the cast structure at 800°C and corrosion resistance in 650°F water is poor. This is probably responsible for a large part of the variability of corrosion resistance previously observed. The corrosion resistance of high carbon heats can be improved by epsilonizing at temperatures below 800°C, but reduction of carbon contamination through improvements in melting practice appears more promising. It is now felt that carbon can be held to less than 0.040 w/o without difficulty. However, factors other than carbon contamination also play a significant part in variability of corrosion resistance. Two heats having essentially the same carbon content, 0.041 w/o, and silicon contents, 3.82 and 3.77 w/o, were found to have 14 day corrosion rates of -0.35 mg/cm²/hr for one heat and -1.50 to -3.0 mg/cm²/hr for the other. Localized pitting attack has been observed for most heats tested so far. Possible factors controlling variability, such as alloy segregation, impurities, excess microstructural constituents, etc., remain to be evaluated.

Small ternary additions of Mo, Nb and Cu to arc-melted button samples have resulted in corrosion rates of less than 1 mg/cm²/hr, with 0.2 w/o Mo showing the lowest rate of -0.68 mg/cm²/hr at 105 days. Similar Al additions appear to destroy corrosion resistance, the samples being consumed in 0-3 days. Uncontrolled variables in melting practice used to prepare cast rods of these alloys have apparently prevented duplicating these results and obtaining a clear-cut indication of the effectiveness of the Mo, Nb and Cu additions in improving corrosion resistance and widening the usable silicon range. Work along these lines is continuing.

Further work on the corrosion mechanism of bare U₃Si indicates that 1 to 3% of the hydrogen liberated during corrosion in 650°F water is absorbed by the alloy, but that no hydride precipitation or hardness increase occurs. This is in contrast to 20-25% absorption for gamma phase alloys with attendant hydride precipitation and large hardness increase.

X-ray diffraction analysis of the metallic-appearing phase formed on the surface of U₃Si during exposure to 650°F water indicates formation of a FCC phase with a lattice parameter of 4.93 Å. Apparently, this phase is not U₃Si₂ as at first suspected, but may be a U-Si compound of high Si content or uranium carbide. Inter-diffusion of U₃Si and pure Si at 750°C in pressure bonded couples have produced a similar phase at the U₃Si surface. In addition, reaction of U₃Si with graphite at 800°C has shown a similar phase.

4. UO₂ Development

A defected specimen failed in the fifth Chalk River UO₂ test. The UO₂ in the 19.5 w/o enriched rod melted and the cladding burst. A large crater was formed near the center of the rod and the Zircaloy-2 clad adjacent to the crater was heavily oxidized. The bursting of the cladding is believed to have resulted from expansion caused by fusion. The heat flux was estimated to be 1.2×10^6 Btu/ft²-hr, which was twice the anticipated maximum heat flux and almost three times the maximum PWR design heat flux.

I. U-3.8 w/o Si Alloy Development

As indicated in the last resume (WAPD-PWR-PM-282) the desirability of fabricating the epsilon phase U-Si alloys by coextrusion was questioned for several reasons. It was found, for example, that a core-clad interdiffusion layer of alpha uranium formed and resulted in rapid bondline attack in 650°F water. It was found also, that the existence range of the desirable U₃Si epsilon phase was extremely narrow and that melting and heat treating invariably resulted in an excess of alpha or delta phases (or both) in the microstructure. The presence of these phases was detrimental to corrosion resistance, especially in the case of extruded rods because they lead to stringer formation and early failure by longitudinal splintering. In addition, the presence of carbon as a contaminant introduced during melting decreased thermal stability of the epsilon phase and caused some de-epsilonization during extrusion. While the possibility of avoiding these bad features of coextruded rods exists, it appeared that more rapid progress and more promising results might be achieved by avoiding extrusion and using the alloy in the cast condition. This is the procedure which is now being emphasized and which is reflected in the following discussions.

A. Clad U-3.8 w/o Si with an Aluminum Alloy Barrier (W. A. Bostrom)

Sample fuel elements which had been prepared by brazing extruded and epsilonized U₃Si rods into Zircaloy-2 tubes using an Al-6 w/o Cu barrier layer have failed in corrosion test after times of 16 to 50 days in 680°F water and 56 to 77 days in 650°F water. As previously indicated, the 16 day failure in 680°F water was probably due to an inadvertent overheating of the autoclave, exposing the samples to 750-800°F steam for several hours.

A typical section through the defect of an element which failed after 56 days exposure to 650°F water is shown in Figure 1. Figure 2 is a higher magnification photomicrograph of the core-barrier-oxide area of Figure 1. It appears that corrosion oxide initially builds up at the base of the defect, producing a force which tears the apparently weak bond between the barrier and core and peels the cladding and barrier alloy from the core. This exposes more core surface, sustaining this mechanism until severe external bulging and splitting of the cladding occurs. Figure 3, which is a section through the defect of an element exposed 77 days in 650°F water, offers further evidence for this mechanism. There is no rapid bondline attack between barrier and core alloy itself. This is consistent with previous findings which indicated that no alpha uranium interdiffusion layer will form if aluminum (which does not form a silicide and deplete the core surface of silicon) is used as a barrier layer.

Of particular interest in Figures 1, 2, and 3, is the finding that the U₃Si core alloy, when clad, does not fail by disintegration even when large areas of fuel are exposed. For all samples examined the core alloy remained in one piece and simply corroded away at the exposed surface. This is in direct contrast to gamma phase U-Mo and U-Nb alloys which are subject to internal hydriding and rapid disintegration when large areas of fuel are exposed to hot water.

It is apparent from the photomicrographs that several possibilities exist for improving the life of the clad fuel elements. These are indicated below and will be evaluated during the next report period.

1. The core-clad bond strength may be improved by restricting the formation of thick interdiffusion layers. The subject elements were brazed in one operation at 850°C. This temperature was too low to effect good clad-to-barrier bonds and too high to restrict barrier-to-core interdiffusion. This difficulty can be overcome by brazing in two operations. In the first operation the inside of the cladding tube is bonded to the barrier at a high temperature (about 950°C). In the second operation the core alloy is brazed to the barrier at a relatively low temperature (700-750°C). Several fuel elements have been prepared in this way and are now in test.

2. The barrier layer thickness used for the first elements was dictated by the ability of the Al-Cu alloy to flow and fill the gap between clad and core at 850°C. It is considered entirely too thick and resulted in some attack of the Al alloy itself. Thinner barrier layers can be applied using the brazing technique noted above; In this connection other Al-base alloys known to have better corrosion resistance in 650°F water than the one employed are being investigated.

3. The corrosion rate of the core alloy in 650°F water is relatively high compared to that of gamma phase alloys. This permits more rapid build-up of oxide at the defect. Reduction of the corrosion rate from 1 to 2 mg/cm²/hr to less than 1 mg/cm²/hr through ternary additions and improvements in melting practice is a distinct possibility as indicated in Section D, below.

4. Reduction in the thickness of the Zircaloy-2 cladding from 0.030 in. to about 0.015 in. will help to prevent peeling of the cladding from the core and restrict bulging to the immediate area of the defect, thus preventing unduly large areas of fuel from being exposed which would in turn result in general bulging of the cladding as corrosion progresses.

B. Hot Water Corrosion of Al-Base Barrier Layer Alloys (W. A. Bostrom and I. Cohen)

Several Al-base alloys are being tested in 650°F water as bare samples or as couples bonded to Zircaloy-2. Couples involving the binary Al-6 w/o Cu alloy and Zircaloy-2 have been in test for 106 days. While the Al alloy shows evidence of oxidation there is no apparent bondline attack. Bare samples of this alloy are corroding at a rate of +0.01 mg/cm²/hr after 112 days in 650°F water. Other Al alloys, X2219 (Al-6 Cu-.09 Fe-.07 Si-.29 Mn-.10 V-.13 Zr), M400 (Al-1 Ni-1 Fe) and M388 (Al-1 Ni-.5 Fe), being screened as possible cladding alloys, are undergoing extensive corrosion tests in 680°F water in the bare condition. While the data obtained are not directly applicable to the use of these alloys as barrier materials, determination of their relative behavior in hot water will be helpful. The corrosion rates observed for these alloys in 680°F water are too high (about 60 times that for Zircaloy-2) to be considered as suitable cladding alloys. But the rates are much lower (about 0.008 mg/cm²/hr) than for the epsilon U₃Si alloy (0.5 to 2 mg/cm²/hr). Hence, their use as barrier layers appears quite promising.

Al-5 w/o Si and Al-12 w/o Si alloys have also been tested in 650°F water in the form of welding rods. Attack in this case was rather severe, complete oxidation occurring in 35 days. However, the use of these alloys as the brazing component between flat Zircaloy-2 plates have withstood exposures in excess of 1200 hours in 680°F water tests conducted by Armour Research Foundation. These alloys, therefore, are also being considered as possible barrier materials.

C. Brazing of Al to Zircaloy-2 at Relatively Low Temperatures (W. E. Bond)

Several techniques have been considered for reducing the temperature required to braze Al-base alloys to Zircaloy-2 and thus permit brazing to be carried out without excessive reaction between the aluminum alloy and the U_3Si fuel. Preliminary results were promising in several cases and were suggested to the PWR Fuel Element Subdivision for further investigation. These are indicated below. Until an improved technique is developed, the method described in the Section A, above, while unsatisfactory for production purposes, is suitable for preparing fuel element samples for material tests and is being used for this purpose.

a). The use of Zirconium hydride as a flux has permitted bonding of Al-6 w/o Cu to Zircaloy-2 strips at 800°C and 750°C (Figure 4A). At 800°C wetting and flow of the Al-alloy is quite good, but several interdiffusion layers (which have not been evaluated for corrosion resistance) form. At 750°C, flow of the Al alloy is not as good but the bond obtained appears sound and less alloying with the clad is encountered.

b). Handy and Harman Flux for brazing to titanium has permitted bonding to Zircaloy-2 strips at temperatures as low as 700°C (Figures 4B and C). The suitability of this flux (and the Zirconium hydride) when applied to the inside of Zircaloy-2 tubes has not been suitably evaluated.

c). Ultrasonics has been considered as a possible means of breaking up the refractory oxide film on the cladding during brazing. Preliminary results obtained on the inside surface of a Zircaloy-2 tube placed in contact with a transducer at 20 kilocycles while immersed in Al-11.6 w/o Si alloy at 850°C is indicated in Figure 4D. A very good bond with essentially no alloying is indicated.

d). Al has been evaporated on the inside surface of Zircaloy-2 tubes held either at room temperature or 750°C. Very uniform Al film thicknesses varying from 0.001 to 0.005 in. have been obtained in this way and appear quite promising. Subsequent brazing tests, however, have not been made.

e). Zinc and copper have been deposited on the inside of Zircaloy-2 tubes by replacement from solution. The coatings produced are uniform in thickness. Zinc is deposited in a heated bath and is well bonded to the cladding. Copper was deposited at room temperature and was tightly adherent. Subsequent brazing has not been suitably evaluated.

f). Dipping of Zircaloy tubes into molten Al alloy baths was also considered as being promising, but has not as yet been evaluated.

g). Wiping of molten Al-11.6 w/o Si alloy over the Zircaloy-2 surface by rotating a rod inside the Zircaloy-2 tube at 850°C has produced good clad-to-barrier bonds in preliminary tests.

D. Corrosion Resistance of Bare U₃Si Cast Rods (I. Cohen and W. E. Bond)

It was previously reported that the corrosion rates observed for duplex melted and epsilonized U₃Si ingots were lower than those of extrusions prepared from the same ingots. It was also shown that the corrosion rate of the extruded material was not improved, and in most cases became worse when the extrusions were re-epsilonized for 1 week at 800°C. Several heats of the binary alloy, therefore, were prepared in the form of cast rods to obtain additional information on the corrosion resistance of cast material.

The first cast rods were induction melted in BeO-washed graphite crucibles and cast to 5/8 in. diam in graphite molds. Chemical analyses determined for four such heats are shown in Table I along with corrosion data obtained in 650°F water. It is apparent that the silicon contents for the four heats are quite uniform (3.76 to 3.81 w/o) but the carbon contents are very high (0.132 to 0.384 w/o). Samples epsilonized 1 week at 800°C show decreasing corrosion rates and improved corrosion life with decreasing carbon content.

All of the samples, however, were subject to non-uniform and severe surface pitting during corrosion. Metallographic examination of the samples after epsilonization indicated that epsilonization was essentially complete in the 0.132 w/o C heat, but not complete in the others (Figure 5A to D). An attempt was made to promote further epsilonization by reheat treating for an additional week at temperatures below 800°C. The results, shown in Figure 6A to D, indicated appreciable improvement in microstructures for all but the very high carbon heat. This was reflected also in improved corrosion resistance as indicated in Table I, but the pitting attack still occurred. It appears from these results that the pronounced decrease in peritectoid transformation temperature resulting from carbon contamination can be somewhat overcome by a decrease in epsilonizing temperature. Improvements in melting practice and preparation of BeO-washed graphite crucibles, designed to reduce carbon contamination, appear to be a more promising avenue of approach. This is now being done, with the majority of more recent heats falling below 0.04 w/o C.

