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WAPD-PMM-15

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RESUME OF URANIUM ALLOY DATA-VIII

By

B. Lustman

February 25, 1955

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Resume of Uranium Alloy Data - VIII

B. Lustman

February 25, 1955

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INTRODUCTION

Much of the activity during the last resume period has been devoted to exploration of the factors affecting the variability of corrosion life of clad U-Mo rods noted in WAPD-MM-491. This study has consisted of an exploration of the corrosion properties as a function of various treatments both of clad and unclad specimens. It was first suspected that initial hydrogen content of core and/or cladding might be an important variable. However, evaluation of the corrosion life of clad rods with respect to initial hydrogen content revealed no trend whatsoever. Similarly, in case of unclad material, no clear-cut difference was noted in corrosion properties of vacuum-annealed material versus those of samples annealed in hydrogen; if anything, the latter showed improved properties, although the differences observed can hardly be considered significant. Attention was next directed to micro-segregation. It has been found that the corrosion properties of unclad samples can be considerably improved by annealing so as to eliminate coring; such coring, arising during solidification particularly in case of the duplex melting procedure, persists through hot extrusion. By homogenizing billets prior to their extrusion, the corrosion properties of unclad extruded samples can be appreciably improved. An X-ray method is being developed which shows promise of quantitatively measuring the extent of micro-homogeneity by measurement of X-ray line breadth.

That homogeneity is only part of the answer to the variability problem is shown by the observation that the corrosion properties of unclad samples of extrusions made from pre-homogenized billets can be still further improved with respect to corrosion resistance by annealing after extrusion even at temperatures lower than those employed for the billet homogenization. While this observation may be explicable on the basis of the improved homogenization possible in the finer worked structure of the extruded material, it is presently considered more likely that grain size control resulting from post-extrusion annealing is responsible for the improvement; some observations detailed below on hydride formation support this explanation.

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Another factor leading to early failure of clad rods is believed to be lack of bonding between core and clad. The incidence of unbonded or partially bonded extrusions appears to be much greater than was hitherto suspected. Post-extrusion working, straightening of rods, and residual internal stresses may each contribute to unbonding and hence early failure.

Some further observations have been made on the appearance of hydride in corrosion-tested gamma-phase alloys. About 22% of the hydrogen released from the corrosion reaction has been found to enter the metal. About 20 ppm of hydrogen enters the metal before precipitation of hydride platelets is observed. However, long before the appearance of hydride platelets, etching effects at the gamma grain boundaries are observed. Whereas, with the metallographic technique usually employed, grain boundaries can be revealed only with difficulty in gamma-quenched samples, they are evident after very short etching treatments in samples corrosion tested for a short time prior to metallographic examination. Note that the grain-boundary etching effects are not revealed by electrolytic polishing although hydride platelets are readily shown even without etching. Cathodically hydrided specimens show a penetration of the grain-boundary etching effect to a depth ten or more times greater than that to which hydride plates penetrate during the same time of treatment. Whether the grain boundary etching effect is evidence of precipitation of a hydride phase or of grain boundary enrichment in hydrogen is as yet unsettled. In any case, the above results indicate that the rate of grain boundary diffusion of hydrogen (or precipitation or both) is several orders of magnitude faster than that of volume diffusion. Thus the improvement noted above on post-annealing pre-homogenized extrusions may arise from grain growth and a consequently slower rate of diffusion of hydrogen into the base metal.

On further exposure of specimens to corrosion, the number of hydride platelets increases (although the width and amount of grain boundary etching effect does not appear to change). The amount of hydrogen absorbed increases linearly with the amount of corrosion observed, and the hardness also increases continuously. It is believed that when a certain level of hardness (and brittleness) is attained, the samples can no longer resist the volume expansion and stresses resulting from formation of the corrosion oxide and hence fail discontinuously.

Closer scrutiny of the hydride platelets formed during corrosion (or cathodic treatment) indicates that they consist of at least two metallographically distinguishable parts. The center of the platelets is appreciably harder than the matrix and exhibits a well-defined outline. This center portion is surrounded by a rather ragged gray border which is not appreciably different in hardness from the matrix. No conclusions have been reached as to the identity of either of these members.

As discussed at the last panel meeting (WAPD-PMM-6), none of the defected or undefected metallic samples from the Chalk River in-pile X-rod loop test (CR-WAPD-Met 4A) showed signs of accelerated corrosion failure. Sections through the defect in the metallic rods revealed only slight corrosion at the

base of the defect. One of the two defected UO_2 samples failed and split the cladding at one end of the rod and slightly bulged the cladding at the other end. The two undefected UO_2 samples and the other defected sample were unaffected by the exposure. Activity traverses indicate that the failed sample was made with low density oxide at each end, whereas the defected sample which survived showed a more uniform distribution of oxide.

Further information has been accumulated on the irradiation behavior of U-Mo and U-Si samples. The observation made quite some time ago that the initial corrosion rate (prior to discontinuous failure) of irradiated bare gamma-phase uranium-molybdenum alloys is identical with that of unirradiated samples was confirmed. Irradiation of bare gamma-phase samples to 8000 MWD/T burnup caused a flux-dependent decrease in density amounting to over 7% in the samples exposed to maximum flux. While the irradiation time (12 weeks) was more than sufficient to cause transformation in the samples exposed in the maximum flux regions whose temperatures are calculated to have risen well above $500^\circ C$, appreciable density decrease was also observed in the low flux samples whose temperatures were insufficient to have caused appreciable transformation. It is believed that the density decrease must arise from formation of voids in the samples. No non-uniform deformation or warpage of the samples was observed. Note that clad samples irradiated up to 17,000 MWD/T showed no dimensional changes. Density decreases of over 3% were also noted in the epsilonized U_3Si samples which were exposed for only about 3000 MWD/T at temperatures calculated to be about $300^\circ C$. These samples showed rapid corrosion failure after irradiation.

Work is continuing on characterization of UO_2 powder with respect to particle size, density, surface area, crystallite size, and O-U ratio. Apparatus has been ordered or is under construction for permeability and pore distribution measurements, as well as for thermogravimetric and differential thermal analysis. Experiments have been initiated on the corrosion behavior of UO_2 as a function of water composition. The absorption and desorption of water from UO_2 is being studied out-of-pile and arrangements are being made for in-pile cycling in water environments (water-logging tests).

I. Variability of Corrosion Properties

A. Effect of Melting Practice

Since it was considered possible that variability in corrosion properties of U-12 Mo was due to differences in melting technique, a comparison was made in the as-cast condition of material that was induction melted with the same material later duplex melted. For the duplex melting operation the particular induction melt was consumably arc-melted. For the induction melt it was convenient to cut one sample from the top and bottom of each ingot and after arc-melting five samples were cut from the top and bottom of each billet machined for extrusion. Table I summarizes the one week corrosion results in $650^\circ F$ water for nine different ingots. It is obvious that no significant difference exists in the corrosion rates of the two types of material. It is interesting to note that the two high carbon materials are corroding at a faster rate than the low carbon

(about 0.01% C) alloys. This agrees with previously reported observations. When duplex melted samples were annealed at 900°C for 24 hours and water quenched, the corrosion rates are approximately halved. Unfortunately no samples were available from the induction melts for this treatment. It appears thus that arc-melting per se does not deteriorate the corrosion properties of induction melted material.

B. Effect of Extrusion Temperature on Corrosion Properties

Two extrusions were examined in this study; one (MO2C1-16) was extruded clad with Zircaloy-2 after heating for 10 minutes at 863°C and the other (MM431-10) was extruded bare after heating for 5 minutes at 1057°C. The cladding was stripped from MO2C1-16 and all subsequent tests were made on unclad specimens from each extrusion. The rod extruded at the lower temperature has a severely stringered appearance and corrosion samples from this material failed in 14 days testing in 650°F degassed water. The rod extruded at 1057°C is only slightly stringered and failed in 28 to 42 days testing in 650°F degassed water. The structures of these extrusions are shown in Fig. 1 and the corrosion curves are shown in Fig. 2. Samples of these rods were also heated at 900°C for 24 hrs and water quenched. The corrosion rates of both extrusions have been lowered appreciably by this treatment with MO2C1-16 having a weight loss of 280 mg/cm² at 21 days (0.51 mg/cm²/hr) compared to 160 mg/cm² (0.32 mg/cm²/hr) for MM431-10 in the same time period. These samples are still in test. It thus appears that the increased homogeneity resulting from a higher extrusion temperature appreciably improved corrosion properties.

C. Homogenization of U-12 Mo Extrusion Billets

It has been known for some time that a homogenization treatment at 900°C will greatly improve the corrosion resistance of unclad extruded U-12 Mo. A study is now being made to determine if homogenization of the extrusion billet prior to extrusion will have the same beneficial effect and to determine if the variability in corrosion properties of extruded U-12 Mo can be eliminated in this manner.

For this purpose a duplex melted ingot, 4 inches diameter, was extruded to 2 inches diameter at 900°C, the size for final extrusion billets. From this bar four billets were machined; two billets for extruding clad with Zircaloy-2 and two billets for extruding unclad. Five 1/8 inch thick slices were also cut from this bar for examination. One billet of each type and one slice were heat treated at 1000°C for 48 hours and furnace cooled for homogenization. The two clad rods were extruded at 870°C while the bare extrusion billets were heated to 1025°C for extrusion. The extrusion of the unhomogenized bare rod was unsuccessful and no test material was obtained. Sections of both clad rods were cold drawn 17% and 30% reduction in area.

After extrusion and drawing, the cladding was stripped from parts of each rod for corrosion testing and metallographic examination. Defected clad specimens of each rod have been submitted for corrosion testing but no results are yet available.

The effectiveness of the homogenization treatment in eliminating coring can be seen in Fig. 3. As extrusion-clad the core material exhibits a highly worked cored pattern but when homogenized prior to extrusion, this pattern has been eliminated.

The corrosion results are shown in Table II. Corrosion tests are being run on the slices from the first extrusion or extrusion billet in three conditions; as extruded, 1000°C for 48 hr and F.C. (treated with billets), and 900°C for 24 hr in a helium-filled Vycor bulb and water quenched. After 14 days in 650°F water the average rate for two samples of each condition is -0.53, -0.55 and -0.26 mg/cm²/hr for the as-extruded, 1000°C, and 900°C treatments respectively. From this it has been concluded that the homogenizing treatment used for the extrusion billets was not optimum and can be improved by further studies. Whether the furnace atmosphere, the cooling rate, or the homogenization times and temperatures cause the observed differences is not known.

When tested in the as-extruded or extruded and drawn conditions, the material homogenized prior to extrusion has a considerably improved rate over the unhomogenized. After 14 days testing as-extruded, the unhomogenized samples have begun to fail and are badly cracked, the rate being -2.88 mg/cm²/hr, while the homogenized material is lightly attacked and has a rate of -0.66 mg/cm²/hr. The cold drawing has certainly not decreased and may even have improved the corrosion properties of both the unhomogenized and the homogenized material. Results obtained in the past have also indicated no change in corrosion rates of unclad samples due to cold work.

When samples from each condition are heat treated at 900°C for 24 hours in a helium-filled Vycor bulb and water quenched, the rates after 3 days in 650°F are approximately -0.10 mg/cm²/hr for all conditions. The reason for this improvement is not known but it obviously would be desirable to duplicate such rates in the as-extruded condition.

To determine the effect of prior homogenization on thermal stability, samples were heated to 500°C for one week and water quenched. The unhomogenized material completely disintegrated after 24 hours in 650°F water while the homogenized material, though badly attacked was still intact. In this case cold drawing has decreased the corrosion resistance as would be anticipated from the effect of cold work in accelerating transformation. When given a 900°C treatment for 24 hours prior to the 500°C one-week treatment, the rates of the homogenized material are about half of those for the unhomogenized.

The material homogenized and extruded bare has a rate of -0.40 mg/cm²/hr after 3 days corrosion and a 3 day rate of -0.09 mg/cm²/hr if heated to 900°C for 24 hours and water quenched. This again emphasizes that homogeneity is not the only criterion for good corrosion resistance.

D. Effect of Homogenizing Temperature on Corrosion Properties

The effect of homogenizing temperature and cooling rate on the corrosion properties of U-12 Mo is being studied. Samples from extrusion M02C1-16 have been treated at (1) 700°C - 24 hr - W.Q., (2) 900°C - 24 hr - W.Q., (3) 900°C - 24 hr - slow cool, (4) 1000°C - 1/2 hr - W.Q., (5) 1000°C - 48 hr - W.Q., and (6) 1000°C - 48 hr - slow cool. The material has a cored structure in the as-extruded form (Fig. 1A). The 700°C treatment was found by metallographic inspection to have eliminated much of the coring while the treatments at 900°C and 1000°C result in metallographically uniform structures. However, when the samples are compared after 7 days corrosion in 650°F water (Fig. 4), the distribution of hydride reveals that considerable segregation still remained in the 700°C sample.

The corrosion data for this material are plotted in Fig. 5. Although the 700°C heat treatment decreased the extent of the coring, the corrosion rate was nearly the same as for the as-extruded condition. The 900°C heat treatments greatly improved the corrosion resistance, and the 1000°C heat treatments improved the rates still more than for the 900°C treatment. The slow cooled samples appear to have somewhat higher rates than the water-quenched samples cooled from both 900°C and 1000°C.

In Fig. 5 it can be seen that the mode of hydride formation differs greatly between the extruded, 700°C heat treated, and 900°C heat treated samples. In the first two of these, areas hydride rapidly in the region of elongated stringers which offer a path of low corrosion resistance and lead to failure in short times; whereas in the 900°C heat treated sample, the hydride needles form randomly and to a much lesser extent. The grain boundaries of all three samples etch very readily, indicating the presence of concentration gradients or a second phase, presumably a hydride, at the grain boundaries. The very fine grain size of the extruded and 700°C annealed samples are particularly to be noted.

