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WAPD-PMM-238

METALLURGY AND CERAMICS

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UNITED STATES ATOMIC ENERGY COMMISSION

RESUME OF URANIUM ALLOY DATA-VII

By
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Resumé of Uranium Alloy Data - VIII

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June 1, 1955

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INTRODUCTION

The use of UO_2 as the fuel material for the first FWR core was recently made official. However, work on uranium-base alloys will be continued. Instead of concentrating on U-12 w/o Mo, emphasis will be shifted to alloys which have more attractive nuclear properties and which permit flexibility in reactor design and low cost fuel element fabrication. Accordingly, a new metal alloy development program is being initiated. This program is divided into four major parts described briefly below. It is requested that the Panel Members consider this program and comment on its adequacy and fruitfulness of the various lines of investigation.

I. U-3.8 w/o Si Alloy Development

Of the U-base alloys presently known the epsilon phase U_3Si alloy appears to be the most likely to overcome the major objections raised for gamma phase alloys and to be most promising for rapid development into a superior fuel element. U_3Si is not subject to discontinuous failure resulting from hydrogen absorption as are the gamma phase alloys. Thus, once it is learned how to fabricate and clad such a material satisfactorily one of the major failings noted for gamma phase alloys will have been eliminated. Since failure does not occur through hydride formation, there is no need for using a hydrogen getter such as Zr as a cladding. Cheaper cladding materials, such as Al and stainless steel, can be considered. Since U_3Si is thermally stable up to $930^\circ C$, as compared with about $400^\circ C$ for gamma phase alloys, larger fuel element diameters can be used without reaching dangerously high central temperatures. This would make the penalty for using claddings of high absorption cross section, such as stainless steel, less severe. The high thermal stability of U_3Si would also permit bonding of core to clad by methods involving low temperature brazing, etc. so that core and clad may be thoroughly inspected separately prior to bonding. This method of

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cladding also holds promise from the standpoint of minimizing fabrication costs. Advantage is taken of these very desirable features of U_3Si in an intensive work program designed primarily to solve the bonding and fabrication problems. A brief outline of the contemplated work follows:

A. Investigation of Stainless Steel as a Cladding for U_3Si

1. Direct bonding of stainless steel to U_3Si by
 - a. Coextrusion
 - b. Hot working of extruded U_3Si rod and stainless steel tubing
2. Intermediate layers applied in the molten condition (Cu-base brazes, Al, Al-Si alloys, Al-Ni alloys, Al-Fe alloys, Al-Ni-Si alloys, etc.) by
 - a. Hot dipping the U_3Si or stainless steel tubing followed by coextrusion or hot working.
 - b. Brazing core to cladding.
3. Intermediate layers applied in the solid condition (electroplated Cr and tubes or foils of Nb, V, Al and Al alloys) by
 - a. Coextrusion
 - b. Hot working

B. Investigation of Zircaloy-2 as a Cladding for U_3Si

1. Direct bonding of Zircaloy to U_3Si by
 - a. Coextrusion
 - b. Hot working
2. Intermediate layers of Al or Al-Ni alloys applied by
 - a. Hot dipping of U_3Si followed by brazing to Zircaloy tubing
 - b. Coextrusion of hot working of U_3Si with Al and Zircaloy tubing
3. Intermediate layers of electrodeposited Cr and tubes or foils of Nb, V, Ni and U-Nb alloys applied by
 - a. Coextrusion
 - b. Hot working

C. Properties of U_3Si

1. Effect of homogenization or corrosion rate of U_3Si
2. Correlation of corrosion rate, hydrogen content, hardness and pertinent physical property measurements.
3. Measurement of hydrogen distribution between core, clad and interface in Zircaloy-clad and stainless steel clad elements after corrosion testing.
4. Rate of interaction of hot pressed compacts of U_3Si with Zr, molten Al, alloys of Al with Si, Ni, Fe, Ni-Si, Cr, Nb, V, Cu-base brazing alloys and other materials.

D. Irradiation Studies on

1. Bare U_3Si to establish changes in physical properties, density and corrosion resistance.
2. Clad U_3Si to determine if cladding restraint helps retain fuel element integrity and properties.

II. Basic Metal Alloy Development

This part of the program is devoted primarily to exploring in greater detail those aspects of uranium alloy behavior uncovered in the U_3Si program. In addition, it is aimed at providing basic information which will permit better and faster development of radiation and corrosion-stable uranium-base alloys.

A. Alloying Behavior of Uranium

1. Magnetic susceptibility measurements on the following to determine effects of alloying elements in promoting thermal stability of the gamma phase.
 - a. U-Mo alloys with varying Mo contents
 - b. U-Mo alloys with minor additions of Nb, Pt, Zr, etc.
 - c. U with minor additions of gamma stabilizers such as Ti, V, Cr, Nb, and Zr.
 - d. U_2Mo during ordering to epsilon
2. Electrical resistivity and temperature coefficient of electrical resistivity measurements on the following to explain anomalous negative temperature coefficients.
 - a. U-Mo alloys of varying Mo contents

- b. U-Nb alloys of varying Nb contents
 - c. U with minor additions of V, Cr, Ti and Zr.
3. Specific heat and resistivity measurements on
- a. U_2Mo to determine order-disorder equilibrium and kinetics
 - b. U-Mo alloys with minor additions of Pt, Nb, Cr, etc. to determine effects of additions on kinetics of order-disorder kinetics of U_2Mo phase.

B. Uranium-Base Alloys with Transition Phase Structures

1. Determination of crystal structure of alpha prime phase
2. Identity of structures produced in U-base alloys
3. Determination of existence range of alpha prime phase
4. Kinetics of formation as affected by alloy additions and heat treatment
5. Kinetics of decomposition of alpha prime phase as affected by alloy additions
6. Effect of residual stress on promoting formation of alpha prime phase

C. Thermal Stability of Gamma Phase Alloys

1. U-Nb-Zr Alloys
 - a. Optimum composition for thermal stability by diffusion of Zr into U-Nb alloys followed by transformation heat treatments
 - b. Diffusion rates in U-Nb-Zr system
 - c. Corrosion resistance of promising alloys
2. Effect of multiple alloying additions versus larger amounts of single additions on gamma stability. Single additions and multiple combinations of Mo, Nb, Zr, Ti, Cr, V, etc. will be investigated.

D. Corrosion Mechanism in U and U-Base Alloys

1. Measurement of mobility of hydrogen in alpha U, gamma U (as stabilized with additions of Mo, Nb, etc.) and U_3Si .
2. Identification of hydride phase formed during corrosion of gamma phase alloys by measuring decomposition pressure as a function of temperature.

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3. X-ray diffraction and magnetic susceptibility measurements for confirmation of nature of hydride phase in large grained samples of gamma phase alloys.
4. Determination of metal and water composition effects on formation of hydride phase and its distribution.
5. Relation of corrosion behavior of U and U-base alloys in oxygen, water and steam.

III. Aluminum Cladding Alloy Development

The progress made at ANL in extending the range of usefulness of Al-base alloys in high temperature water has indicated considerable promise for a cheap Al-base cladding alloy. The addition of 1 w/o Ni to 2S Al has eliminated blistering noted for unalloyed Al at temperatures of 250°C or above. However, the corrosion rates are much too high for 650°F service. In addition, the rates are found to be still higher, by a factor of five, in dynamic tests as compared to static autoclave tests. Considerable erosion and impingement effects are also noted in dynamic tests. It is planned to follow closely ANL developments and also to cooperate with ALCOA Research Laboratories who have initiated a program on Al alloys for high temperature water. The following tasks are considered most important in connection with future Al alloy development.

- A. Coordination of the ALCOA program on static corrosion tests with dynamic and in-pile corrosion tests.
- B. Compatibility of Al with U and UO_2 at 630°F and higher.
- C. Investigation of powder metallurgy product, SAP, and incorporation of Ni, Zr, Ti, etc powder to improve corrosion resistance and strength properties.
- D. Investigation of solution rate of Al_2O_3 in high temperature water as a function of temperature.

IV. Irradiation Effects

The program on irradiation effects, aside from the work which is directed towards evaluation of U_3Si , is to be devoted primarily to determining the limitations on the use of unalloyed uranium when irradiated under clad restraint, the effects of structure of fissionable material on irradiation behavior and the effects of irradiation on crystal and metallographic structure. Specific items to be investigated follow.

A. Effect of Restraint on Irradiation Stability of Uranium

1. Determination of stress required to prevent dimensional changes in alpha uranium as a function of exposure, hardness level as achieved by alloying, and amount of initial texture.

2. Evaluation of effect of cladding on mechanical, corrosion and physical properties after irradiation of gamma phase U-base alloys and alpha U.

B. Relation between Structure and Irradiation Behavior

1. Effect of irradiation on X-ray and metallographic structures of UO_2 , U and U alloys.
2. Effect of structure of fissionable materials, such as UO_2 , UC, U_3Si , gamma phase alloys, alpha prime alloys and unalloyed U on irradiation behavior.

Experiments designed to fulfill the aims of the future work program, especially as they concern the U-3.8 w/o Si alloy, are just getting started. Most of the activity during the last resume period has been devoted to continued exploration of possible factors which might be responsible for observed variability in the corrosion life of U-12 w/o Mo alloy. This work, which is being rapidly deemphasized to permit vigorous attack on the U-3.8 w/o Si alloy development, is summarized briefly below.

Several factors which were considered as possible contributors to variability in U-Mo alloys were found to have little or no effect on corrosion life. Included in these are initial hydrogen content, vacuum versus various inert gas annealing atmospheres, induction versus duplex melting and extrusion temperature. On the other hand, micro-segregation, which is present to a greater or lesser degree in all induction or duplex melted material, is found to be a major factor affecting corrosion life. This microsegregation can not be satisfactorily eliminated by simply raising the extrusion temperature. The salt bath heating cycle employed for extrusion is much too short (about 9 minutes) to effect homogenization. Gross coring, however, can be largely eliminated by a high temperature homogenization treatment either before or after extruding the billets. In the case of coextrusion of clad rods homogenization of the billet prior to extrusion is indicated because of adverse corrosion effects resulting from extensive core-clad interdiffusion.

The corrosion life of U-12 Mo bare extruded rods in 650°F water is appreciably improved the higher the homogenizing temperature. Annealing for 24 hours at 900°C, for example, results in a failure time of 35 days. The same annealing time at 1000°C increases the corrosion life to 42 days while 3 minutes at 1100°C increases the life to 56 days. Increasing the annealing time at either 900 or 1000°C decreases the corrosion rate, as expected, but time to discontinuous failure is not affected. Likewise, increasing the cooling rate from the homogenizing temperature decreases the corrosion rate but has little effect on corrosion life. This emphasizes the importance of hydride, which is responsible for discontinuous failure, and the need for a clearer understanding of the factors which control its formation and distribution in gamma phase alloys.

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A considerable improvement in corrosion resistance is realized when U-12 Mo is subjected to a low temperature anneal (400°C for 5 weeks) following the homogenizing treatment. The 35 day corrosion rate, for example, is reduced from -1.0 to -0.11 mg/cm²/hr and the samples have undergone 42 days of test without failure. This low temperature treatment appears to be optimum both from the standpoint of temperature and time. The improvement is not associated with gross transformation of gamma to alpha but is associated with age hardening. Metallographically examined specimens, so treated, indicate a pronounced effect on the appearance of hydride needles. In gamma quenched material the needles are coarse. In the aged material the needles are very evenly distributed, fine and much shorter. The hydrogen content of the latter material is less than for gamma quenched material for the same corrosion time. It would appear from these results that some unknown impurity or coherent transformation, which affects hardness, strains the alloy lattice and inhibits hydrogen absorption and needle growth. The possibility exists, therefore, that unknown impurities and stress play important roles in the variability of corrosion. This suggests a more complete investigation than has been made to date on the properties of very pure U-base alloys. Such an investigation is included in the future work program.

That stress in itself is an important factor was shown by corrosion testing bent rods of bare U-12 Mo. Less hydride needles developed on the tension than on the compression side of the sample. In a clad rod the surface of the core is under tension. This may account, at least partially, for the increased corrosion life of defected clad rods as compared to bare rods. Cathodically treated bare rods which were stressed in bending were previously shown to develop differently oriented hydride platelets on the compression and tension sides, the platelets forming first on the tension side. This apparent discrepancy indicates that temperature of treatment is important. The cathodic treatment was carried out at 100°C while the corrosion tests were at 343°C.

Another significant finding which gives rise to the promise of developing a satisfactory U-Nb-Zr alloy stems from a metallographic examination of a corrosion tested sample of Zircaloy-2 clad U-10 Nb alloy. This sample had been coextruded, cold drawn 31%, homogenized at 900°C for 24 hours, aged at 400°C for 5 weeks, defected and corrosion tested in degassed water at 650°F for 28 days. The sample, cross-sectioned through the defect, showed that one of the diffusion layers, adjacent to the partially transformed core alloy, has excellent corrosion resistance. This layer, which apparently contains less than 10% Nb and some unknown quantity of Zr, corroded less than the core alloy itself and less than other diffusion layers closer to the cladding. In addition, no transformation structure, like that in the core alloy could be seen in this diffusion layer. Further work is contemplated to identify this layer.

Further information has been obtained on the irradiation behavior of U-Mo samples. The defected U-12 Mo sample being irradiated in the Chalk River X-3 Loop (CR-WAPD-Met 6) to an estimated maximum exposure of 4000 MWD/T with a surface temperature of 688°F has now been exposed for about 9 weeks (about 2000 MWD/T). No sign of accelerated corrosion, as determined by loop water activity, has been noted. Similar results were

obtained for the defected U-12 Mo specimen exposed to 1200 MWD/T in the HB-5 Loop (MTR-WAPD 13-Met 1) with a core-clad interface temperature of 710°F. Additional corrosion data on the four defected clad samples of U-10.5 Mo, irradiated to 2800 MWD/T in the MTR failed in 45-58 days in post-irradiation tests. Three of five control samples have lasted over 145 days. This indicates that irradiation does lower the corrosion life of U-Mo alloys. Other data on samples which were exposed to very high burnups of 6500 to 17,300 MWD/T also indicate reduced corrosion life. These samples received a 750°C heat treatment which is known to produce considerable clad-core interdiffusion. However, unirradiated control samples given this same treatment appear to have appreciably longer corrosion lives. Other samples of bare U-12 Mo, irradiated to maximum exposure of 1700 MWD/T lasted as long as the control samples in 650°F water. Hardness tests made on these samples after irradiation indicated an increase of up to 40 points DPH. On subsequent corrosion testing further hardness increases were obtained. At failure the hardness apparently reaches a level somewhat over 400 DPH, as do unirradiated samples.

Samples of bare U-10.5 Mo, irradiated to 12,000 MWD/T display better dimensional stability than U-12 Mo and U-13.5 Mo. Less density decrease is observed the lower the Mo content. The observed density decreases for these alloys are much higher than would be expected from transformation of the gamma phase, indicating that irradiation, per se, is the major factor responsible for the changes.

Three samples of pure U, which were alpha rolled to produce a high degree of preferred orientation (MTR-WAPD 4-Met 4), were examined after exposures up to 400 MWD/T. These samples were restrained during exposure by calibrated Inconel springs. The specimens grew in length, without buckling, and decreased in diameter into a tapered shape because of diameter restraint at one end. Maximum stress exerted on the springs was 6100 psi. Higher exposures will be obtained on additional specimens in an effort to obtain the stress required to prevent growth as indicated in the program for future work.

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I. Variability of Corrosion Properties

A. Effect of Melting Practice

The corrosion testing intended to determine whether difference in melting techniques could be a major factor responsible for variability in corrosion life of U-12 w/o Mo is essentially completed. The results, tabulated in Table I, confirm the preliminary data and indicate that no appreciable differences exist between the corrosion rates and corrosion lives of induction melted and duplex melted samples. Annealing of the duplex melted samples at 900°C for 24 hours halves the corrosion rate but does not affect corrosion life. It may be concluded, therefore, that arc melting does not adversely affect the corrosion properties of induction melted material.

B. Effect of Extrusion Temperature

From preliminary corrosion data, it was reported in WAFD-PMM-15 that U-12 Mo alloys extruded at 1900°F exhibited superior corrosion resistance than similar material extruded at 1600°F. It was felt that the benefit came about because of increased homogenization as a result of using the higher extrusion temperature. However, additional data does not confirm this, apparently because insufficient time was allowed to permit homogenization to proceed at 1900°F. The corrosion data in Table II for ingot J 875, from which a billet was extruded at 1600°F and at 1900°F, shows similar corrosion rates and identical failure times for both extrusions. The longitudinal views of these two extrusions are shown in Figs. 1 and 2 and it is seen that one is about as severely cored as the other. Thus, no more coring was eliminated in the 1900°F extrusion during its heating-up period than was eliminated in the 1600°F extrusion. As expected, homogenizing for 24 hours at 900°C, following extrusion, resulted lower corrosion rate and longer lives for both extrusion temperatures.

On the other hand, other data included in Table II for extrusions Mo2Cl-16 and MM 431-10, and reported in WAFD-PMM-15, strongly indicates that extruding at the higher temperature is much more desirable. For these two extrusions, the material extruded at 1900°F had double the corrosion life and half the corrosion rate (at 7 days) of samples extruded at 1600°F. The metallographic examination of longitudinal sections of these two extrusions, Figs. 3 and 4, showed the 1900°F extrusion to be almost entirely free of micro-coring whereas the 1600°F extrusion was more severely cored than those shown in Figs. 1 and 2. Thus, in this case, most of the coring was eliminated during the 1900°F extruding and the resulting corrosion resistance was good. Homogenizing after extrusion again shows longer corrosion lives and lower corrosion rates for both the 1600 and 1900°F extruded material. The longer corrosion life of gamma quenched MM 431-10 over that of Mo 2Cl-16 is explained by differences in sample size.

Hence, it is concluded that the higher temperature of extrusion is desirable only if most of the coring is eliminated during the heating cycle of the process. As this varies somewhat from extrusion to extrusion, it is probably better to completely eliminate coring prior to extrusion by some appropriate homogenization treatment. (See Section C on The Homogenization of U-12 Mo Extrusion Billets)

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C. Homogenization of U-12 w/o Mo Extrusion Billets

As indicated in WAPD-PMM-15 a study is being made to determine if homogenization of billets prior to extrusion will have the same beneficial effects on improving corrosion resistance as the same homogenization applied to unclad extruded U-12 w/o Mo rods. Sufficient data have been obtained from corrosion testing of unclad and defected clad samples in 650°F water to enable evaluation of the effects of homogenization prior to extrusion.

The results obtained from samples of extruded fuel billets, heat treated in various ways, are indicated in Table III. It is apparent that some improvement in corrosion life is obtained for samples annealed at 900°C for 24 hours in Vycor tubes and bulb quenched. Samples which were annealed at 1000°C for 48 hours (in a dynamic vacuum) and those which were reannealed at 900°C for 24 hours (in Vycor tubes) showed no improvement in corrosion life over the as-extruded billet samples. It appears, therefore, that little if any improvement in corrosion life of billet samples can be expected as a result of annealing the billets. It is felt that the random arrangement and lack of continuity of the cored billet structure (as compared to the longitudinal orientation of coring in extruded rods) is responsible for this.