Two of the more recent duplex melted ingots, prepared from induction melted material (BeO-washed graphite crucibles), were found to have the same carbon content, 0.041 w/o, and nearly the same silicon content, 3.77 and 3.82 w/o. Samples from these ingots, which were originally intended for subsequent extrusion into rods, were corrosion tested in 650°F water after the ingots had been epsilonized 7 days at 800°C. Despite similar chemical compositions considerable difference in 14 day corrosion rates were observed. The ingot with the slightly lower Si content had a 14 day corrosion rate of -1.5 to -3.0 mg/cm²/hr. This heat has been analyzed by Nuclear Metals, Inc., using a preoxidation technique which normally gives higher silicon values and found to contain 3.93 w/o Si. The other ingot had a 14 day corrosion rate of -0.35 mg/cm²/hr. Both of these heats showed local pitting attack, about half (16 out of 32) samples tested from the first heat failed by cracking or disintegration within 28 days while the samples of the better heat showed a corrosion rate of -0.90 mg/cm²/hr after 35 days. Another duplex melted ingot, having a carbon content of 0.094 w/o and a sili-

con content of 3.80 w/o (nominal) had a 7 day corrosion rate of -1.57 to -1.97 $\text{mg}/\text{cm}^2/\text{hr}$ and showed no localized pitting. The reason for these differences in behavior has not as yet been established. Variations in alloy segregation or in amounts and types of residual microstructural constituents is suspected and is being investigated. It is apparent, however, that gross-carbon content is not responsible for the difference.

Besides investigating the corrosion resistance of cast rods prepared from heats induction melted in BeO-washed graphite crucibles, other types of melting crucibles are being considered. Heats have been melted in BeO, MgO, ZrO_2 and Al_2O_3 crucibles and cast into silica investment molds. Chemical analyses, microstructure and corrosion properties of these heats will be obtained during the next report period.

E. Corrosion of Bare Ternary Alloys (W. E. Bond and I. Cohen)

The corrosion tests of U-3.8 w/o Si alloys containing small ternary additions of Mo, Nb, Cu, Ta and Al were continued in 650°F water: Four sets of samples were involved and tested separately. The first set were prepared as arc-melted buttons by the Armour Research Foundation. These included alloys containing 0.2 w/o Mo, Nb, Cu, Ta and Al. The other three sets were prepared at Bettis using different melting practices. The results are included in Table II along with the chemical compositions and melting practice employed.

The arc-melted button samples indicated that ternary additions of Mo, Nb and Cu were beneficial to both life and corrosion rates. The Mo addition showed the lowest rate, -0.68 $\text{mg}/\text{cm}^2/\text{hr}$ at 105 days. This is to be compared with the binary U_3Si alloy which had a 42 day rate of -1.2 $\text{mg}/\text{cm}^2/\text{hr}$. The aluminum addition resulted in very poor corrosion resistance, samples disintegrating in 0-3 days. The Ta addition caused little change in corrosion resistance over that of the binary alloy.

Earlier data had shown that arc-melted button samples deteriorated in corrosion resistance if they were subsequently induction melted. This was attributed to uncontrolled variables in the melting process which are reflected in the results obtained with the cast rods prepared at Bettis. The first set of these rods, as seen in Table II, were induction melted in BeO-washed graphite crucibles and cast to $5/8$ in. diam in graphite molds. Chemical analysis indicated that silicon and carbon varied considerably from heat to heat. The two high carbon heats (0.125 and 0.181 w/o) failed to epsilonize completely when heated for 1 week at 800°C . The corrosion resistance of all, except the lower carbon (0.090 w/o) heat, was generally poor.

The second set of samples were melted in pure BeO crucibles. They were more consistent in silicon content and the carbon was relatively low (0.014 to 0.042 w/o). A maximum of about 0.015 w/o C was expected from the raw materials, suggesting that some was introduced during casting in graphite molds. The corrosion rates for the Mo, Nb and Cu bearing alloys, however, was 2 to 3 times higher than those observed for the arc-melted buttons. The samples were subject to non-uniform surface pitting, suggesting alloy segregation which was not apparent from the microstructures. The latter indicated a random distribution of residual alpha and delta particles. The Al-bearing alloy again showed poor corrosion resistance even though the amount of Al present was very low (0.07 w/o).

The third set of cast rods were intended to determine more accurately the optimum Mo concentration in the range 0.1 to 0.3 w/o. The lower Mo heats were melted in ZrO₂ crucibles while the other was melted in BeO-washed graphite. All were cast to 3/8 in. diam rods in silica investment type molds to avoid carbon contamination from this source. No chemical analyses or microstructures are as yet available. However, the seven day corrosion rates are indicated in Table II. The corrosion rates are higher than expected and again suggest that uncontrolled variables in the melting practice is responsible for the poor showing of the 0.2 w/o Mo alloy.

F. Mechanism of Corrosion of Bare Epsilonized U-3.8 w/o Si Alloys (R. A. Wolfe)

Various factors which are believed to have an influence on the corrosion mechanism of bare, epsilonized U-3.8 w/o Si alloys are being investigated as indicated below:

1. Nature of the Subscale Formed During Hot Water Corrosion

The formation of a metallic appearing layer has been observed between the corrosion oxide and the unaffected core alloy surface during corrosion in 650°F water. This layer may be seen in Figure 7 for an arc-melted button sample of U-3.8 w/o Si - 0.2 w/o Nb alloy which had been exposed for 7 days in 650°F water. Both the subscale and residual delta (U₃Si₂) particles dispersed in the alloy matrix have the same appearance and are unattacked by electrolytic chromic-hydrofluoric acid etching. It is also noted that there is no primary grain boundary between the delta particle and the subscale at the area of contact. This led to the supposition that the subscale was U₃Si₂ and that the corrosion reaction took the form

It was believed that U was preferentially oxidized leaving a high concentration of Si at the oxide-fuel interface and formation of a U₃Si₂ layer. Recently obtained X-ray data, however, leaves the identity of this subscale layer in doubt. A sample of the layer sufficient in size to obtain an X-ray pattern was removed from a U-3.8 w/o Si - 0.2 w/o Cu alloy which had been corrosion tested 21 days in 650°F water. The sample was found to have a face-centered-cubic (FCC) structure with a lattice parameter of 4.93 Å. This same structure was found for the similar layer formed on a binary U-3.8 w/o Si alloy sample. The structure does not correspond to U₃Si₂, but has the same structure and about the same lattice parameter as UO, UN and UC. The sample size was not sufficiently large to obtain an accurate lattice parameter measurement for comparison with those of the above compounds. However, it appears unlikely that the layer is UO since the latter is relatively unstable and forms only when availability of oxygen is extremely limited. Also, the low nitrogen content, less than 0.004 w/o, of the alloy makes the formation of UN unlikely in the quantity observed. However, carbon contents between 0.013 and 0.38 w/o, have been shown for different heats of U-3.8 w/o Si. While no correlation between carbon content and amount of the subscale layers is now available, it is possible that the layer is a carbide. Additional data are needed to test this. Another possibility is that the layer is a U-Si phase of very high Si content. However, no such FCC phase has been reported in the U-Si system.

It has not been possible to obtain a sufficient quantity of the subscale layer for density or chemical analysis because of its irregular geometry and thin cross section. However, arc-melted button samples are being prepared corresponding to the compositions of higher U-Si compounds. Also a pressure bonded diffusion couple was prepared with U_3Si and Si as the components. The interdiffusion layers observed after heating for 4 hours at $750^{\circ}C$ in vacuum are illustrated in Figure 8. The pure silicon component of the couple was found cracked after diffusion, but two diffusion layers apparently remained. It is interesting to note the similarity in appearance of the white layer adjacent to the core of this diffusion couple and that formed during exposure to high temperature water. An attempt is being made to obtain a thicker layer for X-ray identification. The second layer of Figure 8 was identified by X-ray diffraction as β - USi_2 (or U_2Si_3). Thirteen diffraction lines were obtained and their intensities correspond closely with those reported for the hexagonal β - USi_2 phase. This experiment is being repeated in an effort to retain all diffusion layers.

In another experiment a sample of U_3Si was packed in graphite and annealed in an inert atmosphere at $800^{\circ}C$ for 2-1/2 hours. A reaction occurred over about half of the sample surface. Figure 9 shows a cross section of the sample. X-ray diffraction showed that the top layer was again β - USi_2 . Apparently, U combined with carbon and became detached from the surface, the silicon concentration at the surface increasing to form β - USi_2 . It is also noted in Figure 9 that a white diffusion layer forms between the core alloy and the β - USi_2 . This layer also resembles that formed during corrosion.

It appears from the above results that the subscale layer formed on U_3Si during hot water corrosion and in the diffusion experiments described is a result of preferential surface reactions in which the surface of the core alloy is more readily depleted of U than Si. A positive identification of the subscale and unidentified diffusion layers, however, remains to be determined before any predictions as to its effect on the corrosion resistance of U-Si alloys can be made.

2. Effect of Hydrogen on Corrosion of U_3Si

It was found that a partial pressure of hydrogen (over and above the saturation pressure of water at $650^{\circ}F$) during corrosion of bare U_3Si samples has a significant effect on the rate of corrosion. Corrosion samples of epsilonized U-3.77 w/o Si were tested in $650^{\circ}F$ water in an autoclave with 800 psi hydrogen pressure. The samples were obtained from extrusion No. 462 which had previously been tested under normal conditions and found to have a very low corrosion rate. As indicated in Figure 10 the weight loss versus time is shown for this material under the two test conditions. For the first 7 days of test the corrosion rates were about the same for the two test conditions. In the next corrosion period, however, samples tested under high hydrogen pressure displayed an accelerated corrosion rate which remained constant for the next 21 days. Thus, there appears to be two characteristic corrosion rates for the two test conditions. During the 7 to 28 day test period the rate was $-0.66 \text{ mg/cm}^2/\text{hr}$ for the samples tested under standard conditions and $-1.33 \text{ mg/cm}^2/\text{hr}$ for those tested under high hydrogen pressure. To determine the effect of pressure alone, another run using 800 psi of argon will be made.

Specimens were periodically removed from both the test at saturation pressure and the test with the 800 psi partial pressure of hydrogen. Samples from these specimens were analyzed by hot extraction at 950° to 1050°C for total gas content calculated as 100% hydrogen. The results are listed in Table III. It is apparent that U_3Si does absorb hydrogen during corrosion testing, but the amount absorbed is small. Approximately 1% to 3% of the hydrogen produced during corrosion of U_3Si was absorbed by the specimens. This is to be contrasted with 20% to 25% hydrogen absorption by gamma phase U-Mo alloys. The results are consistent with earlier hydrogen overvoltage studies which indicated a slight slope change in the overvoltage curve for U_3Si and was interpreted as a slight tendency for hydrogen absorption. Metallographic examination after corrosion testing revealed no evidence of hydride precipitation. Also no increase in hardness after 28 days of exposure was detected for the specimens tested at saturation pressure.

The amount of hydrogen absorbed per unit weight loss was nearly the same for both test conditions (Table II). This result is not consistent with the fact that the rate of corrosion is approximately doubled by the presence of 800 psi hydrogen in the autoclave. It appears, therefore, that the increase in corrosion by this hydrogen pressure in the autoclave is not related to the absorption of hydrogen by the sample. The investigation of the hydrogen pressure effect will be continued. It is quite likely, of course, that the effect shown in Figure 10 is merely indicative of sample and test reproducibility.

3. Study of Al-Alloy Barriers by Pressure Bonding

In addition to brazing of U_3Si rods to Zircaloy-2 tubes using various Al-alloy barriers, it was considered desirable to use the pressure bonding technique to obtain data on clad-barrier and core-barrier diffusion and to determine the effect of diffusion on the corrosion mechanism of clad U_3Si . Also, data were desired on the distribution of hydrogen between clad, barrier and core. Earlier work on pressure bonding of U-Mo alloys at Battelle Memorial Institute and U_3Si at Sylvania Electric Products (SEP) indicated that large diffusion zones could be readily obtained and corrosion attack in the individual zones could be readily followed.

Sandwich type samples were prepared by inserting a 0.030 in. thick Al-6 w/o Cu disc and a cylindrical U_3Si sample into a closed end (0.030 in. thick) Zircaloy-2 cup and pressure bonded for 30 minutes at 500°C. The open end of the cup was then sealed by welding a Zircaloy-2 end plug to the rim of the Zircaloy-2 cup. A defect, 0.040 in. diam, was drilled through the closed end of the cup and the adjacent barrier layer. Two such samples were corrosion tested in 650°F water. The cladding bulged at the defect after 4 days exposure. Metallographic examination indicated that the fuel-barrier interface had been severely attacked. These results are in contrast with those obtained by SEP on similar pressure bonded samples which lasted 35 days in 650°F water.

Another pressure bonded sample was sectioned and examined without corrosion testing. It showed a 0.001 in. thick core-barrier diffusion layer. This is considerably less than that observed in brazed fuel element samples which did not show rapid attack at the fuel-barrier interface. It appears, therefore, that the pressure bonded samples do not behave in corrosion as do the brazed elements. Despite this, work will be continued on pressure bonded samples to obtain a clearer understanding of the fuel-barrier characteristics.