The possible effect of grain size on hydride formation may be inferred from Fig. 6 which shows an area of fine grains adjacent to an area of very large grains which formed at the surface of samples treated at 1000°C for 48 hours, water-quenched and then corrosion tested in 650°F water for 14 days. This duplex structure of fine and coarse grain areas is typical of the samples treated at 1000°C for 48 hours. The extent of hydriding appears to be greater in the fine grained area and the plates in this area are coarser. From this observation it appears that fine grained material should be more susceptible to corrosion-crack propagation and therefore have a shorter corrosion life. Note also that the grain boundaries in this sample are well delineated. There is no apparent effect of grain size on corrosion rates. The samples treated at 900°C and water-quenched, 900°C and slow cooled and 1000°C for 1/2 hour and water-quenched all have a grain size of ASTM #6 to 7. Their rates differ, however, and are -0.56, -0.69, and -0.27 mg/cm²/hr, respectively after 21 days corrosion. The samples treated at 1000°C for 48 hours have duplex structures of fine grained areas (ASTM #5-6) and coarse grained areas (ASTM #1). The rates at 21 days corrosion are -0.32 mg/cm²/hr for the water-quenched samples

and $-0.38 \text{ mg/cm}^2/\text{hr}$ for the slowly cooled samples. Thus, it appears that the effects of homogenizing temperature and cooling rate on corrosion rates are more pronounced than the possible effects of grain size on corrosion rate. It is possible that the coarser-grained samples may show a longer life prior to discontinuous failure because of the lower rate of diffusion of hydrogen from grain boundaries into the matrix.

The relation of hydrogen content to corrosion weight loss per unit area was found to be linear for this material when homogenized at a temperature of 900°C or 1000°C , using a sample $3/8$ inch diameter by $1/4$ inch thick as shown in Fig. 7. The ratio of ppm of H_2 to mg/cm^2 corrosion is 1.7, and for the sample size mentioned, the amount of hydrogen picked up by these samples is approximately 20% of the calculated amount produced by the corrosion reaction. It thus appears that in spite of the grain size differences observed, the amount of hydrogen pickup is the same. It is conceivable that in case of the 1000°C samples, insufficient grain coarsening was obtained to affect appreciably the rate of hydrogen diffusion into the matrix.

E. Effect of Annealing Atmosphere

As part of the program to determine the causes of variability in U-12 w/o Mo alloys, a study is being made of the effect of various annealing treatments upon hydrogen content, hydride formation, hardness, corrosion rate, and corrosion life. Samples have been annealed 24 hours at 900°C in vacuo, or in atmospheres of helium, oxygen, tank hydrogen, and hydrogen from the decomposition of UH_3 . All samples were annealed in a vertical Vycor tube furnace and were quenched by water cooling the outside of the tube after removing the furnace. The results obtained thus far are summarized in Table III. Annealing at 900°C for 24 hours greatly improves the corrosion properties of this material regardless of the atmosphere used. The greatest improvement in rate results from annealing in helium or tank hydrogen; both contained some oxygen and water vapor since no effort was made to dry the gases. The tank oxygen samples were annealed in oxygen until a heavy scale formed ($\sim 1/2$ hour) and the remainder of the 24 hours in vacuo. These samples have approximately the same corrosion rate as the samples annealed in hydrogen produced by the decomposition of UH_3 .

Hydrogen concentration as a function of total corrosion is shown in Fig. 8. From this plot it is apparent that the amount of hydrogen present after a given amount of corrosion is essentially independent of the pre-corrosion treatment. About 22% of the hydrogen produced by corrosion is absorbed by the sample.

Fig. 9 indicates the manner in which hardness varies with increasing hydrogen pickup during corrosion testing. Again it can be seen that there is very little effect due to pre-corrosion test treatment of the material.

The microstructures shown in Figs. 10A and 10B are representative of the as-extruded and as-annealed for 24 hours at 900°C conditions, respectively. A standardized electro-etch was used on all samples in this series, and it should be noted that the grain boundaries are not visible in Fig. 10. Structures after a 3 day corrosion test in 650°F degassed water are shown in Figs. 11, A, C, and D

which are as-extruded, annealed 24 hours at 900°C in vacuo, and in tank hydrogen respectively. The samples annealed in other environments showed similar microstructures to Fig. 11D. Here it can be seen that grain boundaries are visible in all materials except the as-extruded, and needles have begun to appear in the vacuum, UH₃ hydrogen, and oxygen annealed samples. This places the solubility of hydrogen in U-12 w/o Mo at least with respect to platelet formation between 17.7 and 26.9 ppm. The hydride in the as-extruded material has a different form and appears to follow the concentration contours of the coring.

The appearance of the hydride and the structures after 14 days corrosion testing in 650°F water are shown in Figs. 11B, 12A, and 12B which are as-extruded, annealed in vacuum, and annealed in tank hydrogen, respectively. The appearance of samples with other annealing treatments is similar to the hydrogen annealed sample. In the as-extruded material the hydride has become the continuous phase and disintegration of the sample occurred during the following 7 day test period. The hydride needles in the vacuum annealed sample have grown considerably thicker and more numerous. The number of needles in the hydrogen annealed samples has increased considerably but they do not appear to be thickening appreciably. Thus with increasing corrosion testing time the following changes successively take place in the hydride morphology in annealed samples:

1. The formation of thin bands outlining the grain boundaries.
2. The appearance of scattered needles.
3. An increase in the number of needles until a thick interconnecting network is formed.

The various annealing atmospheres do not appear to affect this order of change but only the corrosion time required to reach any given stage of hydriding.

Samples annealed in the various atmospheres were also cathodically hydrided for 40 hours at 100°C. With the exception of the oxygen annealed samples it was found that heavy needles were formed at the surface to a depth of about 0.003 inch, grain boundaries were outlined to a depth of about 0.035 inch, and the center was "clean", duplicating the stages of hydriding found in corrosion samples. The oxygen sample was unique in that scattered needles appeared throughout the bulk of the material as well as at the surface. Similarly the appearance of the cathodically-hydrided as-extruded sample is similar to that of the corrosion-tested material shown in Fig. 11A.

F. Homogenization of U-Mo Alloys as Measured by X-ray Line Broadening Techniques

An X-ray study has been started on the problem of measuring quantitatively microsegregation in cast and extruded uranium-molybdenum alloys. Samples in the as-cast condition give broadened lines in which the K α doublet is unresolved. Examination of X-ray lines from samples which have received successively longer anneals at 900°C reveal that a given line first shifts slightly in 2 θ as it becomes sharper and then finally resolves the K α doublet.

A series of X-ray spectrometer tracing are shown in Fig. 13 for a U-12% Mo alloy induction-melted and cast (ingot Y-78). In this drawing the angle values have been superimposed, but the intensity values are only relative and should not be compared.

The Fourier transform method of A.R. Stokes is being used to find the broadening function by which the broadened line is obtained from the fully annealed line. This broadening function is determined by the distribution of d values due to the microsegregation. The effect of quenching stresses is assumed to be small as may be seen by comparing the as-received with the one hour at 600°C spectrometer tracing in Fig. 13. Preliminary results indicate that the distribution of concentrations in as-received material is assymetric and skewed toward lower concentrations.

G. Effect of Quenching Rate of Gamma Phase

Work to determine the effect of cooling velocity from the gamma annealing temperature upon the corrosion resistance of U-12 w/o Mo alloys has begun. In a preliminary experiment samples were annealed 24 hours at 900°C in vacuo and quenched by dropping into molten Wood's metal held at 100°C. The surface of the material was quite clean after this treatment but many fine cracks were visible on all surfaces. The average crack depth was about 0.075 inch and a few cracks extended to the center of the sample; the cracks appear to propagate intergranularly. Unfortunately, no corrosion results could be obtained as the sample broke into small pieces after 3 days at 650°F, presumably along the cracks formed during quenching. It is not known whether these cracks are caused by the high quenching rate or whether other factors are responsible.

H. Effect of Internal Stress

Samples are now in test for determination of effects of residual macroscopic stress on corrosion life. No results are available as yet. It was determined that as-extruded clad rods show a residual tensile stress on the core alloy. A longitudinal slit through such a rod tends to close. Such a stress distribution is to be expected from the fact that the core alloy has twice the expansivity of Zircaloy.

I. Effect of Initial Hydrogen Content

Analysis of the initial hydrogen contents of both clad and core of the specimens shown in Fig. 3 of WAPD-MM-491 failed to show any correlation with failure time.

II. Mechanism of Corrosion Attack

A. Neutron Diffraction of Cathodically Deuterided Samples

Results have been received from Drs. Corliss and Hastings of the Brookhaven National Laboratories on the neutron diffraction experiment upon hydrided and deuterided uranium-12% molybdenum. No diffraction peaks for

uranium hydride or deuteride were detected. The background was higher than would normally be expected, indicating incoherent scattering from an isotropic distribution of hydrogen throughout the metal matrix. An upper limit of 1% was placed on the possible amount of crystalline UH_3 present. Metallographically, 5 to 8% of a platelet phase was visible.

B. Magnetic Susceptibility Measurements

A differential magnetometer has been constructed to measure the magnetic susceptibility of hydrided U-Mo samples at liquid nitrogen temperatures. This equipment is capable of detecting ferromagnetic material if the product of the mass and the susceptibility exceeds 10^{-3} . This method was not sufficiently sensitive to detect the hydride in corrosion samples. As the permeability of uranium hydride is not known, an upper limit to the mass of hydride present cannot be set. An experiment is in progress to determine the magnetic properties of the hydride. A more sensitive arrangement for measuring magnetic susceptibility is under construction.

Arrangements have been made with Dr. J. Goldman of Carnegie Institute of Technology to measure the susceptibilities of hydrided samples from liquid helium to room temperatures. Measurements will also be made upon UO_2 samples to determine if this method would be suitable for measuring the uranium to oxygen ratio by the difference in magnetic moments of the U^{+4} and U^{+6} ions.

C. Effect of Water Additions

Additional corrosion data are now available for the duplex melted, hot extruded (unclad), U-12 Mo alloy tested in 650°F degassed water with additions of 50 ppm of nickel as nickel sulphate, 50 ppm of platinum as chloroplatinic acid, and 12 ppm of platinum as colloidal platinum. The corrosion data are illustrated for the four conditions in Fig. 14 and in Table IV, the hardness data in Fig. 15, and the hydrogen analyses in Fig. 16.

The samples tested in degassed water are seen to corrode with a continually increasing corrosion rate until failure occurs at about forty days total test time. The hardness increases approximately linearly with test time (see Fig. 15). The values are not yet available for samples tested at longer times but from information gained from other alloys it is probable that the hardnesses from samples tested for longer times will be quite high. The hydrogen content also increases with increased corrosion time. The metallography essentially confirmed the other observations in that increased corrosion time produced increasing amounts of "hydride" phase.

Samples tested in the colloidal platinum solution behaved identically in every way with samples tested in plain degassed water. It should be pointed out, however, that the initial 12 ppm concentration of colloidal platinum is actually the total amount of impurities in the water that will pass through an S and S 589 White Ribbon filter. The impurity level for pure distilled water is normally less than 2 ppm. The final concentration of colloidal platinum is not known but the test water is presently being analyzed for this constituent.

Both the nickel sulphate addition and the platonic chloride addition had a pronounced effect on all the parameters measured. From Fig. 14 it may be noted that samples tested in these media corrode with a constant rate instead of the increasing rate observed in degassed water. The samples tested in degassed water exhibit corrosion rates that increase continuously with test time up to about 25 days. The rate during the next period deviates from this regular increase, corresponding to first signs of failure. At this point edges of the sample begin to chip off due to the heavy build-up of hydride. The samples tested in platonic chloride solution exhibit the most consistent rates, corroding at about 0.2 mg/cm²/hr for a period of about 35 days. During the 35-42 day test period, however, one of the samples cracked in two and the other had a portion spall away. The surfaces were still shiny, semi-metallic and the edges were not rounded which again indicates that the hydride concentration is not especially high. A portion of the cracked sample was removed for observation while the remainder was returned to test with the other sample. The test conditions were slightly different for the 35-42 day test in that the test water was changed for the first time and a slightly different addition was made. The first solution was found to be a platinum plating solution and contained a small amount of lead acetate whereas the fresh solution consisted entirely of chloro-platonic acid. Whether this influenced the results is unknown but fresh material from the same source is being tested in a fresh solution.

It will be seen from Fig. 16 that samples tested in solution of nickel sulphate and platonic chloride pick up hydrogen at a much slower rate than do samples tested in degassed water. This is further illustrated by Figs. 17-19 which show the microstructures of samples that have been corrosion tested in degassed water, degassed water plus 50 ppm Ni⁺⁺, and degassed water plus 50 ppm Pt⁺⁺⁺⁺ respectively. The sample tested for 28 days in platonic chloride solution (Fig. 19) showed but a very few needles and a hydrogen concentration of 39 ppm while the sample tested for the same length of time in nickel sulphate solution (Fig. 18) showed quite a few more needles and had a hydrogen content of 47 ppm. On the other hand, a sample tested for 25 days in degassed water contained the large amount of hydride shown in Fig. 17 and had 368 ppm of hydrogen. Note also that grain boundary etching effects are observed as in case of the samples shown in Figs. 11 and 12.

• The effect of Ni⁺⁺ and Pt⁺⁺⁺⁺ in the water on the increase in hardness of corrosion specimens is a little difficult to evaluate due to the limited data but what little there is would indicate that the increase in hardness during corrosion is not directly correlated with total hydrogen concentration. For example, samples tested for 28 days in solution of nickel sulphate and platonic chloride exhibit a hardness of 375 DPH units and a hydrogen content of from 40 to 50 ppm. Samples tested in degassed water for lesser periods of time but having the same hardness value contain from 100 to 140 ppm of H₂ or from 2 to 3 times as much total hydrogen. It would seem, therefore, that the increase in hardness is not solely a function of hydrogen content but also may be a function of hydrogen distribution.