While homogenization did not result in marked increase in the corrosion life of billets prior to extrusion, it materially improved corrosion life of bare rods extruded from homogenized billets. This was true also of rods which were cold drawn, either 17 or 30% after extrusion. The results are shown in Table IV. For material not homogenized before extrusion, the extruded and extruded-drawn samples all failed in 14-21 days, because of excessive segregation lined up parallel to the rod axis. Annealing at 900°C for 24 hours subsequent to extrusion or drawing improves the corrosion life of material which was not pre-homogenized and does not produce any added improvement in corrosion life of material which did receive a pre-homogenization heat treatment. It can be concluded, therefore, that homogenization of billets, prior to extrusion, is effective in improving the corrosion life of bare extruded rods and that subsequent cold drawing of extruded rods is not, in itself, detrimental to corrosion life.

To determine the effect of homogenization on the thermal stability of extruded rods, samples from each condition were annealed at 500°C for 7 days subsequent to extrusion and tested in 650°F water. The unhomogenized sample completely disintegrated in one day while the homogenized material, though badly attacked, was still intact. The latter samples disintegrated in 1 to 7 days. When given a 900°C treatment for 24 hours prior to the 500°C one week treatment, samples from all conditions failed in 1 to 7 days. Therefore, it is concluded that there is an appreciable increase in thermal stability from the prior homogenization treatment.

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As a further evaluation of thermal stability, samples from each condition were annealed at 400°C for 5 weeks both with and without a 900°C anneal for 24 hours prior to the low temperature anneal. Without the prior gamma quench, the unhomogenized extrusions which were annealed at 400°C failed in 7 to 14 days. The corrosion life for the pre-homogenized, extruded and drawn material is 14 to 28 days while the pre-homogenized and extruded material has lasted 28 to 42 days. In agreement with the results from annealing at 500°C, considerable improvement in thermal stability through prior homogenization is evident. All of the samples annealed at 900°C before the 400°C anneal are still in test after 28 days with rates of -0.10 to -0.14 mg/cm²/hr. These low 28 day rates indicate that more complete homogenization was attained by the gamma quench subsequent to extrusion than was accomplished by the homogenization prior to extrusion.

In order to determine the effect of a low temperature recrystallization treatment, unclad samples from each condition were annealed at 600°C for one hour. The results, as seen in Table IV, reveal two significant observations. First, the samples which were not pre-homogenized have a corrosion life which is about half of the life for those which were pre-homogenized. This further displays the effectiveness of the prior homogenization. It is also note-worthy that the corrosion life for all samples annealed at 600°C is significantly less than the as-extruded or extruded-drawn condition with the exception of the prehomogenized-extruded condition where the life was identical for both conditions. The decrease in corrosion life of recrystallized extruded or extruded and drawn samples may be due to elimination of beneficial surface stresses which affect the morphology of hydride formation.(See Section I).

It was erroneously reported in WAPD-PMM-15 that the unclad extruded rod was homogenized prior to extrusion (condition D in Table IV). However, metallographic examination of this material has since disclosed excessive segregation and the material, therefore, was not prehomogenized. It is interesting to note that the corrosion life for the unhomogenized bare extrusion is identical to the life of the unhomogenized clad extrusion in both the as-extruded and 900°C annealed conditions. Thus, the presence of cladding during extrusion does not influence the corrosion properties of the core alloy itself.

Corrosion tests are being conducted on simulated fuel elements with 0.040 inch diameter defect holed through the cladding and the results to date are shown in Table V. Specimens from the extruded and extruded-drawn rods are still in test after 70 days while specimens (from the extruded rods) which were annealed at 400°C for 5 weeks subsequent to extrusion are still in test after 7 days. However, when defected specimens from the extruded rods were annealed at 500°C for one week, those specimens from the unhomogenized rods failed catastrophically in the first 7 day period while the specimens from the prehomogenized extrusion are still in test after 7 days. These data are in good agreement with the results of tests on unclad samples.

The remainder of the duplex melted ingots discussed in Section A on the effect of melting variables were again corrosion tested after fabrication to extruded rods to determine the effects of prior homogenization as well as extrusion temperature. Sections of some ingots were homogenized at 900 and 1000°C in a dynamic vacuum while others received no homogenization prior to extrusion. Extrusion temperatures used were 1600 and 1900°F. Since no two ingots were processed in the same way only general comparisons can be made. The results are listed in Table VI.

It appears, from Table VI, that homogenization prior to extrusion at 1600°F has no effect on corrosion rate and only a slight effect on extending corrosion life. On the other hand homogenization prior to extrusion at 1900°F appears to be detrimental to both corrosion rate and life. However, very severe pitting attack was observed in the homogenized samples extruded at 1900°F. This pitting has not been previously encountered and is attributed to some uncontrolled fabrication variable rather than to the material itself. The same material homogenized after extrusion does not exhibit this pitting attack. It should be emphasized that these ingots were initially induction melted in a variety of ways and impurity contents vary considerably from one melt to another. While this was seen to have no effect (with the exception of carbon) on corrosion properties of the cast ingots, their effects on extruded samples may have clouded the influence of homogenization and extrusion temperature on corrosion behavior.

It is interesting to note that the samples extruded at 1600°F without prior homogenization did not corrode rapidly. Apparently, this material was not as severely cored as other material given the same treatment (See Section B). In addition it is apparent that the two high carbon alloys derived considerable benefit from the prehomogenizing and post homogenizing treatment. The high carbon alloy represented the only non-homogenized extrusion which exhibited poor corrosion properties. These observations indicate that much of the variability observed in U-Mo alloys is associated with variability in the melting and casting practice which results in different degrees of coring and different impurity concentrations. While improvements in melting practice can be made, it appears advisable to employ a homogenizing treatment prior to extrusion to offset some of these variables which may be difficult to control during fabrication.

Additional data on the effect of heat treating at 400 and 500°C, with and without a prior gamma quench, will be obtained on these extrusions.

D. Effect of Homogenization on Corrosion Properties of Extruded U-12 Mo

The preliminary study of the effect of homogenization and cooling rate on the corrosion properties of extruded U-12 w/o Mo has been completed. The corrosion properties for the various heat treated conditions of U-12 w/o Mo extrusion No. Mo 2C1-16 are listed in Table VII. From these results and from metallographic studies of annealed samples and corrosion tested samples (as reported in WAPD-PMM-15) the following has been concluded.

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a. Effect of cooling rate

Those samples which were furnace cooled have slightly higher corrosion rates than the water quenched samples (Table VII) but the difference is not sufficient to affect corrosion life. For example, the samples annealed at 900°C for 24 hours and water quenched had a 28 day rate of -1.47 mg/cm²/hr while those furnace cooled from the same temperature had a 28 day rate of -2.16 mg/cm²/hr, yet all of these samples failed in 28-35 days.

In an additional experiment to determine the effect of cooling rate identical samples of a duplex melted and extruded U-12 Mo rod were annealed at 900°C for 24 hours in vacuum. One sample was allowed to cool by radiation while the other was quenched with a helium blast. The results are shown in Table VIII. It can be seen that the corrosion life, about 35 days, is the same for both samples and confirms the data in Table VII. The corrosion rate of the slow cooled sample is again higher than that of the quenched sample. It is postulated that the improved rate of the quenched samples, in both cases, may be due to compressive residual surface stresses which tend to decrease the size and improve the distribution of hydride platelets. This effect would disappear as the surface corrodes away exposing the essentially stress-free center.

As a result of both cooling rate experiments it is concluded that corrosion life is not appreciably affected by cooling rate but that a fast cooling rate is preferred for bare samples to reduce corrosion rate.

b. Effect of grain size

This subject was discussed in WAPD-PMM-15, page 8. No effect of grain size on corrosion rate was observed. However, the extent of hydriding is greater in the fine grained samples and the platelets are coarser. From this observation it appears that the fine grained material should be more susceptible to corrosion-crack propagation and therefore have a shorter corrosion life. However, the results are obscured by the presence of fine grained areas in the coarse grained samples and consequently this study should be repeated with uniform coarse grained samples.

c. Effect of temperature

It has been found that the corrosion resistance of U-12 w/o Mo is adversely affected by the presence of micro-coring and that a high temperature anneal (for example, 1000°C for 48 hours) is necessary to eliminate this coring from extruded material not previously homogenized. As seen in Table VII, the 1000°C annealing treatments have resulted in lower 28 day corrosion rates than the 900°C annealing treatments, with all samples failing, however, in 28 to 35 days. Thus, only improvement in corrosion rate resulted by a 100°C increase in homogenization temperature. An appreciable increase in corrosion life of the extruded rod is attained with either the 900°C-24 hr anneal or the 1000°C-48 hr anneal, while the

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700°C-24 hr anneal has shown no improvement. It is apparent that the time at the latter temperature was too short to permit complete homogenization.

From the above work it is apparent that a more detailed study is needed to establish the effects of annealing time and temperature on the completeness of homogenization and resultant corrosion properties of U-12 Mo. Accordingly, bare samples from both an extruded fuel billet and an extrusion clad and stripped rod have been annealed at 600, 700, 800, 900 and 1000°C for time periods varying from 30 minutes to three weeks. These samples are being examined using metallographic and X-ray diffraction techniques and corrosion tested in 650°F degassed water. Data so far obtained are insufficient for proper evaluation.

In addition to the above program the effect of annealing time on the corrosion properties of duplex melted and extruded samples of U-12 Mo were determined for annealing temperatures of 900, 1000 and 1100°C. Annealing was carried out in vacuum with the results shown in Table IX. Somewhat longer corrosion life and lower corrosion rates were realized for samples annealed at 1000°C over those annealed at 900°C. Also, it was found that annealing longer than 1/3 hour at either 900 or 1000°C improves the corrosion rate but does not appreciably affect the corrosion life.

The samples treated at 1100°C were inductively heated. Three minutes heating at this temperature resulted in a significant increase in corrosion life. However, the sample heated for one hour failed prematurely. In this test the temperature was rather uncertain. It is believed that the relatively short corrosion life of this sample was due to partial melting and alloying with the sample holder.

It is concluded from the data so far accumulated on effects of homogenization temperature and time that the higher the homogenization temperature the longer the corrosion life and the lower the corrosion rate, increasing the time of homogenization at either 900 or 1000°C results in appreciable reduction in corrosion rates, reflecting more complete elimination of microcoring. The fact that longer corrosion life does not result from longer homogenizing times indicates that other variables so far unexplained, play a part in hydride formation and distribution which is ultimately responsible for disintegration of the samples.

E. Effect of Annealing Atmosphere

Determination of the effects of annealing atmospheres (900°C for 24 hours) was reported in WAPD-PMM-15. This work was completed, the final results being listed in Table X. All new data agree with those previously reported in that new values for hydrogen content and hardness fall on the curves of Figures 8 and 9 included in WAPD-PMM-15. It is apparent from Table X that disintegration of the samples (with possibly the exception of the one annealed in vacuum) occurs when the hardness reaches a level of 400 to 430 DPH. It appears that discontinuous failure in the U-12 Mo alloy results when sufficient hydrogen is introduced to raise the hardness to this level, at which point the U-12 Mo matrix cannot withstand further stresses

induced by the hydride platelets. Annealing in hydrogen or helium resulted in the lowest corrosion rates and longest corrosion lives, possibly by influencing the distribution of hydride platelets. This reasoning is consistent with the observation that the total hydrogen concentration varies considerably for the different samples, but the hardness at failure remains approximately the same.

F. Effect of Fabrication Condition

Since induction melted and chill cast U-12 Mo ingots were found to be insensitive to homogenization treatments, an investigation was initiated to determine the effects of composition, heat treatment and corrosion test time in 650°F degassed water upon the corrosion rate, hydrogen content and hardness of these cast alloys. Alloys containing 10.7, 12, 14 and 15 w/o Mo were corrosion tested in both the as-cast and gamma quenched conditions (900°C for one week in vacuum followed by water quenching.). The results are summarized in Table XI. It can be seen that homogenization results in somewhat lower corrosion rates and considerably shorter corrosion lives. Comparison of the data with that included in Table X for the U-12 Mo alloy, indicates that the homogenized cast alloy has characteristics similar to the extruded and homogenized material.

Hydrogen concentration as a function of total corrosion is shown in Figure 5. This curve is similar to the one for duplex melted, extruded alloys (Figure 8 of WAPD-PMM-15) and indicates that about 22% of the hydrogen produced by corrosion is absorbed by the sample. For these alloys the amount of hydrogen present after a given corrosion time appears to increase with increasing Mo concentration on the as-cast alloys. The U-10.7 Mo alloy appears to absorb hydrogen at a slower rate in the as-cast condition than in the annealed condition. This sample is still in test after 35 days, at which time its hydrogen concentration is 506 ppm and its hardness is 460 DPH. The higher Mo alloys have considerably higher hydrogen concentrations at shorter time intervals and have disintegrated in 35 days or less. The higher hardness and lower hydrogen concentration of the U-10.7 Mo alloy may be associated with an aging effect which inhibits hydrogen absorption. Figure 6 illustrates the manner in which hardness varies with total corrosion for these alloys.

Microstructures which are typical of these alloys in the as-cast condition are shown in Figs. 7a and 7b, which represent the U-12 w/o Mo alloy as cast and after 7 days corrosion testing in 650°F water, respectively. The segregation is quite apparent in Fig. 7a and it should be noted in Fig. 7b that the hydride platelets are quite short and appear to be concentrated at the grain boundaries. The presence of inclusions at the grain boundaries possibly accounts for nucleation of the hydride phase. Although this type of hydride formation is similar to that observed for as extruded material it should be noted that the corrosion life of this alloy is 28-35 days while the as-extruded material fails in 14-21 days. As previously reported, coring in the extruded material results in a stringered structure which is more susceptible to corrosion attack.

Structures typical of the annealed materials are shown in Figs. 8a and 8b which are the U-12 w/o Mo alloy as homogenized and homogenized and corrosion tested one week in 650°F water, respectively. Fig. 8a indicates that the homogenization treatment has removed all microscopically observable traces of segregation and produced a more uniform distribution of inclusion. Fig. 8b shows that the hydride structures produced during corrosion testing have a more general distribution and are similar to those observed in extruded and homogenized alloys. As indicated in Table XI however, the corrosion life of this annealed, cast alloy is relatively short (14-21 days) as compared to 21-28 days minimum for the extruded and homogenized U-12 w/o Mo alloys. The reason for this apparent discrepancy is not clear.

The corrosion behavior of several extrusions of duplex melted U-12 Mo alloys in the as-extruded, extruded plus gamma quenched, as-cold drawn, and drawn plus gamma quenched conditions are being investigated. Table XII summarizes the data to date. It is seen that although the corrosion rates vary considerably for as-extruded samples, the corrosion lives are fairly consistent. The same is true for as-cold drawn samples. The variation seems to be limited to one testing period, which is probably nothing more than the statistical variation present in any material. Gamma quenched samples show some differences in their rates but the samples that have failed have done so in the same testing period. As expected, the extruded and gamma quenched samples have longer corrosion life and lower corrosion rates than the extruded samples. All samples will be tested to failure.

Quite a few U-10.5 Mo extrusions are being studied in a manner similar to the U-12 Mo extrusions and these results are also included in Table XII. The alloys are the same core materials used for the study of the effect of various barrier layers on the corrosion of simulated defective fuel elements (See Section III). It is a little early to draw many conclusions regarding these materials, but all of the as-extruded samples failed in about the same time which was something less than 21 days. As-drawn samples of Mo3a2-8 exhibited early failures but other than that the as-drawn samples behaved quite similarly to the as-extruded samples. Additional testing time on the gamma quenched samples is necessary before any conclusions concerning them can be made.

It is interesting to note that there is no clear cut indication that cold drawing deleteriously affects either the 10.5 or 12 Mo alloys. As many instances can be found where cold drawing slightly improves the fuel as can be found where it harms it.

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

An X-ray study has been completed on the problem of micro-segregation in cast uranium 12 w/o Mo alloys. A Fourier transform method was used to obtain the broadening function by which the broadened line is obtained from the fully annealed line. It is assumed that this broadening function is determined by the distribution of d values due to the micro-

segregation.

Time in Hrs at 900°C	Width at Half Maximum of Concentration Distribution Function		Corrosion Rate After 7 days in 650°F degassed Water mg/cm ² /hr
	a/o	w/o at 12w/o	
0	10.7	5.1	.14
1	5.8	2.7	.11
2	3.4	1.6	.10
4	2.3	1.1	.10
6	2.1	1.0	.09
8	2.1	1.0	.09

In the early stages of homogenization the line broadening technique is satisfactory for giving a quantitative measure of degree of homogeneity. During the final stages of homogenization where the change in X-ray line breadth is small this technique breaks down due to the finite number of harmonics used in the Fourier analysis of the peaks.

H. Effect of Low Temperature Annealing of U-12 w/o Mo Alloys

Past experience has shown that annealing at 400°C for periods of 3 to 5 weeks, subsequent to the gamma quench homogenization, greatly improves the corrosion rate and corrosion life of U-12 Mo alloys. The mechanism of this improvement is now being investigated.

Samples from an unclad extrusion (MM 431-13) of U-12 Mo are being corrosion tested in various conditions of heat treatment as shown in Table XIII.

Unlike the majority of U-Mo extrusions, this material in the extruded condition is only slightly segregated. As a result, the as-extruded corrosion life is as good as the gamma quenched condition and likewise, the 35 day corrosion rate is only slightly greater as-extruded than for the gamma quenched condition. The 343°C anneal has had little effect upon the corrosion rate and corrosion life. The 400°C anneal, however, has reduced the 35 day rate to approximately 1/10 of the rate for the gamma quenched condition. No failures have yet occurred in 42 days of testing for these samples. It is important to note that when the 400°C anneal is not preceded by a gamma homogenizing treatment, the corrosion resistance is relatively unaffected.

As seen in Fig. 9, examination of corrosion tested samples has revealed that the formation of hydride platelets during corrosion is markedly different for the samples which were gamma quenched and annealed at 400°C. The platelets in these samples are very short and thin and are approximately 1/10 of the length of the average needle in gamma quenched samples. These fine platelets are more numerous than those found in other samples but the over-all hydride content is much less for the samples annealed at 400°C.