II. Basic Metal Alloy Development

A. Alloying Behavior of Uranium

1. Specific Heat Measurements on U-Base Alloys (R. F. Boyle and E. K. Halteman)

Additional specific heat measurements have been made on U-15 w/o Mo samples to support previous data indicating that the epsilon phase in the U-Mo system is actually an ordered form of the gamma phase. The epsilon phase was previously shown as having a molybdenum existence range of 31 to about 32.7 a/o Mo. Its crystal structure is $C11b \cdot MoSi_2$ type. The unit cell is tetragonal and the space group $D_{17}^{17} - 14/mm$. The lattice parameters are $a_0 = 3.427 \text{ \AA}$, $c = 9.834 \text{ \AA}$, $c/a = 2.871$. The three samples which analyzed 15.2 w/o Mo (30.4 a/o) were gamma-quenched (900 C-24 hrs-W.Q.) and then heat treated in a stepwise fashion from 590°C to obtain various degrees of ordering as indicated below:

Sample:	Y-85(11)	Y-85(2)	Y-85(3)
Heat Treatment:	590→570°C in 109 days	590→550°C in 110 days	590→500°C in 124 days
Phase Present:	epsilon	epsilon	epsilon
Phase Present after Sp. Ht. Measurements	gamma	gamma	gamma

Figure 11 is a plot of specific heat versus temperature for the three samples. The temperature identifying each curve represents the lowest temperature reached on each sample during the ordering heat treatment. Note that the evolution of the latent heat of ordering causes a sharp rise in specific heat at about the same temperature as that of the final ordering temperature. The samples receiving final ordering treatments at 570, 550 and 500°C release the latent heat of ordering at 560, 551 and 500°C, respectively. The break in the curves cannot be located exactly, but the agreement with final ordering temperature is quite good.

The above experimental results correlate well with existing order-disorder theory of AB and AB₂ alloys and indicate that the epsilon phase is actually an ordered form of gamma with an AB₂ type of structure.

The specific heat samples were examined in an X-ray spectrometer prior to their being heated in the specific heat apparatus. From the areas of the diffraction peaks the Bragg and Williams long range order parameter S was computed. The structure factor was corrected for the composition being 30.4 a/o Mo rather than the ideal value of 33-1/3 a/o. The superlattice line was 1.5° in θ different from the normal lattice line. As the two lines were so close together the temperature factor was neglected. A computation using the temperature factor that was used in the original structure determination of the epsilon phase showed that neglecting this factor would change the value of S by less than 0.01. The results are shown in Figure 12. The point for the 400°C sample is quite low. This sample was at the final ordering temperature of

400°C for 23 days while the other samples were at their final temperatures for longer times (72, 93, and 102 days). One would not expect the 400°C sample to be at equilibrium as it had spent the least time at the lower temperature.

U-Nb samples corresponding to AB_3 , AB_2 , AB , A_2B and A^3B compositions are being prepared for specific heat measurements to determine if³ an order-disorder reaction occurs in this system. The AB_3 and AB_2 compositions have been received and are being machined.

2. Resistivity of U-Alloys at Low Temperatures

The liquid nitrogen cryostat built for determining electrical resistivities of U-Mo alloys at low temperatures is being replaced by a new liquid helium cryostat to permit measurements to lower temperatures. This was considered desirable since the maximum in the resistivity anomaly observed in gamma phase U-Mo alloys may not be detected unless temperatures below -196°C are reached. Some measurements are now being made on U-9 to -13.5 w/o Mo down to liquid helium temperatures at the Westinghouse Research Laboratories. Results will be available for the next resume. Hall coefficient measurements are also being made on these alloys.

B. Uranium Base Alloys with Transition Phase Structures (M. W. Burkart)

An effort is being made to determine the habit plane for the diffusionless transformation of gamma to the alpha prime phase. Coarse grained specimens of U-5 w/o Mo have been prepared by prolonged annealing at 1000°C. The largest grains in these specimens have been outlined and photographed. After finding their orientations from Laue patterns, they will be treated to produce the alpha prime phase for which the habit plane will be determined. Preparations have been made to end quench a U-5 w/o Mo rod from 1000°C. This experiment is designed to determine the effect of cooling rate upon the formation of the alpha prime phase and the decomposition of the gamma phase.

The kinetics of the thermal decomposition of the alpha prime phase are also being investigated. Specimens of U-5 w/o Mo, water-quenched from 900°C to produce the alpha prime phase, have been annealed at 400°C for various periods of time between 10 and 100 hours. Preliminary results indicate that the alpha prime phase is still present after 10 hours at 400°C. After 20 hours there is no metallographic evidence of alpha prime. The X-ray diffraction results show a poorly developed alpha pattern and the presence of another phase which may be either gamma, epsilon or alpha prime. With increased annealing times there appears to be a gradual development of a good alpha phase diffraction pattern.

Since the alpha prime phase readily decomposes at 400°C, it is apparently different from the phase which has been observed surrounding hardness impressions in annealed U-Mo specimens. In this case the phase could be observed after more than 400 hours at 400°C. An attempt is being made to obtain a satisfactory Weissenberg pattern of this phase in order to identify it.

C. Thermal Stability of Low Zr-Nb Alloys of Uranium (M. W. Burkart)

A series of U-Nb alloys containing between 2 to 12 w/o niobium have been successfully pressure bonded to zirconium. The diffusion couples are being annealed between one and three weeks at 1050°C to promote diffusion. The microstructure of a couple annealed for three weeks at 1050°C is shown in Fig. 13. Metallographically it has been possible to distinguish the presence of at least six different diffusion layers in the couple. X-ray identification of the layers is now in progress.

Diffusion couples were also prepared using strips of tantalum foil as markers to denote the position of the couple interfaces prior to diffusion. These couples will be used to measure marker movement and will be chemically analyzed to determine the diffusion coefficients of the components. From the porosity which has been observed on the uranium alloy side of the couple interface, it appears that the uranium has the highest diffusion coefficient.

Additional specimens are being annealed at 400°C after the diffusion treatment to determine the thermal stability of the gamma phase over a range of niobium and zirconium concentrations. Couples will also be corrosion tested to determine the corrosion resistance of the gamma phase over a range of compositions.

D. Magnetic Susceptibility Measurements (E. K. Halteman)

The magnetic susceptibility apparatus has been rebuilt to allow better temperature control of the sample. A metal, liquid nitrogen cryostat has been designed, built, made vacuum tight and assembled in position above the magnet. The resistance thermometer for measuring the sample temperature is being calibrated. It is planned to measure the magnetic susceptibility of U-Mo alloys as a function of temperature (before and after introduction of the hydride phase by exposure to hot water). This will indicate the difference in tendency toward ferromagnetism in U-Mo gamma phase alloys with and without the presence of the hydride phase. In this connection the possibility has been raised that the hydride platelets represent a body centered cubic phase which is only slightly different in lattice parameter from the gamma matrix and for this reason cannot be identified by X-ray diffraction.

Prior to dismantling the old magnetic susceptibility apparatus, some measurements were made on hydrided U-12 w/o Mo samples. These measurements were made at a fixed temperature, that of liquid nitrogen, and at a fixed field strength of 3230 gauss. A sample containing 155 ppm of hydrogen had a susceptibility of 2.2×10^{-3} emu. If one assumes that 25 ppm of hydrogen is the solubility limit, the remaining 130 ppm would form UH_3 or $(\text{U}_{1-x}\text{Mo}_x)\text{H}_3$ platelets and the magnetic moment per gram of this sample would be 7.1. The magnetic moment of UH_3 at the same value of temperature and field strength, on the other hand, has been reported as 18.0 (Guen, D. M., J. of Chem. Physics 23, 1708, 1955). Since the matrix alloy is about 25 a/o Mo, one might expect the hydride to be $(\text{U}_{0.75}\text{Mo}_{0.25})\text{H}_3$. This would have a magnetic moment per gram almost equal to that of UH_3 as the Mo atoms are almost equal in size to the U atoms and the hydrogen makes so little a contribution to the mass. Thus, the platelet material does not have a large enough magnetic moment to be UH_3 .

An alternate approach would be to consider the platelet material to be pure UH_3 and have the magnetic properties of bulk UH_3 . One can then compute that 51 ppm of hydrogen are needed to give the observed susceptibility and that the remaining 104 ppm of hydrogen are in solution. As it is known that platelets are visible microscopically below 100 ppm of hydrogen it is concluded that the platelets are not UH_3 on the basis of magnetic moments at fixed temperature and field strength. It is planned to measure the magnetic moment as a function of temperature and field strength.

E. Identification of the Hydride Phase in Corrosion Tested Gamma Phase U-12 w/o Mo Alloys
(W. E. Bond)

It was previously reported (Resumé X) that the hydride decomposition pressure of U-12 w/o Mo samples corroded for various times in 650°F water to introduce the hydride phase followed the expression

$$\log P_{\text{mm}} = \frac{-1235}{T} + 5.315.$$

The samples involved in the hydride decomposition runs were examined metallographically and compared with samples corrosion tested in the same way but not subjected to further tests. The latter are shown in Figures 14 and 15 along with the hydrogen content and corrosion rates after 2, 4, 7, 14 and 21 days exposure to 650°F water. It will be noted that evidence of hydride precipitation occurs within 2 days, that the hydride forms first at grain boundaries and then platelets are nucleated, for the most part, at grain boundary intersections. With increasing corrosion time (and hydrogen content) the number of platelets increase, the platelets became coarse and the corrosion rate increases. At high magnifications (1000X) isolated platelets are observed in the sample tested 2 days and containing as little as 20 ppm of hydrogen. There also appears to be a hydride gradient from edge to center of the 1/4 in. diam cylindrical samples exposed to hot water for relatively short times (2 to 4 days).

After the hydride decomposition runs of samples exposed for 7, 14 and 21 days in 650°F water, there was evidence of changes in the appearance of the hydride. This was most pronounced in the sample exposed for 21 days. The latter sample, which had a corrosion rate of $-1.8 \text{ mg/cm}^2/\text{hr}$ and contained 1347 ppm of hydrogen was held for 1 day at 154°C during the hydride decomposition run. Very little decrease in hydrogen occurred during the run (because of the very small volume of the apparatus) so that changes in hydride appearance is attributed solely to decomposition effects. As seen in Figure 15D, the original coarse platelets have apparently decomposed and reformed locally to much finer platelets having a more uniform distribution within the matrix. The samples corroded for 7 and 14 days did not show as much change even though the decomposition temperatures were higher (240 and 325°C) and times were longer (2 and 6 days).

One of the samples exposed to 650°F water for 14 days (containing 815 ppm of hydrogen) was evacuated for 24 hours at 406°C to remove the hydride phase. Figure 16A, B and C illustrates the structure at the center and edge after dehydriding. Based on the appearance of the hydride, a gradient of 120 ppm at the center to 0 ppm at the surface is estimated. Radial cracking at the outside edge occurred. The cracks appear to be intergranular and occur to a depth of about 0.5 mm. Decomposition of the hydride and its removal with an attendant increase in density apparently caused crack-

ing. The density of the gamma phase U-12 w/o Mo alloy is 16.9 gm/cc while that of the hydride has been estimated as about 13.2 gm/cc.

Traces can be seen in Figure 16C where the hydride platelets originally existed. These appear as actual depressions or voids in the metallographically prepared surface. Their presence may account for the finding that molecular hydrogen can be re-introduced in samples which once contained platelets. This could not be done, even at high temperatures, for samples which were not first exposed to high temperature water.

A new apparatus is being constructed to carry out a detailed program designed to determine the thermodynamic properties of the hydride phase and to obtain more data on the U-Mo-H₂ system. This now appears feasible since it has been found possible to remove and re-introduce hydrogen in the gamma phase U-Mo alloys after hot water exposure.

F. U-Nb Phase Diagram (R. B. Roof, Jr.)

X-ray diffraction data on the U-10 w/o Nb alloy had previously indicated the existence of a face centered cubic phase in the U-Nb system. To obtain more information on this phase, its identity and composition, alloys corresponding in composition to U₃Nb, U₂Nb, UNb, UNb₂ and UNb₃ were prepared as arc-melted buttons. Ten samples of each alloy were heat treated at 1100°C for five days to homogenize the structure. X-ray diffraction patterns were obtained on each of the samples to provide a check on homogeneity, to determine lattice parameter as a function of composition and to provide a record of the original condition of the samples prior to subsequent heat treatment studies.

The homogenization treatment resulted in a significant reduction in alloy segregation present in the as-arc-melted samples. The diffraction lines were sharper and more symmetrical in shape following homogenization. However, only the (110) diffraction line was sufficiently sharp to obtain accurate 2θ values. The lattice parameters, therefore, were determined from the (110) reflection. Figure 17 shows the lattice parameter versus composition (both in w/o and a/o) for the U-Nb alloys quenched from 1100°C. The lattice constant for gamma uranium was determined from an extrapolation of data relating lattice parameter with temperature (Crystal Data, p. 473). The lattice parameter versus w/o Nb curve shows a significant difference from that reported by B. A. Rogers (Iowa State College Quarterly Summary Report No. ISC-609 dated June 16, 1955). The probable error in the parameters of lattice constant and composition is shown by the size of the rectangles comprising the points of the curve. This curve will be used to determine the compositions of the two phases in alloys quenched from the two-phase gamma and gamma prime field.

III. Corrosion Results on U-Mo and U-Nb Clad Fuel Elements in 650°F Water (I. Cohen)

Routine corrosion tests of duplex-melted Zircaloy-2 clad and extruded defected fuel elements in 650°F water are being completed. The results indicate that the corrosion life variability that was found for induction cast and extruded fuel elements has been overcome to a large extent by using duplex-melted alloys. Fuel element samples of extruded U-12 w/o Mo defected with an 0.040 in. diam hole have survived 224 days of test with no failures. This can be compared with the 49 to 256 days failure time for defected samples of induction cast and extruded material tested earlier. Four out of six defected fuel elements of duplex-melted and extruded U-10.5 w/o Mo have also survived 224 days of test in 650°F water with one failure occurring in the 168-182 day period, and the other failure occurring in the 210-224 day period. Extruded fuel elements with 1 w/o Pt added to U-8 w/o Mo and 0.5 w/o Pt added to U-12 w/o Mo now have 252 days of test with no failures recorded.