The effect of nickel and platinum additions therefore seems to be one of inhibiting hydrogen absorption by the samples. This results in

prolonging the life of the samples. These data also show that increasing amounts of hydride cause accelerated corrosion behavior and figure prominently in the ultimate failure of test specimens.

D. Microscopic Observations on Hydride Platelets

A metallographic study was made of the structural characteristics of hydride platelets in each of two gamma quenched U-12% Mo samples, one of which had been cathodically hydrided, the other corrosion tested in 650°F water for 28 days. The platelets in both samples were similar in appearance and, as can be seen by the typical illustration shown in Fig. 20A, they apparently consist of two parts, an inner, well outlined plate surrounded by a rather ragged gray border. The possibility of this structure being an artifact was investigated by subjecting the samples to mechanical, acid, and electrolytic polishing and/or etching, all of which revealed a duplex hydride structure.

The results of an attempt to show a difference in the hydride platelet components by scratch hardness are shown in Fig. 20B. When a Knoop indenter under a constant load is moved, parallel to the 172° included angle, across a polished sample surface the scratch width is made by the 130° included angle of the diamond. A series of such scratches made with a 10 gram load resulted in a matrix scratch width of 2.2μ, tapering to a width of 1.2μ in the inner part of the platelet. The tapering width decrease is explicable if the center part of the platelet is harder than the matrix, but the outer part only slightly different in hardness. Interference microscope measurements revealed the particular scratched hydride platelet to be less than 0.1μ below the matrix. This surface depth is insufficient to account for the observed differences in scratch width on the basis of geometry alone. It thus appears that the center part of the platelet is appreciably harder than the matrix while the outer rim differs only slightly if at all from the matrix hardness.

A U-12% Mo sample 3/8 inch in diameter that had been vacuum annealed and cathodically hydrided for 40 hours at 100°C was examined metallographically. Etching electrolytically in any one of several electrolytes developed a 1/16 inch thick rim of selectively attacked, wide grain boundaries around the outside of the sample (Fig. 21) leaving the grain boundaries in the central portion unetched. It is planned to study this wide boundary effect by electron microscopy in an effort to determine the possible presence of a phase. From the fact that the penetration of the grain boundary etching effect is about ten times as great as the penetration of platelets, it may be inferred that at 100°C grain boundary diffusion of hydrogen is about 100 times as rapid as volume diffusion.

A heat through put test was conducted on an extruded Zircaloy-2, U-12% Mo clad rod. The sample 12 inches long, 0.3 inch in diameter with an 0.030 inch thick clad was heat treated for 19 days at 500°C prior to testing to partially transform the alloy to $\delta + \epsilon$. A 0.040 inch diameter defect hole was drilled through the clad to a depth of 0.002 inch into the core alloy. The test ran for 44 hours under the following conditions: the sample was heated by electrical resistance, the loop water contained 25 cc of H₂/kg, the

approximate water temperature was 575 to 580°F and the probable surface temperature 650°F.

Photographs of the test results are shown in Fig. 22. Fig. 22A is a cross section through the ruptured defect area. Fig. 22B is a high magnification photograph taken in the banded area of Fig. 22A above. It is believed that this band represents a hydrided area as a result of corrosion in the previously transformed core alloy. It will be noted in Fig. 22B that the gray areas thought to be hydride nucleate around patches of the transformed material. Cooling the sample to below the Curie temperature caused it to become slightly magnetic, indicating the presence of hydride. This sample thus illustrates the importance of hydride as an intermediary in the corrosion not only of the gamma phase but also of transformed material.

E. Hydrogen Overvoltage Studies

Equipment has been set up for measuring hydrogen overvoltage of U-Mo samples as suggested at the last panel meeting. No results are available as yet.

III. Alloy Development

A. Bare Alloys

U-Mo-Pt

One of the gamma phase samples of the 15 Mo + 4.8 Pt alloy tested in 650°F water for approximately 300 days without cracking was analyzed for hydrogen and found to contain only about 50 ppm. Samples of the same alloy were annealed at 500°C for 5 weeks and then corrosion tested in 650°F degassed water. This annealing treatment converted all but the grain boundary phase to epsilon. The unknown grain boundary phase that was present in the gamma quenched material was isotropic to polarized light after the annealing treatment. The transformation at 500°C destroyed the corrosion resistance of the alloy as the samples disintegrated in less than one week of testing in 650°F water.

The reasons for the outstanding behavior of this material in the gamma-quenched condition at least may reside in the nature of hydride attack. Note in Fig. 23 that hydride does not appear to penetrate the matrix either as platelets or at grain boundaries but rather forms a heavy interwoven network at the surface. An understanding of the reasons for this different mode of attack would be of obvious importance.

Additional data are now available concerning the samples of U-Mo-Pt from arc melted buttons that were reported in WAPD-MM-491. The beneficial effect of adding platinum to a U-Mo base binary alloy is seen from Table V to be quite pronounced. Not only is the life of samples in the as-melted or gamma quenched conditions significantly prolonged by platinum additions but samples annealed for varying lengths of time at 400 and 500°C also derived large benefits from the platinum additions. Increasing amounts of platinum are seen to cause greater improvements.

U-Mo-Nb Ternary Alloys

Table VI summarizes the corrosion data of alloys of U-Mo-Nb currently being tested along with those of some previously tested alloys. As is readily seen from Table VI the lives of these alloys vary considerably from melt to melt. The cause of this variation is, at the present time, unknown but some of these samples have shown phenomenal corrosion lives when compared with U-Mo alloys. For example, samples of gamma quenched U + 7 Mo + 2 Nb stood up in 343°C degassed water for about 150 days while samples of U + 9 Mo failed in about 20 days.

U-Mo-X Ternary Alloys

Table VII summarizes the most recent data for samples of U + 7 and 9 w/o Mo containing small additions of Cr, Ti, and V that are currently being examined for corrosion resistance. It will be seen that some discrepancies occur in the data, but, in general, large increases in corrosion lives are effected by each of these additions when the material is tested in the gamma condition. It is doubtful that either Cr, Ti, or V contribute significantly to the thermal stability but in the case of vanadium, at least, the results may be obscured by the fact that a grain boundary precipitate occurred when the samples were annealed at 900°C. Samples of U-Mo-V were annealed at 700 and 800°C also but the precipitate was still visible metallographically.

U-Zr-Nb

The U + 10 Zr + 4 Nb alloy that was induction melted and chill cast has been corrosion tested in 343°C water after gamma quenching and after annealing at 400 and 500°C. Table VIII indicates the results.

When samples of this alloy are water quenched in a bulb from 900°C the "alpha prime" structure results. From Table VIII it is seen that this structure has a test life of from 28 to 70 days with a corrosion rate of less than 0.2 mg/cm²/hr. Both this life and rate are comparable to those of the best unclad U-Mo alloys. This alloy exhibits noticeable but limited thermal stability as evidenced by the fact that its corrosion life is not drastically impaired by a one-week anneal at 400°C. In this respect it is probably about equivalent to a 9 or 9.5 w/o Mo alloy.

B. Transformation in U-Mo Alloys and Effect on Corrosion Properties

The investigation of the effect of low temperature annealing on the corrosion resistance of gamma quenched U-Mo alloys is being continued. Latest results are listed in Tables IX and X. The very long corrosion life of a 9 w/o Mo-U alloy gamma quenched and annealed at 343°C for 7 weeks, previously reported as 56 to 70 days, may be unreal. A recheck sample of this material had a corrosion life of 14-28 days which is more in line with other data. Corrosion data and X-ray spectrometer data for samples annealed long times are summarized in Table X.

It is interesting to note that even though samples of U-12 Mo show complete transformation after annealing at 400°C the corrosion life is not seriously impaired. These samples remained in test for approximately the same period of time as gamma quenched samples which for this alloy was 14-28 days. This is contrasted to a corrosion life of about one day after complete transformation at 500°C. The 13.5 and 15 w/o Mo alloys showed some transformation to ϵ after this 140 days at 400°C but the corrosion resistance was apparently unaffected as failure time was quite similar to that of gamma quenched specimens.

The apparent decrease in corrosion life after annealing at 343°C for over 200 days is unexplained by the X-ray spectrometer data, for none of the alloys above 9 w/o Mo showed any evidence of transformation. No metallographic data are available.

C. Vacuum Melting in Urania Crucible

A "high-purity" U-12 w/o Mo alloy has been made by remelting duplex melted material in a urania crucible in vacuo. This material was held at 1300°C for 8 hours. The ultimate vacuum attained was 10^{-6} mm of mercury. The material was subsequently annealed 24 hours at 900°C in vacuo and water quenched. The purpose of this experiment was to prepare an alloy as free as possible from impurity and inclusion effects. The microstructure, shown in Fig. 24, consists of a relatively clean matrix with two types of inclusions at the grain boundaries. These inclusions have not as yet been identified, although one type appears to be non-metallic, possibly UO_2 , while the other is metallic. Hydrogen analysis of the as-annealed material showed 0.28 ppm present. The corrosion rate of this material after one week in 650°F water is 0.17 mg/cm²/hr. Cathodic hydriding for 40 hours at 100°C produced only a few scattered needles at the surface.

D. Corrosion Life of Extruded Rod Elements

Routine corrosion testing of end-plugged extruded rod elements of various alloys is being continued. These rods have three holes 0.040 inch in diameter and about 0.05 inch deep drilled through the cladding. Generally, three to six such rods were tested for a given condition. The data in Table XI are for the three rods showing longest corrosion life since in many tests one or two rods fail in an exceptional manner. Note the long corrosion life for the 12 Mo, 13.5 Mo, and 10 Nb alloys in 650°F water. The 680°F data indicate that the 10 Nb alloy in the as-extruded condition is superior to the U-Mo alloys, while the 750°F steam test is a very severe treatment for all alloys.

All available data for the 10 Nb alloy are summarized in Table XII. Note especially that the 400°C annealing that produces transformation of U-Nb alloys, and the 800°C annealing that produces core-clad interdiffusion, do not appear to markedly affect corrosion life of the clad rods; 70 days testing is believed to be a significant time since deleterious results were produced in U-Mo alloys for 800°C annealing in a shorter time than this.

E. Corrosion Life of Extruded and Cold-Drawn Clad U-12 w/o Mo Alloy

Additional corrosion data have been obtained for cold drawn materials in the form of simulated fuel elements with 0.040 inch diameter defect holes through the cladding. The latest results are summarized in Table XIII. These data appear to indicate an exceedingly detrimental effect of cold drawing upon the corrosion life of the rods regardless of subsequent heat treatment. It has been observed, however, that cold drawn rods tend to fail by splitting near the ends. This is believed to indicate that corrosion has progressed along the core-clad interface rather than through the bulk of the core. Inasmuch as this material was not subjected to any treatments which would produce a highly corrodible layer at this interface, it is believed that the poor and/or variable corrosion life of the cold drawn rods is due to poor bonding. It is suspected that the metallurgical bond formed during hot coextrusion is broken at least partially during the cold drawing operation. Tests by the Fuel Element Subdivision have indicated that some of the cold drawn rods are unbonded. This condition offers a good explanation for the extreme variability of drawn rods such as 1101-1-7 (for two samples one failed within 7 days, the other is still in test after 49 days), particularly if the bond is not broken throughout the entire length of the rod from which the simulated fuel elements are made.

The corrosion results for bare samples obtained by stripping the cladding from coextruded rod are summarized in Table XIV. It is apparent that no significant difference exists between as-drawn and as-extruded material with respect to corrosion life or corrosion rate. This indicates that cold-working is not detrimental to the corrosion resistance of the alloy itself and the decrease in life observed for cold-drawn fuel elements is probably due to rupture of the core-clad bond during the cold drawing operation.

IV. Irradiation Effects - Uranium-Base Alloys

A. Pre-Post Tests of Uranium-Molybdenum Alloys

1. MTR Irradiation of Clad U-Mo Alloy Samples (MTR-WAPD 11-Met 1)

The three remaining control samples of U-10.5 w/o Mo (see WAPD-MM-491, p. 16) which had been corrosion tested earlier in 650°F water with the irradiated samples were continued in test. One of the three as-extruded samples failed in the 145 to 158 day test period. The two remaining samples have survived 172 days without failure and are continuing in test.

2. MTR Irradiation of Clad U-Mo Alloy Samples (MTR-WAPD 11-Met 3) (MTR-WAPD 11-Met 4)

Corrosion testing of defected Zircaloy-2 clad specimens of U-9 w/o Mo, U-10.5 w/o Mo, U-12 w/o Mo, and U-13.5 w/o Mo alloys containing 5 w/o uranium-235 has continued. These specimens had previously been irradiated in MTR process water to estimated burnups ranging from 6500 to 17,300 MWD/T. Results of the corrosion tests in 650°F static water are summarized in Table XV.

As previously mentioned in WAPD-MM-491, all of these specimens were heat treated for 1/2 hour at 750°C prior to irradiation thus causing core-clad interdiffusion. The data indicate, as have previously been observed, that the corrosion life is greatly shortened by irradiation in case of fuel elements so mistreated. In order to evaluate the effects of the 750°C heat treatment on the corrosion life without irradiation, a group of unirradiated specimens were fabricated from the same extruded rod as the irradiated specimens. Half of these control specimens will be tested in the as-extruded condition and half as heat treated at 750°C for 1/2 hour.