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It is apparent, therefore, that the improved corrosion resistance is related to the slow rate of growth and small maximum size of the hydride platelets formed in samples annealed at 400°C. As seen in Table XIII, the hardness of this material is greatly increased by the 400°C anneal. This hardening may be due to coherent precipitation of transformation products or to precipitation of impurities acting as a hardening constituent. The lattice is thus strained and resists the growth of the hydride platelets during subsequent corrosion testing. As a result, a limited amount of hydride is formed. Since the hydride itself has poor corrosion resistance and accelerates the rate of corrosion, the samples with the fine needles are more corrosion resistant. The fact that the same hardness increase is obtained, with or without the prior gamma quench, and that only the gamma quenched and annealed samples display the low corrosion rate, indicates that a more general dispersion of hardening precipitate is obtained for the latter treatment and is responsible for the fine evenly distributed hydride needles. Additional annealing times at 400°C will be investigated.

I. Effect of Internal Stress

As previously reported in WAPD-FMM-15 the effects of residual macroscopic stress on the corrosion behavior of U-12 Mo is being investigated. Two extruded rod samples of Zircaloy-2 clad and one bare sample were stressed, making use of a bending jig, to approximately 95,000 psi. The clad samples were defected with 0.040" diameter holes on the tension and compression sides. These samples, along with two clad and defected, but unstressed, samples were inserted in 650°F degassed water. All clad samples have completed 42 days of corrosion testing without failure. The bent bare sample was removed from the bending jig after 5 days of corrosion test time and found to have relaxed considerably. On restressing the rod broke, at the point of maximum deflection, with a brittle failure. Metallographic inspection of the fracture, Figure 10, revealed a dense network of hydride needles on the compression side. On the tension side the hydride needles are long, thin and more randomly dispersed. It is apparent, therefore, that the state of stress has considerable influence in the density and form of the hydride needles. It is planned to check the amount of relaxation to be expected at 650°F before testing additional bare samples.

It should be pointed out at this point that previously reported results of cathodically hydrided specimens which were similarly stressed in bending indicated that the hydride needles appeared first on the tension side and later on the compression side of the specimen. In addition, the needles were perpendicular to the tension direction (penetrated the specimen to more than half diameter) and parallel to the compression stress. The results reported above do not confirm the previous information possibly because of differences in test temperature. The cathodic hydriding treatment was run at 100°C while corrosion tests were run at 343°C. Whether or not cathodic hydriding fails to simulate corrosion data on stressed samples will be checked as more data is obtained.

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II. Mechanism of Corrosion Attack

A. Effect of Water Additions on Corrosion of U-Mo

All of the samples of the duplex melted, hot extruded (unclad), U-12 w/o Mo alloy tested in 650°F degassed water with additions of (1) 50 ppm of nickel sulfate, (2) 50 ppm of platinum as chloroplatinic acid, and (3) 12 ppm of platinum as colloidal platinum have now failed. The corrosion, hardness, and hydrogen analysis data are illustrated for the four conditions in Table XIV. Also included in this table are the data from reruns of the same alloy tested in degassed water containing 50 ppm of Ni and Pt. The data summarized in Table XIV is shown graphically in Fig. 11, 12 and 13 which plot the weight loss, hydrogen pickup, and hardness increase, respectively, as a function of time. The rerun in the nickel sulphate was performed in an identical manner with the original test but the rerun in chloroplatinic acid was slightly different than the original test. The first 35 days of the initial test was performed in a solution of chloroplatinic acid containing about 1% of lead acetate and the solution was never changed. After 35 days fresh solution consisting entirely of chloroplatinic acid was used for each test period. The rerun was conducted using chloroplatinic acid without lead acetate.

From the first test, the nickel sulphate addition apparently prolongs the life of U-12 Mo by about a factor of two. The results of the rerun indicate that this may be a little optimistic and that life is improved by only 50-75%, increasing the life from less than 40 days in degassed water to more than 60 days in water containing 50 ppm of Ni. From Table XIV, Fig. 11 and 12, it is readily seen that the rate of hydrogen pickup is much less, for the equivalent corrosion, for samples tested in nickel sulphate solution than for samples tested in degassed water. In view of this it is proposed that the increased life is due to the decreased rate of hydrogen pickup which is presumably due to the nickel acting as a hydrogen depolarizer. This action is one of increasing the rate of combination of atomic hydrogen formed during corrosion to molecular hydrogen. (It has previously been demonstrated that molecular hydrogen in the water has little effect on the corrosion properties of U-Mo alloys.) It is interesting to note that the hardness values attained are as high as those reached for specimens tested in degassed water despite the somewhat higher hydrogen concentration of the latter. It is felt that the introduction of hydrogen increases hardness, thus stressing the lattice, until a hardness of slightly more than 400 DPH is reached. At this point the metal is unable to withstand further stress and cracking occurs. This reasoning appears to be in line with the findings previously discussed in Section E.

Oxide fingers (Fig. 14) have been observed to exist in samples prior to cracking but their contribution to hardening or cracking has not been adequately established. Many cracks that have been observed appear to initiate at these oxide fingers but the probability of catching a crack at the proper stage is rather small and hence makes the morphology of cracking difficult to determine.

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Additional data on the effect of pure chloroplatinic acid indicate that this acid contributes little to extending the life of U-12 Mo but that a small amount of lead acetate added to the solution results in longer test lives of samples. This is based solely on the fact that samples tested for 35 days in chloroplatinic acid solution containing lead acetate lasted longer than samples tested for their entire life in pure chloroplatinic acid solution. The hydrogen pickup and hardness increase closely parallel one another in the initial test periods but after 28 days the sample tested in pure chloroplatinic acid shows more hydrogen. Additional testing will be done with lead acetate. The hydrogen contents of samples tested in water containing pure chloroplatinic acid are much lower than that of samples tested in degassed water even though the corrosion life is about the same. Samples that contain only about 150 ppm of H_2 crack severely. This compares with over 600 ppm H_2 in cracked samples tested in degassed water.

It is concluded, therefore, that water additions of both nickel sulphate and chloroplatinic acid greatly reduce the percentage of the hydrogen produced during corrosion that is absorbed by the samples. In the case of the nickel sulphate addition the life of the samples is prolonged but in the case of the pure chloroplatinic acid addition little benefit in specimen life is realized. Some question exists concerning the effect of adding small amounts of lead acetate to the chloroplatinic acid solution.

B. Hydrogen Overvoltage Studies

Cathodic polarization curves have been obtained for uranium and several uranium alloys. All values were obtained at 25°C using stirred solutions saturated with hydrogen. All samples were allowed to equilibrate under open circuit conditions overnight. For each curve successive readings were taken at 20 minute intervals as it was found that for most values of current density no appreciable change in potential occurred after 15 minutes. All values were corrected for the IR drop through the solution but no correction has been applied for concentration polarization effects.

The values obtained for unalloyed uranium are shown in Fig. 15. A neutral phosphate solution was used for which the reversible hydrogen potential is 0.66 volts. The hydrogen overvoltage W is given by the following expression:

$$W = 0.94 - 0.28 \log C.D.$$

where C.D. is the current density in milliamps/cm² and W is in volts. The lower potentials obtained for the decreasing current density curve are presumably due to the occurrence of surface hydriding at the higher current densities.

Fig. 16 indicates the values obtained for a U-12 w/o Mo alloy vacuum induction melted and subsequently annealed for 24 hours at 900°C and water quenched. These curves were obtained for increasing current density only and indicate the effect of electrolytes with various pH values. Al-

though the shapes of the curves vary considerably the following expression for overvoltage applies to all.

$$W = 0.50 \pm 0.11 \log C.D.$$

It is believed that the inflection which occurs at a current density of about 3×10^{-6} amps/cm² is related to the absorption of atomic hydrogen by this material.

Also shown in Fig. 16 is the curve obtained for this U-12 w/o Mo alloy after the surface had been hydrided cathodically for 40 hours at 100°C in a buffered phosphate solution. The hydrogen overvoltage obtained was:

$$W = 0.64 \pm 0.09 \log C.D.$$

It should be noted that the inflection in this curve occurs at about the same current density as the smaller inflection observed for the unhydrided samples.

Polarization curves obtained for a U-12 w/o Mo alloy prepared by induction melting and chill casting are shown in Fig. 17. A neutral phosphate electrolyte was used. The hydrogen overvoltage for this material is given by the equation:

$$W = 0.61 \pm 0.13 \log C.D.$$

The relatively small amount of hysteresis presumably indicates that appreciable surface hydriding does not occur. It can be seen that this curve is similar to the appropriate curve of Fig. 16 except that the potentials are displaced upward. It has been observed that the corrosion life of this material is approximately twice that of the induction vacuum melted material.

Fig. 18 shows the results obtained using a neutral phosphate solution for a U-15 w/o Mo-4.8 Pt alloy and a chill cast U-10 w/o Nb alloy. The curve obtained for the U-Mo-Pt alloy is similar to the curve for unalloyed uranium except for much lower potentials and the relatively slight hysteresis of the alloy curve. This is in agreement with the observation that hydriding of both of these materials is primarily a surface effect. The hydrogen overvoltage for the U-15 w/o-4.8 Pt alloy is given by the following equation:

$$W = 0.48 \pm 0.30 \log C.D.$$

The curve for the U-10 w/o Nb alloy shows an inflection at about 10^{-7} amps/cm² for increasing current but no inflection when the current is decreasing. This presumably indicates that hydriding occurs both internally and at the surface. The overvoltage is given by:

$$W = 0.62 \pm 0.16 \log C.D.$$

A platinized U-12 w/o Mo sample was prepared by electrolytically depositing platinum on the surface of the vacuum induction melted U-12 w/o Mo alloy described above. The platinum was in the form of a thin black fairly adherent film. Fig. 19 indicates the values obtained using a buffered phosphate electrolyte. The reasons for the unusual shape of the curve are not known at this time although it is believed that the inflection at 10^{-4} amps/cm² is related to the porosity of the platinum layer. The hydrogen overvoltage is given by the following equation:

$$W = 0.01 / 0.12 \log C.D.$$

This low value is in agreement with the published data for platinized surfaces.

Thus far no obvious relationship has been found between hydrogen overvoltage values and corrosion life or corrosion rate for the alloys examined.

C. Role of Zircaloy-2 in the Corrosion Mechanism

In order to determine if the Zircaloy-2 cladding improves corrosion life of defected clad U-12 w/o Mo extrusions, a program has been initiated to determine the corrosion behavior of rods clad with an element which is not a hydrogen getter. For this purpose samples of U-12 Mo were melted in Mo crucibles to ensure good bonding. These will be extruded in the normal fashion, defected and corrosion tested in 650°F degassed water.

To obtain much needed information on the role of core-clad interdiffusion layers on corrosion properties, several samples of extrusion-clad U-10 Nb and U-12 Mo were heated at 900°C for time intervals varying from 1 day to 13 days. Longitudinal sections from these samples were polished metallographically and the diffusion layer thicknesses and location with respect to cladding and core alloy are being measured. An X-ray identification of the diffusion layers will be made. Samples will then be corrosion tested in 650°F degassed water to establish which diffusion layers are subject to accelerated attack.

III. Alloy Development

A. Uranium Molybdenum Phase Diagram

An investigation has been completed to determine the location of the $\alpha/\epsilon/\epsilon'$ phase boundary. Previous work with samples annealed for five weeks indicated that the boundary shifted toward lower molybdenum concentrations at higher temperatures, i.e. the ϵ field widened at higher temperatures as shown by the dotted line in Fig. 20. Several series of samples were given long duplex anneals of at least 90 days. The results of these experiments showed that ϵ field did not widen and in fact was much narrower than previously believed. The new $\alpha/\epsilon/\epsilon'$ boundary occurs at 31.2 ± 0.3 a/o Mo.

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The alpha plus epsilon phase field can be divided into two regions, the dotted line in Fig. 20 shows the approximate line of demarcation. In the low molybdenum region the rate of precipitation of the alpha phase exceeds the rate of ordering of the gamma phase to epsilon. The alpha first forms by the diffusion of molybdenum atoms out of a given region, the regions which are now enriched in molybdenum are now more easily ordered into the epsilon phase. In the high molybdenum region the rate of ordering exceeds the rate of alpha precipitation. Thus, samples of high Mo content annealed at 550°C would order during the initial stages of transformation to an epsilon of a given composition. At this temperature where T/T_c is very nearly one the order parameter, S , will be considerably less than one and it will be impossible to obtain perfect order. Thus a pure epsilon phase having the correct stoichiometric ratio will be difficult to form and it will be equally as difficult for the uranium atoms to agglomerate and precipitate as alpha. After long anneals of about 100 days at 550°C the sharp twin bands in the epsilon phase lose their original sharpness and the alpha begins to appear as a fine intragranular precipitate.

B. Bare Alloys

1. U-Mo-Pt Ternary Alloys

Additional data for samples cut from arc melted buttons of U-Mo-Pt ternary alloys are included in Table XV along with previously reported information concerning these alloys. Corrosion data for one additional heat treatment are now available, that is, 900°C/24 hr/W.Q. / 400°C/35 days/W.Q. It would appear from this data that the platinum addition is actually detrimental to the U-12 Mo for this one particular heat treatment. This is inconsistent with the effects of platinum additions when annealing at 500°C. Here, it will be remembered, considerable benefit was derived from the platinum both in respect to rate and failure time. Samples from the U-12 Mo-0.6 Pt alloy that were γ Q and then annealed at 500°C for 7 days failed in test in about 84 days whereas samples from the U-12 Mo alloy fabricated, annealed and tested at the same time failed in about 7 days.

This data on the 400°C annealing is also inconsistent with data on alloys previously tested and on the other alloys currently being tested. A sample of an arc melted button of U-12 Mo-0.5 Pt, tested some time ago, that was γ Q and annealed at 400°C for 5 weeks, stood up in 650°F water for 84 days, after which it cracked severely. This was about the same as or slightly longer than the corrosion life of the gamma quenched sample. Table XVI summarizes the data for samples of U-8 Mo-1 Pt and U-12 Mo-0.5 Pt which are currently being examined in various heat treated conditions. Both of these alloys were duplex melted and co-extruded at 1600°F. The testing times are not yet long enough to be of much significance, but samples of U-12 Mo-0.5 Pt that were γ Q and annealed at 400°C for 35 days still look good after 14 days testing time. While this is not particularly outstanding, it is significantly longer than the 1-7 day life reported in Table XV for samples of similar composition and heat treatment.

In view of other data, therefore, the poor corrosion lives of the samples annealed at 400°C reported in Table XV seem out of line. It is felt that additions of platinum do improve the corrosion properties of as-cast and annealed U-Mo alloys.

2. U-Nb Binary Alloys

Table XVII summarizes the present status of the corrosion data for U-8, 10 and 12 Nb alloys tested in various conditions. The extruded, extruded plus gamma quenched, and extruded plus gamma quenched plus annealed at 400 and 500°C samples are corroding about as expected from previous information. Annealing for as little as 7 days at 400°C or 2 days at 500°C is sufficient to completely destroy the corrosion resistance of both 8 and 10 w/o Nb alloys when tested in the bare form. The metallographic examination of samples annealed at 400°C revealed that after 7 days an alpha rich precipitate was present at the grain boundaries which grew rapidly with continued annealing. After 2 days annealing at 500°C no grain boundary precipitate was visible but the matrix had transformed to a structure resembling the distorted alpha phase. After 7 days at 500°C this acicular matrix disappeared and was replaced by a transformation structure that closely resembled the 400°C heavy grain boundary precipitation of alpha and niobium solid solution. Figures 21 and 22 show typical structures of these alloys.

The X-ray data essentially confirm the metallographic observations with the exception of the samples annealed for 2 days at 500°C. The structure was not clear cut "distorted alpha" as might be expected from the metallography, but was instead broad gamma with some indication of alpha being present.

The hardness increases to about 550 DPH units after a 7 day anneal at 400°C but decreases steadily thereafter and after 35 days annealing time the hardness is about 450 DPH units. The hardening was not quite as pronounced when annealing at 500°C but here too the hardness reached a peak value, about 420 DPH units in 2 days, and decreased with additional annealing.

The poor corrosion behavior of the cold drawn samples is not too well understood but there are X-ray and metallographic indications that some alpha phase is present in these samples. Fig. 23 shows the metallographic appearance of a remnant of a cold drawn sample corrosion tested for one day in 650°F degassed water, containing patches of a dark etching constituent that could be either alpha or hydride. Since the sample analyzed over 200 ppm of H₂, however, it is believed that the grey areas in Fig. 23 are hydride which formed in regions of previously high alpha content.

Gamma quenching cold drawn samples does not restore the corrosion resistance observed when gamma quenching extruded samples. The sample size was considerably less for homogenized cold drawn samples than for homogenized extruded samples but it is not felt that this is the major factor contributing to the inferior corrosion properties of cold drawn material.

3. U-Nb-Pt Ternary Alloys

One ternary alloy, U-10 Nb-1 Pt, is being studied with respect to its corrosion resistance after extruding, drawing, gamma quenching, and gamma quenching and annealing at 400 and 500°C. Table XVIII summarizes the present status of this study. It is seen that platinum affords some improvement in the corrosion resistance for practically all conditions except the cold drawn. Here, as in the binary alloys, samples failed during the first day of corrosion testing. It is important to note, however, that gamma quenched cold drawn samples of U-Nb-Pt behave similarly to gamma quenched extruded samples.

The metallography is not yet completed, but annealing at 400°C for 21 days does not produce the heavy grain boundary precipitate that was observed in the binary alloys. There appears to be a very fine precipitate within the grains that causes the matrix to stain during preparation but it is not well resolved. Annealing at 500°C for two days causes straight line striations to appear in the grains but no cross-hatching as was observed for U-Nb binary samples receiving the same annealing treatment. Continued annealing at 500°C causes an alpha rich precipitation at the grain boundaries that closely resembles that seen in the binary alloys, but after 7 days at 500°C, this precipitate has by no means absorbed the entire matrix. There is little doubt but that this ternary alloy shows less metallographic evidence of transformation than the corresponding U-Nb alloy for identical heat treatments. The X-ray spectrometer tracings are ill defined and show no big differences over the tracings for the binary alloys.

The hardness increases to about 600 DPH units after a 7 day anneal at 400°C and continues to harden with additional annealing. After 35 days the hardness is about 630 DPH units.

C. Vacuum Melting in Urania Crucible

The corrosion characteristics in 650°F water of the "high purity" U-12 w/o Mo alloy described in WAPD-PMM-15 have been determined. The results are shown in Table XIX. There is no readily apparent reason for the extremely short corrosion life of this alloy. It would appear the removal of impurities is detrimental to corrosion life. Possibly, lack of impurity nucleation centers results in formation of large hydride platelets rather than numerous very fine platelets observed in impure samples annealed at 400°C. This possibility deserves more attention. It is planned to zone refine some uranium to obtain as pure a product as possible. This can then be alloyed with pure Mo in uranium crucibles under vacuum and by arc melting in water-cooled copper crucibles. A detailed study and comparison of aging effects, thermal stability and corrosion behavior can then be made with alloys of conventional purity.