Cold drawing extruded fuel elements more than 50% R.A. reduces the corrosion life of U-12 w/o Mo alloy to less than 28 days in 650°F water. The shortened life of cold drawn samples can be attributed to transformation of gamma to alpha phase and/or destruction of the core-clad bond during fabrication. The corrosion life of cold drawn elements has been extended in two ways: first, by decreasing the amount of cold reduction to 40% or less; second, by a recrystallization and stress-relief anneal for extruded material cold drawn over 40%. Defected fuel elements made from duplex-melted and extruded alloy, cold drawn 17%, have now been in test 252 days with no failures. Samples made from the same extrusion but cold drawn 30% have failed in 224 to 252 days. Defected elements fabricated from duplex-melted and prehomogenized (1000°C for 48 hours) ingots which were extruded and cold drawn 17 and 30% have survived 252 days test with no recorded failures. Similar sample elements cold drawn 40% have been in test 112 days with no failures. Defected samples cold drawn 53% and given a recrystallization and stress-relief anneal in the gamma region for 10 minutes at 700°C have been in test for 154 days without any failures.

The corrosion results of Zircaloy clad and defected samples of extruded U-10 w/o Nb duplex melted alloy indicate variability in time to failure. Elements of this alloy failed in 84 to 196 days of test in 650°F water with one element still in test after 252 days. This variability is not found in U-10 w/o Nb - 1 w/o Pt and U-12 w/o Nb alloys. The latter elements have been in test 224 days, while the former have 252 days of test time with no recorded failures. The use of a Nb barrier layer between core and clad in U-10 w/o Nb alloy increases the corrosion life of extruded U-10 w/o Nb and also allows the alloy to be homogenized after coextrusion with Zircaloy-2. Defected samples with the barrier layer were homogenized at 900°C for 24 hours and now have over 252 days of test time with no recorded failures. These tests are also being continued.

IV. Irradiation Effects - Uranium-Base Alloys

A. Irradiation of Transformed Specimens of U-Mo Alloys (M. L. Bleiberg)

It was previously reported in Resume' X (WAPD-PMM-282) that the electrical resistivity, hardness and density measurements on irradiated specimens of alpha-transformed U-9, -10.5, -12 and -13.5 w/o Mo indicated that the alpha plus epsilon phases had reverted to the gamma phase as a result of neutron bombardment. Microstructures, however, failed to show the expected gamma phase structure after irradiation. In fact, no significant differences in structure before and after irradiation were observed. This is illustrated in Figures 18 and 19 for the U-9 w/o Mo alloy before and after irradiation at two levels of magnification (250X and 1500X). The lamellar structure of the thermally transformed alloy is still present after irradiation.

To resolve the discrepancy between microstructure and physical measurements an X-ray diffraction pattern of the thermally transformed and irradiated U-9 w/o Mo specimen, No. A-7, whose microstructure is shown in Figures 18 and 19, was obtained using the double crystal spectrometer at Hanford Atomic Products Operation. This pattern along with that of an unirradiated control specimen is shown in Figure 20 in the range of 33 to 42 degrees in 2θ . It indicates conclusively that the room temperature stable alpha plus epsilon phases have reverted to the high temperature stable gamma phase during irradiation. It may be seen from Figure 20 that the background of the diffraction pattern on the irradiated sample was about 80 counts per second and that the recorder response was logarithmic. If the alpha phase were present in the irradiated sample, in the same concentration as the control sample, then the maximum alpha peak would be easily detected. Its intensity in the unirradiated sample corresponds to 33 counts per second. Thus, its peak would have been observed in the irradiated sample and would have shown an intensity about 33 counts per second above background (or 113 counts per second). It is possible, however, for alpha to be present in the irradiated sample and not be detected, if its concentration had been reduced to about one third of its original value. In this case detection of the peak above background would be questionable.

Five gamma phase peaks were observed for the irradiated sample. Using the values obtained for the lattice constants at the five peak locations and the Nelson and Reilly extrapolation method, an accurate lattice parameter of $3.4203 \text{ \AA}$ was calculated for the irradiated alloy. This corresponds to a Mo content of 8.8 w/o as determined from a plot of lattice parameter versus Mo content of U-Mo gamma phase alloys. The Mo content, so obtained, agrees exactly with the chemically analyzed ingot from which the sample was fabricated.

An additional diffraction pattern was obtained on the irradiated sample across the (110) plane ($2\theta = 37.3^\circ$) at a slow speed ($0.1^\circ/\text{min}$) so as to determine the extent of line broadening due to alloy segregation. The value of the instrumental broadening was determined by using an annealed single crystal of aluminum. The broadening due to the sample alone was then determined using the Warren formula. If it is assumed that the line broadening was due solely to a Mo concentration gradient in the irradiated sample, then the maximum concentration gradient was found to be $\pm 0.5 \text{ w/o Mo}$. This gradient was shown earlier to be roughly equivalent to that obtained by homogenizing an as-cast sample of U-9 w/o Mo for 16 hours at 900°C .

The above results leave little doubt as to the irradiation-induced phase reversal and strongly suggest that the gamma phase formed on irradiation of thermally transformed samples is essentially homogeneous with respect to Mo. On this basis, the appearance of lamellae in the microstructure of the irradiated sample must be interpreted as a "ghost" structure. Possibly, this might come about by precipitation of impurities which outline the original lamellae and fail to redissolve during irradiation or which may dissolve and then reprecipitate. Another explanation may involve differences in crystallographic orientation of extremely fine submicroscopic grains within the original lamellae. This may account for differences in etching characteristics even though only the gamma phase is present and the alloy is homogeneous.

The alpha-transformed specimens which were irradiated in the Materials Testing Reactor to maximum exposures of about 800 MWD/T were corrosion tested for 24 hours in 650°F water. These specimens were compared to unirradiated control specimens which were similarly corrosion tested. The control specimens were held at 300°C for 6 weeks to simulate the thermal treatment of the irradiated specimens in-pile. These results are shown in Table IV. It may be seen that the unirradiated U-9 and -10.5 w/o Mo control specimens disintegrated after this corrosion test while the irradiated specimens did not. Similarly in the U-12 and -13.5 w/o Mo alloy specimens, the corrosion rate of the unirradiated specimens was considerably higher than the irradiated specimens. These results further verify the neutron-induced phase reversal effect. The corrosion rates for the transformed and irradiated samples, however, are higher than for material in the gamma-quenched condition.

The design of an in-pile experiment in which the kinetics of the phase transformations in U-Mo and other alloy systems will be followed by resistivity measurements is continuing. The contemplated capsule design (3/8 in OD by about 3 in. long) will accommodate a wire specimen, 0.040 in diam by 5 in. long, bent in a "U" shape. The current and potential leads will be run through a KOVAR-to-glass seal and the capsule will be evacuated and filled with helium gas. The resistance of the sample will be measured by means of the current-potential method and will be recorded continuously on a modified 12 point recorder. Tentatively, the first run will involve four samples irradiated in the liquid nitrogen facility at Brookhaven. The specimen compositions and heat treatments follow:

- 1). U-15 w/o Mo - gamma-quenched
- 2). U-15 w/o Mo - gamma-quenched and transformed to the ordered epsilon phase
- 3). U-9 w/o Mo - gamma-quenched and isothermally transformed to alpha plus gamma
- 4). U-9 w/o Mo - gamma-quenched and isothermally transformed to alpha plus epsilon

B. Pre-Post Irradiation Tests on U-Nb Alloys (L. J. Jones)

1. Clad U-Nb Alloys

Ten samples of Zircaloy-2 clad natural U-10 w/o Nb, fabricated in various manners and irradiated in MTR process water to a maximum exposure of 840 MWD/T, have been in corrosion test in 650°F water for 35 days without failure. Only four unirradiated control samples out of the original ten control samples remain in test after 26 days. The corrosion data are summarized in Table V. No explanation for the apparent improvement in corrosion life due to irradiation is known. The control specimens were fabricated from the same extrusions and in an identical manner to the irradiated specimens. Corrosion testing of both groups of specimens is performed in the same autoclave at the same time.

2. Unclad U-Nb Alloys

The microhardness of unclad natural U-10 w/o Nb, irradiated in the gamma-quenched and transformed conditions, is shown in Table VI. The hardness values shown are averages of five impressions made across the diameter of a transverse section using a 5 kg. load and a 136° diamond indenter. No significant changes in hardness across the diameter of the samples were observed, indicating little or no effect due to the bulk temperature of the material during irradiation. The pre-irradiation hardness is a maximum during the early stages of transformation and decreases as transformation proceeds. After irradiation, the hardness of the gamma-quenched material showed an increase which was apparently dependent upon exposure. The hardness of all transformed specimens decreased due to irradiation. Thus these decreases in hardness again indicate a reversion toward gamma. As with density and electrical resistivity results, the hardnesses of the irradiated specimens indicated that an equilibrium condition between the gamma-quenched condition and the fully transformed condition was approached.

No apparent changes in microstructure due to irradiation were observed at magnifications available with light microscopy. Pre and post microstructures of a gamma-quenched sample, a partially transformed sample, and a fully transformed sample are shown in Figure 21. Notice in particular that, although the properties of the gamma-quenched specimen (Figure 21B) and the partially transformed specimen (Figure 21D) are similar after irradiation, the microstructure appears to be entirely different. It is postulated that the affected zones during irradiation individually are so small that structural changes would be observable only at very high magnification. In essence, the original structure remains as a "ghost" structure.

Samples cut from each of the seven irradiated specimens have been corrosion tested in 650°F static water. The results are shown in Table VII, together with the corrosion rates of unirradiated material. Apparently, the corrosion properties of gamma-quenched material are greatly impaired by irradiation. Notice that the corrosion resistance tends to be inversely proportional to exposure. Insufficient results are available to indicate any improvement of corrosion resistance in the transformed specimens due to irradiation. It would appear from the other property changes that an improvement should be found due to the reversion toward the gamma phase.

C. Pre-Post Irradiation Tests on U-Si Alloys

Seven specimens of unclad natural U-3.8 w/o Si, sealed in NaK filled capsules, are being irradiated in the A-31 NE position of the MTR. These specimens were machined from a Zircaloy-2-U₂Si coextrusion. The unsuppressed thermal flux in this position is estimated to be 2.7×10^{14} nv. A 2 cycle irradiation should yield a maximum exposure of approximately 1900 MWD/T. The specimens are scheduled for discharge February 27, 1956. When the samples are returned to Bettis, changes in physical properties and corrosion properties will be measured. A similar experiment, using cast U-3.8 w/o Si, is planned. The program will be initiated as soon as the preliminary evaluation of cast material is completed by the Alloy Development Group.

D. Volume Expansion Studies on Clad Hollow Cylinders of Uranium

Specimens are being fabricated for an irradiation experiment on Zircaloy-2 clad natural uranium having a hollow center. Specimen size has been dictated by the ease of fabrication. Specimens are 0.304 in. OD by 2 in. in length. Core dimensions are 0.244 in. OD by 0.096 in. ID by 1 in. in length. All specimens will be given a beta-quenched treatment in order to reduce the degree of anisotropy. For irradiation, the specimens will be sealed into NaK filled capsules. Currently, calculations are being made to determine the stress pattern within the core and clad due to both thermal and irradiation effects.

V. Properties and Preparation of UO₂

A. Powder Preparation (J.C. Clayton, R.E. Cowan)

Work was continued on the preparation of UO₂ by various methods for irradiation and fabrication tests as well as for investigation of the physical and chemical properties of the oxide itself.

1. Hydrogen Reduced UO₃

Because the properties of uranium dioxide prepared by hydrogen reduction of UO₃ closely resemble those of MCW powder, this method has continued to be used to produce uniformly enriched UO₂ and oxide containing additives for irradiation tests.

In attempting to reclaim rejected enriched sintered compacts it was found that dissolution occurs very slowly unless the oxide is crushed prior to acid treatment. It was demonstrated, however, that rapid dissolution can easily be brought about by air oxidation of the UO₂ to U₃O₈ at 800°C. The resulting U₃O₈ powder can then be readily dissolved in nitric acid for subsequent conversion into UO₂ by standard techniques. This method of dissolution may prove to be of importance in the reclamation of spent oxide cores.

2. Activated UO₂

In order to determine the action of ball milling in improving the sinterability of UO₂, slurries of Mallinckrodt oxide (64 ml. distilled water/200g. UO₂) were ball milled for 12-16 hours and dried in a vacuum oven at 70°C. When hydrostatically pressed at 55,000 psi and sintered in hydrogen at 1750°C, pellets were obtained with densities up to 97% of theoretical. Chemical analyses indicated that considerable oxidation took place during ball milling; the O/U ratios were increased from 2.03 to 2.15. Further studies are being made to determine the separate effects of particle size reduction and high O/U ratio.

3. Oxygen Doped UO₂

Samples of uranium oxide with O/U ratios around 2.1 to 2.2 were prepared by controlled oxidation of Mallinckrodt UO₂ at 150-250°C. These samples were annealed in vacuo at 250°C for three days and 750°C for two weeks. The presence of U₃O₈ could not be detected by X-ray analysis. These powders were pressed at 175,000 psi and chemical analyses indicated that the O/U ratios were essentially unchanged. However pellets with O/U ratios of 2.2 sintered at 1550°C for 20 hours in flowing argon were found by chemical analyses to have reverted to UO_{2.0}. Similar results were obtained with U₃O₈ powders pressed and sintered under the same conditions. Chemical analyses are in progress to determine whether any change in O/U ratio occurs in oxygen doped compacts sintered in static nitrogen at 1550°C for 10 hours. This program will be continued in an attempt to find a method of sintering high O/U ratio pellets which will preserve oxygen content.