3. MTR Irradiation of Clad U-Mo Alloy Samples (MTR-WAPD 11-Met 7)

Two defected specimens each of Zircaloy-2 clad as-extruded natural U-10.5 w/o Mo and U-12.0 w/o Mo, which had been irradiated in MTR process water to a maximum estimated exposure of 3000 MWD/T, have been corrosion tested in 650°F static water for 3 days without failure. The test is continuing. After it has been determined that the sample materials will not fail prematurely, additional samples of each alloy will be put into test.

4. Irradiation of Clad U-Mo Alloys (MTR-WAPD 11-Met 8)
(MTR-WAPD 11-Met 9)

Samples of as-extruded Zircaloy-2 clad U-10.5 w/o Mo alloy and U-12 w/o Mo alloy, enriched to 3.6 w/o uranium-235, which have been irradiated in MTR process water to an estimated maximum exposure of 3600 MWD/T, have been discharged from the reactor and returned to WAPD. The specimens will be defected by drilling a 0.040 inch hole through the cladding and corrosion tested to failure in 650°F static water. These samples are a part of the group of samples fabricated for the CR-WAPD Met-4A loop test and a comparison will be made of the corrosion behavior of samples irradiated in the two reactors. The second train of samples, currently being irradiated to an estimated maximum exposure of 6500 MWD/T, is scheduled for discharge at the March 7 shutdown.

5. MTR Irradiation of Unclad U-Mo Alloy Samples (MTR-WAPD 12-Met 1)
(MTR-WAPD 12-Met 3)

Three samples of U-10.5 w/o Mo and three samples of U-10.5 w/o Mo irradiated to a maximum exposure of 2000 MWD/T have each been sectioned into four pieces. These samples are being corrosion tested in 650°F (343°C) static water. It is planned to remove samples periodically for hardness and metallographic examination in order to study more quantitatively the course of the corrosion. The samples have currently been corrosion tested for two days, and the corrosion rates of all the samples are still comparable to the corrosion rates of the unirradiated control samples.

6. MTR Irradiation of Unclad U-Mo Alloy Samples (MTR-WAPD 12-Met 3)

Three samples of gamma-quenched U-12 w/o Mo, three samples of gamma-quenched U-13.5 w/o Mo, and one sample of U-13.5 w/o Mo that was 60% gamma and 40% epsilon (by X-ray measurements) have been irradiated to a

maximum exposure of 8200 MWD/T during a 12-week exposure at MTR. All samples were enriched to 5 w/o uranium-235. The calculated temperatures of the highest flux sample are 522°C at the center of the sample and 334°C at the surface. The changes in dimensions of three samples, which were originally 0.187 inch in diameter by 2.000 inches long, are shown in Table XVI. The maximum decrease in density was 6.65% for the maximum exposure gamma quenched sample, while the epsilonized sample (irradiated in the highest flux) showed a density decrease of 7.61%.

This marked decrease in density was quite unexpected, particularly in view of the observation that the clad samples listed in Table XV showed no appreciable dimensional changes when exposed to much higher burn-ups. While undoubtedly the samples exposed in the higher fluxes attained temperatures sufficient to cause appreciable, if not complete, transformation in 12 weeks, the volume changes on transformation are insufficient to explain the observed effects. Certainly, the temperatures attained in the low flux samples are insufficient to have caused transformation, yet the density decrease in these samples is appreciable. Note that the specimens after irradiation appear to be smooth and unmarked. Further metallographic observation should prove quite instructive.

B. In-Pile Tests of U-Mo Alloys

1. Irradiation of Clad U-Mo Alloys and UO₂ in X-Rod Loop (CR-WAPD Met-4A)

The test section was returned to Bettis and the specimens of U-10.5 w/o Mo and U-12 w/o Mo (specimen details and test conditions are given in WAPD-MM-485 and WAPD-MM-491) were removed for examination on December 29. The thickness of the crud deposit, which seemed to be uniform over the entire length of the composite rod, was determined photographically to be 0.0055 inch. Diametral measurements revealed that no dimensional changes had occurred as a result of irradiation. Sections were removed from three samples for metallographic examination of the base of the defect. It was observed that the core material had corroded only slightly at the base of the defect. It is currently planned to cut a defected and an undefected sample of each fuel alloy, which had been irradiated in adjacent positions, into a number of 3/16 inch thick wafers for a determination of fission gas release at temperatures up to the melting point of the alloy. Defects in the form of 0.040 inch holes will be drilled into the remaining undefected samples and all samples which have not been used for fission gas or metallographic examination will be corrosion tested to failure in 650°F water.

A number of defected unirradiated natural and enriched control samples have been corrosion tested in 650°F water for more than 82 days. The results are tabulated in Table XVII. Note that the corrosion lives of many of these samples are surprisingly short and further that the longer-lived specimens, with few exceptions, are those extruded at the higher temperatures. These observations may well tie in with the effect of homogeneity on variability of corrosion life noted in Section I above.

2. Irradiation of Clad U-12 w/o Mo in X-Rod Loop (CR-WAPD Met 6)

Thirteen samples of double melted Zircaloy-2 clad U-11 w/o Mo and U-12 w/o Mo, enriched to 3.6 w/o uranium-235, have been sent to Chalk River for insertion into the X-3 loop on February 28, 1955. The sample charging order in the reactor is tabulated below:

Composition	Reactor Charging Order	Sample No.	End Closure
12.1 w/o Mo (MO3c2-3)	1 (Top of Reactor)	N 50	bonded
	2	N 51	"
	3	N 52	"
	4	N 53	"
	5	N 54	"
	6	N 56	"
	7 (Center Line)	N 55*	"
11.1 w/o Mo (MO3c2-1)	8	N 60	unbonded
	9	N 61	"
	10	N 62	"
	11	N 63	"
	12	N 64	"
	13 (bottom of reactor)	N 65	"

* Sample defected with a 0.040 inch flat bottom drill to a depth of less than 0.001 inch into the core material. The exposed strip of core material is approximately 0.008 inch x 0.040 inch.

Samples of bare core material have been corrosion tested in 650°F water for a cumulative time of 616 hours. The corrosion rates are as follows:

Corrosion Time (hr)	Weight Loss of MO3c2-1* (U-11.1 w/o Mo)			Weight Loss of MO3c2-3 (U-12.1 w/o Mo)		
	Sample #1 mg/cm ² /hr	Sample #2 mg/cm ² /hr	Sample #3 mg/cm ² /hr	Sample #1 mg/cm ² /hr	Sample #2 mg/cm ² /hr	Sample #3 mg/cm ² /hr
41	.60	.53	.53	.21	.29	.26
168	.41	.39	.40	.32	.34	.32
263	.46	.44	.46	.41	.46	.41
431	.39	.51	.45			
448				2.3	1.5	1.2
616	1.3	1.7	1.3			

* In-pile defected sample from extrusion MO3c2-1

C. Tests of Other Alloys

1. Irradiation of U-3.8 w/o Si Alloy (MTR-WAPD 12-Met 5)

Both ends of each irradiated specimen were cut on an underwater cutoff wheel for metallographic examination and hardness measurements. Density measurements were made on the remaining middle section of the specimens and are

shown in Table XVIII. Specimen #8 shattered on one end in the cutoff wheel vise and it is presumed that the density measurement was affected to an unknown degree by the presence of moisture in the many cracks in the specimen since the sample was not artificially dried before the weight in air was taken. The decrease in density appears to be uniform for all specimens with the exception of specimen #8 and not a function of integrated neutron flux exposure. These results are to be compared with those in Table XVI. The density of the irradiated specimens (14.92 to 14.97 gm/cm³) is lower than the density of the material in the as-extruded condition (15.34 gm/cm³). A very interesting fact is to be noted if it can be assumed that the as-extruded material was partially epsilonized and that the specimens transformed as a result of irradiation to the alpha plus epsilon phase. In support of this assumption Bitsianes has reported that the maximum density decrease between cast and epsilonized U-Si alloys was approximately 3.5% (CT-3309, "Alloys of Uranium and Silicon, II The Epsilon Phase") which compares with the density decreases of 3.5% to 3.9% as measured between the unirradiated and irradiated specimens. The specimen ends are now being prepared for metallographic examination in order to determine whether a phase change has occurred. The dimensional changes in specimen #16 (reported in WAPD-MM-491) indicates that the volume has increased by 4.5% which compares with the density decrease in this specimen of 3.7%. Note that the maximum temperatures attained in this experiment are probably no higher than about 300°C which is far below the temperature required for de-epsilonization.

Five of the middle sections of the irradiated specimens along with five control specimens which had been heat treated for 6 weeks at 200°C, 300°C, 400°C, and 500°C in evacuated Vycor tubes and at 400°C in a NaK filled capsule, were corrosion tested in 650°F water for 22 hours. These results are shown in Table XIX. Three of the irradiated specimens disintegrated during this test period and the remaining two specimens showed a marked increase in corrosion rates (-6.56 and -14.26 mg/cm²/hr).

The control specimens, which were tested in the same autoclave as the irradiated specimens, showed a corrosion rate similar to the specimens which were not heat treated for 6 weeks. A comparison of the corrosion rates of two specimens which had received similar heat treatments, one in an evacuated Vycor tube and one in NaK filled capsule, indicated that the NaK environment had little or no effect on the corrosion resistance of this material. The two remaining irradiated specimens and the control specimens will be corrosion tested for another 24 hour test period.

2. MTR Irradiation of Clad U-Nb Alloy Samples (MTR-WAPD 11-Met 11)

Ten specimens of Zircaloy-2 clad natural uranium-10 w/o niobium have been shipped to the MTR for irradiation in process water to a maximum exposure of 2600 MWD/T. Two specimens each of the following conditions are to be irradiated.

- a. Extruded + cold drawn + annealed at 800°C for 4 hours.
- b. Extruded + annealed at 800°C for 4 hours.
- c. Extruded + homogenized at 900°C for 24 hours.

- d. Extruded + 0.5% cold swaged + annealed at 800°C for 4 hours.
- e. Extruded + 0.5% cold swage + homogenized at 900°C for 24 hours.

Length and diameter measurements will be obtained before and after irradiation. Defects will be placed in the irradiated samples after their return to WAPD and the corrosion resistance of the defective samples determined in 650°F static water. It is expected that preliminary results will be available by June 1, 1955.

3. MTR Irradiation of Clad U-Nb Alloy Samples (MTR-WAPD 12-Met 7)

Four samples of Zircaloy-2 clad natural U-10 w/o Nb, canned in NaK, have been shipped to the MTR for irradiation to an estimated burnup of 2000 MWD/T. The purpose of this experiment is to determine the effect of irradiation on the dimensional stability and corrosion resistance of clad U-10 w/o Nb, irradiated in a manner to yield core-clad interface and core central temperatures equivalent to those predicted for PWR fuel rods.

Two defected specimens, one as-extruded and one homogenized at 900°C for 24 hours, are to be irradiated. An unirradiated defected specimen from the same extrusion has been corrosion tested 217 days in 650°F static water without failure. Two undefected specimens of extruded Zircaloy-2 clad U-10 w/o Nb, homogenized at 800°C for 4 hours and 900°C for 24 hours respectively, are also to be irradiated.

Length and diameter measurements of all specimens will be obtained before and after irradiation. The corrosion resistance of the two defected specimens will be determined in 650°F static water after irradiation for comparison with the corrosion resistance of unirradiated specimens. The two undefected specimens will be sectioned and the microstructure examined for phase changes due to irradiation.

V. Uranium Oxide Development

A. UO₂ Preparation Studies

A number of runs have been made in which UO₂ was prepared by oxidation of uranium foil by both high pressure and low pressure steam. The materials as prepared by both methods were similar in appearance and pressing characteristics; however, the UO₂ prepared by low pressure steam oxidation generally had somewhat higher oxygen to uranium ratios. As indicated later this discrepancy may be due to the presence of water in the high pressure steam oxidized material. An apparatus for determination of water in UO₂ is now being constructed to check this point.

It has been observed that, although the UO₂ prepared by the low pressure steam oxidation of foil is not pyrophoric as has been reported by other workers, the material does gain weight rather rapidly when attempting to weigh it following its preparation. This effect may be due to either oxidation or

water adsorption. Experiments are now being conducted to determine the cause of this effect. In addition, studies are being made of the keeping properties of the various UO_2 preparations as a function of the humidity and temperature.

B. UO_2 Powder Characterization

Lattice parameters and crystallite sizes were determined by X-ray diffraction for the various UO_2 powders. The lattice parameters were converted to oxygen-uranium ratios using data published by Herring and Perio (Bull. Soc. Chim. 351, (1952)). These parameters, as well as the oxygen to uranium ratios determined by weight analysis are shown in Table XX.

It can be seen that the values of oxygen to uranium ratio as determined by X-ray diffraction, are not significantly different from two, whereby the oxygen to uranium ratios as determined by weight analysis are higher than two for the low pressure powders and lower than two for the high pressure powders.

Since trace quantities of higher or lower oxides or of free uranium would not show up in the X-ray analyses, whereas they would in the chemical analysis, the discrepancy between the O/U ratios as determined by the two methods may indicate the presence of higher oxides in the low pressure material and the presence of free U or water vapor in the high pressure material. As indicated previously these points are now being investigated.

The general shapes of the UO_2 powders, prepared by hydrogen reduction of UO_3 (Mallinckrodt) and by steam oxidation of the metal, were described in the previous report. Since that report, a detailed study was made of the microstructure of Mallinckrodt UO_2 . Most of the effort was applied to the +100 -80 sieve fraction of this powder. This fraction contains particles which passed through 177 μ openings and were retained on a sieve having 149 μ openings. By polishing the particles in cross-section it was shown that each particle is composed of smaller units about 1 μ - 15 μ which are held together in a spongy mass.

By etching the polished surfaces it was shown by light and electron microscopy that the smaller units are aggregates of individual crystals about 1/2 - 4 μ held together in very compact masses. Photographs A and B, Fig. 25, are light micrographs showing the as-polished structure of a particle and the etched structure of the same area.