D. Corrosion Life of Extruded and Cold Drawn Clad Alloys

Routine corrosion testing of extruded rod elements, end-plugged and defected as described in WAPD-PMM-15 is being continued. The

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data obtained to date are summarized in Table XX. In the case of binary U-Nb alloys it is apparent that no adverse effect occurs due to annealing of the clad rods at 900°C. However, a 5 week anneal at 400°C, after homogenization at 900°C, resulted in failure of one of the U-8 Nb samples in 14-28 days. This is to be compared with over 70 day life of as-extruded and homogenized samples. Cold drawn samples, in general show early failures. Homogenizing after cold drawing seems to improve corrosion resistance of as-drawn material but the adverse effects of cold drawing are not completely eliminated. Short time results on material that was cold drawn, homogenized and annealed at 400°C for 5 weeks appear erratic, but relatively early failures are probable. From the data so far accumulated it may be concluded that the binary U-Nb alloys display best corrosion resistance in the extruded or gamma quenched conditions. Cold drawing and aging (conditions which result in partial transformation of the gamma phase) are detrimental to corrosion resistance. It is too early to make conclusions regarding the effect of Nb concentration in these samples.

One of the U-10 Nb fuel element samples which had been cold drawn, homogenized at 900°C for 24 hours and annealed at 400°C for 5 weeks was removed from corrosion test after 28 days (before it had failed). This sample is not included in the Table. It merits special attention because metallographic examination through the defect clearly indicates the progress of corrosion. Fig. 24A indicates that the Zircaloy cladding was partially transformed from alpha to beta during the high temperature treatment. Below the cladding are at least three core-clad interdiffusion layers which apparently corrode at different rates. The thick layer, adjacent to the Zircaloy has a Widmanstätten structure. This layer which is probably high in Zr and low in U and Nb corrodes faster than the layers below it and faster than the core alloy. Next to this layer is what appears to be a brittle layer with a columnar grain structure. Below it is another layer adjacent to the core alloy. It appears to have excellent corrosion resistance since the corroding section has a diameter at least as small as that of the partially transformed Zircaloy cladding. While the compositions of each layer are not now known, it is probable that the corrosion resistant layer is a ternary alloy of U-Nb-Zr with a Nb content somewhat below 10 w/o and a relatively low Zr content. More work is planned in an effort to determine the composition of this alloy layer and investigate its properties separately. Fig. 24b and c, at higher magnification show details of structure in the various layers and the lack of transformation in the corrosion resistant layer. The core itself has an X-ray determined structure consisting mostly of alpha with some gamma. It might be concluded from this that a U-Nb-Zr alloy, containing less than 10 w/o Nb and a small amount of Zr, may be found to have excellent thermal stability and corrosion resistance.

The presence of a niobium barrier between cladding and core of U-10 Nb does not appreciably affect corrosion properties as one might expect. The addition of 1% Pt to the U-10 Nb appears to have increased the corrosion life of cold drawn rods somewhat. The extent of the increase, however, will not be known until corrosion test time is lengthened.

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U-12 Mo-0.5 Pt alloy shows superior corrosion resistance in all heat-treated conditions over the U-8 Mo-1 Pt alloy. However, both alloys fail early in the cold drawn condition. Homogenization after cold drawing improves corrosion life, no failures being recorded in the U-12 Mo-0.5 Pt alloy after 42 days for the cold drawn and homogenized samples and after 14 days for the cold drawn, homogenized and low temperature annealed samples.

The effect of Pd, Pt, Nb, Mo, 15 Mo-5 Pt and U-10 Nb as barrier layers between the Zircaloy-2 cladding and U-10.5 Mo alloy core were investigated. The results so far obtained are also listed in Table XX. The bonding to the core alloy was not satisfactory with Pd and Pt barriers and early failures resulted. Nb and Mo appear promising as barrier layers, permitting 900°C homogenization treatments for 24 hours without creating a poor corrosion resistant diffusion zone. However, additional corrosion test time is needed before proper evaluation can be made.

E. Effect of Heat Treatment on Corrosion of Cold Drawn U-12 Mo Clad Extrusions

Because of practical considerations it would be desirable to cold draw after extruding clad fuel elements. Cold drawing has been shown to be deleterious to clad U-12 Mo extrusions. For this reason a more detailed study was initiated to determine the possibility of eliminating the bad effects of cold drawing by a subsequent heat treating operation. Two induction melted and cast ingots of U-12 Mo were homogenized at 900°C for 48 hours prior to coextrusion with Zircaloy-2 cladding. The extruded rods were then cold drawn 31 and 53% reduction in area. Clad (bare end), bare and completely clad samples, the latter defected by drilling 0.040" diameter holes through the cladding, are being corrosion tested in 660°F de-gassed water in various conditions of heat treatment. The samples were heated for 10 minutes and 0.5, 1, 4, 8 and 24 hours at 600 and 700°C to effect stress relief and recrystallization. Other samples were heat treated for 10 minutes, $\frac{1}{2}$, 1 and 24 hours at 900°C.

Data so far obtained on bare samples are listed in Table XXI. The corrosion rates of the bare samples heat treated at 600 and 700°C show no improvement over the as-drawn samples. The 900°C anneal was beneficial in all cases. A plot of total corrosion versus test time for the latter is shown in Fig. 25 and illustrates increasing corrosion resistance with increasing homogeneity.

Cracking of bare samples annealed at 600 and 700°C was attributed to the presence of pipe and porosity in the center of each rod as revealed by micro-examination of cross sections and longitudinal sections of several samples. Oxide stringers were found to follow the porosity. The cylindrical surfaces of the samples, on the other hand, were bright and metallic after 14 days corrosion test time. Lack of similar failures in the 900°C annealed samples was probably due to improved corrosion resistance realized by the high temperature anneal. Bare end specimens, annealed at 900°C for 24 hours failed within 7 days by severe bond attack. No bond attack

was associated with shorter annealing times at this temperature and all times at lower temperatures. These specimens, however, all cracked in short time intervals because of internal porosity.

Early results of the tests on defected clad fuel elements are listed in Table XXII. The as-cold drawn fuel elements, those annealed 8 and 24 hours at 700°C and those annealed 24 hours at 900°C failed in less than 14 days. The latter samples apparently failed early because of severe bond attack. The remaining specimens are still in test.

Because of the porosity present in the induction melted and cast material, it is planned to repeat the above tests using duplex melted, extruded and cold drawn material. Despite the poor quality of specimens so far tested, however, it appears that there is a good possibility of using a short time high temperature heat treatment which will eliminate the bad effects of cold drawing on corrosion life without causing serious core-clad interdiffusion.

F. Effect of Defect Size on Corrosion Properties of Clad U-12 Mo

A program was initiated to study the effect of defect size on the corrosion properties of U-12 Mo extruded clad rods. Defect diameters of 0.003, 0.013, 0.020, 0.040 and 0.080" were drilled through the cladding. No failures have occurred in 42 days of test time in 650°F degassed water. This study is designed to reveal whether increasing the area of exposed alloy within relatively narrow limits is directly related to corrosion life. This study, together with that indicated in Section II C, should indicate the importance of a hydrogen getter or non-getter as a cladding material.

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)

It was previously reported (WAPD-PMM-15) that three of the five control samples of U-10.5 w/o Mo had failed when tested in 650°F water. Two failed in 33-45 days and the third in 145-158 days. The remaining two samples were continued in test and now have accumulated 228 days of testing time without failure. It was previously reported that of the eight samples irradiated to a maximum exposure of 2800 MWD/T four failed in less than 45 days, these failures being attributed to bad end closure welds. The remaining four irradiated samples failed in 45-58 days, indicating that irradiation was responsible for decreased corrosion life. The remaining two control samples will be continued in test to obtain complete data.

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 contain-

ing 5 w/o uranium-235 has continued. These specimens had been heat treated at 750°C for $\frac{1}{2}$ hour prior to irradiation and irradiated in MTR process water to estimated burnups ranging from 6500 to 17,300 MWD/T. The additional results of the corrosion tests in 650°F static water are summarized in Table XXIII.

As previously mentioned in WAPD-PMM-15 two additional groups of control specimens were prepared to determine if the observed decrease in corrosion life was a result of irradiation damage or damage caused by core-clad interdiffusion resulting from heat treatment. Two groups of control specimens are being tested; one group of eight specimens in the same autoclave as the irradiated specimens and a second group of sixteen specimens in a separate autoclave. Half of each group are in the as-extruded condition and half as heat treated at 750°C for $\frac{1}{2}$ hour. The control specimens being corrosion tested in the same autoclave as the irradiated specimens have undergone 21 days test without failure. Of the specimens being tested in a separate autoclave, the two U-9 w/o Mo samples which were heat treated failed in the 14-28 day test period. All others are continuing in test after 28 days of corrosion testing. While it may be too early to draw definite conclusions, the results so far indicate that irradiation or irradiation plus heat treatment rather than the heat treatment alone was responsible for the early failures.

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

Twenty defected specimens of U-12 w/o Mo and three defected specimens of U-10.5 w/o Mo, irradiated in MTR process water to maximum exposures of 1200 MWD/T, have been corrosion tested in 650°F static water. Also tested in the same autoclave were eight control specimens of U-12 w/o Mo and one control specimen of U-10.5 w/o Mo. All specimens have failed in less than 22 days of test, with the exception of four irradiated U-12 w/o Mo specimens. The estimated exposures of the four remaining specimens encompass the entire range of exposures for this experiment. Failure of control specimens occurred as early as the 0-7 day test period. No correlation of corrosion life and exposure is evident. It is believed that the relatively poor corrosion behavior of this group of specimens is due to poor cladding, which was caused by the overheating of the extrusion billets in the salt bath prior to extrusion. For this reason no further work is contemplated on this experiment.

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

The second train of samples of as-extruded Zircaloy-2 clad U-10.5 w/o Mo and U-12 w/o Mo alloys, enriched to 3.6 w/o uranium-235, which were irradiated in MTR process water to an estimated maximum exposure of 6500 MWD/T were received at WAPD (MTR-WAPD 11-Met 9). These samples will be defected by drilling a 0.040 inch hole in the cladding and corrosion tested to failure in 650 F water along with the first train of similar samples exposed to an estimated maximum exposure of 3600 MWD/T (MTR-WAPD 11-Met 8).

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5. MTR Irradiation of Clad U-Mo Alloy Samples (MTR-WAPD 11-Met 10, MTR-WAPD 11-Met 13, MTR-WAPD 11-Met 14, MTR-WAPD 11-Met 15)

A series of four experiments of Zircaloy-2 clad U-9 w/o Mo, U-10.5 w/o Mo, U-12 w/o Mo, and U-13.5 w/o Mo alloy samples in the as-extruded condition has been initiated. The first experiment consists of 24 natural U-Mo specimens, which have been irradiated six weeks in MTR process water to an estimated maximum exposure of 2800 MWD/T. The other three experiments consist of 24 specimens each of 5 w/o enriched U-Mo alloys, which are to be irradiated in MTR process water 12 weeks, 24 weeks, and 51 weeks to estimated maximum exposures of 7,000, 14,000 and 24,000 MWD/T respectively. After irradiation, the specimens will be defected and corrosion tested to failure in 650°F static water.

6. MTR Irradiation of Clad U-Mo Alloy Samples (MTR-WAPD 11-Met 12)

Four specimens each of Zircaloy-2 clad 5 w/o enriched U-9 w/o Mo and U-10.5 w/o Mo, transformed to alpha plus epsilon, have been irradiated in MTR process water for three weeks to an estimated maximum exposure of 2000 MWD/T. Specimens will be measured for any dimensional and structural changes due to irradiation.

7. MTR Irradiation of Clad U-Mo Alloy Samples (MTR-WAPD 11-Met 16)

Seven specimens of Zircaloy-2 clad 3.6 w/o enriched U-12 w/o Mo, in the as-extruded condition, were charged March 28 into MTR process water for nine weeks irradiation to an estimated maximum exposure of 5000 MWD/T. These specimens were fabricated from the same extrusions and in the same manner as the specimens for the Chalk River CR-WAPD-Met 6 Loop Test. After irradiation, the specimens will be defected and corrosion tested to failure in 650°F static water.

8. MTR Irradiation of Unclad U-Mo Alloys (MTR-WAPD 12-Met 1)

Three samples of U-10.5 w/o Mo and three samples of U-12 w/o Mo, which were irradiated to a maximum exposure of 1700 MWD/T, have been corrosion tested in 650°F (343°C) water at saturation pressure for a total of 28 days. The time to failure for both these sample groups and the unirradiated control samples are shown in Table XXIV. One U-12 w/o Mo sample failed in 20-22 days, and one U-12 w/o Mo sample and two U-10.5 w/o Mo samples failed in 22-28 days. Of the two remaining samples, the U-12 w/o Mo sample is a high exposure sample (1580 MWD/T) while the U-10.5 w/o Mo sample is a lower exposure sample (1450 MWD/T). The control samples for this experiment failed in 21-35 days.

It appears therefore, that irradiation up to 1700 MWD/T has had little effect on the corrosion behavior of unclad U-10.5 w/o Mo and U-12 w/o Mo alloys. It should be noted here that the results of a previous experiment (MTR-WAPD 7-Met 1) on seven cast buttons exposed to somewhat higher burnup (about 2500 MWD/T) indicated that irradiation accelerates the time to failure for unclad U-12 w/o Mo samples. Since the condition of the

material and the exposures were different in the two experiments a comparison of results at this stage may not be significant.

In order to obtain a better understanding of the mechanism of corrosion in U-Mo alloys, sections of each of the six irradiated corrosion test samples mentioned above were removed from test after 1 day, 3 days, and 11 days. These samples have been mounted and lapped, and the corrosion induced hardness changes measured. The results are shown in Table XXV. Hardness increased approximately 40 points DPH for the sample exposed 1700 MWD/T and correspondingly smaller increases in hardness were obtained for samples subjected to shorter exposures. Subsequent corrosion testing results in further hardness increases. It would appear from this that strain induced by irradiation results in increased hardness and reduces the amount of additional strain that can be introduced by subsequent corrosion testing before failure occurs. This possible explanation for reduction in corrosion life due to irradiation will be checked in other experiments by recording hardness as a function of exposure and correlating this with corrosion life.

9. MTR Irradiation of Unclad U-Mo Samples to High Burnups
(MTR-WAPD 12-Met 2, 3 and 6)

Seven gamma quenched U-10.5 w/o Mo samples which were irradiated to a maximum exposure of 12,000 MWD/T have been returned to WAPD. The irradiation induced dimensional and density changes have been measured and are shown in Table XXVI. A plot of the density change versus exposure is shown in Fig. 26 together with the changes previously reported on a series of U-13.5 w/o Mo and U-12 w/o Mo samples which were irradiated to a maximum exposure of 7300 MWD/T.

It is apparent from Fig. 26, that in the range of 13.5 w/o to 10.5 w/o Mo, decreasing the amount of molybdenum increases the stability of the material. Metallographic examination of all these samples will be made. It is estimated that a density increase of approximately 0.5% would be expected if complete transformation occurred. It is evident, therefore, that the observed changes were a result of irradiation rather than transformation.

Banding of the same sort as previously reported on the U-12 w/o Mo and U-13.5 w/o Mo samples was also noted on the U-10.5 w/o Mo samples, with the additional observation that the location of the bands is not dependent on the position of the sample in the individual capsule. Metallographic studies of these bands remain to be completed.

10. Irradiation of Transformed Specimens of U-Mo Alloys (MTR-WAPD 12-Met 4)

An experiment was initiated to establish the effects of irradiation on partially transformed U-Mo alloys. Twenty specimens of U-Mo alloys were sealed into NaK filled Zircaloy-2 capsules and were inserted into the MTR on April 18, 1955 for a 6 weeks irradiation in a maximum flux of 3×10^{14} neutrons/cm²/sec. The sample conditions and their physical

properties are summarized in Table XXVII.

In order to interpret the effects of irradiation on partially transformed samples the annealing kinetics of U-9, 10.5, 12 and 13.5 w/o Mo alloys at 525°C are currently being studied by means of electrical resistivity measurements. It has been observed that at temperatures between -196°C to 150°C, these alloys in the gamma quenched condition exhibit a negative temperature coefficient of electrical resistivity which is increasingly negative for smaller amounts of molybdenum. As the gamma phase is transformed to alpha plus epsilon the coefficient of electrical resistivity becomes less negative and finally changes sign. Also, as transformation of the gamma phase proceeds in these alloys, the inflection point in the electrical resistivity versus temperature curve, beyond which the temperature coefficient is positive, is moved progressively toward lower temperatures. By assuming that the relationship between electrical resistivity and test temperature is linear between -25 and 125°C, the coefficient of electrical resistivity may be calculated in this temperature range and related to transformation time for each alloy. This was done and the results are indicated below:

<u>Hrs at 525°C</u>	<u>U-12 w/o Mo (°C-1)</u>	<u>U-13.5 w/o Mo (°C-1)</u>
0	$-.092 \times 10^{-3}$	$-.051 \times 10^{-3}$
8	$-.101 \times 10^{-3}$	$-.041 \times 10^{-3}$
25	$-.073 \times 10^{-3}$	$-.021 \times 10^{-3}$
48	$-.037 \times 10^{-3}$	$+.021 \times 10^{-3}$
76	0	$+.120 \times 10^{-3}$
312	$+.088 \times 10^{-3}$	$+.179 \times 10^{-3}$

The coefficient of resistivity, calculated on the above basis, is seen to change sign after 76 hours of transformation at 525°C for the U-12 w/o Mo alloy and after about 35 hours for the U-13.5 w/o Mo alloy. While the time at which the sign changes from minus to plus does not indicate that transformation is complete (since longer transformation times result in increasingly positive values), the indications are that the U-12 w/o Mo alloy is more stable than the U-13.5 w/o Mo alloy. Information of this type is believed to be helpful in later tests on irradiated material first transformed to the same extent.

The electrical resistivity measurements performed at -196°C on pre-irradiated samples indicates that the start of transformation occurs later for U-10.5 w/o Mo than for U-Mo alloys of either lower or higher Mo contents. This is shown below:

<u>Alloy</u>	<u>Start of Transformation at 525°C</u>
U-9 w/o Mo	15 hours
U-10.5 w/o Mo	35 hours
U-12 w/o Mo	32 hours
U-13.5 w/o Mo	25 hours

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B. In-Pile Tests of U-Mo Alloys

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

The remaining four defected, unirradiated, natural and enriched control samples of U-10.5 and U-12 w/o Mo were continued in corrosion test. One of these, U-10.5 w/o Mo, failed in 117 to 124 days. This represents the only one of eight samples, which were extruded at 1750°F, to last over 82 days. The other three control samples, all U-12 w/o Mo, were extruded at 1950°F and are continuing in test after 124 days. The higher extrusion temperature appears to have improved corrosion life.

The samples irradiated to an estimated maximum exposure of 1545 MWD/T have been defected and will be corrosion tested in 650°F water shortly.