4. Silica and Carbon Doped UO₂

Because distillation of silica from the sintering furnace could cause reaction of SiO₂ with the UO₂, a series of silica doped pellets were made to determine the sensitivity of sintered UO₂ to this impurity. Silica was added to UO₂ powder in amounts up to 1600 ppm. The compacted powders were sintered in either hydrogen or argon and corrosion tested in degassed water at 650°F and 2200 psi.

Hydrogen sintering was found to reduce the silica content appreciably. Pellets which originally contained 1600 ppm silica and were sintered in hydrogen for 8 hours at 1750°C were found to contain only 200 ppm silica after sintering. Likewise, hydrogen sintering for 2 hours at 1450°C reduced the amount of silica from 1100 to 860 ppm. Sintering in argon, however, did not reduce the silica content. Pellets containing silica in amounts up to 1600 ppm were obtained by sintering in argon for 10 hours at 1550°C. Corrosion tests of the doped pellets which had been sintered either in hydrogen or argon failed to cause adverse affects after an exposure of 21 days.

Since the presence of silica in amounts up to 1600 ppm does not cause corrosion failure and since silica is actually removed from UO₂ during hydrogen sintering, it was concluded that silica contamination from sintering furnaces is not detrimental to the corrosion resistance of UO₂. Accordingly, work on this phase of the doping program will be discontinued.

It was previously reported in WAPD-PWR-PM-282 that the presence of carbon during the sintering of UO₂ could lead to the formation of uranium carbide at the grain boundaries. The presence of this second phase could then result in the disintegration of the pellets during corrosion testing.

To test this hypothesis, carbon doped UO₂ powders were prepared and the compacted pellets were sintered in argon for various times and temperatures. Chemical analyses after sintering showed that the carbon content of sintered pellets was extremely variable and in none of the sintering runs were consistent impurity contents maintained. Attempts to introduce carbon into the pellets by sintering in direct contact with carbon were also unsuccessful; the carbon content after sintering was only 20 ppm. Pellets containing 6500 ppm carbon (present as polyvinyl alcohol and Sterotex) were also sintered in argon and the carbon content was reduced to only 20 ppm. It is thought that carbon removal takes place as a result of the reaction of carbon with water vapor present in the sintering atmosphere. Corrosion tests carried out on all sintered pellets which contained appreciable carbon before sintering failed to cause breakup or significant weight changes after an exposure of 22 days.

Further attempts to introduce carbon will be made in an effort to determine the cause of corrosion failure of UO₂ Compacts.

B. Storage Stability (J. C. Clayton)

It has been reported that UO_2 may have a tendency to pick up both water and oxygen on standing, the amount being a function of its mode of preparation as well as atmospheric conditions during exposure. Since it is highly undesirable for UO_2 intended for use in the PWR to undergo changes in storage which will greatly alter the nature of the material, studies were made of the storage stability of UO_2 prepared by different methods. Employing the technique indicated in the PWR specifications for UO_2 , fifty-gram samples were placed in a 10-cm. Petri dish and uniformly exposed to air in a drying oven at $30 \pm 2^\circ\text{C}$ for one month. Some correlation was observed between the surface area and storage stability of the various UO_2 powders. Powders prepared from ammoniumdiuranate with a surface area of $35\text{--}60\text{ m}^2/\text{cc}$ increased 2-4% in the amount of U(VI); hydrided steam oxidized UO_2 with a surface area of $22.6\text{ m}^2/\text{cc}$ increased 1.5% in U(VI); and MCW oxide with a surface area of $6.2\text{ m}^2/\text{cc}$ increased only 0.2% in U(VI) content. The amount of water pickup was rather low in all cases (0.01-0.05%).

Uranium oxide samples containing 2-6% silica were found to have a marked susceptibility towards air oxidation at room temperature.

C. Thermal Analyses (J. C. Clayton)

Thermogravimetric and differential thermal analysis (DTA) curves have been obtained for Mallinckrodt, ammonium diuranate precipitated and steam oxidized UO_2 . Preliminary results are in substantial agreement with ORNL studies. In all cases a weight loss, due to the evolution of water, occurred around 100°C . On heating in air, both the DTA and weight change curves indicated two exothermic oxidation reactions, $\text{UO}_2 \rightarrow \text{U}_x\text{O}_y \rightarrow \text{U}_3\text{O}_8$. For high pressure steam oxidized ammonium diuranate precipitated and Mallinckrodt UO_2 , the intermediate compound was U_3O_7 . However, UO_2 prepared by the low pressure steam oxidation method oxidized to a compound with an O/U ratio of 2.22 (U_4O_9 , U_2O_5). The composition of these intermediate oxides will be checked by X-ray diffraction methods. The stability range of U_3O_8 was between $400\text{--}600^\circ\text{C}$ and varied with the type of UO_2 . The U_3O_8 then began to lose oxygen gradually, reaching an O/U ratio of 2.55 at 1400°C . On cooling there was a gradual increase in weight and the oxide reverted to U_3O_8 .

D. Fabrication and Sintering of UO_2 (T. R. Padden)

Study of the relative importance of the various factors affecting the sinterability of UO_2 has continued. In this connection compacts were pressed to various densities from as-received MCW- UO_2 , the -325 mesh sieve fractions and the +325 sieve fractions. These were then sintered in hydrogen at 1750°C for times ranging from 2 to 64 hours. Density measurements and open and closed porosity determinations have been made and micro-structural studies are in progress. The following primary observations have been made:

1. Densification of the compacts resulted primarily from decreases in open porosity.

2. Maximum densification occurred within the first 16 hours of sintering. Maximum density is achieved after approximately the same sintering time regardless of original densities of the compacts.

3. The green densities of the pellets pressed from MCW as-received powder determined their final densities. Compacts having original green densities of 51%, 57.7%, 69.5% and 73% of theoretical density sintered to 79.2%, 87.79%, 95.2% and 96.9% respectively.

4. The differences in the maximum sintered densities for the series which had the various green densities resulted almost entirely from the amounts of the residual open pore volume.

5. The closed porosities varied only slightly between 2 and 64 hours.

6. The sieve size fraction of MCW oxide appears to have little influence on the final sintered densities providing the pellets are pressed to high green densities.

7. Observation of microstructure for the series of compacts made from as-received MCW oxide showed that: (a) Grain size increases with sintering time; (b) grain size is more uniform the higher the green density; (c) there seems to be an apparent variation in density on a microscale in both green and sintered compacts and this variation is more obvious the lower the green density for the same sintering conditions; (d) the grain size in the high density areas is in general larger than that in the surrounding matrix; and (e) with different pressing and sintering conditions but with the same powder it is possible to obtain compacts having the same density and approximately the same open and closed pore volume fractions but with different pore volume distributions and grain sizes.

E. Stability of UO_2 in Water (S. Aronson)

Long term tests on the stability of UO_2 compacts in water have continued. Specimens have now been exposed for 94 days in degassed water at 650°F, 77 days in degassed water maintained at a pH of 10.5 at 650°F, and 98 days in degassed steam at 750°F. In general, the appearance and weights of the compacts have not changed significantly. However, weight losses of several milligrams were noted for some samples, and there was a small deposit of powder in some containers. This may have been due to an erosive rather than a chemical action.

F. Surface Area and Density of UO_2 Powders (S. Aronson, J. C. Clayton)

Surface area and density measurements have been performed on UO_2 powders prepared from two types of ammonium diuranate. The ammonium diuranate powders were prepared from uranyl nitrate by precipitation with either ammonium hydroxide (ADU-13) or urea (ADU-14). The surface area and density values of the diuranates were 72.4 m^2/cc and 5.06 g/cc for ADU-13 and 28.2 m^2/cc and 5.15 g/cc for ADU-14. The diuranates were pyrolyzed to U_3O_8 and then reduced with hydrogen to UO_2 . The specific area and density of the UO_2 derived from ADU-13 were 59.9 m^2/cc and 11.11 g/cc respectively. The values for UO_2 prepared from ADU-14 were 60.4 m^2/cc and 11.34 g/cc.

These surface area values are the highest obtained on UO_2 powders to date. The largest area measured previously was 22.6 m^2/cc for UO_2 prepared by steam oxidation of UH_3 . However, British workers have reported surface

areas as high as 100 m²/cc. The data are as yet insufficient to determine whether there is some relationship in surface area between the parent ammonium diuranates and the derivative UO₂ powders. This point will be investigated further. The high densities of these powders are probably due to their high O/U ratios (2.08-2.14). Densities around 11.2 have been reported in the literature for UO₂ powders with O/U ratios of 2.10.

The surface areas of several UO₂ green compacts, prepared from MCW UO₂ by pressing to 68% theoretical density, were determined. The value obtained was 1.09 m²/g as compared with 0.63 m²/g for the original powder. It appears that pressing breaks up the powder to some extent, increasing its surface area.

To check the accuracy of the surface area measurements, a determination was made on a National Bureau of Standards TiO₂ powder of known surface area. The value obtained for the specific area was in good agreement with the known value.

A krypton adsorption apparatus has been constructed for surface area measurements on low surface area uranium oxides. Whereas the nitrogen adsorption technique is generally applied to powders having specific areas of 1 m²/g or greater, the krypton method is applicable to powders having specific areas as low as 0.01 m²/g. A preliminary determination of the surface area of MCW UO₂ gave a value for the specific area which agreed with that obtained by the nitrogen method.

A helium displacement apparatus for measuring densities of UO₂ compacts has been constructed and calibrated. This unit will be used to study variations in density and porosity occurring in UO₂ upon pressing and sintering.

A high pressure mercury porosimeter for measuring pore size distribution in UO₂ powders has been constructed. This equipment will permit measurement of pore diameters from about 85,000 Å at 25 psi to about 38 Å at 55,000 psi.

Preliminary experiments indicated that modification of the equipment was necessary. These changes have been made and recalibration of the volume measuring system is in progress.

G. UO₂-O₂ Equilibrium and Kinetics (S. Aronson)

Study of the equilibrium and kinetics of the system UO₂-O₂ has been continued in an effort to gain information regarding the structure and reactivity of UO₂ under various conditions.

As was reported in WAPD-PWR-PMM-282, samples of uranium oxide having O/U ratios from 2.03 to 2.67 were prepared and annealed in vacuo for various times at temperatures of 200, 360 and 700°C. Although X-ray analyses have not been completed, some definite results can be reported.

It was found that samples which were slowly oxidized at temperatures of approximately 200°C take up oxygen to an apparent O/U ratio of 2.16 without significant change in lattice parameter. As the apparent O/U ratio is increased from 2.16 to 2.30, the lattice becomes tetragonal with a constant c/a ratio of 1/0.11. This behavior may indicate that, under conditions of slow oxidation at low temperatures, the oxygen is taken up inhomogeneously with the formation of an entirely new phase, presumably U_3O_7 , and that this phase begins to show up on the diffraction patterns only after sufficient conversion has occurred. Beyond this point the cubic pattern disappears and that of the new phase becomes predominant.

The X-ray diffraction patterns of samples annealed at 200°C are decidedly different from those of the unannealed samples. Those annealed for 2 weeks show two distinct cubic phases, the α consisting of $UO_2 + x$ and the β probably consisting of U_4O_9 . For powders with O/U ratios between 2.00 and 2.16, the cubic α lines are sharp and the β lines diffuse while in the range 2.16 to 2.25, and α lines are diffuse and the β lines sharp. That further annealing is necessary in order to improve the crystallinity of the phases was confirmed by the fact that sharper patterns were obtained for samples annealed for 4 weeks. These results are in general agreement with the phase diagram of Gronwald in the composition range $UO_{2.00} - UO_{2.25}$ at temperatures of approximately 200°C. However, the exact positions of phase boundaries of the α and β cubic phases are still uncertain.

X-ray diffraction patterns of samples of $UO_{2.08}$ and $UO_{2.10}$ annealed at 700°C show only the α -cubic phase. This is also in agreement with Gronwald's phase diagram which shows a region containing only the α -cubic phase $UO_2 + x$ in this temperature and composition range. On the basis of Perio's diagram, a mixture of the α and β phases would have been expected.

Calculations are now being made to determine whether a lattice contraction occurs in the α -cubic phase as the quantity of oxygen in the lattice increases.

H. Kinetic Studies in Water (S. Aronson)

Work has continued on the rates of oxidation and reduction of UO_2 and U_3O_8 powders in 650°F water containing oxygen and hydrogen in order to better understand the reactivity of uranium oxides in water under various conditions.

As was reported in WAPD-PWR-PMM-282, samples of UO_2 and U_3O_8 powder have been exposed to 650°F water containing 100 cc H_2 /Kg for periods of 5 to 55 days. The O/U ratio of the UO_2 powders did not change beyond the range of analytical error. Chemical analyses of the U_3O_8 samples showed that the oxygen content decreased at an approximately linear rate. After 55 days, the powder attained an O/U ratio of 2.26. X-ray diffraction patterns of the samples indicate that the orthorhombic U_3O_8 phase is transformed into the α -cubic phase of UO_2 and that the amount of UO_2 present increases with exposure time.