The particles in Mallinckrodt powder are friable but are held together by stronger forces than would be exhibited from mere agglomeration of crystal aggregate units. The particles are readily broken down by very light grinding with a spatula on glass; however, they are not broken down by shearing in viscous medium such as petroleum jelly. On reaction with HNO_3 the particles quickly disintegrate into the crystal aggregates which then continue to react as individual units. Photographs A, B, and C, Fig. 26, are light micrographs of mounted and polished samples of the +80 fraction (particles above 177 μ), the 325 fraction (44 μ to 53 μ) and the fines fraction (0 to 44 μ).

The as-polished structures in the 80 and 325 fractions and as far down into the fines as could be observed by this technique, were not significantly different from that observed in the 100 fraction described above. Although the primary crystal size in these fractions have not yet been determined, it would appear that the structure of the particles is independent of size at least down to about 20 μ .

Repeated attempts to determine the fine structure in a low pressure steam oxidized powder were unsuccessful. In this connection three UO₂ materials having known structures and a sample of the steam oxidized powder were polished and etched in the same mount. The expected structures were observed in the control samples but no fine structure was observed in the steam oxidized powder. Apparently the crystal size in this material is below the resolution of the light microscope, and the crystal aggregate size may be the same as the particle size.

C. Irradiation Program

1. Fission Monitoring

A method for monitoring pile irradiations of fuel element materials has been agreed upon. The monitor is to consist of a few milligrams of the fuel material in question and is to be identical to it in both chemical and isotopic composition. The monitor is to be sealed into a small length of quartz capillary tubing which will in turn be sealed into an aluminum capillary so that the quartz may be crushed without losing any of the sample. The entire unit will be held in a special container located in the end cap extension of the specimen. In this manner, it is expected that the gaseous fission products as well as the solid ones will remain in the monitor for subsequent determination.

After the irradiation, the monitor is to be removed and analyzed radiochemically for a typical fission product of known yield. Cs¹³⁷ has been selected as the primary monitor because it has approximately the same fission yield from both U²³⁵ and Pu²³⁹, and the probability of its formation by non-fission processes is expected to be negligible.

2. MIR - A-Piece Cyclor (WAPD-19 Met-1)

Six Zircaloy clad UO₂ specimens 0.400 inch O.D. x 4.5 inches long have been prepared and shipped for irradiation in the A-piece thermal cycling experiment at MIR. The samples were prepared from both Mallinckrodt and steam oxidized UO₂ by hot pressing and by cold pressing and then sintering. The cold pressed and sintered specimens have a density 92% of theoretical whereas the hot pressed Mallinckrodt is 81% dense and the steam oxidized 87%. The specimens will be irradiated for six weeks in a flux of 3 x 10¹⁴ n.v. achieving a maximum center temperature of 2500°C. During this period the specimens will be cycled approximately 4000 times.

3. MIR - KAPL Cycling Experiment

Four specimens of UO₂ have been shipped to MIR for irradiation in the KAPL cycling installation. Three of the specimens consist of Mallinckrodt UO₂ cold pressed and sintered to 90% density. The other specimen is

4. MTR - HB-5 Loop Test

5. MIR - WAPD 14-Met 3

The capsules containing the specimens have been opened and the specimens examined superficially. All of the natural UO_2 specimens appear normal; however, two of the enriched samples which were in the high flux region exhibited extensive damage. This was undoubtedly due to the specimens having been inadvertently irradiated in a flux much higher than that calculated to give allowable interface temperatures between the UO_2 and the clad. The actual temperatures were estimated to be of the order of 1700°C at the interface and at least 4000°C at the center. One of the specimens had bulged and split at one end and exposed the oxide. It appears that the damage resulted from melting of the UO_2 and reaction with the clad. The other specimen was damaged in the central portion of the rod but the nature and extent of damage has not been determined. These results support the validity of the heat transfer calculations and should provide an opportunity to assess the extent of reaction between the UO_2 and the Zircaloy clad as well as what occurs in an element whose center temperature has exceeded the melting point of the UO_2 .

6. MIR - WAPD 14-Met 2

- 26 -

SECRET

REF ASSURE

- a. 70% dense - cold compacted
- b. 80% dense - cold compacted
- c. 90% dense - cold compacted
- d. 92-95% dense - sintered

The specimens received an irradiation of 2000 MWD/T with center temperatures ranging from 1407°C for 70% dense material to 2037°C for the 90% dense. The examination of the pellets already opened will determine which of the remaining specimens are to be cut open. One-half of each pellet was examined and photographed with the stereo camera. The two low density samples appear sintered and possibly melted in the center. In the 90% dense cold compacted sample the two pellet halves were not in contact. The half examined exhibited no change other than the presence of several gross cracks. The sintered sample had a fractured surface and appeared to contain one or two gross cracks. The photographs of several of the pellets are shown in Fig. 27. It is planned to section four additional pellets on the cutoff wheel in a plane 90° to the weld.

7. Chalk River X-1 Rod Loop Test (CR-WAPD-Met 4A)

The 6.1% enriched steam oxidized UO₂ samples hot pressed to 80% density have been measured, examined, and photographed. One of the two defected specimens containing a 5 mil hole defect was found to have ruptured at one end of the specimen. The other defected specimen gave no outward appearance of specimen damage. The specimen which failed exhibited an 80 mil bulge at the point of failure in comparison to an original diameter of 0.3 inch as shown in Fig. 28A. A slight bulge appeared at the other end of the rod (Fig. 28B). The defects in the two specimens were examined closely for a possible difference in their condition. The specimen that ruptured appeared to have a clogged defect. Some of the material in the defect is magnetic indicating it might be crud. However, it may have been put there during shipment or when the crud was wiped off the rest of the specimen. The defect in the second specimen was apparently clear of obstructions. The undefected specimens exhibited no dimensional changes.

Gross activity measurements were taken on each specimen at 10, 20, and 30 cm in air using a Victoreen ionization chamber. As shown in Fig. 29 the defected ruptured UO₂ specimen fell about 10% below a smooth curve corresponding to the flux position of the specimens. The other defected UO₂ specimen fell on the curve. However, all the defected U-Mo specimens in the same train fell 15 to 20% below the curve (Fig. 30) while the undefected U-Mo specimens were on the curve. The data were corrected for the amount of U₂₃₅ in each specimen; however, in view of the fact that the U-Mo and the UO₂ specimens had different amounts of U₂₃₈ and different atoms associated (O₂ vs. Mo) a direct comparison of the two types of specimens is not valid until a detailed analysis is made and corrections are applied. However, the curves are self consistent for the same type of material and in view of the results, it appears that some fission activity was lost from the defected U-Mo specimen as well as from the UO₂.

Each of the four UO_2 specimens was scanned longitudinally through a 3/16 inch slit in 4 inches of lead using the same ionization chamber to see if density variations of the UO_2 could be determined by variations in longitudinal activity. The data appear to indicate (see Figs. 31, 32, 33, 34) that the two undefected and the defected ruptured specimens had high density in the middle and low density in the ends. The variations in apparent density ranged from approximately 10 to 30%. The second defected specimen showed little or no variation in apparent density. Future work to be done on these specimens includes fission gas measurement, fission product leaching and metallographic examination.

8. Second Chalk River X-1 Rod Loop Test (CR-WAPD-Met 5)

Because of the large variation in density of the defected specimen in the first Chalk River X-1 rod test, the possibility exists that failure may have resulted from absorption of water in the low density portion of the specimen. In order to eliminate this source of failure, the test is being repeated with uniform, high density compacts.

Eleven Zircaloy clad UO_2 rods were shipped from WAPD January 23, 1955 for insertion in the X-1 loop at Chalk River. This second test is scheduled for four months irradiation at a flux of 2×10^{13} n.v. The defected specimen consisted of cold pressed and sintered steam oxidized UO_2 having a 5 mil defect. The remaining specimens are tabulated below.

No. Specimens	Source	Method of Compacting	Density
3	Steam Oxidized	Hot Pressed	94%
1	Mallinckrodt	Hot Pressed	89%
1	Mallinckrodt	Cold Pressed and Sintered	92%
3	Steam Oxidized	Cold Pressed and Sintered	88%
2	Mallinckrodt	Hydrostatically Pressed	90%

9. Water Logging Experiments

The above mentioned eleven Zircaloy Clad UO_2 rods scheduled to be inserted in the X-1 loop at Chalk River were corrosion tested at 680°F for 4 days in degassed water. The defected sample gained 100 mg which it retained on being heated in vacuo for 18 hours at 112°C and for 15 hours at 200°C. Upon being heated for 3-1/2 hours at a pressure of 10^{-6} mm Hg at 400°C, a weight loss of 28.4 mg from the rod was recorded.

It is not known whether the weight gain was due to water absorption alone or to a combination of reaction of the environment with the UO_2 as well as absorption of the water. A program has been started to investigate the cause of the gain in weight. Initially, a clad specimen of cold pressed and sintered steam oxidized UO_2 having a 5 mil hole defect was exposed to degassed water at 625°F along with two additional unclad specimens of Mallinckrodt and steam oxidized UO_2 . After an exposure of one hour the steam

oxidized specimens had disintegrated. The remaining specimens were then exposed for successive one-hour periods. After three hours the two unclad Mallinckrodt specimens achieved a constant weight which was an increase of approximately $1/4$ of one percent of the initial weight. The defected steam oxidized specimen is still gaining weight after five hours exposure. At this point the increase in weight over the initial value was 0.8%.

Another defected clad specimen of cold pressed and sintered steam oxidized UO_2 and two specimens each of unclad Mallinckrodt and steam oxidized UO_2 were exposed to cold degassed water at a pressure of 2000 psi. After 15 hours all of the specimens exhibited a slight weight increase; however, after being dried for 24 hours in vacuo at $120^\circ C$, all of the specimens decreased in weight to a value slightly below their initial value before exposure to cold water. These results indicate that a chemical reaction may occur in the high temperature degassed water. A control sample is now being similarly dried to see if any weight change occurs in it. Water logging of these specimens will be tested as a function of their compacting method (structure and density), defect size, source material and test medium. Finally, the effects of thermal cycling on the oxide structure will be examined. These experiments are being repeated in hydrogenated water.

10. MTR Water Logging Tests

The design of the autoclave and specimens for the MTR rabbit water logging experiment has been reviewed and the test parameters have been fixed. The specimens will be 90% dense natural UO_2 3 inches long with 0.355 O.D. clad in 0.400 inch Zircaloy. The design provides for a 0.015 inch water annulus in a flux of 1×10^{14} n.v. The specimens should be ready for insertion into MTR by the end of February.

A facility is now being designed by the Physics Department which will enable the testing of defected prototype fuel elements for water logging and other cyclic exposure effects under conditions corresponding to those likely to be encountered in the PWR. It is expected that this facility will be completed in April.

D. The Reaction of Zirconium with UO_2

Work at the Battelle Memorial Institute under subcontract to WAPD on the reaction of UO_2 with zirconium has continued. The method previously used for this study, viz., the packing of zirconium cylinders in UO_2 powder has been abandoned in favor of one in which the powders are mixed and compacted before heating.

A number of compacts $1/2$ inch in diameter x $1/2$ inch high containing zirconium and UO_2 powder in the ratio of 5 to 1, 1 to 1, and 1 to 5 have been prepared by mixing -230 +250 mesh fused $UO_{2.004} \pm 0.004$ with -70 +80 mesh zirconium and compacting at 100,000 psi. These were heated in vacuo at $825^\circ C$ for 36 hours along with zirconium powder and UO_2 control samples. Microscopic examination subsequent to reaction revealed that the zirconium particles in both the 1 to 5 and the 1 to 1 zirconium to UO_2

samples were incased in a reacted layer about 0.002 inch thick, whereas the 5 to 1 zirconium to UO_2 samples had thinner layers of reacted material. Although X-ray analyses have not yet been done it is not believed that the layers are ZrO_2 . There is no evidence of a second phase in the UO_2 on the basis of the microscopic examination.

Chemical analyses were performed by leaching the compacts in nitric acid to remove the free uranium metal and UO_2 and subjecting the residue ($\text{ZrO}_2 + \text{Zr}$) to vacuum fusion for oxygen determination. The residues from the vacuum fusions were then analyzed for uranium. It was found by this method that the Zr in the case of the 1 to 5 and the 1 to 1 Zr to UO_2 compacts contained about 4% uranium; the 5 to 1 compact contained 0.4% uranium. On the basis of these analyses, it is believed that the reaction may have produced free uranium metal as a product and that this may have diffused into the Zr to form an alloy which was resistant to the nitric acid leach solution. The smaller degree of reaction in the case of the 5 to 1 zirconium to UO_2 compact is attributed to the fact that the zirconium was not completely surrounded by UO_2 in the compact.

The possibility that UO is a product of the reaction rather than uranium is now being checked. Arc melting of U and UO_2 in the volume ratio of 1 to 1 produced no evidence of reaction.

E. Zr- UO_2 Phase Diagram

The equilibrium diagram of UO_2 and Zr is being determined at Battelle under subcontract to WAPD. In this connection a number of UO_2 -Zr compositions have been prepared by arc melting UO_2 and Zr in a water cooled copper hearth. This technique was found to work very well for compositions up to approximately 80 w/o UO_2 . However, difficulty was experienced in preparation of samples containing 85 and 93 w/o UO_2 and it is expected that powder metallurgical techniques will have to be employed in the preparation of these specimens. Samples containing 20, 30, and 70 w/o UO_2 were heat treated at 1300°F for 240 hours. A preliminary metallographic examination indicates the presence of only two phases. X-ray analyses are not yet complete.