2. Irradiation of Clad U-Mo in Chalk River X-Rod Loop (CR-WAPD-Met 6)

The thirteen specimens of Zircaloy-2 clad U-11 w/o Mo and U-12 w/o Mo, were inserted into the Chalk River X-3 Loop on March 10. The calculated temperature at the point at which fuel is exposed to high temperature water for the one defected specimen is 688°F. After two months exposure (about 2000 MWD/T) the radioactivity of water samples removed from the loop indicate that the corrosion rate of the exposed fuel is extremely low. The water activity has been running continuously at about 2000 counts/min/ml.

3. Irradiation of Clad U-12 w/o Mo in the HB-5 Loop (MTR-WAPD 13-Met 1)

The Zircaloy-2 clad 3.6 w/o enriched U-12 Mo sample, defected, was discharged April 18 after six weeks irradiation to an exposure of 1200 MWD/T. The calculated core-clad interface temperature during test was 710°F. The bare fuel material was exposed to neutral water (pH = 7) for the first three weeks and to water containing LiOH (pH = 9.5 - 10) for the last three weeks.

The average activity of water samples taken during the first three weeks of test was approximately 1200 counts/min/ml. This activity was reduced during the last three weeks to 120 counts/min/ml after the LiOH addition. A spectrographic analysis of a water sample showed a high Mn content, indicating that the activity in the loop water was mainly from stainless steel corrosion. It was also found that the water activity was reduced to zero after passing through the ion exchanger, indicating that solids or solubles were responsible for the activity rather than fission gases which would not be removed by the ion exchanger.

This specimen has been returned to WAPD. It will be sectioned at the defect and examined metallographically for corrosion effects.

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C. Tests of Other Alloys

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

It was indicated in WAPD-PMM-15 that density decreased approximately 3.7% when U-3.8 w/o Si alloy was irradiated to an estimated maximum exposure of 2500 MWD/T. An extensive effort was made to determine if the density decrease was associated with transformation of the epsilon phase to alpha plus epsilon as a result of irradiation. Attempts to reveal the microstructure metallographically, however, have not as yet been fruitful. Chemical and electro-chemical etchants, which performed satisfactorily on unirradiated U-3.8 w/o Si, stained or anodized the irradiated samples. Investigation of a wide range of chemical etchants and concentrations, current densities and voltages for electrolytic etching and bath temperatures have not produced satisfactory structures. Cathodic vacuum etching and other methods are being investigated. Progress in remote polishing techniques has made it possible to prepare U-Mo and U-3.8 w/o Si alloys for etching in 10 to 15 minutes using master slave manipulators. This compares with several hours previously required to prepare a sample for etching.

2. MTR Irradiation of Clad U-Nb Alloy Samples (MTR-WAPD 11-Met 17)

Twelve specimens of Zircaloy-2 clad natural uranium-10 w/o niobium have been charged into MTR process water for six weeks irradiation to an estimated maximum exposure of 2600 MWD/T. Two specimens of each of the following conditions are being irradiated.

a.	Extruded	/	900°C-24 hrs	/	700°F-5 weeks
b.	"	"	"	/	750°F-5 weeks
c.	"	"	"	/	865°F-5 weeks
d.	"	/	800°C-4 hrs	/	700°F-5 weeks
e.	"	"	"	/	750°F-5 weeks
f.	"	"	"	/	865°F-5 weeks

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 defected samples determined in 650°F static water.

3. MTR Irradiation of Unclad U-Nb Alloy Samples (MTR-WAPD 12-Met 8)

Seven specimens of unclad uranium-10w/o niobium, canned in NaK, are being irradiated for six weeks in the MTR to an estimated maximum exposure of 2000 MWD/T. The irradiation consists of three specimens homogenized at 900°C for 24 hours and one specimen each homogenized at 900°C for 24 hours followed by the aging treatments shown below.

a.	400°C	- 2 weeks	- W.Q.
b.	450°C	- 2 weeks	- W.Q.
c.	500°C	- 2 weeks	- W.Q.
d.	550°C	- 2 weeks	- W.Q.

The effect of irradiation on the dimensional stability, density, hardness, electrical resistivity, corrosion rate, and micro-structure will be determined. Pre-irradiation properties of these samples are shown in Table XXVIII.

4. Irradiation of Restrained Unalloyed Uranium (MTR-WAPD 4-Met 4)

Three specimens of unalloyed natural uranium, which were rolled in the alpha region so as to produce a high degree of preferred orientation, were assembled into NaK filled Zircaloy-2 capsules and irradiated for a maximum burnup of about 400 MWD/T. The specimens were assembled in the capsules so that they were forced to grow in-pile against a calibrated Inconel-X spring. Also, one end of each sample was drilled so that a thermocouple well extended into the middle of the specimen. Stainless steel clad chromel-alumel thermocouples were inserted into the wells and extended out of the reactor to permit continuous recording of the central temperatures of the uranium specimens. These containers were returned to the Hot Laboratory and disassembled and the following observations were made:

(1) The uranium specimens grew in length without buckling or warping so that it was possible to determine the stress exerted on the spring by the increase in length of the uranium specimens.

(2) The specimens decreased in diameter as follows: the diametrical decrease in the region of the thermocouple well was approximately equal to the clearance that existed between the specimen and the thermocouple well prior to irradiation. The diametrical decreases in the regions not restrained by the thermocouple well appeared to be greater toward the end of the specimen with the smallest diameter directly in contact with the spring.

(3) The irradiated springs were recalibrated and it was found that the spring constants had not changed from their unirradiated value.

The specimens were photographed and the negative enlarged to about 8 x from which length measurements were obtained. These results are summarized below:

Specimen No.	Estimated Exposure (MWD/T)	Length (in.)		Diameter at Spring Sect. (in.)				Stress Exerted By Uranium (psi)
		Pre	Post	L	Pre	Post	D	
#2	400	.752	.870	.118	.251	.233	.018	2930
#3	200	.752	.897	.145	.251	.235	.016	3410
		.753	1.007	.254	.251	.223	.028	6140

The results of the temperature measurements are not clear since the data have not been forwarded from the MTR. Verbal communication has indicated that the thermocouple exposed to the maximum neutron flux shorted out and the temperature recorded for the next highest neutron flux position was about 250°F. From these results, the following temperatures

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are estimated at the center of the uranium specimens:

<u>Specimen No.</u>	<u>Estimated Temp. (°C)</u>
# 6	60 to 100°C
# 3	121°C
# 2	250 to 300°C

It is planned to irradiate two additional assemblies similar to this to maximum exposures of about 600 MWD/T and 1200 MWD/T respectively.

D. In-Pile Tests of Other Alloys

1. Irradiation of Clad U-10 w/o Nb in the HB-5 Loop (MTR-WAPD 13-Met 2)

A Zircaloy-2 clad 5 w/o enriched U-10 w/o Nb specimen, defected with a 0.040" hole through the cladding, ran for one three week fuel cycle in the HB-5 loop in the MTR. The calculated temperature at the bottom of the defect was 705°F. Water counts for the first two weeks of test were 600 counts/min/ml or less. Data for the last week of operation have not been received to date. Currently, this specimen is in the coffin at MTR pending a decision on the operation of the HB-5 loop. This specimen may be reinserted in the loop on May 30.

V. Uranium Oxide Development

A. Preparation of UO_2

1. High Pressure Steam Oxidation

As indicated previously the O/U ratio of the UO_2 prepared by this method was always less than two, i.e. 0.96 to 1.99. The water content of the as-prepared powder averaged about 0.5%. It was found, however, that the water content could be reduced to below 0.05% by heating in hydrogen for twelve hours at 800°C. This treatment also causes the color to change from black to brown, but the analysis of the powder does not change. The amount of U(VI) before and after treatment is below $\pm 0.2\%$, the limit of accuracy of the wet chemical methods employed. Thus far, all attempts to detect free uranium have been unsuccessful.

Analyses indicate that some oxidation occurs on cold pressing at 100 T.S.I. Oxygen-uranium ratios as high as 2.15 have been found. The water content is unaffected however.

2. Hydrogen Reduced UO_3

When it was found that compacts made of UO_2 prepared by steam oxidation were more prone to disintegrate in water than compacts made of Mallinckrodt UO_2 if carbon were present, it was decided to abandon the steam oxidation method for the preparation of enriched powder and adopt the method employed by Mallinckrodt. Uranium dioxide is prepared by this method by first preparing uranyl nitrate hexahydrate, pyrolyzing it to UO_3 , grinding the powder and reducing it to UO_2 in dry hydrogen (0.1 - 0.2 liter/hr g) at 800°C. Depending on the length of the reduction period and the temperature, samples have been made having O/U ratios of 2.05 (6 hrs at 550°C) to 2.01 (50 hrs at 800°C). It was found that oxide containing 2.5% or greater U(VI) exhibited poor cold pressing characteristics.

3. Carbon Doped UO_2

A series of samples containing between 50 and 800 ppm of carbon UO_2 are being prepared in support of a program designed to determine the sensitivity of UO_2 sintered compacts to carbon. Thus far an attempt was made to prepare a sample of UO_2 containing 400 ppm carbon. This was made by dissolving an amount of sugar in the uranyl nitrate solution such that the desired amount of carbon would be uniformly dispersed throughout the UO_2 on pyrolysis of the solution and reduction to UO_2 . Subsequent analysis of the powder indicated that most of the carbon was lost in processing. Another attempt is being made to prepare the sample by a modified procedure.

4. Oxygen Doped UO_2

In order to determine the effect of composition on the physical properties of UO_2 , a series of samples of UO_2 are being made up with oxygen-uranium ratios above two. These are being prepared by reacting as-received Mallinckrodt UO_2 with a measured quantity of oxygen at a temperature of $150^\circ \pm 10^\circ C$. A total of eleven samples were prepared ranging in O/U ratio from 2.0 to 2.5. There are some indication that those samples having O/U ratios above 2.3 consist of more than one phase.

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B. Microscopic Examination of UO_2 Powders and Compacts

1. Observations on Powders

The structure of the +100 -80 sieve fractions of Mallinckrodt UO_2 which was prepared in 1954 was compared with that prepared in 1951. These were found to be identical. A comparison of these powders with that prepared at Bettis by the hydrogen reduction of UO_3 was also made. The Bettis prepared UO_2 was found similar in microstructure to the Mallinckrodt material, the particle size of the as-manufactured Bettis material was found to be much larger than that of the Mallinckrodt material. Moreover the Bettis material contains a sizeable proportion of particles with a much higher density.

An "active" UO_2 powder prepared by ball milling UO_3 in N sulfuric acid in the manner suggested by Battelle and subsequently reducing in H_2 , has been examined microscopically. This was found to be structurally similar to the fines fraction in Mallinckrodt powder but smaller in particle size. This small particle size may account in large measure for the high final densities obtained in compacts sintered from this type material.

Further examination of the high pressure steam oxidized material indicates that there are actually two types of powder obtained by this method. One type consists of very thin sheets which tend to curl while the other type consists of equiaxed particles having a smaller specific area. This latter type is the more frequently observed type.

2. Observations on Compacts

It was reported previously that a second phase has been found in compacts which have been sintered in a carbon resistor furnace as well as in compacts to which polyvinyl alcohol has been added as a binder. In general, the concentrations of second phase which have been observed metallographically have been too low for X-ray analysis. However, one sample made from Mallinckrodt UO_2 , in which polyvinyl alcohol was used as a binder, contained a sufficient amount to identify this phase tentatively as UC_2 .

C. Desintering of UO_2

A series of tests have been initiated to determine the effect of long-time exposure of UO_2 in high temperature water and steam. The observations made thus far are summarized in Table XXIX. Weight changes will be recorded after the samples have undergone a fourteen-day exposure.

The results shown in Table XXIX as well as the results obtained on four additional short-term tests indicate that samples sintered in argon in a carbon resistor furnace disintegrate in degassed (0.03 cc O_2 /kg H_2O) or hydrogenated water (12-25 cc H_2 /kg H_2O) while identical samples sintered in hydrogen in a molybdenum wound alundum muffle furnace are good without exception. Additional studies on the mode of attack of these carbon containing UO_2 specimens appear to substantiate the conclusion previously reached, viz., that the carbon concentrates in the grain boundaries and disintegration in the consequence of attack of the carbide at the grain boundaries.

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D. Surface Area and Density of UO₂ Powder

Measurements of the surface area of UO₂ powders prepared by different methods are being continued. Particular effort was put on the evaluation of the validity of the techniques being employed for these measurements. The results are summarized in Table XXX.

It is apparent from these data that adsorbed gases and vapors interfere with the measurement of the surface area of UO₂ by the nitrogen adsorption method. Degassing at 100°C for a reasonable length of time is incomplete; heating under vacuum at 400°C increased the as-measured surface area by 20% over that determined after outgassing at 100°C. The precision of the measurements is estimated to be within $\pm 10\%$.

It will be noted that UO₂ prepared by high pressure steam oxidation of the metal has approximately twice the specific area of Mallinckrodt powder. A specific area value of 3.9 sq meters/g reported previously for high pressure steam oxidized powder is apparently not typical for this type of powder.

Measurements of the density of UO₂ powders by the helium displacement method have been compared with the less time consuming measurements made by the displacement of various liquids. This was done in an effort to determine the applicability of the latter method. The results are tabulated in Table XXXI.

It will be noted that in the case of the high pressure powder the density values obtained using liquids are 1-2% lower than those obtained using helium, whereas closer agreement is obtained in the case of Mallinckrodt powders when they have been given comparable preparative treatments. This appears to indicate that the open pores in the Mallinckrodt powder are larger than those in the steam oxidized powder and the liquid is thus better able to penetrate the Mallinckrodt powder. It will also be noted that there appears to be a progressive decrease in the "helium" density of the Mallinckrodt powder with increase in time and temperature of heat treatment. Since the temperatures involved are too low to expect closing up of pores by sintering, this is attributed to progressive oxidation of the samples and lowering of density toward that of U₃O₈. This throws some doubt on the surface area results obtained may be due to partial conversion to a higher oxide. The validity of these results will be checked by chemical analysis.

In general it has been found that the measured density of high pressure steam oxidized powder approaches the theoretical value 10.96 g/cc, whereas the measured density of Mallinckrodt powder is considerably below the theoretical value. Thus it is likely that the steam oxidized powder consists of dense granules while the Mallinckrodt contains an appreciable number of closed pores. On the basis of the increase in density of the fired samples it appears that these pores may shrink somewhat on firing although this effect may also be due to an increase in oxygen-to-uranium ratio. This point will be checked.

E. Magnetic Susceptibility Studies

A series of oxide samples having oxygen to uranium ratios ranging between 2.0 and 2.67 (UO₂ to U₃O₈) are being prepared for magnetic susceptibility

measurements by the Magnetism Department of the Carnegie Institute of Technology. It is expected that both the slope of the Curie-Weiss plot in the temperature range, 40°K to room temperature, and the behavior of the susceptibility temperature curve below 40°K will provide a quantitative indication of the oxygen content. It is also hoped that additional information regarding the construction of the UO_2 will be gleaned from the measurements. Samples of high pressure steam oxidized material will also be measured in order to determine whether free uranium or uranium hydride is present in the samples. Since uranium hydride is ferromagnetic, its presence can be determined by measuring the field dependence of the magnetization.

F. Diffusion Studies

Escape of fission gases from UO_2 can occur by means of one or both of two mechanisms, macro-channel diffusion and interstitial lattice diffusion. In order to determine the relative importance of these two processes in causing migration, a study of the rates of diffusion, and diffusion coefficients for rare gases in UO_2 has been undertaken. It is also the purpose of the program to study the mechanism by which lattice diffusion occurs and to determine the effect of radiation on the overall diffusion process. The problem is now being analyzed in order to determine the experimental model which will be most amenable to mathematical treatment.

G. The $UO_2 - O_2$ Equilibrium

In view of the current lack of detailed information regarding the $UO_2 - O_2$ equilibrium at various temperatures, work has been initiated to determine the equilibrium constants under conditions likely to be encountered in the utilization of UO_2 for the PWR core. In addition, the kinetics of the reaction will be studied as a function of temperature, pressure, and surface conditions. Equipment is now being assembled for these measurements. Provision is also being made to study the diffusion of oxygen in UO_2 . From electrical conductivity and transference number measurements, it may be possible to elucidate the defect structure of UO_2 and arrive at an understanding of the mode of diffusion of oxygen in UO_2 .

H. The Reaction of Zirconium with UO_2

Work at the Battelle Memorial Institute under subcontract to Bettis on the reaction of UO_2 with zirconium has continued. The reaction is being studied by two methods; one involving powder mixtures and the other involving sandwiches of massive zirconium and dense fired UO_2 .

The powder experiments are performed by compacting mixtures of one part zirconium and four parts fused UO_2 to a density of 70% theoretical and heating the compacts in vacuo at various temperatures for various times. The extent of reaction is determined by chemical analysis for U and O_2 in the Zr-rich phase as well as by metallographic examination.

At 825°C the reaction proceeds rapidly and equilibrium is attained in less than 60 hours. The reaction is considerably slower at 700°C and equilibrium was not attained after even nine days at temperature.

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The sandwich-type experiments are performed by cladding high density fired UO_2 pellets in zirconium or Zircaloy-2 and inserting them in an autoclave where they are heated to a given temperature with the application of a high external pressure. Under these conditions the cladding deforms sufficiently to make a good contact with the UO_2 . The extent of reaction is determined by metallographic examination and by X-ray analysis.

No noticeable reaction was observed at 750°F after twenty days. Considerable reaction was observed, however, after ten days at 1300°F . X-ray analysis indicated the presence of alpha uranium and alpha zirconium adjacent to the UO_2 . Another region adjacent to this region consisted of the delta inter-metallic compound and alpha zirconium.

The region adjacent to the UO_2 which contained the alpha uranium corroded out completely after being exposed to water only one hour at 650°F .

I. Zr- UO_2 Phase Diagram

Work on the determination of the equilibrium diagram of UO_2 and Zr is being continued at Battelle under subcontract to Bettis.

Metallographic and X-ray analysis of alloys containing 26.0, 71.1, and 80.7 w/o zirconium in UO_2 indicates that a minor phase is present in addition to two major phases. The major phases are UO_2 and zirconium solid solution while the third phase was identified as alpha uranium.

J. Thermal Conductivity of UO_2

The thermal conductivity of UO_2 at temperatures between 1000°C and the melting point is being determined for Bettis by the Armour Research Foundation. Although preliminary tests with alumina indicated that the method was basically sound, so much difficulty was experienced with the apparatus that it was decided to rebuild it completely. The parts of the new apparatus are now being constructed. The new design employs resistance heating rather than induction heating. It is anticipated that the construction of the apparatus will be completed by the end of April.

K. Hot Laboratory Equipment

1. Density Measuring Equipment

A special balance has been constructed for remote measurement of UO_2 densities. The technique employed is one of mercury displacement. The overall accuracy for a 1 g sample is $\pm 0.5\%$.

A micro-manipulator is being constructed on the same mounting base to provide a method of taking samples at intervals across the diameter of the irradiated fuel specimen.