Samples of U_3O_8 have also been exposed to water containing 5cc H_2 /Kg for periods of 5 to 60 days. Samples removed after 40 days had O/U ratios of 2.64, indicating that some reduction had occurred. Samples removed after 50 and 60 day exposures are currently being analyzed to see if further reduction is occurring.

A mechanism which may be applicable to the reduction process in water has been proposed by English workers (AERE-C/R-886) for the reduction of U_3O_8 in hydrogen at temperatures of 500°C and above. They proposed that reduction occurs by the diffusion of oxygen out of the U_3O_8 lattice accompanied by a phase change in the oxygen-deficient U_3O_8 lattice with the formation of the cubic phase of UO_2 .

To further elucidate the mechanism of the reaction, reductions will be studied at other concentrations of dissolved hydrogen. Surface area measurements will be performed on exposed samples and the concentrations and lattice parameters of the phases present will be determined by X-ray analysis.

Samples of UO_2 and U_3O_8 powder have been exposed to water containing 2cc O_2 /Kg for 5 to 10 days. The UO_2 and U_3O_8 samples removed after 5 days had O/U ratios of 2.06 and 2.69 respectively. The samples removed after 10 days had thin layers of yellow green powder on the surface indicating that the oxidation did not occur homogeneously. A new group of samples has been prepared for exposure. These powders will be mixed thoroughly after each three or four day exposure period to better insure homogeneous reaction.

I. In-Pile Fission Gas Release Experiment (R. C. Koch, J. M. Markowitz)

The in-pile fission gas release experiment has been operating at the Brookhaven National Laboratory reactor since December 27. The purpose of this experiment is to measure the relative amounts of fission gases released and their rate of release from a uranium dioxide specimen under irradiation. Fission gas emanation from the specimen is swept out of pile into an analytical apparatus by means of a stream of helium gas. There, continuous monitoring of the helium gas stream is performed with a gamma-ray spectrometer, and a second spectrometer permits quantitative analysis of gas samples. An in-pile furnace provides for control of the specimen temperature. Specimens are formed in the shape of flat plates (0.1 in. x 0.5 in. x 1.0 in.) to minimize thermal gradients. They are fabricated by hydrostatically pressing ball-milled MCW powders to 50,000 psi followed by sintering in hydrogen to about 97% theoretical density. Pile ambient temperature and neutron flux in the specimen neighborhood are, respectively, about 20°C and 5×10^{10} n/cm² sec.

Initial results show a low level of emanation activity for pile ambient temperature conditions; the level increases somewhat at higher specimen temperatures. A new specimen will be inserted during the next reactor shutdown, after which quantitative data should become available.

J. Diffusion Studies (A. Auskern)

As mentioned in WAPD-PWR-PMM-282, two types of diffusion couples are being investigated--a compound pellet, consisting of a layer of enriched UO_2 pressed onto a layer of natural UO_2 and a sintered natural UO_2 pellet upon which a thin layer of enriched UO_2 has been vacuum deposited.

A diffusion couple of the first type has been prepared and analyzed. This couple was sintered in hydrogen at 1750°C for 10 hours and centerless ground to obtain dimensional uniformity. Layers, about 0.004 in., were removed for analysis by hand grinding the pellet on fine ground abrasive cloth. Isotopic analysis was done by emission spectrography. Although this analytical method was not completely satisfactory in determining small concentration differences in the low concentration range, a curve was obtained of U^{235} concentration versus distance. An "average" diffusion constant of $5 \times 10^{-9} \text{ cm}^2/\text{sec}$ was calculated.

The significance of a diffusion constant calculated from these data is not clear. It is assumed that for true bulk diffusion the diffusing ion moves through a stable lattice, i.e., one whose density and size does not change during the diffusion process. In the experiment a number of processes are operative during the firing. Along with bulk diffusion, diffusion occurs along grain boundaries and on free surfaces. Both of these latter processes have diffusion constants which are considerably greater than that for bulk diffusion. Grain boundary diffusion is essential for the densification that takes place during sintering and is an important mechanism in the early stages of firing. It is in the latter stages of firing, after densification has been completed, where bulk diffusion becomes the major process.

Studies on compound pellets are being extended to include the effect of O/U ratio, additives and sintering atmosphere on the extent of material transport during sintering.

The determination of the true bulk diffusion coefficient is being done on diffusion couples of the second type (vacuum deposition of enriched UO_2 onto a sintered pellet). A number of pellets of this type have been prepared.

A quantity of O^{18} enriched water was used to prepare UO_2 by the low pressure steam oxidation method. Chemical analysis of uranium oxide prepared in this manner shows an O/U ratio of 2.07. This material will be used to make diffusion couples for the determination of the diffusion coefficient of oxygen in uranium dioxide.

A number of methods have been investigated for obtaining very thin layers of UO_2 from the diffusion surface. The main difficulty encountered by hand grinding techniques has been to maintain parallel cuts of uniform thickness. A sample holder has been designed which shows promise of improving and simplifying this portion of the work.

The feasibility of using U^{233} as a diffusion tracer is being investigated.

VI. UO₂ Irradiation Program

1. MTR-WAPD-14-Met-8 Irradiation of Half Length PWR Reference Rods (R. C. Koch and J. D. Eichenberg)

Four half length PWR reference rods canned in NaK capsules were irradiated for three weeks in position L-45 of the MTR. The thermal flux in this position was estimated to be 4×10^{14} nv, producing a maximum central temperature of 2600°C in the UO₂ rods. When the capsules were opened, it was found that the UO₂ in the two samples in the highest flux had melted and caused the cladding to bulge and split. No change was noted in the appearance or dimensions of the two end samples in the train which were exposed to lower fluxes.

Analyses of the fission monitors indicate the following burnups and average fluxes at the respective positions:

Position	Burnup MWD/T	Average Flux (nv)
Top of pile	376	1.1×10^{14}
7-1/2" from top of pile	1260	4.1×10^{14}
15" from top of pile	2060	7.8×10^{14}
22-1/2" from top of pile	1040	3.3×10^{14}

The accuracy of these analyses is estimated to be 20%. These results indicate that the flux in the L-45 position is appreciably higher than that estimated by the MTR personnel. The central temperature of the specimen in the maximum flux position is now estimated to be approximately 4000°C rather than the anticipated 2600°C. This higher temperature was sufficient to produce the melting phenomenon which was described above.

2. MTR-WAPD-19-Met-1 & 2 - Irradiation Cycling of Steam Oxidized and MCW UO₂ Rods (R. R. Fouse)

A density measurement has been completed on a section of a hot pressed Mallinckrodt sample from the second A-piece cyclor test. This sample was cycled approximately 7,500 times into and out of a high thermal neutron flux region in the MTR and received about 2000 MWD/T exposure.

The density measurement was made on a small piece weighing 293 mg by weighing it on a pool of mercury and then measuring the force required to submerge it. As measured by this method the density was $90.2 \pm 1\%$ of theoretical. The pre-irradiation density determined by measuring and weighing the whole pellet was 89.2% of theoretical. Density measurements will be made on other samples in the group.

3. MTR-WAPD-19-Met-4 A-Piece Cyclor (R. R. Fouse)

Dimensional measurements have been completed on eight natural UO₂ specimens, each 9-3/4" long, which were cycled into and out of a thermal neutron flux of 1×10^{14} nv approximately 10,000 times for a total estimated burnup of 1250 MWD/T.

There were no significant changes in diameters. However, specimens with 0.150 in. end clearance grew an average of 0.0065 in. while those with zero end clearance grew 0.010 in. While a maximum warpage of 0.0125 in. was found at the center of one specimen, the average warpage was 0.006 in., the same as that for a set of similar unirradiated samples.

4. MTR-WAPD-19-Met-5-A-Piece Cyclor (R. R. Fouse)

The four full length 5.5 w/o enriched UO_2 specimens being irradiated in the second A-Piece cyclor at an unsurpressed flux of 3.5×10^{13} nv have been rescheduled for an indefinite length of time sufficient to provide a total of at least 10,000 MWD/T. At present the cyclor is not operating because of a frozen hydraulic cylinder. Replacement cylinders furnished with the A-Piece cyclor did not fit because some dimensional changes were made in the final blue prints. Therefore, it was necessary to order exact duplicates of those presently in the cyclors. The cyclor should be back in operation by February 26.

5. MTR-WAPD-19-Met-6 (R. R. Fouse)

Eight natural samples similar to those described in MTR-WAPD-19-Met-4 but compacted without PVA were discharged December 26 after an exposure of approximately 2000 MWD/T and 12,500 power cycles into and out of the maximum flux of the first A-Piece cyclor.

6. MTR-WAPD-19-Met-8 (R. R. Fouse)

Four full length natural UO_2 specimens having diametral clearances of 0.005 in. and 0.010 in. and end clearances of 0.070 to 0.090 in. were charged into the first A-Piece cyclor at the MTR on December 26. They will remain in the reactor for a minimum of 6 cycles during which time they will receive approximately 12,500 power cycles and a burnup of approximately 2000 MWD/T.

7. CR-WAPD-Met-4A (R. R. Fouse and R. C. Koch)

Analysis of the fission gas released from an 80% dense undefected specimen containing hot pressed UO_2 has been completed. The specimen had about 1500 MWD/T exposure along with the defected specimen in the first UO_2 Chalk River test. A total of 10.1 per cent of the total calculated Kr^{85} was released at temperatures up to 1000°C. Ten per cent of the gas was released at room temperature, 0.02% between 27°C and 250°C, 0.02% between 250°C and 600°C, and 0.07% between 600°C and 1000°C. An analysis of the gas remaining in the specimen will also be made.

An autoclave leaching test on a portion of this specimen has been terminated and analyses will be made for representative long-lived fission products in the sample, in the water and on the autoclave walls to determine the distribution of the leachable species.

8. MTR-WAPD-17-Met-2 (R. R. Fouse)

A test is being prepared for insertion in a rabbit facility at MTR,

It will consist of NaK capsules containing 1.05 w/o enriched UO_2 samples, each 4 in. long. The samples will have 0.008 in. diametral clearances and will be irradiated in various positions in the rabbit facility to give estimated heat fluxes of 300,000, 400,000 and 500,000 Btu/hr-ft² in order to determine when and if center melting will occur. Two methods of obtaining actual heat fluxes will be used. One method involves a measurement of the differential thermal expansion between the sample and the capsule and the second method involves analyses of fission samples from the specimens. Eight capsules will be used in this test, two each containing UO_2 samples at the three heat fluxes and two containing empty clad samples as standards for the differential thermal expansion measurements.

9. MTR-WAPD-13-Met-6 (R. R. Fouse)

A defected UO_2 specimen, 4.7 w/o enriched, which had been cold pressed and sintered to 93% of theoretical density was discharged from the HB-5 facility at MTR after five reactor cycles of operation. The maximum heat flux estimated for this specimen was 600,000 Btu/hr-ft²-°F.

The sample operated for six weeks in the high flux position without appreciable cycling. Following this it was cycled in periods of 5 minutes in the high thermal neutron flux region and 5 minutes in a flux that was lower by a factor of 10. During the fourth reactor cycle the periods changed to 1 hour in and 7 hours out. In the last 3 weeks before shutdown the specimen was cycled fast and slow and left stationary for about equal periods of time.

Although analysis of the radiochemical data has not been completed for the test period, in general the specimen behaved in much the same way as the defected UO_2 specimen in CR-WAPD-Met-7. The general level of activity remained fairly constant over the entire test period. Delayed neutron peaks of a regular nature occurred during the cycling operations. No extreme bursts of activity were noted.

10. L-42 Loop Cycler (R. R. Fouse)

Two test sections are being prepared for a proposed test in the HB-5 loop at MTR when it is reinstalled as a vertical cycling loop in the L-42 lattice position. Both test sections will consist of one defected sample and one undefected sample each 10-1/4 in. long. All the samples will have 0.060 in. end clearance and a maximum of 0.008 in. diametral clearance.

The first test section will be fabricated from Mallinckrodt UO_2 according to PWR reference design. The alternate test section will be fabricated from Mallinckrodt UO_2 containing 0.2 w/o TiO_2 and pressed into pellets with a 2 to 1 L/D ratio and sintered at 1500°C in H_2 . The pellets containing TiO_2 will be placed in the clad as sintered without centerless grinding to a specific dimension.

The specimens will be fabricated by February 7.

11. CR-WAPD-Met-7 Third Chalk River UO_2 Defect Test (R. R. Fouse, R. C. Koch)

This test, consisting of one defected and one undefected sample each containing 95% dense, 4.7 w/o enriched UO_2 was discharged from the X-1 loop facility at Chalk River on November 7 and returned to Bettis on December 15.

Preliminary examination of the specimens was made and the undefected sample was punctured for fission gas release.

Neither sample showed any change in diameter but there was an 0.3% increase in length for the defected sample. In addition, the defected sample showed a weight gain of 118 mg as compared with a 22 mg weight gain for the undefected sample. The weight gain of the undefected sample and part of the weight gain of the defected sample is probably due to a whitish crud along one side which is presumed to have been deposited there during storage or shipment while the specimens were in a horizontal position.

The defected specimen was vacuum dried for 24 hours at 120°C and showed no loss in weight although a slight amount of fission gas apparently came off at this time. Data on fission gas release for both specimens will be available as soon as the radiochemical analyses are complete.

Two of the three fission monitors in the loop were obtained intact and have been processed. The burnup values are 6700 MWD/T between the two specimens and 6000 MWD/T at the bottom of the lower specimen. The corresponding thermal neutron flux values are 3.9×10^{13} neutrons/cm² at the middle and 3.8×10^{13} neutrons/cm² at the bottom end of the lower specimen.