F. Thermal Conductivity of UO_2

The thermal conductivity of UO_2 at temperatures between 1000°C and the melting point is being determined for WAPD by the Armour Research Foundation. The apparatus for these measurements has been completed, calibrated, and tested with samples of Al_2O_3 . The conductivity measurements obtained at Armour were in good agreement with those obtained at MIT. Samples of UO_2 are now being prepared for measurement. It is expected that preliminary results will be obtained before the end of February.

G. Physical and Chemical Properties of UO₂

The volumetric gas adsorption apparatus for determination of the surface area of UO₂ has been altered to give more accurate results.

The surface area of a sample of high pressure steam oxidized UO₂ which had been previously measured and reported on, was remeasured in the improved apparatus after outgassing for one hour at 100°C. A value of 3.9 meters² per gram corresponding to an average particle diameter of 0.14 μ was obtained. This is approximately twice the area obtained in the apparatus previously employed. Measurements are being made to determine the decrease in surface area with heat treatment of the powder. An attempt will be made to correlate these results with the sintering characteristics of the powders.

Equipment for the determination of the real and apparent densities of UO₂ samples is being completed. Also, a mercury porosimeter is being constructed in an effort to obtain information regarding the pore distribution in UO₂.

A comprehensive program has been outlined and initiated to study the reaction kinetics of the uranium oxides with oxygen, hydrogen, and their mixtures in the presence of water and steam. The effect of additives and pH on the nature and rate of the corrosion process will be investigated in detail.

The first group of samples consisting of specimens of recently received Mallinckrodt powder, high pressure steam oxidized powder, low pressure steam oxidized powder, and high density (91-94% theoretical density) cold pressed and sintered compacts (1750°C) made from these powders were exposed in water containing only 0.02 cc O₂/Kg H₂O at 650°C. All of the compacts began to disintegrate after only one days exposure; however, the Zircaloy cup in which the Mallinckrodt powder was contained corroded in the spots where powder contacted the walls. The cup in which the Mallinckrodt cold pressed and sintered compact was contained did not corrode; however, Chemical analysis of the Mallinckrodt powder indicated the presence of 100 ppm of fluoride which undoubtedly accounts for the corrosion of the Zircaloy container. The fact that the container holding the sintered Mallinckrodt compact did not corrode must indicate that the fluoride is volatilized during sintering. It is not known positively why the compacts disintegrated; however, it is believed that this may be due to reaction of the UO₂ with the water since hydrogen was not present to inhibit the reaction. In addition to performing analysis on the powder and compacts in an effort to determine the cause for this phenomenon, the tests are being repeated to check the results.

Table I - Corrosion Rate of As Melted U-12 Mo After 7 Days in 650°F Water

* The induction-melted ingot was used as a consumable electrode in arc-melting.

<u>Heat #</u>	<u>Induction Melt*</u>		<u>New Heat #</u>	<u>Ind. Melt Consumably Arc-Melted (Duplex Melt)</u>			
	<u>Bottom</u>	<u>Top</u>		<u>Bottom</u>	<u>Gamma Quenched</u>	<u>Top</u>	<u>Gamma Quenched</u>
X M 7	0.37	-	J 833	0.34	0.16	0.33	0.18
X M 8	0.63(0.2% C)-		J 835	0.57	0.39	0.68	0.29
X M 9	0.34	-	J 831	0.30	0.12	0.31	0.14
X M 10	0.32	-	J 829	0.33	0.14	0.32	0.14
X M 11	0.53(0.1% C)-		J 830	0.47	0.30	0.44	0.27
X M 13	0.36	-	J 832	0.29	0.16	0.35	0.14
X M 14	-	0.35	J 879	0.33	0.13	0.34	0.14
X M 15	-(11.6 Mo)-		J 881	0.25	0.16	0.29	0.16
X M 19	0.30	-	J 854	0.30	0.15	0.28	0.12
Average (hi C excluded)	0.34	0.35		0.31	0.15	0.32	0.15

Table II - Effect of Pre-Extrusion Homogenization on 650°F Corrosion Properties
of Stripped Extruded Clad Rod

Pre-Extrusion Condition	Extrusion Condition	Post Extrusion Heat Treatment	Corrosion Rate (cumulative) mg/cm ² /hr			
			1 day	3 day	7 day	14 days
Extrusion Billet	As extruded to billet size	None		-.28	-.35	-.53
"	"	1000°C/48hr/furnace cool		-.20	-.32	-.55
"	"	900 C/24hr/water quench(in bulb)		-.11	-.14	-.26
None	As extruded to clad rod	None	-	-.50	-.59	-2.88
"	"	500°C/7da/W.Q.	Dis.			
"	"	900°C/24hr W.Q./500°C/7da/W.Q.	-0.51			
1000°C/48hr/F.C.	"	None	-	-.29	-.38	-.66
"	"	500°C/7da/W.Q.	-2.29			
"	"	900°C/24hr/W.Q./500°C/7da/W.Q.	-0.27			
None	As extruded & cold drawn 17%	None	-	-.49	-.51	-.68
"	"	500°C/7da/W.Q.	Dis.			
1000°C/48hr/F.C.	As extruded & cold drawn 17%	900°C/24hrW.Q./500°C/7da/W.Q.	-1.24	-.25	-.30	-.34
"	"	500°C/7da/W.Q.	-5.07			
"	"	900°C/1da/W.Q./500°C/7da/W.Q.	-0.52			
None	As extruded & cold drawn 30%	None		-.50	-.51	-.66
"	"	500°C/7da/W.Q.	Dis.			
"	"	900°C/1da/W.Q./500°C/7da/W.Q.	-1.01			
1000°C/48hr/F.C.	As extruded & cold drawn 30%	None		-.27	-.32	-.36
"	"	500°C/7da/W.Q.	-.44			
"	"	900°C/1da/W.Q./500°C/7da/W.Q.	-0.40			
None	As extruded to clad rod	900°C/24hr/W.Q.		-.09	-	-
1000°C/48hr/F.C.	"	"		-.06	-	-
None	As extruded & cold drawn 17%	"		-.09	-	-
1000°C/48hr/F.C.	"	"		-.10	-	-
None	As extruded & cold drawn 30%	"		-.07	-	-
1000°C/48hr/F.C.	"	"		-.11	-	-
1000°C/48hr/F.C.	As extruded to bare rod	None		-.40	-	-
"	"	900°C/24hr/W.Q.		-.09	-	-

34

Table III - The Effects of Various Annealing Atmospheres and Corrosion
Test Time Upon the Corrosion Properties of a U-12 w/o Mo Alloy

		as ext.	900°C/24hrs vacuum	900°C/24hrs Tank He	900°C/24hrs Tank H ₂	900°C/24hrs UH ₃ H ₂	900°C/24hrs Tank O ₂
0 days	H ₂ Conc.	1.1	1.6	0.8	12.6	6.4	0.21
	DPH 30 kg	309	296	302	316	302	288
3 days	H ₂ Conc.	65.1	26.5	17.7	16.6	29.0	29.5
650°F	Corr. Rate mg/cm ² /hr	-0.87	-0.26	-0.14	-0.11	-0.25	-0.22
	Total Corrosion	62.7	18.7	10.0	7.8	17.9	15.9
	DPH 30 kg	331	315	312	315	318	314
7 days	H ₂ Conc.	386	93	41	112*	63	65
650°F	Corrosion Rate	-1.15	-0.40	-0.19	-0.15	-0.31	-0.26
	Total Corrosion	193	68	31	26	52	44
	DPH 30 kg	355	331	326	333	334	
14 days	H ₂ Conc.	1210	420	115	105	144	
650°F	Corrosion Rate	-3.25	-0.64	-0.26	-0.23	-0.41	-0.36
	Total Corrosion	1092	215	87	77	137	121
	DPH 30 kg	425	352	350	354		
21 days	H ₂ Conc.	disint.	886	338	280	474	
650°F	Corrosion Rate	"	-0.98	-0.38	-0.36	-0.53	
	Total Corrosion	"	494	191	181	267	
	DPH 30 kg	"					
28 days	H ₂ Conc.	"	disint.	634	708		
650°F	Corrosion Rate	"	"	-0.59	-0.57	-0.88	
	Total Corrosion	"	"	396	383		
	DPH 30 kg	"	"				
35 days	H ₂ Conc.	"	"				
650°F	Corrosion Rate	"	"	-0.97	-1.09		
	Total Corrosion	"	"				
	DPH 30 kg	"	"				

* Being checked

WAPD-PMM-15

Table IV - Corrosion Data for Gamma Quenched U-12 Mo Alloy in 650°F Water with Various Additives

Water Addition	Cumulative Rate (mg/cm ² /hr)							Observations
	<u>7*</u>	<u>14</u>	<u>21</u>	<u>28</u>	<u>35</u>	<u>42</u>	<u>49</u>	
50 ppm Ni ⁺⁺	-0.23	-0.23	-0.29	-0.26	-0.32	-0.32	-0.32	Thick oxide readily removed by brushing. Of two samples remaining after 49 days, one cracked in three pieces 42-49 days. Surfaces still smooth semi-metallic.
50 ppm Pt ⁺⁺⁺⁺	-0.13	-0.17	-0.18	-0.20	-0.20	-0.26		Loose powdery oxide easily removed by washing. One of two samples cracked 35-42 days. Surfaces still smooth semi-metallic. Test conditions inadvertently changed at 35-42 days.
12 ppm Colloidal Platinum	-0.15	-0.24	-0.32	-0.32	-0.60			Behavior similar to degassed water. Test discontinued after 35 days.
<u>No Addition</u>	<u>5*</u>	<u>10</u>	<u>15</u>	<u>20</u>	<u>25</u>	<u>30</u>	<u>35</u>	<u>40</u>
	-0.16	-0.22	-0.28	-0.33	-0.37	-0.52	-1.1	Cracked
								Severely
								Loose powdery oxide easily removed by washing. Dark, smooth, metallic-gray surface initially, changing to dull semi porous with increased testing time.

* Time in Days

TABLE V

Corrosion of U-Mo-Pt Ternary Alloys in 650°F Water

Composition w/o	A		B		C		D		E		F		G	
	X	Y	X	Y	X	Y	X	Y	X	Y	X	Y	X	Y
9 Mo 0.3 Pt	0.2	84-98	0.08	42-56	0.3	14-28	47	1-7	--	0-1	--	0-1	--	0-1
	0.2	70-84	0.06	> 84	0.2	14-28	--	0-1	--	0-1	--	0-1	--	0-1
9 Mo 0.6 Pt	0.08	> 98	0.04	70-84	0.02	56-70	61	1-7	--	0-1	--	0-1	--	0-1
	0.08	> 98	0.04	> 84	0.03	28-42	42	1-7	--	0-1	--	0-1	--	0-1
9 Mo 1.2 Pt	0.05	> 98	0.02	> 84	0.003	> 84	9	7-14	0.04	14-28	--	0-1	--	0-1
	0.05	> 98	0.02	> 84	0.003	> 84	8	7-14	0.05	14-28	--	0-1	--	0-1
12 Mo 0.3 Pt	0.17	> 98	0.12	> 84	0.06	> 84	0.63	14-28	0.07	> 84	0.06	14-28	0.26	1-7
	0.17	> 98	0.10	> 84	0.06	> 84	0.68	14-28	0.08	> 84	0.18	14-28	0.42	1-7
12 Mo 0.6 Pt	0.12	> 98	0.05	> 84	0.04	> 84	0.34	28-42	0.02	> 84	0.09	> 70	0.25	7-14
	0.12	> 98	0.06	> 84	0.04	> 84	0.40	42-56	0.07	14-28	0.08	> 70	0.83	7-14

X - mg/cm²/hr

Y - Failure Time in Days

A - As melted

B - 900°C/24 hrs/W.Q.

C - " " " + 400°C/7 days/W.Q.

D - 400°C/35 da/W.Q. (No initial homogenization)

E - 900°C/24 hr/W.Q. + 500°C/2 da/W.Q.

F - " " " + 500°C/7 da/W.Q.

G - " " " + 500°C/21 da/W.Q.

Table VI - Corrosion Life in Days of Unclad U-Mo-Nb Alloys in 650°F Water

Composition w/o		Fabrication Method	A *	B	C	D	E	F
6 Mo 3 Nb	"	Ind. melted-extruded	42-56	28-42	28-42	0-1	0-1	0-1
			42-56	98-112	14-28	0-1	0-1	0-1
		Button		42-56	1-7	0-1	-	-
7 Mo 2 Nb	"	Ind. melted-extruded	28-42	140-154	154-168	1-7.		
			28-42	154-168	154-168	1-7	0-1	0-1
		Button	42-56	28-42	7-14	0-1	0-1	0-1
			42-56	28-42	14-28	0-1	0-1	0-1
9 Mo 0.5 Nb	"	Ind. melted-extruded	14-28	14-28	7-14	0-1	0-1	0-1
			14-28	14-28	14-28	0-1	0-1	0-1
		Button	28-42	28-42	14-28	0-1	0-1	0-1
			28-42	28-42	14-28	0-1	0-1	0-1
9 Mo 1.4 Nb	"	Button		168-184	28-42	1-7	-	-
		Ind. melted-extruded	56-70	42-56	42-56	14-28	0-1	0-1
			56-70	42-56	42-56	28-42	0-1	0-1
9 Mo 1.5 Nb	"	Button	70-84	28-42	42-56	1-7	0-1	0-1
			>98	28-42	28-42	1-7	0-1	0-1
10.5 Mo 0.5 Nb	"	Ind. melted-extruded	14-28	56-70	42-56	28-42	1-7	0-1
			14-28	70-84	14-28	56-70	1-7	0-1
		Button	42-56	42-56	1-7	1-7	28-42	1-7
			42-56	42-56	28-42	1-7	28-42	1-7
10.5 Mo 1.5 Nb	"	Ind. melted-extruded	28-42	28-42	14-28	28-42	42-56	14-28
			14-28	14-28	14-28	28-42	42-56	14-28
		Button	1-7	7-14	14-28	1-7	14-28	0-1
			70-84	14-28	28-42	1-7	28-42	0-1
12 Mo 0.5 Nb	"	Ind. melted-extruded	28-42	42-56	14-28	28-42	42-56	28-42
			14-28	28-42	140-154	28-42	42-56	28-42
		Button	42-56	7-14	1-7	7-14	28-42	28-42
			42-56	14-28	1-7	7-14	42-56	28-42

* A - As melted

B - 900°C/24 hrs/W.Q.