2. Corrosion Testing

A shielded autoclave capable of handling several curies of radioactive materials has been constructed for corrosion and leaching tests on

sections of irradiated UO_2 elements. Provisions have been made for controlling corrosion conditions and for periodic sampling of the autoclave water. The samples are tested in a porous bottom stainless steel cup which is placed in a spring loaded holder for remote handling.

3. Fission Gas Apparatus

An improved apparatus for puncturing irradiated specimens and extracting the contained fission gases has been constructed and is now being tested. A new system for separating and diluting the gases is being designed to work in conjunction with this apparatus.

L. UO_2 Irradiation Program

1. MTR-WAPD 14-Met 1

The purpose of this study was to determine the effect of radiation on the dimensional stability and the state of aggregation of clad UO_2 as well as the degree of fission gas release. The following specimens were irradiated in the MTR to a burnup of 5,600 MWD/T. (See Table XXXII)

Three of the specimens have been opened and described in a previous report. The remaining specimens are to be analyzed for fission gas release and for the presence of solid fission products.

2. MTR-WAPD 14-Met 3

The specimens employed in this test were designed to have sufficiently high central temperature in-pile to produce sintering or melting of the UO_2 in order to determine the resultant effects. (See Table XXXIII)

The Zircaloy cladding of all of the specimens containing steam oxidized UO_2 had either bulged or split. A water analysis was made of a control specimen of this series and it was found that the UO_2 contained 0.5% water. It has been calculated that the presence of 0.1% of water in the UO_2 is sufficient to burst the clad. It is concluded therefore that the failure of these specimens was due to the presence of water in the UO_2 and accordingly, they have been discarded.

Of the four Zircaloy-clad Mallinckrodt natural UO_2 specimens, only one exhibited any change in external appearance as a result of irradiation. This specimen had bulged in the center approximately 0.007 in. and decreased in length 0.06 in. As the specimen was being cut open for observation, NaK was seen escaping from the specimen. Subsequently, an appreciable amount of NaK was found in the specimen. The UO_2 appears to have sintered and melted during irradiation, leaving fissures extending from the center to the specimen edges. It is believed that the NaK entered the specimen through an undetected defect in the clad and caused the observed bulging during irradiation. Two of other Mallinckrodt specimens were cut open and found to have either sintered or melted in the center. The specimens had a hollow core approximately 1/8 in. in diam.

The remaining Mallinckrodt specimen was punctured and analyzed for fission gas release. It was found that approximately 5% of the estimated

fission gas present was released at room temperature. This work is described in more detail in a later section.

3. MTR-WAPD 14-Met 4

This experiment is an extension of MTR-WAPD 14-Met 3 and consists of the specimens listed in Table XXXIV. The specimens have been irradiated in the MTR for nine weeks at 2×10^{14} nv.

4. MTR-WAPD 14-Met 6

The purpose of this experiment is to compare the irradiation behavior of hot pressed specimens with the behavior of the cold pressed and sintered specimens now being irradiated in MTR-WAPD 14-Met 5. (See Table XXXV) The experimental conditions are as follows:

5. MTR Waterlogging Tests

a. Rabbit

UO₂ specimens with cladding defects were cycled in the MTR rabbit facility forty times. The specimens were immersed in water pressured to 2000 psi with He to simulate waterlogging conditions in the PWR. The samples have been returned to Bettis and will be examined in the near future. The experimental conditions for this test are tabulated in Table XXXVI.

b. Super-rabbit

This test is similar to the Rabbit experiment except that the specimens used will be full length prototype fuel elements. It is expected that this facility will be completed in July. (See Table XXXVII)

6. MTR-WAPD 19-Met 1

The purpose of this experiment is to determine the effects on UO₂ of radiation cycling under temperature conditions similar to those of PWR. As originally planned, the specimens were to have been irradiated for six weeks in a flux of 3×10^{14} nv. However, because of a breakdown in the hydraulic system, during which no cycling occurred, the specimens received approximately two weeks of irradiation under static conditions. Accordingly it was decided to cycle the specimens for another three week period.

The estimated control temperature of the specimens was 1424°C. The specimens have been removed from the MTR after 1800 cycles and will be shipped to WAPD during the week of May 16.

7. MTR-WAPD 19-Met 2

This is a duplicate of experiment MTR-WAPD 14-Met 1 except that the arrangement of the specimens in the cyclor has been altered to take into account the flux gradient along the specimen train. The specimens were inserted into the MTR on April 18.

8. CR-WAPD-Met 4A

The object of this experiment was: (1) to determine what would happen to a defected UO_2 specimen when irradiated in water and (2) to determine whether fission product activity would be released to the water during irradiation. (See Table XXXVIII)

In addition to the results already reported, examination of sections taken from both defected specimens revealed gross cracking of the UO_2 . There also was some evidence of sintering in the centers. Provisions are being made to analyze these specimens for fission gas release and solid fission products. In addition, their densities will be determined and they will be subjected to fission product leaching tests.

9. CR-WAPD-Met 5

The purpose of this experiment is to study the waterlogging of defected specimens using high density UO_2 to determine if failure of the defected specimen in CR-WAPD-Met 4A was due to water absorption in the low density compacts.

The specimens in Table XXXIX were to be exposed for four months at a flux of 2×10^{13} nv.

All of the specimens are 0.344 in. in diameter and range in length from 3 in. to $5\frac{1}{2}$ in.

Irradiation of these specimens was halted prematurely because of a leak developed in the loop. The specimens have been returned to WAPD and superficially examined. There is no evidence of rupturing in any of the specimens. However, the diameter of the defected specimen has increased uniformly from 0.4045 in. to 0.4110 in. In addition, it exhibited a weight increase of 0.59 gms. The specimen will be dried in a vacuum oven to remove any water which may be present and then re-weighed. The defect appeared clean and unobstructed. The results obtained with this defected specimen are not surprising in view of the results of an out-of-pile autoclave test performed on a control specimen. This indicated that the pellets comprising the specimen would disintegrate in water with a small increase in weight; the disintegration being caused by the pickup of carbon by the pellets during firing in a graphite resistance furnace.

Two additional specimens, one of which was defected, have been prepared for this test and have been shipped to Chalk River. The UO_2 for these specimens was prepared by the decomposition of uranyl nitrate and subsequent reduction in hydrogen. The pellets were sintered in a hydrogen atmosphere in a molybdenum-wound alundum-muffle furnace to insure that no carbon would be picked up. Control specimens exposed to water at 650°F for 14 days have shown no change in appearance or dimensions.

The specimens were inserted May 9 and after five days at full power the activity level in the water is only 10^4 counts/min. This is approximately the same as the level in the loop containing the U-Mo specimens. A series of experiments are now in process to determine the effect of simple thermal cycling out-of-pile on the structure of the oxide and on the propensity of the element to waterlog as a result of the treatment. Initially, four specimens were cycled between 550 and 1050°F: a solid Zircaloy rod 0.4 in. diam x 5 in. long, an empty Zircaloy cladding of the same size with end caps, and two clad UO₂ specimens. One of the UO₂ rods is 0.4 in. OD x 12 in. long and the other 0.4 in. OD x 5½ in. long. The cladding of both rods is 0.028 in. thick. The rods contain cold pressed and sintered MCW UO₂ pellets, 90.5% dense, with 0.001 in. diametral clearance between the clad and the pellets. The specimens were held at each temperature for ten minutes with a 15 second travel time between temperatures.

After 500 cycles no dimensional changes could be detected in any of the specimens. After 1000 cycles, the 12 in. long UO₂ specimen had increased approximately 0.04% in length, and the Zircaloy rod and tube both decreased approximately 0.1% in length. There was no change in diameter of the UO₂ and Zircaloy tube specimens within the accuracy of measurement. The solid Zircaloy rod exhibited an increase in diameter of approximately 0.2% at one end. All of the specimens exhibited a slight warpage. The specimens will be sectioned and examined metallographically.

10. Fission Gas Analysis

Experimental measurement of the escape of fission product gases from irradiated UO₂ specimens has been initiated. First measurements were made on a sample of natural Mallinckrodt UO₂ which was cold pressed to 74.3% theoretical density. The sample (specimen No. 7C of MTR-14 Met 3) was irradiated to about 800 MWD/T as estimated from an analysis of the Al-Co monitors associated with this sample.

The specimen was punctured at room temperature under vacuum and xenon and krypton were adsorbed on activated charcoal in a U-tube trap immersed in liquid nitrogen. Non-fission gases were pumped through the trap into a gas buret by means of a Toepler pump. The rate of loss of the fission gases from the specimen was monitored by measuring the increase of the activity in the charcoal due to volatile radioactive species. It was observed that after about one hour the activity level was constant. No activity was observed during periodic monitoring of the gases which were pumped through the traps into the buret. This indicated that the trapping method used was quantitative for fission gases.

When the specimen was punctured, the pressure in the system rose from 30 μ to 1100 μ . This gas, plus other non-fission gas released at room temperature, measured 3.6 cc NTP. It was assumed that this was primarily the helium in which the specimen was sealed.

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After the trap containing the liberated fission gases had been replaced, the temperature of the specimen was raised to 120°C and the above procedure was repeated. After about 30 minutes the activity in the U-tube trap leveled off at about 12 mr/hr and about 1.5 mls NTP of "helium" was measured in the buret.

While the temperature of the specimen was being raised further, the experiment was terminated by a failure of the ceramic furnace tube.

The sample of fission gas liberated at room temperature was analyzed by sealing a small known aliquot of the gas into an ampoule and counting on a gamma-ray spectrometer. In addition to the 540 Kev peak due to Kr⁸⁵, three other peaks were observed at approximately 27 Kev, 80 Kev, and 163 Kev.

The amount of Kr⁸⁵ liberated at room temperature was determined by calibrating the counter with a standard sample of Na²² (0.5 Mev γ). The value obtained was 2.3 millicuries, which was about 5% of the total Kr⁸⁵ expected for a 800 MWD/T burnup of the specimen.

The peaks at 80 and 163 Kev may be associated with 5.3 day Xe¹³³ and 12 day Xe^{131m} respectively. Half-life measurements on these peaks which are in progress indicate that they are decaying with half-lives similar to those of the above species. The disintegration rate of the 163 Kev species was estimated at 0.25 millicuries at about 100 days after shutdown. This value corresponds to about 64 millicuries of Xe^{131m} at shutdown. This is about 5% of the amount of Xe^{131m} expected in this specimen.

The disintegration rate of the 80 Kev gamma emitter is about a factor of three higher than that attributed to Xe^{131m}. If this peak is due solely to the five day Xe¹³³, it would predict an excessive disintegration rate for this species at shutdown. Therefore, the identity of this isotope as well as the one emitting the 27 Kev gamma, is not known at this time. More complete information on these species is being sought at this time.

TABLE I

Corrosion Properties of U-12 Mo Alloys in Various
Conditions in 650°F Water

Sample No.	A		B		C	
	X	Y	X	Y	X	Y
J 829	0.3	> 56	0.3	42-56	0.15	42-56
J 831	0.3	> 56	0.3	42-56	0.13	42-56
J 854	0.3	7-14	0.3	> 56	0.13	42-56
J 881	No Data		0.3	42-56	0.16	42-56
J 832	0.4	28-42	0.3	42-56	0.15	42-56
J 879	0.4	14-28	0.3	> 56	0.13	42-56
J 835*	0.6	14-28	0.6	14-28	0.3	14-28
J 830*	0.5	28-42	0.4	28-42	0.3	28-42

A - As-cast (induction melted)
B - As-cast (duplex melted)
C - Duplex melted / 900°C/24 hr/W.Q.

X - Corrosion rate in mg/cm²/hr
Y - Corrosion life in days

* - High carbon material

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TABLE II

Effect of Extrusion Temperature on Corrosion Properties
of U-12 Mo Alloys in 650°F Water

<u>Material</u>	<u>Ext. Temp. (°F)</u>	<u>Heat Treatment</u>	<u>Corrosion Rate (mg/cm²/hr)</u>							
			<u>Time - days</u>							
			<u>3</u>	<u>7</u>	<u>14</u>	<u>21</u>	<u>28</u>	<u>35</u>	<u>42</u>	<u>49</u> <u>56</u>
J 875	1600	As ext.	-0.50	-0.59	-2.4	D				
J 875	1600	900°C/24 hr/W.Q.	-0.09	-0.14	-0.27	-0.39	-0.58	-1.2	(1) -1.4	D
J 875	1900	As ext.	-0.40	-0.53	-0.67	D				
J 875	1900	900°C/24 hr/W.Q.	-0.09	-0.14	-0.30	-0.40	-0.55	-1.1	(2) -1.6	D
Mo 2C1-16	1600	As ext.	-0.79	-1.1	-4.0	D				
Mo 2C1-16	1600	900°C/24 hr/W.Q.	-0.19	-0.21	-0.33	-0.56	-1.5	D		
MM 431-10	1900	As ext.	-0.73	-0.46	-0.55	-	-1.3	-	C	
MM 431-10	1900	900°C/24 hr/W.Q.	-0.24	-0.20	-0.27	-	-0.35	-	-0.82	- D

D - Disintegrated

C - Cracked-up

(1) One of two samples disintegrated

(2) Two of three samples disintegrated

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TABLE III

Effect of Homogenization Prior to Extrusion on 650°F
Corrosion Properties of Extruded Billet Material

<u>Condition</u>	<u>Corrosion Life</u> <u>(days)</u>
As-extruded to billet size (no pre-homogenization)	21-28
1000°C/48 hr/F.C. (with billets)	21-28
1000°C/48 hr/F.C. (with billets) / 900°C/24 hr/W.Q.	21-28
1000°C/48 hr/F.C. (check samples)	21-28
900°C/24 hr/W.Q.	28-35
900°C/24 hr/W.Q. (check samples)	21-42

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TABLE IV

Effect of Homogenization Prior to Extrusion on 650°F Corrosion
Properties of Stripped Extruded and Extruded-Drawn Rods

<u>Pre-extrusion Heat Treatment</u>	<u>Extrusion Condition</u>	<u>Post Extrusion Heat Treatment</u>	<u>Corrosion Life (days)</u>
None	A	None	14-21
"	A	F	0-1
"	A	G	1-7
"	A	H	35-49
"	A	I	7-14
"	A	J	>28
"	A	K	7-14
1000°C/48 hr/F.C.	A	None	21-28
"	A	F	1-7
"	A	G	1-7
"	A	H	35-42
"	A	I	28-42
"	A	J	> 28
"	A	K	21-28
None	B	None	14-21
"	B	F	0-1
"	B	G	1-7
"	B	H	28-42
"	B	I	7-14
"	B	J	> 28
"	B	K	7-14
1000°C/48 hr/F.C.	B	None	35-49
"	B	F	1-7
"	B	G	1-7
"	B	H	28-42
"	B	I	14-28
"	B	J	> 28
"	B	K	21-28
None	C	None	14-21
"	C	F	0-1
"	C	G	1-7
"	C	H	28-35
"	C	I	7-14
"	C	J	> 28
"	C	K	7-14
1000°C/48 hr/F.C.	C	None	35-49
"	C	F	1-7
"	C	G	1-7

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TABLE IV (Contd.)

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<u>Pre-extrusion Heat Treatment</u>	<u>Extrusion Condition</u>	<u>Post Extrusion Heat Treatment</u>	<u>Corrosion Life (days)</u>
1000°C/48 hr/F.C.	C	H	28-42
"	C	I	14-28
"	C	J	> 28
"	C	K	14-21
None	D	None	14-21
"	D	H	35-49

Symbols

- A - As extruded to clad rod
- B - As extruded and cold drawn 17%
- C - As extruded and cold drawn 30%
- D - As extruded to bare rod
- F - 500°C/7 da/W.Q.
- G - 900°C/24 hr/W.Q. / 500°C/7 da/W.Q.
- H - 900°C/24 hr/W.Q.
- I - 400°C/5 wk/W.Q.
- J - 900°C/24 hr/W.Q. / 400°C/5 wk/W.Q.
- K - 600°C/1 hr/W.Q.

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TABLE V

Effect of Homogenization Prior to Extrusion on 650°F
Corrosion Properties of Defected Clad Rods

<u>Pre-extrusion Heat Treatment</u>	<u>Extrusion Condition</u>	<u>Post Extrusion Heat Treatment</u>	<u>Corrosion Life (days)</u>
None	A	None	70
"	A	I	7
"	A	F	0-7
1000°C/48 hr/F.C.	A	None	70
"	A	I	7
"	A	F	7
None	B	None	70
1000°C/48 hr/F.C.	B	None	70
None	C	None	70
"	C	F	7*
1000°C/48 hr/F.C.	C	None	70

* Two samples are in test; one of these samples has bulged at the defect hole after 7 days corrosion.

Symbols same as for Table IV.

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TABLE VI

Effect of Homogenizing Prior to Extrusion on the Corrosion
Properties of Duplex Melted U-12 Mo Alloys

Ingot No.	Homogenization Treatment	Ext. Temp. (°F)	A		B	
			X	Y	X	Y
J 829	1000°C - 48 hrs	1600	0.26	>21	0.24	>14
"	"	"	0.31	>21	0.21	>14
J 831	900°C - 24 hrs	1600	0.34	>21	0.24	>14
"	"	"	0.28	>21	0.23	>14
J 854	None	1600	0.28	>21*	0.16	>14
"	"	"	0.25	>21*	0.17	>14
J 881	1000°C - 48 hrs	1900	0.9	14-21**	0.20	>14
"	"	"	1.3	7-14**	0.19	>14
J 832	900°C - 24 hrs	1900	0.67	14-21**	0.21	>14
"	"	"	0.43	14-21**	0.20	>14
J 879	None	1900	0.22	>21	0.19	>14
"	"	"	0.22	>21	0.16	>14
J 835***	900°C - 24 hrs	1600	0.37	>21	0.44	>14
"	"	"	0.39	>21	0.43	>14
J 830****	None	1600	1.4	7-14	0.43	>14
"	"	"	0.5	14-21	0.43	>14

A - As extruded

B - Extruded / 900°C/24 hrs/W.Q.

X - Weight loss in mg/cm²/hr at 7 days

Y - Failure time in days

* - Cracked in two pieces after 21 days in test

** - Very severe pitting attack contributed to the high rate and early failure

*** - 0.2 w/o C

**** - 0.1 w/o C

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TABLE VII

Corrosion Properties of Unclad Samples of Extruded
U-12 w/o Mo Tested in 650°F Water

<u>Condition</u>	<u>ASTM Grain Size</u>	<u>Corrosion Rate 28 days (mg/cm²/hr)</u>	<u>Corrosion Life (days)</u>
As extruded	11 - 12	--	14 ⁽²⁾
700°C/24 hr/W.Q.	11 - 12	--	14 ⁽²⁾
900°C/24 hr/W.Q.	6 - 7	-1.47	28 - 35
900°C/24 hr/F.C.	6 - 7	-2.16	28 - 35
1000°C/30 min/W.Q.	6 - 7	-0.42	35 - 49
1000°C/48 hr/W.Q.	(1)	-0.51	28 - 35
1000°C/48 hr/F.C.	(1)	-0.69	28 - 35

- (1) Duplex grain structure with grains ASTM No. 1 and larger at the surface and ASTM No. 5 to 7 in the center.
- (2) Discontinued after 14 days because sample was nearly disintegrated.
- *

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TABLE VIII

Effect of Cooling Velocity upon the Corrosion
of a U-12 w/o Mo Alloy

	<u>Corrosion Rate (mg/cm²/hr) at</u>					
	<u>3 da</u>	<u>7 da</u>	<u>14 da</u>	<u>21 da</u>	<u>28 da</u>	<u>35 da</u>
900°C/24 hr/slow cool	-0.19	-0.29	-0.43	-0.64	-0.93	disint.
900°C/24 hr/He quench	-0.09	-0.13	-0.25	-0.36	-0.62	disint.