The defected specimen was sectioned at one end. Although the examination has not been completed, no unusual characteristics were observed.

12. CR-WAPD-Met-8 Fourth Chalk River UO₂ Defect Test (R. R. Fouse)

A full length defected UO₂ specimen described in WAPD-FWR-PMM-282 was discharged from the X-3 loop at Chalk River. As previously reported, several bursts of activity occurred late in October following a series of pile trips; however, during November the short lived species of activity apparently disappeared from the coolant water. This would seem to indicate that leaching of fission products from the UO₂ had ceased, possibly because the defect had become plugged.

13. CR-WAPD-Met-9 Fifth Chalk River UO₂ Defect Test (R. R. Fouse, R. C. Koch)

Four 10-1/4 in. long UO₂ rods enriched to 8.35 w/o U²³⁵ and one 10-1/4 in. long UO₂ rod enriched to 19.5 w/o U²³⁵ were inserted in the X-1 loop at Chalk River. The 19.5 w/o rod and 2 of the 8.35 w/o rods were defected. The rods were arranged so that the one having the highest enrichment would be in the highest flux level at the center of the reactor. Three hours after start-up of the reactor an extremely large burst of activity caused the pile to trip although attempts were made to shield the loop so that operation could be continued. It was found necessary to withdraw the test after 20 hours of intermittent operation due to a build-up of an extraordinarily high level of activity. On examination of the specimens it was found that the 19.5 w/o enriched rod, which was estimated to have operated at a maximum heat flux of 533,000 Btu/hr-ft², burned out somewhat below its center forming a rather large crater and exposing what was once molten UO₂. The Zircaloy-2 clad in the immediate vicinity of the crater was heavily oxidized.

In order to determine whether the melting of the UO_2 was confined to the immediate area of the crater or whether it had occurred throughout the length of the rod, the bottom and top of the specimen were sectioned close to the end cap. Examination revealed that the interior of the rod had melted almost to the end cap and to within approximately $1/32$ in. of the edge of the pellet. Three distinct concentric zones were distinguished (see Fig. 22). The outer zone resembled the original sintered material. The zone immediately adjacent to it was compared to columnar crystals which had recrystallized from the melt. The center zone had a rather porous crystalline appearance.

On the basis of the degree of melting in the specimen, a calculation was made of the heat flux. For a range of melting temperatures from 2400°C to 2800°C the heat flux was 1.3 to 1.4×10^6 Btu/hr-ft 2 - $^\circ\text{F}$. The fission monitors from the test were examined and the following flux and burnup values were determined:

Specimen	Enrichment (w/o U^{235} in UO_2)	Ave. Flux (Neutrons/cm 2)	Ave. Burnup (MWD/T)
x-4-1	8.35	1.45×10^{13}	26
x-4-2	8.35	2.71×10^{13}	53.4
x-4-3	19.5	3.67×10^{13}	164
x-4-4	8.35	3.88×10^{13}	73.9
x-4-5	8.35	3.21×10^{13}	60.4

By positioning the specimens on the flux plot and weighting them for enrichment it was determined that the 19.5 w/o rod produced 43% of the measured output of the in-pile assembly. Based on a 65 KW output, an average heat flux of 1.2×10^6 Btu/hr-ft 2 - $^\circ\text{F}$ was calculated.

Three sections of the ruptured specimen together with one section of the specimen immediately above it in the loop assembly were pressure mounted in Kelon and sectioned longitudinally. Microscopic examination essentially confirmed the results observed microscopically. On the ruptured specimen a narrow band of oxide was found apparently in the as-sintered condition. Progressing inward toward the center the structure showed increasing grain growth followed by an area of what appeared to be 100% dense material. The major part of the central area was composed of 100% dense UO_2 particles separated by voids. On the end pellet the narrow band of sintered material extended around the diameter and the upper surface of the pellet with a concave contour along the upper surface.

The pellet from the adjacent 8.35 w/o enriched rod showed no visible change from its original condition. A layer of ZrO_2 was found on the inside of the Zircaloy-2 clad in all the sections. In the ruptured specimen a maximum thickness of 0.00067 in. of ZrO_2 was found while the average thickness was 0.00023 in. From the length of exposure time and the thickness of oxide formed, the temperature of the inside of the cladding was estimated to be 900 - 1000°F . From this figure, a heat flux of about 1.2×10^6 Btu/hr-ft 2 was also estimated. In the adjacent 8.35 w/o undefected specimen the maximum ZrO_2

thickness was 0.00011 in. and the average was 0.00007 in. Part of the ZrO_2 in this sample can be explained by the fact that the specimens were assembled in air with interference fit end caps and, on welding in a helium atmosphere, the entrapped air in the undefected specimens may have caused oxide formation.

The failure of this specimen is thus attributed to the volume expansion occurring upon fusion of the oxide, the resultant pressure within the fuel element and release of this pressure by squirting of the molten oxide through a local break in the oxide. The fact that the fuel element was undisturbed dimensionally at locations away from the break, that no excessive oxide build-up was evident over the general cladding surface, and that the edges of the broken-through section showed a transformed structure in the Zircaloy clad at the break reinforces this explanation.

14. CR-WAPD-Met-10 (R. R. Fouse)

A new UO_2 test section is being prepared for the X-1 loop at Chalk River. Based on the CR-WAPD-Met-9 failure an enrichment figure of 6.9 w/o U^{235} in UO_2 has been chosen to yield a maximum heat flux of 420,000 Btu/hr-ft² of from the center specimen. As in the previous test, there will be five 10-1/4 in. long rods. In addition to the variations in heat flux there will also be variations in axial and diametral clearances as follows:

<u>Specimen Position</u>	<u>Clearances</u>		<u>Defect</u>	<u>Heat Flux</u>
	<u>Axial</u>	<u>Diametral</u>		
Top	0.060 in.	0.008 in.	0.005 in. hole	346,000
2	0.0-0.005 in.	0.0015 in.	0.005 in. hole	400,000
Middle	0.060 in.	0.008 in.	None	420,000
3	0.060 in.	0.008 in.	0.005 in. hole	400,000
Bottom	0.0-0.005 in.	0.005 in.	None	346,000

The specimens will be fabricated according to standard production techniques using automatic Stokes presses and continuous sintering furnaces. The specimens are scheduled for shipment to Chalk River by the end of January.

15. HIR-WAPD-114A Statistical Irradiation Experiment (J. D. Eichenberg)

This experiment is designed to study the effects of irradiation on the properties of various types of uranium oxides. To obtain as much information as possible from a limited number of samples, the experiment has been arranged so that the results will be amenable to statistical analysis. As presently conceived, each train will consist of samples embracing the following variables:

<u>Type of Sample</u>	<u>Density</u>	<u>O/U Ratio</u>	<u>Additive</u>	<u>Enrichment</u>
Unsintered	60%	2.00	-----	Low High
	70%	2.10		
		2.25		
		2.67		
Sintered as received powder	70%	2.00	-----	Low High
	78%	2.00		
	86%	2.00		
	94%	2.00		
Sintered Ball milled powder	94%	2.00	TiO ₂ Ce ₂ O ₃ *	Low High
	98+%	2.00		

* May be included

At the present time, no suitable method has been found to sinter uranium oxides containing O/U ratios higher than 2.00 and still maintain the desired ratio. Therefore, unsintered samples of various O/U ratios are included in the test to ascertain the effect of this variable on the irradiation behavior. Each train will consist of 40 samples and trains will be irradiated for suitable periods of time so that the maximum exposure sample in each train will receive a burnup of 2000 MWD/T, 4000 MWD/T, 8000 MWD/T, and 16,000 MWD/T respectively.

The primary variables to be measured after irradiation are dimensions and fission gas release although measurements such as grain size and UO₂ density will be measured on at least some of the samples.

Approval was received from Hanford for the irradiation of this experiment. Manufacture of the samples will start as soon as information on permissible maximum enrichments is received from Hanford. This information is dictated by physics and heat transfer considerations which are currently being calculated at Hanford.

16 WAPD-14-Met-12 X-ray Diffraction Effects on Irradiated Uranium Oxides (J. D. Eichenberg)

A double crystal spectrometer suitable for obtaining diffraction patterns on irradiated materials is currently being constructed at Bettis. An experiment is being designed to determine the effect of irradiation on those properties of various uranium oxides which can be determined by X-ray diffraction techniques. The experiment is still in the design stage, but it has been decided to irradiate the following materials in the first test:

1. MCW UO_{2.00}
2. High pressure steam oxidized UO_{2.00}
3. U₃O₈

In addition, samples having higher O/U ratios coupled with various heat treatments will be included if it can be shown that the spectrometer will resolve the lines from this type of sample.

17. Out-of-Pile Thermal Cycling (J. E. Eck)

Five sintered UO_2 filled PWR fuel rods and one empty cladding have accumulated 10000 thermal cycles between the temperatures of 550 and 1050°F.

The net dimensional changes which have occurred are as follows:

1. Lengths have increased from 0.16% to 1.6%.
2. Diameters have changed from -0.23% to 1.0%.
3. Axial runout at the center of the rod has changed from 0 to 0.048 in. with the average of the six rods equal to 0.020 in.

Visual and X-ray inspections of the rods do not show any material damage other than a few cracked pellets and a considerable number of small particles lodged in the spaces between the pellets.

The rods have been replaced in test and will be examined again at 15000 cycles. At that time the rod which shows the least damage will be replaced by a rod of PWR reference design constructed with clearances close to the maximum values which will be allowed in production. This rod will also have been heat treated for two hours at 1300°F in vacuo.

18. WAPD-22-Met-1 (J. E. Eck)

A proposal has been submitted to the MTR project engineer outlining the method and design of equipment for the measurement of fuel temperature as a function of heat flux in a UO_2 fuel rod. The method involves the inclusion of three stainless steel clad thermocouples. Temperatures will be measured at the mid point of the rod - in the center of the fuel and at the clad interface - and at the end cap interface.

TABLE I

Corrosion of Bare U₃Si Cast Rods in 650°F Water

Heat	w/o Si	w/o C	Heat Treatment	No. Samples	Avg. Negative Corrosion Rates at Indicated Days					
					3	7	14	24	28	35
989 (BeO-washed Gr)	3.76	0.132	800°C/7 days	6	0.76(6)	1.08(5)	1.04(5)	1.44(4)	1.41(4)	1.30(3)
			do + 750°C/7 days	3	1.87(3)	1.50(3)	1.38(3)	1.34(3)	1.50(3)	
			do + 700°C/7 days	3	2.67(3)	1.84(3)	1.74(3)	1.62(3)	1.53(3)	
919 BeO-washed (Gr)	3.81	0.154	800°C/7 days	6	3.84(4)	1.96(3)	1.58(2)	2.25(2)		
			do + 750°C/7 days	3	1.78(3)	1.45(3)	1.35(3)	1.48(3)	1.72(3)	
			do + 700°C/7 days	3	2.00(3)	1.63(3)	1.63(3)	1.64(3)	1.42(2)	
995 BeO-washed (Gr)	3.79	0.190	800°C/7 days	6	Dis.(6)					
			do + 750°C/7 days	3	2.85(3)	2.06(3)	1.87(3)	1.65(2)	1.28(1)	
			do + 700°C/7 days	3	2.65(2)	2.58(2)	2.06(1)	1.82(1)	1.69(1)	
			do + 650°C/7 days	3	2.60(1)					
933 (BeO-washed Gr)	3.78	0.384	800°C/7 days	6	6.35(1)					
			do + 725°C/7 days	3	3.46(1)					
			do + 700°C/7 days	3	5.50(2)	3.61(2)	2.38(1)			
			do + 675°C/7 days	3	3.45(1)					

NOTE: Numbers in parentheses indicate samples surviving the corrosion test period.

TABLE II

Corrosion of Cast Ternary Alloys in 650°F Water

<u>Composition, w/o</u>	<u>Melting Crucible</u>	<u>Mold</u>	<u>Corrosion Rate</u> <u>mg/cm²/hr</u>
U-3.8 Si	Arc Melted Button		-1.2 (42 day)
U-3.8 Si-0.2 Mo	"		-0.68 (105 ")
U-3.8 Si-0.2 Nb	"		-0.83 (77 ")
U-3.8 Si-0.2 Cu	"		-0.87 (84 ")
U-3.8 Si-0.2 Ta	"		-1.37 (77 ")
U-3.8 Si-0.2 Al	"		Disint.
U-3.8 Si-0.2 Mo	BeO-Washed Graphite	Graphite	-1.90 (35 day)
U-2.9 Si-0.125 C-0.18 Nb*	"	"	Disint.
U-3.79 Si-0.090 C-0.12 Cu*	"	"	-1.25 (42 day)
U-3.8 Si-0.181 C-0.19 Al*	"	"	Disint.
U-3.85 Si-0.042 C-0.17 Mo*	Pure BeO	Graphite	-1.20 (21 day)
U-3.84 Si-0.014 C-0.20 Nb*	"	"	-1.81 (21 ")
U-3.85 Si-0.023 C-0.2 Cu*	"	"	-1.85 (21 ")
U-3.95 Si-0.039 C-0.07 Al*	"	"	-2.8 (7 ")
U-3.8 Si-0.1 Mo	ZrO ₂	SiO ₂ Investment	-1.56 (7 day)
U-3.8 Si-0.2 Mo	" 2	"	-6.90 (7 ")
U-3.8 Si-0.3 Mo	BeO-Washed Graphite	"	-1.34 (7 ")

* Analyzed values; all others are nominal.