C - " " " / 400°C/ 7 da/W.Q.

D - 900°C/24 hrs/W.Q. / 400°C/35 da/W.Q.

E - " " " / 500°C/ 2 da/W.Q.

F - " " " / 500°C/ 7 da/W.Q.

Table VII - Corrosion Behavior of U-Mo-X Alloys in 650°F Water

Composition w/o	As Melted		900°C/1 da/W.Q.		900°C/1 da/WQ/400°C/7 da	
	Rate (mg/cm ² /hr)	Failure (Days)	Rate (mg/cm ² /hr)	Failure (Days)	Rate (mg/cm ² /hr)	Failure (Days)
7 Mo	26	1-7	22	1-7	--	0-1
	22	1-7	7.5	1-7	--	0-1
7 Mo 0.3 Cr	1.3	14 *	0.4	7-14	2.3	7-14
	1.3	14 *	0.7	7-14	5.0	7-14
7 Mo 0.6 Cr	0.04	84-98	12	1-7	--	0-1
	0.04	>98	6	1-7	--	0-1
7 Mo 1.0 Cr	0.2	14-28	0.03	28-42	--	0-1
	0.2	14-28	0.03	>84	29	1-7
7 Mo 0.3 Ti	0.4	42-56	2.3	1-7	--	0-1
	0.1	84-98	2.8	7-14	--	0-1
7 Mo 0.6 Ti	0.6	>98	0.4	7-14	--	0-1
	0.2	>98	0.2	>84	--	0-1
7 Mo 1.0 Ti	0.2	>98	0.07	42-56	--	0-1
	0.2	7-14	0.07	>84	--	0-1
7 Mo 0.3 V	1.1	7-14	0.3	14-28	1.0	14-28
	1.1	7-14	0.3	14-28	0.8	7-14
7 Mo 0.6 V	0.08	42-56	2.3	1-7	--	0-1
	0.08	42-56	1.8	1-7	--	0-1
7 Mo 1.0 V	0.04	56-70	48	1-7	--	0-1
	0.04	56-70	47	1-7	--	0-1
9 Mo	0.6	14-28	0.1	14-28	1.0	14 *
	0.6	14-28	0.2	14-28	1.0	7-14
9 Mo 0.3 Cr	0.1	56-70	0.07	14-28	0.5	7-14
	0.1	42-56	0.06	14-28	3.6	1-7
9 Mo 0.6 Cr	0.1	28-42	0.03	>84	31	1-7
	0.1	42-56	0.03	>84	38	1-7
9 Mo 1.0 Cr	0.2	14-28	0.06	28-42	0.8	7-14
	0.2	14-28	0.15	14-28	0.8	14 *
9 Mo 0.3 Ti	0.2	56-70	0.1	>84	0.5	1-7
	0.1	70-84	0.2	14-28	0.5	7-14
9 Mo 0.6 Ti	0.1	>98	0.2	>84	0.6	1-7
	0.2	>98	0.3	56-70	0.6	7-14
9 Mo 1.0 Ti	0.1	>98	0.3	42-56	--	0-1
	0.1	>98	0.2	70-84	--	0-1
9 Mo 0.3 V	0.1	56-70	0.2	42-56	0.1	42-56
	0.1	56-70	0.1	56-70	0.2	42-56
9 Mo 0.6 V	0.05	56-70	2.4	1-7	1.4	1-7
	0.1	70-84	9.1	1-7	1.5	1-7
9 Mo 1.0 V	0.1	42-56	0.06	28-42	65	1-7
	0.06	56-70	18.6	1-7	48	1-7

* Sample was almost entirely corroded. Not retested.

Table VIII - Corrosion Data for U-10 Zr-4 Nb in 343°C Water

Heat Treatment	Corrosion Rate (mg/cm ² /hr)	Life (Days)
900°C/24 hr/W.Q.	0.18	28-42
	0.18	42-56
	0.13	28-42
	0.17	56
900°C/24 hr/W.Q. / 400°C/7 da/W.Q.	0.29	14-28
	0.29	14-28
900°C/24 hr/W.Q. / 400°C/35 da/W.Q.	15	7-14
	--	0-1
900°C/24 hr/W.Q. / 500°C/2 da/W.Q.	--	0-1
	--	0-1
900°C/24 hr/W.Q. / 550°C/7 da/W.Q.	--	0-1
	--	0-1

Table IX - Effects of Low Temperature Annealing

Heat Treatment	Failure Time in Days in 343°C Water							
	6	7	9	9.8	10.7	12	13	15 %Mo
900°C/24 hr/W.Q.	0-1	0-1	14-28	14-28	28-42	14-28	7-14	7-14
300°C/60 da/W.Q.		7-14		28-42	28-42	14-28		
300°C/79 da/W.Q.	7-14	14-28	14-28					
300°C/140 da/W.Q.	7-14	7-14	7-14					
343°C/49 da/W.Q.			(14-28 56-70)					
343°C/105 da/W.Q.		1-7	7-14			14-28		
400°C/140 da/W.Q.		0-1	0-1	1-7	28-42	14-28	14-28	

TABLE XCorrelation Between Corrosion Life and X-Ray Structure

<u>Wt. % Mo</u>	<u>300°C - 140 Days</u>		<u>343°C - 210 Days</u>		<u>400°C - 140 Days</u>	
	<u>Life</u>	<u>X-Ray Structure</u>	<u>Life</u>	<u>X-Ray Structure</u>	<u>Life</u>	<u>X-Ray Structure</u>
6	7-14 7-14	dist. α				
7	7-14	probably δ + dist. α	1-7 1-7	broadened δ + ϵ + α	0-1 0-1	well resolved ϵ + α
9	7-14 7-14	broadened δ + α	7-14 1-7	broadened δ + ϵ + α	0-1 0-1	well resolved ϵ + α
12	--	--	7-14 7-14	sharp δ	28-42 14-28	sharp ϵ plus broadened α . complete transformation
13.5	--	--	7-14 7-14	sharp δ	14-28 14-28	ϵ + δ
15	--	--	7-14 7-14	sharp δ	14-28 7-14	δ + ϵ

TABLE XI

Corrosion Life of Zircaloy Clad Uranium
Alloy Elements Tested in As-Extruded Condition in High Temperature
Water or Steam with 0.040 in. Holes in Cladding

(Data represents range for three best samples ever tested at each condition)

<u>Alloy Content (w/o)</u>	<u>Test Temperature (°F)</u>	<u>Corrosion Life (Days)</u>
9 Mo.	650	115-143 (1-175-189)
9 Mo.	680	40-54
9 Mo.	750 (steam)	28-59
10.5 Mo.	650	105-183
10.5 Mo.	680	28-96
10.5 Mo.	750 (steam)	58-65
12 Mo.	650	232 (in test)
12 Mo.	680	84-98 (1 in test 98 days)
12 Mo.	750 (steam)	42-63
13.5 Mo.	650	232 (in test)
13.5 Mo.	680	68-96 (1 bulging at one hole-207 da.)
13.5 Mo.	750 (steam)	7-73
10 Nb	650	216 (in test, 5 for 140 da.)
10 Nb	680	208 (in test)
10 Nb	750 (steam)	28-42
12 Mo + 0.5 Nb	680	70-124 (2 rods)
7.5 Mo + 1.5 Nb	650	112-140 (1 in test 140 da.)
7.5 Mo + 1.5 Nb	680	28-54 (1 in test 96 da.)
9 Mo + 1.4 Nb	650	70-98
9 Mo + 1.4 Nb	680	40-54
9 Mo + 1.4 Nb	750 (steam)	42-65
8 Mo + 0.3 Ti	650	14-28
8 Mo + 0.3 Ti	680	14-28
8 Mo + 0.3 Ti	750 (steam)	7-14
6 Mo + 3 Nb	650	112-126 (1 rod)
7 Mo + 2 Nb	650	128-142 (1 rod)
7 Mo + 2 Nb	680	98-112 (1 rod)
9 Mo + 0.5 Nb	650	84-98 (1 rod)
9 Mo + 0.5 Nb	680	28-42 (1 rod)
10.5 Mo + 1.5 Nb	650	196 (1 rod in test)
10.5 Mo + 1.5 Nb	680	180 (1 rod in test)

TABLE XII

Corrosion Life of Zircaloy-Clad U-10 w/o Nb
Alloy Rods (405-7 and 9) with 0.040 in. Holes in Cladding

<u>Condition</u>	<u>Test Temp. (°F)</u>	<u>No. of Rods</u>	<u>Corrosion Life (Days)</u>
As-Extruded	650	1	216 (in test, 5 for 140)
As-Extruded	680	2	208 (in test)
As-Extruded	750 (steam)	2	28-42
343°C(650°F)/42 days	650	2	140 (in test)
343°C(650°F)/42 days	750 (steam)	2	49-63
400°C(750°F)/42 days	650	2	70(in test), 1 for 14-21
800°C/2 hours	650	1	63(in test)
800°C/24 hours	650	1	70(in test)

TABLE XIII

Corrosion Life (Days) of Clad U-12 w/o Mo Alloy
Simulated Fuel Elements with 0.040 in. Hole Defects in Cladding

	<u>650°F Water</u>			<u>750°F Steam (1500 psi)</u>	
	<u>1101-1-7</u>	<u>1101-1-8</u>	<u>1101-1-9</u>	<u>1101-1-8</u>	<u>1101-1-15</u>
As Extruded	42*	63*	--	21-28	35-42
	42*	35-42	--	35-42	42*
As Drawn	0-7	28-35	7-14	0-7	14-21
	49*	7-14	7-14	0-7	21-28
As Drawn + 1/2 hr 600°C	0-7	7-14	--	0-7	0-7
	21-35	28-35	--	0-7	0-7
As Drawn + 8 hrs 600°C	7-14	--	--	--	0-7
	7-14	--	--	--	0-7
As Drawn + 1 wk 400°C	--	7-14	--	--	--
	--	7-14	--	--	--
As Drawn + 3 wks 400°C	--	0-7	--	--	--
	--	0-7	--	--	--

* Still in test

Table XIV - Corrosion Life of Bare U-12 w/o Mo Alloys
in Days and Corrosion Rate in Mg/cm²/hr

	1101-1-8 650°F		1101-1-9 650°F		1101-1-14 650°F		1101-1-15 650°F		1101-1-8 750°F	
	Life	Rate	Life	Rate	Life	Rate	Life	Rate	Life	Rate
As Extruded	7-14	-1.6					7-14	-0.9	1-4	-7
As Ext. + 900°C/24 hrs/W.Q.	--	--					28*	-0.3	--	--
As Ext. + 600°C/1/2 hr	--	--					7-14	-1.3	--	--
As Ext. + 600°C/4 hrs	--	--					7-14	-1.4	--	--
As Ext. + 600°C/8 hrs	--	--					7-14	-1.3	--	--
As Drawn	7-14	-1.5	28-42	-0.4	7-14	-0.9	7-14	-1.2	1-7	-12
(A) As drawn + 900°C/24 hrs/W.Q.	--	--			14*	-0.3	28*	-0.25		
(B) As drawn + 600°C/1/2 hr	7-14	-1.1	14-28	-1.2	7-14	-1.6	7-14	-2.5	1-7	-10
+ 600°C/4 hrs	7-14	-1.0					7-14	-1.7	1-7	-10
+ 600°C/8 hrs			7-14	-1.25			7-14	-1.5		
(C) + 600°C/24 hrs					7-14	-1.0				
+ 400°C/1 wk	14-28	-2.2			3-7	-3.4			4-7	-16
+ 400°C/3 wk	7-14	-7			3-7	-7			4-7	-12
+ 400°C/5 wks	1-7	-5			1*	-5			1-4	-20
(A) + 1 wk 400°C					7*	-0.11				
(A) + 3 wks 400°C					14*	-0.10				
(A) + 5 wks 400°C					7*	-0.11				
(B) + 1 wk 400°C					1-7	-45				
(B) + 3 wks 400°C					0-3	--				
(B) + 5 wks 400°C					0-3	--				
(C) + 1 wk 400°C					1-7	-30				
(C) + 3 wks 400°C					0-3	--				
(C) + 5 wks 400°C					0-3	--				

* Still in test

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Table XV - Corrosion Life in 650°F Water of
Irradiated Annealed Clad Rods

<u>Sample No.</u>	<u>Composition</u>	<u>Estimated Exposure in Mwd/T</u>	<u>Test Days to Failure</u>	<u>Remarks</u>
A 23	U-9.0 w/o Mo	10,100	6 - 9	Longitudinal split at defect
A 26	U-9.0 w/o Mo	15,500	3 - 6	Six longitudinal cracks. General swelling
B 24	U-10.5 w/o Mo	9,500	Continuing in test after 12 days	
B 26	U-10.5 w/o Mo	12,500	Continuing in test after 15 days	
B 27	U-10.5 w/o Mo	15,500	0 - 3	Slight bulge at defect. No cracks at clad
C 21	U-12.0 w/o Mo	10,300	6 - 9	Longitudinal split at defect
C 26	U-12.0 w/o Mo	16,000	0 - 3	Longitudinal split at defect. Swelled over center section.
C 27	U-12.0 w/o Mo	17,300	0 - 3	Longitudinal cracks in cladding. General swelling
D 21	U-13.5 w/o Mo	10,300	6 - 9	Longitudinal split at defect
D 27	U-13.5 w/o Mo	14,000	3 - 6	Longitudinal split at defect