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TABLE IX

Effect of Annealing Time upon the Corrosion of a U-12 w/o Mo Alloy

Temp. (°C)	Time of Anneal	Corrosion Rate (mg/cm ² /hr) at								
		3 da	7 da	14 da	21 da	28 da	35 da	42 da	49 da	56 da
900	1/3 hr	-0.24	-0.32	-0.45	-1.78	disint				
	2	-0.25	-0.30	-0.42	-0.71	-1.44	disint			
	8	-0.20	-0.27	-0.45	-0.62	-0.90	disint			
	24	-0.22	-0.31	-0.51	-0.76	-1.14	disint			
	72	-0.17	-0.26	-0.44	-0.65	-0.96	disint			
	168	-0.17	-0.23	-0.36	-0.49	-0.75	disint			
1000	1/3 hr	-0.12	-0.20	-0.28	-0.36	-1.17	-1.76	disint		
	2	-0.06	-0.14	-0.21	-0.30	-0.39	-1.12	disint		
	8	-0.13	-0.17	-0.24	-0.33	-0.51	-0.87	disint		
	24	-0.10	-0.13	-0.21	-0.30	-0.43	-0.66	disint		
	72	-0.09	-0.11	-0.18	-0.23	-0.28	-0.39	disint		
	168	-0.09	-0.12	-0.20	-0.17	-0.37	disint			
1100*	40 sec	-0.29	-0.44	-0.62	disint					
	3 min	-0.05	-0.11	-0.17	-0.23	-0.29	-0.39	-0.65	-1.20	disint
	1 hr	-0.09	-0.23	-0.32	-0.42	-0.60	disint			

* Inductively heated

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TABLE X

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

Days in 650°F Water		As Ext. <u>H₁</u>	Vacuum <u>H₂</u>	Tank H ₂ <u>H₃</u>	Tank H ₂ <u>H₄</u>	UH ₃ -H ₂ <u>H₅</u>	O ₂ <u>H₉</u>
0	H ₂ Conc. DPH 30 Kg	1.1 309	1.6 296	0.8 302	12.6 316	6.4 302	0.21 288
3	H ₂ Corr. Rate Total Corr. DPH 30 Kg	65.1 0.87 62.7 331	26.5 0.26 18.7 315	17.7 0.14 10.0 312	16.6 0.11 7.8 315	29.0 0.25 17.9 318	29.5 0.22 15.9 314
7	H ₂ Conc. Corr. Rate Total Corr. DPH 30 Kg	386 1.15 193 355	93 0.40 68 331	41 0.19 31 326	46 0.15 26 333	63 0.31 52 334	65 0.26 44 330
14	H ₂ Conc. Corr. Rate Total Corr. DPH 30 Kg	1210 3.25 1092 425	420 0.64 215 352	115 0.26 87 350	105 0.23 77 354	144 0.41 137 357	208 0.36 121 350
21	H ₂ Conc. Corr. Rate Total Corr. DPH 30 Kg	Disint. 886 0.98 494 379	 886 0.98 494 379	338 0.38 191 371	280 0.36 181 366	474 0.53 267 381	467 0.47 238 371
28	H ₂ Conc. Corr. Rate Total Corr. DPH 30 Kg.	 Disint. 634 0.59 396 386	 Disint. 634 0.59 396 386	708 0.57 383 387	1486 0.88 596 416	1333 0.71 477 408	
35	H ₂ Conc. Corr. Rate Total Corr. DPH 30 Kg	 Disint. 1441 0.97 815 421	 Disint. 1441 0.97 815 421	1296 1.09 916 429	Disint. Disint. Disint. Disint.		
42				Disint.	Disint.		

TABLE XI

Effects of Composition Annealing and Corrosion Test Time upon
Various Properties of Induction Melted Chill Cast Alloys

		10.7 w/o Mo		12 w/o Mo		14 w/o Mo		15 w/o Mo	
		As Cast	γQ*	As Cast	γQ*	As Cast	γQ*	As Cast	γQ*
0 days	H ₂ Conc.	0.54	0.40	0.90	0.23	0.30	0.53	0.41	0.18
	DPH 30 Kg	271	271	289	287	314	311	326	328
3 days	H ₂ Conc.	52	13	53	26	61	18	64	23
650°F	Corr. Rate (mg/cm ² /hr)	-0.19	-0.12	-0.20	-0.13	-0.28	-0.07	-0.33	-0.14
	Total Corr. (mg/cm ²)	14	9	14	9	20	5	9	10
	DPH 30 Kg	313	300	317	335	357	343	366	366
7	H ₂ Conc.	52	34	122	57	163	58	181	disint.
	Corr. Rate	-0.15	-0.16	-0.23	-0.19	-0.35	-0.11	-0.43	
	Total Corr.	17	27	39	32	59	18	73	
	DPH 30 Kg	340	337	356	353	369	374	382	
14	H ₂ Conc.	92	70	516	233	713	disint.	747	
	Corr. Rate	-0.12	-0.16	-0.31	-0.29	-1.47		-1.63	
	Total Corr.	40	54	104	97	495	547	547	
	DPH 30 Kg	375	364	372	368	404		413	
21	H ₂ Conc.	141	245	748	disint.	disint.		disint.	
	Corr. Rate	-0.12	-0.16	-0.41					
	Total Corr.	60	81	207					
	DPH 30 Kg	406	391	381					
28	H ₂ Conc.	197	disint.	1241					
	Corr. Rate	-0.14		-1.05					
	Total Corr.	98		705					
	DPH 30 Kg	425		405					
35	H ₂ Conc.	506**		disint.					
	Corr. Rate	-0.40							
	Total Corr.	356							
	DPH 30 Kg	460							

* 900°C for 7 days in vacuo,
water quench

** still in test

TABLE XII

Effect of Fabricating Conditions

Sample No.	Composition w/o		<u>A</u>		<u>B</u>		<u>C</u>		<u>D</u>	
			X	Y	X	Y	X	Y	X	Y
Mo 3a1-1	12	Mo	1.6	14-28	0.2	28-42	0.7	14-28	0.16	> 7
			1.6	14-28	0.2	28-42	1.2	7-14	0.16	> 7
Mo 3a1-3	12	Mo	1.5	7-14	0.4	28-42	2.5	7-14	0.07	> 7
			1.2	14-21	0.4	28-42	1.2	14-28	0.08	> 7
Mo 2a1-7	12	Mo	0.4	21*	0.13	> 7				
			0.5	21*	0.17	> 7				
Mo 3a1-2	10.5	Mo	1.2	7-14	0.15	> 42	1.3	7-14		
			1.3	7-14	0.14	> 42	0.9	14-28		
Mo 3a2-6	10.5	Mo	0.6	7-21	0.20	> 7	1.6	7-14	0.23	> 14
			0.6	7-21	0.16	> 7	1.0	14-28	0.23	> 14
Mo 3a2-8	10.5	Mo	0.9	7-21	0.23	> 7	0.6	1-7	0.02	> 14
			0.9	7-21	0.21	> 7	0.3	1-7	0.02	7-14
Mo 3a2-9	10.5	Mo	0.7	7-21	0.20	> 7	0.6	> 14	0.24	> 14
			0.6	7-21	0.30	> 7	0.6	> 14	0.24	> 14
Mo 3a2-10	10.5	Mo	0.7	7-21	0.21	> 7	1.8	7-14	0.28	> 14
			0.6	7-21	0.20	> 7	1.6	7-14	0.27	> 14
Mo 3a2-12	10.5	Mo	0.6	7-21	1.3	> 7	0.7	> 14	0.21	> 14
			0.5	7-21	0.28	> 7	0.7	> 14	0.25	> 14
Mo 3a2-13	10.5	Mo	1.2	7-14	0.29	> 7	0.3	14-28		0-3
			1.3	7-14	0.79	> 7	0.3	14-28		0-3

A - As-extruded

B - Extruded / 8Q

C - As-cold drawn

D - Drawn / 8Q

* Samples discontinued due to the severe attack.

TABLE XIIICorrosion of Annealed U-12 Mo in 650°F Water

<u>Condition</u>	<u>Annealed Hardness DPH</u>	<u>Corrosion Rate (35 days) (mg/cm²/hr)</u>	<u>Corrosion Life (days)</u>
As-extruded	318	-1.4	35-42
900°C/24 hr/W.Q. (gamma quenched)	318	-1.0	35-42
900°C/24 hr/W.Q. / 343°C/5 wk/W.Q.	321	-0.93	35-49
900°C/24 hr/W.Q. / 400°C/5 wk/W.Q.	458	-0.11	> 42
400°C/5 wk/W.Q.	461	-0.85	35-42

TABLE XIV

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

<u>Water Addition</u>	<u>7</u>	<u>14</u>	<u>28</u>	<u>35</u>	<u>42</u>	<u>49</u>	<u>56</u>	<u>63</u>	<u>70</u>	<u>77</u>	<u>Observations</u>
50 ppm Ni ⁴⁴ (1)											One of two cracked in three pieces 42-49 days. Pieces retested and they cracked 63-70 days. Other cracked 70-77 days.
Rate*	0.23	0.23	0.26	0.32	0.32	0.32	0.30	0.30	0.31	-	
ppm H ₂	-	11	47	-	-	137	-	-	-	454	
DPH**	-	328	370	-	-	410	-	-	-	439	
50 ppm Ni ⁴⁴ (2)											Samples showed chips from edges after 56 days.
Rate*	0.09	0.13	0.21	0.21	0.21	0.23	0.30	cracked			
50 ppm Pt ⁴⁵ (1)											One of two samples cracked in two 35-42 days. Retested pieces and remaining sample cracked severely 49-56 days.
Rate*	0.13	0.17	0.20	0.20	0.26	0.44	cracked				
ppm H ₂	-	24	39	-	60	-	165				
DPH	-	343	371	-	385	-	403				
50 ppm Pt ⁴⁵ (2)											Samples showed corner spalling after 35 days and cracked into pieces 35-42 days.
Rate*	0.13	0.17	0.22	0.37	cracked						
ppm H ₂	16	26	71								
DPH	328	351	375								
12 ppm Colloidal Pt											Behavior similar to degassed water. Test discontinued at 35 days.
Rate*	0.15	0.24	0.32	0.60							
ppm H ₂		113									
DPH		393									
<u>No addition</u>	<u>0</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>		
Rate*	-	0.16	0.22	0.28	0.33	0.37	0.52	1.1	cracked severely		Corners badly spalled and some cracking after 35 days. Severely cracked into pieces after 40 days.
ppm H ₂	2	29	59	134	228	368	-	593	964		
DPH	321	341	364	385	394	407	-	426	480		

* Cumulative rate of weight loss in mg/cm²/hr

** All samples mounted in bakelite for hardness readings

(1) First test

(2) Rerun

TABLE XV

Corrosion of U-Mo-Pt Ternary Alloys (Arc Melted Buttons) in 650°F Water

Composition w/o	A*		B		C		AC-2		C-2		D/2	
	X	Y	X	Y	X	Y	X	Y	X	Y	X	Y
9 Mo	0.58	14-28	0.13	14-28	0.52	7-14	-	0-1	No data		-	0-1
	0.51	14-28	0.15	14-28	0.93	7-14	-	0-1			-	0-1
9 Mo 0.3 Pt	0.12	84-98	0.021	84-98	0.32	14-28	47	1-7	-	0-1	-	0-1
	0.11	70-84	0.021	42-56	0.24	14-28	-	0-1	-		-	0-1
9 Mo 0.6 Pt	0.10	>154	0.014	70-84	0.015	56-70	61	1-7	-	0-1	-	0-1
	0.10	>154	0.014	84-98	0.015	28-42	42	1-7	-		-	0-1
9 Mo 1.2 Pt	0.08	>154	0.006	112-126	0.003	98-112	2.6	7-14	18	1-7	0.03	14-28
	0.08	>154	0.008	112-126	0.003	84-98	1.8	7-14	-		0.05	14-28
12 Mo	0.22	28-42	0.16	42-56	0.06	28-42	0.67	7-14	0.07	14	0.46	28-42
	0.30	28-42	0.26	42-56	0.24	1-7	0.89	7-14	-		0.13	56-70
12 Mo 0.3 Pt	0.15	112-126	0.16	112-126	0.063	98-112	0.63	14-28	0.05	7-14	0.07	>140
	0.15	112-126	0.16	>140	0.063	>140	0.68	14-28	-		0.08	>140
12 Mo 0.6 Pt	0.11	>154	0.13	>140	0.031	>140	0.36	28-42	0.01	1-7	0.04	>140
	0.11	>154	0.13	>140	0.031	>140	0.40	42-56	-		0.07	14-28

A = As melted

B = 900°C/24 hr/W.Q.

C = 900°C/24 hr/W.Q. / 400°C/7 da/W.Q.

AC-2 = 400°C/35 da/W.Q. (No YQ)

C-2 = 900°C/24 hr/W.Q. / 400°C/35 da/W.Q.

D/2 = 900°C/24 hr/W.Q. / 500°C/2 da/W.Q.

X = Weight loss rate (mg/cm²/hr)

Y = Corrosion life (days)

TABLE XVI

Corrosion Properties of Two Duplex Melted and Extruded
U-Mo-Pt Alloys in 650°F Degassed Water

Heat Treatment	U-8 Mo-1 Pt		U-12 Mo-0.5 Pt	
	X	Y	X	Y
As Extruded	.32	> 63	.32	> 63
	.11	> 63	.32	> 63
As Cold Drawn	2.0	7-14	.30	> 28
	2.1	7-14	.31	> 28
Ext. γ Q	.02	42-56	.08	> 56
	.02	42-56	.06	> 56
Cold Drawn γ Q	.26	> 28	.05	> 28
	.22	> 28	.06	> 28
Ext. γ Q $\neq$ 400°C-7 days	.10	7-14	.03	1-7
	.04	7-14	.02	> 28
Ext. γ Q $\neq$ 400°C-21 days	-	0-1	.02	1-7
	-	0-1	.02	> 28
Ext. γ Q $\neq$ 400°C-35 days	-	0-1	.01	> 14
	-	0-1	.01	> 14
Ext. γ Q $\neq$ 500°C-2 days	-	0-1	.03	> 28
	-	0-1	.06	> 28
Ext. γ Q $\neq$ 500°C-7 days	-	0-1	.12	> 28
	-	0-1	.12	> 28
				(discontinued)
Ext. γ Q $\neq$ 500°C-21 days	-	0-1	.19	7-14
	-	0-1	.17	7-14
Ext. γ Q $\neq$ 500°C-35 days	-	0-1	.38	1-7
	-	0-1	.22	1-7

X - Rate of weight loss in mg/cm²/hr
Y - Failure time in days

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TABLE XVII

Corrosion Properties of U-Nb Alloys in 650°F Water

Identity	Composition	A		B		C		D		E		F	
		X	Y	X	Y	X	Y	X	Y	X	Y	X	Y
Mo3a2-3	8 Nb	0.4	7-14	-	0-14	0.4	1-7	-	0-7	-	0-1	-	0-1
		0.5	7-14	0.2	14-28	31	1-7	-	0-7	-	0-1	-	0-1
Mo3a2-1	10 Nb	0.2	14-21	0.03	> 56	47	1-7	0.8	1-7				
		0.2	14-21	0.15	28-42	-	0-1	0.16	7-14				
Mo3a2-4	10 Nb	0.3	1-7	0.04	28-42	-	0-3	1.4	7-14	-	0-1	-	0-1
		0.3	7-14	0.1	42-56	-	0-3	0.8	7-14	-	0-1	-	0-1
Mo3a2-5	10 Nb	0.3	7-14	0.1	28-42	11	3-7	1.3	7-14				
		0.3	1-7	0.04	> 56	-	0-3	1.4	7-14				
Mo3a2-11	10 Nb	-				-	0-3	0.2	> 14				
						-	0-3	0.2	> 14				
Mo3a2-7	12 Nb	0.1	14-28	0.01	> 28	2.4	1-7	0.01	> 28	Data not yet available			
		0.1	14-28	0.01	> 28	3.4	1-7	0.01	14-28				

- A - As extruded
 B - Extruded ∇ 900°C/24 hr/W.Q. (helium filled tube)
 C - As cold drawn
 D - Cold drawn ∇ 900 C/24 hr/W.Q. (helium filled tube)
 E - Extruded ∇ 400°C/7 da/W.Q.
 F - Extruded ∇ 500°C/2 da/W.Q.

- X - Weight loss in mg/cm²/hr
 Y - Failure time in days

TABLE XVIII

Corrosion Properties of U-10 Nb-1 Pt in Various Conditions in 650°F Water

A		B		C		D		E		F		G		H	
X	Y	X	Y	X	Y	X	Y	X	Y	X	Y	X	Y	X	Y
0.1	>42	0.01	>42	-	0-1	0.02	>28	0.7	7-14	-	0-1	4.5	1-7	-	0-1
0.1	28-42	0.02	>42	-	0-1	0.01	>28			-	0-1	3.4	7-14	2.8	7-14

- A - As extruded
 B - Extruded ∇ 900 C/24 hr/W.Q.
 C - As cold-drawn
 D - Drawn and 900°C/24 hr/W.Q.
 E - Extruded ∇ Q ∇ 400°C/7 da/W.Q.
 F - Extruded ∇ Q ∇ 500°C/2 da/W.Q.
 G - Extruded ∇ Q ∇ 400°C/21 da/W.Q.
 H - Extruded ∇ Q ∇ 400°C/35 da/W.Q.

- X - Weight loss in mg/cm²/hr
 Y - Failure time in days

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TABLE XIXCorrosion Data for "High-Purity" U-12 w/o Mo Alloy

<u>Sample</u>	<u>3 days</u>	<u>7 days</u>	<u>14 days</u>	<u>21 days</u>
A	-0.15	-0.17	-0.76	disint.
B	-0.10	-0.18	-0.40	disint.
C	-0.16	-0.18	-1.80	disint.
D	-0.15	-0.17	-0.42	disint.