All samples were epsilonized one week at 800°C

TABLE III

The Absorption of Hydrogen by Bare U_3Si during Corrosion in 650°F Water

<u>Corrosion Conditions</u>	<u>Corrosion Time (Days)</u>	<u>Total Hydrogen (ppm)</u>	<u>Weight Loss (gm)</u>	<u>% Absorption</u>	<u>ppm H_2 Weight Loss</u>
650°F-saturation pressure-2200 psi	0	0.7			
"	3	4.5	0.3025	1.3	12.5
"	7	6.9	0.3853	1.7	16
"	14	16.0	0.8539	1.7	18
"	21	33.1	1.2490	2.4	26
"	28	37.2	1.4011	2.3	26
"	35	57.4	2.0429	2.1	27.5
650°F-saturation pressure+800 psi	14	28.8	1.3057	1.9	21.5
hydrogen-3000 psi	28	49.7	2.4320	1.4	20

TABLE IV

Effect of Irradiation on the Corrosion Resistance of Transformed U-Mo Alloys

(All samples tested in 650°F (343°C) water at saturation pressure)

<u>Specimen No.</u>	<u>Composition</u>	<u>Heat Treatment</u>	<u>Exposure (MWD/T)</u>	<u>Corrosion Rate after 24 hr Test (mg/cm²/hr)</u>
A-13	U-9 w/o Mo	α transformed + 300°C for 6 weeks	---	Disintegrated
A-8	"	α transformed	755	-9.00
A-9	"	"	790	Broke into several pieces
B-8	U-10.5 w/o Mo	α transformed + 300°C for 6 weeks	---	Disintegrated
B-9	"	α transformed	730	-3.86
C-26	U-12 w/o Mo	α transformed + 300°C for 6 weeks	---	-3.59
C-23	"	α transformed	180	-2.83
D-23	U-13.5 w/o Mo	α transformed + 300°C for 6 weeks	---	-0.47
D-24	"	α transformed	170	-0.21

TABLE V

Effect of Irradiation on the Corrosion Life of Zircaloy-2 Clad U-10 w/o Nb

(Corrosion Testing in 650°F Static Water at Saturation Pressure)

Specimen No.	Fabrication History	Heat Treatment	Exposure (MWD/T)	Corrosion Life (Days)
F-7	As extruded	800°C-4 hr-W.Q.	500	O.K. after 35 days
F-9	"	"	840	"
F-12	"	900°C-24 hr-W.Q.	840	"
F-14	"	"	729	"
G-18	Extruded + Cold Swaged	800°C-4 hr-W.Q.	497	"
G-19	Straightened	"	718	"
G-20	"	900°C-24 hr-W.Q.	840	"
G-21	"	"	740	"
H-1	Extruded to 1/2" diam.	800°C-4 hr-W.Q.	729	"
H-7	& cold drawn to 0.325"	"	840	"
F-8	As extruded	800°C-4 hr-W.Q.	Control	O.K. after 26 days
F-10	"	"	"	19-26
F-11	"	900°C-24 hr-W.Q.	"	12-19
F-13	"	"	"	19-26
G-14	Extruded + Cold Swaged	800°C-4 hr-W.Q.	"	19-26
G-15	Straightened	"	"	O.K. after 26 days
G-16	"	900°C-24 hr-W.Q.	"	12-19
G-17	"	"	"	5-12
H-2	Extruded to 1/2" diam.	800°C-4 hr-W.Q.	"	O.K. after 26 days
H-8	& cold drawn to 0.325"	"	"	"

TABLE VI

Microhardness of Irradiated Unclad U-10 w/o Nb Alloy

<u>Specimen No.</u>	<u>Condition</u>	<u>Exposure (MWD/T)</u>	<u>DPH at 5 kg. Load</u>		<u>Change</u>
			<u>Pre</u>	<u>Post</u>	
F-3	900°C-24 hrs-W.Q. (γ Q)	820		347 $\pm$ 13	+ 61
F-4	"	720	286 $\pm$ 16	325 $\pm$ 11	+ 39
F-5	"	500		309 $\pm$ 6	+ 23
F-22	γ Q + 400°C-2 weeks	310	558 $\pm$ 23	367 $\pm$ 11	- 191
F-19	γ Q + 450°C-2 weeks	475	460 $\pm$ 7	369 $\pm$ 10	- 91
G-4	γ Q + 500°C-2 weeks	700	396 $\pm$ 1	311 $\pm$ 22	- 85
G-1	γ Q + 550°C-2 weeks	810	355 $\pm$ 1	338 $\pm$ 25	- 17

TABLE VII

Corrosion Properties of Irradiated Unclad U-10 w/o Nb Alloy

Unirradiated Data

<u>Sample No.</u>	<u>Condition</u>	<u>Corrosion Rate in 650°F Water (mg/cm²/hr)</u>						
		<u>72 hrs</u>	<u>168 hrs</u>	<u>336 hrs</u>	<u>672 hrs</u>	<u>1008 hrs</u>	<u>1680 hrs</u>	
Mo 3A9-11 B	As Extruded	-0.008	-0.007	-0.015	-0.033	-0.043	disintegrated	
		<u>24 hrs</u>	<u>96 hrs</u>	<u>168 hrs</u>	<u>336 hrs</u>	<u>504 hrs</u>	<u>672 hrs</u>	<u>840 hrs</u>
F-25	900°C-24 hrs-W.Q.	+0.037	+0.006	-0.012	-0.12	-0.25	-1.33	disintegrated

Irradiated Data

<u>Sample No.</u>	<u>Pre-Irradiation Condition</u>	<u>Exposure (MWD/T)</u>	<u>Corrosion Rate in 650°F Water (mg/cm²/hr)</u>	
			<u>24 hrs</u>	<u>69 hrs</u>
F-3	900°C-24 hrs-W.Q. (8Q)	820	-4.01	disintegrated
F-4	"	720	-1.87	-4.82
F-5	"	500	-0.23	-4.11
F-22	8Q + 400°C-2 weeks	310	disintegrated	---
F-19	8Q + 450°C-2 weeks	475	"	---
G-4	8Q + 500°C-2 weeks	700	"	---
G-1	8Q + 550°C-2 weeks	810	-42.7 (removed from test)	---

Fig. 1 - Section through failed
element at defect hole
after 56 days in 650°F
water. 7X

Neg.No. 3573B-2

Fig. 2 - Core-Barrier-Oxide Area
of Fig. 1. Acid Polish
50X

Neg.No. 3573B-1

Fig. 3 - Section Through Defect Hole
of Element 77 days in 650°F
Water. Acid Polish 7X

Neg.No. 4030B-1

A. Zircaloy-Al-6 w/o Cu Bond Zr H Flux
800°C 50X
Neg.No. 3791B1-3

B. Zircaloy-Al-6 w/o Cu Bond "Handy Ti
Flux" 700°C 20X
Neg.No. 3750B-3

C. Zircaloy-Al-6 w/o Cu Bond "Handy
Ti Flux" 700°C 500X
Neg.No. 3750B-1

D. Zircaloy-Al-11.6 w/o Si Bond Ultra-
sonic Brazing at 850°C 250X
Neg.No. 20820

Fig. 4 - Types of Bonds Obtained Between Zircaloy-2 and Al-Base
Alloys by Brazing at 700 to 850°C Using Different Techniques

A. 0.132 w/o C
Neg.No. 3557B-3

B. 0.154 w/o C
Neg.No. 3557B-1

C. 0.190 w/o C
Neg.No. 3557B-4

D. 0.384 w/o C
Neg.No. 3557B-2

Fig. 5 - Effect of Carbon Content on the Microstructures of Induction Melted (BeO-washed Graphite Crucibles), Cast Rods of U-3.8 w/o Si After Epsilonizing 1 Week at 800°C

A. 0.132 w/o C
800°C/1 week + 750°C/ 1 week
Neg. No. 3765-B-1

B. 0.154 w/o C
800°C/1 week + 750°C/1 week
Neg.No. 3762-B-1

C. 0.190 w/o C
800°C/1 week + 750°C/1 week
Neg.No. 3767-B-1

D. 0.384 w/o C
800°C/1 week + 700°C/1 week
Neg.No. 3764-B-1

Fig. 6 - Effect of Lower Temperature Epsilonization on the Microstructure of High Carbon U-3.8 w/o Si Alloys

Fig. 7 - Corrosion Interface of a U₃Si Specimen Tested
for Seven Days in 650°F Water 1000X
Neg.No. 3576-B-3

Fig. 8 - Surface Layers Formed on U₃Si Specimen Which
Was Pressure Bonded to Pure Silicon at 750°C
for 4 hours 500X
Neg. No. 4016-B-1

USi_2 (U_2Si_3)

Unidentified white
layer

U_3Si

Fig. 9 - Surface Layers on a U_3Si Specimen Which Was Heated
in Contact with Graphite for 2-1/2 hours at $800^{\circ}C$
Neg.No. 3943-B-1 250X

FIGURE 10
THE EFFECT OF 800 PSI PARTIAL PRESSURE OF
HYDROGEN UPON THE CORROSION OF UNCLAD U_3Si
SPECIMENS IN 345°C WATER.

FIGURE II
SPECIFIC HEAT VS °C
U-15.2 W/L Mo ALLOY
STEPWISE ORDERED

FIGURE 12

LONG RANGE ORDER VS. FINAL ORDERING TEMP.
FOR U - 30.4 ^a/_o Mo ALLOY

Zr Side

U-4 w/o Nb Side

Fig. 13 - Diffusion Zones Formed Between Zirconium and
U-4 w/o Nb Alloy on Annealing 3 Weeks at 1050°C
Neg.No. 3955B1-1 100X

A. Center of Sample
Corrosion Tested 2 Days -0.21
mg/cm²/hr 20 ppm H₂ 250X
Neg.No. 3657B1-2

B. Edge of Sample
Corrosion Tested 2 Days -0.21
mg/cm²/hr 20 ppm H₂ 1000X
Neg.No. 3657B-1

C. Center of Sample
Corrosion Tested 4 Days -0.18
mg/cm²/hr 80 ppm H₂ 250X
Neg.No. 3658B3-2

D. Center of Sample
Corrosion Tested 4 Days -0.18
mg/cm²/hr 80 ppm H₂ 1000X
Neg.No. 3658B-3

Fig. 14 - Hydride Configuration in U-12 w/o Mo Samples
Exposed for Various Times in 650°F Water

A. Corrosion Tested 7 Days
 $-0.79 \text{ mg/cm}^2/\text{hr}$ 270 ppm H_2
 Neg.No. 2964B1-1 250X

B. Corrosion Tested 14 Days
 $-0.88 \text{ mg/cm}^2/\text{hr}$ 815 ppm H_2
 Neg.No. 2964B2-1 250X

C. Corrosion Tested 21 Days
 $-1.8 \text{ mg/cm}^2/\text{hr}$ 1347 ppm H_2
 Neg.No. 2964B3-1 250X

D. After Hydride Decomposition
 1 Day @ 154°C
 Initially Corrosion Tested
 21 Days 250X
 Neg.No. 3361B-4-1

Fig. 15 - Hydride Configuration of U-16 w/o Mo Samples
 Exposed for Various Times in 650°F Water

A. Center Area
Neg.No. 3372B-1

250X

B. Sample Edge
Neg.No. 3372B-2

250X

C. Sample Edge
Neg.No. 3629B-1

1000 X

Fig. 16 - Microstructures of U-12 w/o Mo Samples Exposed 14 Days in 650°F Water (815 ppm H_2) and Evacuated 1 Day at 406°C

U-9 w/o Mo
24 hrs at 900°C, water-
quenched Unirradiated
Neg.No. 3659B-1 250X

U-9 w/o Mo
Gamma-quenched then alpha-
transformed at 525°C for
13 days Unirradiated
Neg.No. 1341B1-1 250X

Same sample as shown above
after irradiation to 0.09
total a/o burnup 250X
Neg.No. H114-2

Fig. 18 - Microstructures of Unirradiated and
Irradiated U-9 w/o Mo Alloy

U-9 w/o Mo
Gamma-quenched then alpha-
transformed at 525°C for 13
days. Held at 300°C for 6
weeks in evacuated Vycor tube.
Neg.No. 4037B-1 1440X

U-9 w/o Mo
Gamma-quenched then alpha-
transformed at 525°C for 13
days and irradiated to 0.09
total a/o burnup 1500X
Neg.No. HL 14-4

Fig. 19 - Microstructures of Unirradiated and
Irradiated U-9 w/o Mo Alloy

Fig. 2CA

A. 900°C-24 hrs-W.Q. (γ Q)
Neg.No. 2443B-3

B. 900°C-24 hrs-W.Q. + Irradiated
to 820 MWD/T
Neg.No. HL 41-1

C. γ Q + 400°C-2 weeks
Neg.No. 2443B-2

D. γ Q + 400°C-2 weeks + Irradiated
to 310 MWD/T
Neg.No. HL 45-1

E. γ Q + 550°C-2 weeks
Neg.No. 2444B-2

F. γ Q + 550°C-2 weeks + Irradiated
to 810 MWD/T
Neg.No. HL 46-1

Fig. 21 - Microstructure of U-10 w/o Nb Alloy - Pre and Post Irradiation
250X

Fig. 22 - Cross Section of the 19.5 w/o Enriched Specimen
of the Fifth Chalk River UO_2 Defect Test 7X
Neg.No. E 186