Table XVI - Change in Density of Bare U-Mo Samples
Exposed to a Maximum of 8000 Mwd/T

<u>Reactor Position</u>	<u>Composition</u>	<u>Estimated Temperatures</u>		<u>Increase in Diameter**</u>	<u>Increase in Length</u>	<u>Density Decrease</u>
		<u>Surface</u>	<u>Center</u>			
1 (min flux)	13.5 w/o Mo-U	124	168	0	0.1%	.54%
2		236	337	.54%	.25%	1.11%
3		302	439	1.07%	.65%	2.75%
4 (max flux)	13.5 w/o Mo-U*	385	565	2.67%	2.35%	7.61%
5	12 w/o Mo-U	400	588	3.21%	2.1%	6.65%
6	"	337	492	.54%	.5%	2.09%
7 (min flux)	"	193	273	.54%	.25%	1.13%

* Epsilonized Sample

** Samples originally 0.187% Dia. x 2.000" long

Table XVII - Corrosion Life of Chalk River Control Samples

<u>Composition</u>	<u>Sample No.</u>	<u>End Closure</u>	<u>Extrusion Temp.</u>	<u>Corrosion Life in 650°F Water</u>
U-10.4 w/o Mo	M 46 (natural)	bonded	1750 F	28-42 days
U-10.5 w/o Mo	M 32 (enriched)*	bonded	1750 F	28-42
U-10.5 w/o Mo	M 30 (enriched)	bonded	1750 F	43-54
U-10.5 w/o Mo	M 34 (enriched)	bonded	1750 F	43-54
U-10.5 w/o Mo	M 31 (enriched)	unbonded	1750 F	43-54
U-10.4 w/o Mo	M 47 (natural)	unbonded	1750 F	55-68
U-10.6 w/o Mo	N 30 (enriched)	bonded	1932 F	69-82
U-10.6 w/o Mo	N 31 (enriched)	unbonded	1932 F	69-82
U-10.5 w/o Mo	M 33 (enriched)	unbonded	1750 F	69-82
U-10.6 w/o Mo	M 36 (enriched)	bonded	1932 F	69-82
U-10.5 w/o Mo	M 35 (enriched)	unbonded	1750 F	In test after 82 days
U-12.4 w/o Mo	N 32 (enriched)	unbonded	1960 F	55-68
U-12.4 w/o Mo	N 33 (enriched)	unbonded	1960 F	In test after 82 days
U-12.0 w/o Mo	N 46 (natural)	unbonded	1950 F	In test after 82 days
U-12.0 w/o Mo	N 48 (natural)	bonded	1950 F	In test after 82 days

* Samples enriched to 3.6 w/o uranium-235

Table XVIII - Density of U-3.8 w/o Si Alloy

<u>Specimen No.</u>	<u>Location in Reactor</u>	<u>"as-extruded"</u>	<u>Density(g/cm³) epsilononized*</u>	<u>% decrease irradiated</u>	<u>after irradiation</u>
	bottom of reactor				
5	1	15.34 $\pm$ 0.01	15.54	14.97	3.8
8	2	(measured on	15.54	15.31	0.2**
10	3	four control	15.54	14.99	3.5
11	4(max flux position)	samples)	15.52	14.92	3.9
16	5		15.53	14.96	3.7
17	6		15.53	14.96	3.7
18	7		15.52	14.96	3.6
	top of reactor				

* 800°C for 91 hours in evacuated vycor tubes

** Sample cracked during a sectioning operation.
Density measurement may be invalid.

Table XIX - Corrosion Behavior of U-3.8 w/o Si Alloy

Sample No.	Condition	Corrosion Rates (mg/cm ² /hr) in 650°F Water							
		Time - hours							
		24	168	336	672	1008	1344	1680	2016
1	epsilonized	-2.98	-1.79	-1.44	-1.34	-1.16	-1.05	-9.30	disintegrated
2	"	-3.04	-1.86	-1.71	-1.75	-1.49	-1.11	disintegrated	
3	"	-2.68	-1.73	-1.39	-1.31	-1.17	disintegrated		
4	"	-2.50	-1.65	-1.36	-1.30	-1.13	-1.05	disintegrated	

Sample No.	Condition	Wgt. before test (gm)	Wgt. after test (gm)	Weight loss (gm)	Rate mg/cm ² /hr
6	epsilonized / 6 wks at 200°C in vacuum	11.5559	11.2008	-.3551	-2.50
13	epsilonized / 6 wks at 300°C in vacuum	11.5217	11.2032	-.3185	-2.24
14	epsilonized / 6 wks at 400°C in NaK filled tube	10.6808	10.3826	-.2972	-2.25
15	epsilonized / 6 wks at 400°C in vacuum	11.7370	11.4503	-.2867	-1.99
19	epsilonized / 6 wks at 500°C in vacuum	10.2571	10.0071	-.2500	-1.98
8	irradiated-reactor position #2	5.5628	disintegrated		
10	#3	6.1652	disintegrated		
11	#4	7.9378	disintegrated		
17	#6	7.0862	6.4666	-0.6196	-6.56
18	#7	7.5812	6.1454	-1.4358	-14.26

See Table XVIII for reactor position.

SECRET

WAPD-PMM-15

50

Table XX - UO₂ Powder Characterization

Powder	Run #	Wt. Analysis Grav. Anal.		X-ray Diffraction		
		o/u	o/u	A ₀ Å *	Crystallite Size A ^Δ o/u	□
Mallinckrodt	---	---	---	5.4689 ±0.0003		1.995 ±0.002
Steam ox 5 psi - 225°C	NOL 1a	2.17	2.244	5.4695 ±0.0050	110 ± 50	1.990 ±0.04
Steam ox 5 psi - 430°C	NOL 4	2.09	---	5.4677 ±0.0020	170 ± 50	2.003 ±0.015
Steam ox 2200 psi - 343°C	NOL 10	1.95 ^x	---	5.4646 ±0.0010	200 ± 50	2.032 ±0.007
Steam ox 2200 psi - 343°C Enriched	EOH 3	1.96 ^x	---	5.4704 ±0.0005	170 ± 50	1.982 ±0.003

* Determined using film in 114.6 cm camera with copper K radiation value of a₀ obtained by extrapolation using Nelson-Riley Function

Δ Determined using the Scherrer formula for the 311 line and assuming Mallinckrodt crystallite size to be infinite i.e. greater than 2000 Å⁰

□ Determined from data given by Herring and Perio (Bu. Soc. Chime 351-7 1952)

x May contain adsorbed water

Mag. 250X - Heat Tinted
As Extruded - Longitudinal View

A

Extrusion M02C1-16

Extruded clad with Zircaloy-2

Ext. Temp. - 1585°F
Soaking Time - 10 min.

Corrosion Life - 14 days
in 650°F H₂O

B

Extrusion MM431-10

Extruded Bare

Ext. Temp. - 1935°F
Soaking Time - 5 min.

Corrosion Life - 28 to 42 days
in 650°F H₂O

Fig. 1 - Comparison of Homogeneity vs Corrosion
Life of Two U-12 Mo Extrusions.

FIG 2 CORROSION OF BARE SAMPLES OF U-12 MO RODS
EXTRUDED AT 1585°F AND 1935°F AND TESTED IN
650°F WATER.

Longitudinal Section 250X

A. Homogenized at 1000°C for 48 hours, furnace cooled and extruded clad. No heat treatment after extrusion.

Longitudinal Section 250X

B. As extruded clad without prior homogenization of billet.

Fig. 3 - Structure of U-12 Mo Ingot J-875 Extruded Clad (A) with and (B) without Homogenization Prior to Extrusion.

A. As extruded hydrogen - 462 ppm
longitudinal view 250X

B. 700°C-24 hr-W.Q. hydrogen - 666
ppm longitudinal view 250X

C. 900°C-24 hr-W.Q. hydrogen - 78
ppm longitudinal view 250X

987 053

Fig. 4 - Microstructure of Homogenized Extruded U-12 Mo
after 7 Days Corrosion in 650°F Water.

FIG 5 EFFECT OF HOMOGENIZATION TEMPERATURE ON
THE CORROSION OF U-12 MO EXTRUSION M02C1-16

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WAPD-PMM-15

Fig. 6 - U-12 Mo 1000°C-48 hrs-
W.Q. corrosion tested
14 days in 650°F water
250X

987

055

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FIG. 7 INCREASE IN HYDROGEN IN U-12Mo DURING CORROSION IN 650°F WATER.

INITIAL HYDROGEN - 0.15 ppm

58

Fig. 8 - Hydrogen Concentration as a Function of Total Corrosion for a U-12 w/o Mo Alloy annealed in Various Atmospheres.

59

A. As extruded-transverse section
1.1 ppm H₂ 250X

B. As annealed 24 hrs at 900°C in
tank hydrogen
12.6 ppm H₂ 250X

Fig. 10 - Typical Initial Structures of A. Duplex melted, as-extruded U-12 Mo, B. Same as annealed 24 hours at 900°C
250X

A. As extruded, 3 days test at 650°F
65.1 ppm H₂

B. As extruded, 14 days test at 650°F
1210 ppm H₂

C. As vacuum annealed, 3 days test
at 650°F
26.5 ppm H₂

D. As tank hydrogen annealed, 3 days
test at 650°F
16.6 ppm H₂

Fig. 11 - Typical Microstructures after Corrosion Testing (all 250X, standard electro-etch). A. As extruded, 3 days in 650°F water. B. As extruded, 14 days in 650°F water. C. Vacuum annealed, 24 hours at 900°C, 3 days in 650°F water. D. Tank hydrogen annealed, 24 hours at 900°C, 3 days in 650°F water.

A. Vacuum Annealed 14 days in test 650°F
420 ppm H₂ - 0.64 Mg/cm²/hr 250X

B. Tank Hydrogen Atmosphere 14 day in test
650°F 105 ppm H₂ - 0.23 Mg/cm²/hr 250X

Fig. 12 - Further Microstructures after Corrosion Testing

A. As vacuum annealed, 14 days test at 650°F

B. As tank hydrogen annealed, 14 days test at 650°F

Fig. 13
X-RAY LINE PROFILES DURING
HOMOGENIZATION OF U-12 MO

LEGEND

- AS REC'D
- - - 1 HR. - 600° C
- 1 HR. - 900° C
- 8 HR. - 900° C
- 24 HR. - 900° C

Fig. 14 - The Influence of Water Additions on the Corrosion
of U-12 Mo in 650°F Water

Fig. 15 - The Influence of Additions to 650°F Water on
The Hardness Increase of U-12 Mo During
Corrosion

Fig. 16 - The Influence of Additions to 650°F Water on
The Hydrogen Pick-up of U-12 Mo During
Corrosion

Fig. 17 - Gamma quenched U-12 Mo. Corrosion tested in 650°F degassed water for 25 days. 250X electro-etched

Fig. 18 - Gamma quenched U-12 Mo. Corrosion tested in 650°F degassed water containing 50 ppm Ni^{++} for 28 days
250X electro-etched

Fig. 19 - Gamma quenched U-12 Mo. Corrosion tested in 650°F
degassed water containing 50 ppm Pt⁺⁺⁺⁺ for 28 days
250X electro-etched

A. Electrolytically Etched 5 seconds in
Chromic-Acetic Acids
78B13 X1000

8 μ
2.2 μ
1.2 μ

B. As Acid Polished
783B12

X1000

Fig. 20 - UH_3 Platelets in Gamma Quenched U-12% Mo
after Corrosion Testing in 650°F Water for
28 days (Wt. loss 282 mg/cm²)

987 068

A

X9

B

X1000

Fig. 22 - Defect Area of a Zircaloy-2 Clad U-12% Mo Rod
Transformed at 500°C after Heat Through Put Test.

Fig. 23 - Cathodically Hydrided 15 Mo-4.8 Pt Alloy
as Gamma Quenched, 40 Hours at 100°C
150X

Fig. 24 - U-12 w/o Mo Melted 8 Hours at 1300°C in Vacuo in Uranium
Crucible Subsequently Annealed 24 hrs 900°C in Vacuo
(900B-1) 250X

A

As Polished
(353B1)

X 1000

B

Same Aggregate
Etched with HNO_3

X 1000
(353B2)

Fig. 25 - Mallinckrodt UO_2 Powder, 100 Sieve Fraction, Mounted in Keylon and Polished in Cross Section

A + 80 Fraction
Particle Size Above 177μ
(1009B) X 500

B 325 Fraction
Particle Size 44 - 53μ
(1008B) X 500

C Fines Fraction
Particle Size 0 - 44μ
(1007B) X 500

Fig. 26 - Mallinckrodt UO₂ Particles Mounted in Keylon
and Polished in Cross Section

987 074

A

90% Dense Cold Compacted UO_2

B

70% Dense Cold Compacted UO_2

Fig. 27 - Photographs of Sectioned Pellets of UO_2 after
5600 MWD/T Burnup

A

Split End

B

Bulged End Opposite Split

Fig. 28 - Photograph of Each End of Split Defected UO_2
Sample from CR-WAPD-Met 4A Test

19

- 79 -

WAPD-PMM-15

WAPD-PMM-15

82

CR - WAPD - MET - 4A
 LONGITUDINAL ACTIVITY OF UO_2 SPECIMEN No. 3
 READINGS TAKEN THROUGH 3/16" SLIT IN 4" OF LEAD
 CROSS HATCHED SECTIONS INDICATE VARIATIONS
 IN DENSITY OF UO_2

FIG. 33