TABLE XX

Corrosion Life of Simulated Fuel Elements Tested
in 343°C Degassed Water with 0.040 in. Defect in Clad

<u>Alloy Content</u> <u>w/o</u>	<u>Sample</u> <u>Condition*</u>	<u>No.</u> <u>Samples</u>	<u>Corrosion Life</u> <u>Days</u>
8 Nb	A	2	> 70
	B	1	> 70
	B	1	56-70
	C	1	14-28
	C	1	> 28
	D	4	0-14
	E	4	> 42
	F	3	0-14
	F	1	> 14
10 Nb	A	6	> 70
	B	4	42-56
	B	1	> 56
	C	6	> 28
	D	8	0-14
	D	1	28-42
	E	3	14-28
	E	3	42-56
	E	3	> 56
	F	2	0-14
	F	2	14-28
	F	5	> 28
12 Nb	A	2	> 42
	B	3	> 42
	C	2	> 14
	D	1	0-14
	D	2	14-28
	D	1	28-42
	D	1	> 42
	E	5	> 42
	F	5	> 14
10 Nb-Nb Barrier	A	2	> 70
	B	2	> 70
	C	1	0-14
	C	1	14-28
	D	1	0-14
	E	4	> 42
	F	4	0-14

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TABLE XX (Contd.)

<u>Alloy Content</u> <u>w/o</u>	<u>Sample</u> <u>Condition*</u>	<u>No.</u> <u>Samples</u>	<u>Corrosion Life</u> <u>Days</u>
10 Nb / 1 Pt	A	3	>70
	B	3	>70
	C	1	14-28
	C	2	>28
	D	2	>42
	E	1	28-42
	E	1	>42
	F	2	>14
8 Mo / 1 Pt	A	3	>70
	B	3	14-28
	C	3	0-14
	D	4	0-14
	E	1	28-42
	E	3	>42
	F	4	0-14
12 Mo / 0.5 Pt	A	2	>70
	B	2	>70
	C	2	>28
	D	4	0-14
	E	4	>42
	F	4	>14
10.5 Mo-Pd Barrier (un- bonded)	A	1	0-14
	A	2	14-28
	B	3	>42
	C	3	0-14
	D	4	0-14
	E	3	0-14
	E	1	14-28
	F	3	0-14
	F	1	>14
10.5 Mo-Pd Barrier (un- bonded)	A	1	0-14
	B	2	>28
	C	1	0-14
	C	1	>14
	D	4	>42
	E	4	0-14
	F	4	0-14
10.5 Mo-15 Mo / 5 Pt Alloy Barrier	A	3	>42
	B	2	14-28
	B	1	28-42
	C	1	0-14
	C	2	>14

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TABLE XX (Contd.)

<u>Alloy Content</u> <u>w/c</u>	<u>Sample</u> <u>Condition*</u>	<u>No.</u> <u>Samples</u>	<u>Corrosion Life</u> <u>Days</u>
10.5 Mo-15 Mo / 5 Pt Alloy Barrier	D	1	0-14
	D	1	>42
	E	1	0-14
	E	1	14-28
	F	1	>14
10.5 Mo-Nb Barrier	A	3	>42
	B	3	>42
	C	2	>14
	D	1	0-14 (un bonded)
	D	2	28-42
	D	2	>42
	E	1	0-14 (un- bonded)
	E	1	28-42
	E	3	>42
	F	5	0-14
10.5 Mo-Mo Barrier	A	3	>42
	B	3	>42
	C	3	>14
	D	3	>14
	D	1	14-28
	E	1	14-28
	E	3	>42
	F	2	0-14
	F	2	>14
10.5 Mo-10 Nb Alloy Barrier	A	1	0-14 (Weld Rupture)
	A	2	>42
	B	2	28-42
	C	2	0-14
	D	1	0-14
	D	2	14-28
	D	1	>42
	E	4	14-28
	F	4	0-14

*A - As extruded

B - Extruded / 900°C/24 hr/W.Q.

C - Extruded / 900°C/24 hr/W.Q. / 400°C/5 wk/W.Q.

D - Extruded / Cold Drawn

E - Extruded / Cold Drawn / 900°C/24 hr/W.Q.

F - Extruded / Cold Drawn / 900°C/24 hr/W.Q. / 400°C/5 wk/ W.Q.

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TABLE XXI

Effect of Annealing on the 650°F Corrosion Properties
of Cold Drawn U-12 Mo Bare Rod

<u>Condition</u>	<u>Heat Treatment</u>	<u>Avg. Corr. Rate-mg/cm²/hr</u>			
		<u>3 days</u>	<u>7 days</u>	<u>14 days</u>	<u>21 days</u>
As cast billet	900°C/48 hrs/W.Q.	-.18	-.21	-.25	-.28
As extruded		-.52	-.56	cracked	
Cold Drawn-31%		-.40	-.39	cracked	
Cold Drawn-53%		-.43	-.50	cracked	
"	600°C/10 min/W.Q.	-.63	-.65	cracked	
"	600°C/30 min/W.Q.	-.78	-.87	cracked	
"	600°C/1 hr/W.Q.	-.95	-1.50	cracked	
"	600°C/4 hrs/W.Q.	-.78	-1.00	cracked	
"	600°C/8 hr/W.Q.	-.71	-.88	cracked	
"	600°C/24 hr/W.Q.	-.78	-.95	cracked	
"	700°C/10 min/W.Q.	-.44	-.63	cracked	
"	700°C/30 min/W.Q.	-.39	-.56	cracked	
"	700°C/1 hr/W.Q.	-.49	-.66	cracked	
"	700°C/8 hr/W.Q.	-.49	-.64	cracked	
"	700°C/24 hr/W.Q.	-.48	-.58	cracked	
"	900°C/10 min/W.Q.	-.09	-.16	-.27	-.40
"	900°C/30 min/W.Q.	-.11	-.15	-.23	-.29
"	900°C/1 hr/W.Q.	-.07	-.13	-.21	-.27
"	900°C/24 hr/W.Q.	-.09	-.13	-.17	-.25

TABLE XXII

Effect of Annealing on the 650°F Corrosion Properties of Cold
Drawn U-12 Mo Defected Fuel Elements in Degassed Water

<u>Condition</u>	<u>Heat Treatment</u>	<u>Corrosion Life - Days</u>
As extruded		> 14
Cold Drawn - 31%		(1) 7-14 (1) > 14
Cold Drawn - 53%		7-14
"	600°C/10 min/W.Q.	> 14
"	600°C/30 min/W.Q.	> 14
"	600°C/1 hr/W.Q.	> 14
"	600°C/4 hr/W.Q.	> 14
"	600°C/8 hr/W.Q.	> 14
"	600°C/24 hr/W.Q.	> 14
"	700°C/10 min/W.Q.	> 14
"	700°C/30 min/W.Q.	> 14
"	700°C/1 hr/W.Q.	> 14
"	700°C/8 hr/W.Q.	7-14
"	700°C/24 hr/W.Q.	0-7
"	900°C/10 min/W.Q.	> 14
"	900°C/30 min/W.Q.	> 14
"	900°C/1 hr/W.Q.	> 14
"	900°C/24 hr/W.Q.	0-7

TABLE XXIII

Corrosion Life in 650°F Water of U-Mo Alloys
Irradiated Clad Rods Annealed $\frac{1}{2}$ hr at 750°C

<u>Sample No.</u>	<u>Composition</u>	<u>Estimated Exposure in MWD/T</u>	<u>Test Days to Failure</u>
A 21	U-9.0 w/o Mo	7,100	Continuing in test after 21 days
A 22	U-9.0 w/o Mo	8,900	14-21
A 24	U-9.0 w/o Mo	8,000	14-21
B 21	U-10.5 w/o Mo	7,100	Continuing in test after 21 days
B 22	U-10.5 w/o Mo	8,900	Continuing in test after 21 days
B 23	U-10.5 w/o Mo	10,100	14-21
B 24	U 10.5 w/c Mo	9,500	26-33
B 25	U-10.5 w/o Mo	8,000	Continuing in test after 21 days
B 26	U 10.5 w/c Mo	12,500	15-16
C 22	U-12.0 w/c Mo	9,900	6-9
C 23	U-12.0 w/o Mo	10,300	12-21
C 24	U 12.0 w/c Mo	10,100	9-14
D 22	U-13.5 w/c Mo	9,500	6-9
D 23	U-13.5 w/c Mo	8,000	9-14
D 24	U-13.5 w/c Mo	8,900	14-21

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TABLE XXIV

Corrosion Results on Irradiated Unclad
U-Mo Alloys

Samples tested in 650°F (343°C) water at
Saturation Temperature

<u>Sample No.</u>	<u>Composition</u>	<u>Exposure in MWD/T</u>	<u>Corrosion Behavior*</u>
11	U-10.5 w/o Mo	1700	Failed in 22-28 days
12	U-10.5 w/o Mo	1450	Survived 28 days
13	U-10.5 w/o Mo	750	Failed in 22-28 days
24	U-12 w/o Mo	1580	Survived 28 days
26	U-12 w/o Mo	1450	Failed in 22-28 days
27	U-12 w/o Mo	750	Failed in 20-22 days
5	U-10.5 w/o Mo	Control	Failed in 21-35 days
6	U-10.5 w/o Mo	Control	Failed in 21-35 days
29	U-12 w/o Mo	Control	Failed in 21-35 days
30	U-12 w/o Mo	Control	Failed in 21-35 days

* Corrosion rates of all samples up until the samples failed was between .15-.30 mg/cm²/hr.

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TABLE XXV

Hardness Changes in Unclad U-Mo Alloys as a Result of Irradiation
and Subsequent Corrosion Testing

Sample No.	Composition	Exposure (MWD/T)	DPH Hardness		Corrosion Tested in 650°F Water		
			Before Irradiation	After Irradiation	1 day	3 days	11 days
11	U-10.5 w/o Mo	1700	275 $\pm$ 5*	318 $\pm$ 5(43)**	328 $\pm$ 2(10)	341 $\pm$ 4(23)	350 $\pm$ 5(32)
12	U-10.5 w/o Mo	1450	"	310 $\pm$ 7(35)	337 $\pm$ 3(27)	330 $\pm$ 4(20)	350 $\pm$ 2(40)
13	U-10.5 w/o Mo	750	"	285 $\pm$ 9(10)	327 $\pm$ 4(42)		373 $\pm$ 2(92)
24	U-12 w/o Mo	1580	307 $\pm$ 3	336 $\pm$ 10(29)	349 $\pm$ 3(13)	366 $\pm$ 4(30)	364 $\pm$ 4(28)
26	U-12 w/o Mo	1450	"	319 $\pm$ 8(12)	363 $\pm$ 2(44)	356 $\pm$ 5(37)	371 $\pm$ 3(52)
27	U-12 w/o Mo	750	"	323 $\pm$ 4(16)	369 $\pm$ 6(46)	366 $\pm$ 6(43)	388 $\pm$ 3(65)

* Standard deviation

** Numbers in parentheses indicate hardness changes

TABLE XXVI

Changes in Dimensions and Density of Unclad
U-10.5 w/o Mo Samples

<u>Sample</u> <u>No.</u>	<u>Exposure</u> <u>(MWD/T)</u>	<u>Percent Increase</u> <u>in Diameter*</u>	<u>Percent Increase</u> <u>in Length</u>	<u>Percent Decrease</u> <u>in Density</u>
42	2720	.3%	.15%	.9%
43	6700	.3%	.5%	1.6%
45	9000	1.1%	.8%	2.7%
47	11,600	1.6%	1.0%	3.5%
48	12,000	1.1%	1.0%	4.4%
50	9850	.8%	.7%	2.3%
51	5250	.5%	.4%	1.4%

* Samples originally 0.187" Dia. x 2.000" long

TABLE XXVII

Pre-Irradiation Data on
Transformed U-Mo Alloys

No. of Samples In-File	Composition	Heat Treatment	Density g/cm ³	Hardness (VHN 5 kilo load)	Electrical Resistivity A-196°C (cm)	Phases Present
1	U-9 w/o Mo	# 1	17.35 ± 0.01	296 ± 9	72.5 ± 0.2	γ
2	U-9 w/o Mo	# 4	17.47 ± 0.01	446 ± 18	31.2 ± 0.1	α + E
1	U-10.5 w/o Mo	# 1	17.15 ± 0.01	306 ± 6	74.6 ± 0.2	γ
2	U-10.5 w/o Mo	# 4	17.46 ± 0.01	388 ± 15	60.3 ± 0.6	α + E
1	U-12 w/o Mo	# 1	16.95 ± 0.01	331 ± 10	76.5 ± 0.3	γ
2	U-12 w/o Mo	# 2	16.98 ± 0.01	324 ± 10	76.0 ± 0.3	γ
2	U-12 w/o Mo	# 3	16.98 ± 0.01	332 ± 8	75.6 ± 0.2	γ + E
2	U-12 w/o Mo	# 4	16.96 ± 0.01	351 ± 13	69.8 ± 0.5	α + E + γ
1	U-13.5 w/o Mo	# 1	16.81 ± 0.01	340 ± 9	79.1 ± 0.3	γ
2	U-13.5 w/o Mo	# 2	16.82 ± 0.01	320 ± 13	78.7 ± 0.3	γ
2	U-13.5 w/o Mo	# 3	16.81 ± 0.01	327 ± 10	76.9 ± 0.5	γ + E
2	U-13.5 w/o Mo	# 4	16.80 ± 0.01	348 ± 8	72.0 ± 0.6	γ + E + α

Heat Treatments

- # 1 - 900°C in kinetic vacuum for 24 hours, water quenched
 # 2 - #1 plus 525°C in evacuated Vycor tubes for 8 hours, water quenched
 # 3 - #1 plus 525°C in evacuated Vycor tubes for 48 hours, water quenched
 # 4 - #1 plus 525°C in evacuated Vycor tubes for 312 hours, water quenched

* Phases present from X-ray and metallographic examination

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TABLE XXVIII

Pre-Irradiation Properties of Uranium-10 w/o Niobium

<u>Heat Treatment</u>	<u>Density</u> <u>(gm/cm³)</u>	<u>Hardness</u> <u>(RA)</u>	<u>Electrical Resistivity</u> <u>($\mu\Omega\text{cm}$)</u>	
			<u>R.T. (26°C)</u>	<u>-196°C</u>
900°C - 24 hrs - W.Q.	16.51	64.5	65.70	71.19
900°C - 24 hrs / 400°C - 2 wks	16.71	76.5	52.15	35.66
900°C - 24 hrs / 450°C - 2 wks	16.76	72.0	44.28	21.80
900°C - 24 hrs / 500°C - 2 wks	16.78	68.5	41.59	18.12
900°C - 24 hrs / 550°C - 2 wks	16.81	66.0	40.21	16.60

TABLE XXIX

UO₂ Corrosion Test ~ 650°C Degassed Water
(0.06 cc O₂/kg max)

<u>UO₂ Powder</u>	<u>Sample Preparation</u>	<u>Density %T</u>	<u>Density %T</u>	<u>Sintering Atmosphere</u>	<u>Total Da in Test</u>	<u>Observations</u>
MCW 1954	4100 -80 sieve fraction as manufactured	-	-	-	4	no change
NUR-3	large pieces of as manufactured powder	-	-	-	4	no change
MCW 1954	as cold pressed	69.5	-	-	4	no change
NUR-1	as cold pressed	68.8	-	-	4	no change
NOH-18	as cold pressed	77.5	-	-	4	no change
MCW 1954	cold pressed and sintered 10 hrs 1725°C ~69	-	-	H ₂ BMI alundum furnace	4	no change
NUR-1	cold pressed and sintered 10 hrs 1725°C ~69	-	-	H ₂ BMI alundum furnace	4	no change
NOH-18	cold pressed and sintered 10 hrs 1725°C ~77	-	-	H ₂ BMI alundum furnace	4	no change
NUR-1	cold pressed and sintered 10 hrs 1725°C ~69	93.8	-	H ₂ Bettis alundum furnace	4	no change
MCW 1954	cold pressed and sintered 10 hrs 1725°C ~69	94.1	-	Argon Bettis carbon furnace	4	disintegrated into powder
NUR-1	cold pressed and sintered 10 hrs 1725°C ~69	94.2	-	Argon Bettis carbon furnace	4	disintegrated into powder
NOH-18	cold pressed and sintered 10 hrs 1725°C ~77	88.5	-	Argon Bettis carbon furnace	4	disintegrated chunks & powder
MCW 1954	cold pressed and sintered 6 hrs 1750°C ~75	92.5	-	Argon Bettis carbon furnace	4	split into two pieces & powder
MCW 1954	cold pressed and sintered 6 hrs 1750°C ~70	87.3	-	Argon Bettis carbon furnace	4	disintegrated into powder
MCW	hydrostatic pressed sintered 4 hrs 1760°C	88	-	H ₂ BMI alundum furnace	5	no change
MCW	hot pressed 1750°C 15 min	95	-	Argon CO ATF graphite die	5	no change

MCW - Mallinckrodt UO₂NUR-1 - Run 1 Bettis UO₂ made from uranyl nitrateNOH-18 - Run 18 Bettis high pressure steam oxidized UO₂

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TABLE XXX

<u>Sample No.</u>	<u>Powder Type</u>	<u>Treatment of Powder</u>	<u>Surface Area (sq. meters/g)</u>	<u>Av. Part. Diam (microns)</u>
H-18-1	high press. steam oxidized	degassed 100°C, 2 hr	.97	.57
H-18-1	high press. steam oxidized	degassed 400°C, 6 hr	1.18	.47
M-1	MCW (1954)	degassed 100°C, 1 hr	.49	1.21
M-2	MCW (1954)	degassed 100°C, 2 hr	.54	1.10
M-2	MCW (1954)	degassed 100°C, 6 hr	.63	.95

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TABLE XXXI

<u>Sample No.</u>	<u>Powder Type</u>	<u>Treatment of Powder</u>	<u>Displacing Fluid</u>	<u>Density (gram/ml)</u>
H-18-2	high press. steam ox.	degassed - 100°C - 1 hour	helium	10.92
H-18-2	high press. steam ox.	degassed - 400°C - 6 hours	helium	10.92
H-18-3	high press. steam ox.	degassed - 100°C - 1 hour	benzene	10.79
H-18-3	high press. steam ox.	dried in vacuo- $\frac{1}{2}$ hr-100°C-deg.	benzene	10.80
H-18-3	high press. steam ox.	dried in vacuo- $\frac{1}{2}$ hr-100°C-deg.	carbon tetrachloride	10.75
H-18-3	high press. steam ox.	dried in vacuo- $\frac{1}{2}$ hr-100°C-deg.	water	10.75
M-1	MCW (1954)	degassed - 100°C - 1 hour	helium	10.13
M-2	MCW (1954)	degassed - 100°C - 2 hours	helium	10.09
M-2	MCW (1954)	degassed - 400°C - 6 hours	helium	10.03
M-3	MCW (1954)	dried in vacuo- $\frac{1}{2}$ hr - 100°C-deg.	benzene	10.19
M-3	MCW (1954)	dried in vacuo- $\frac{1}{2}$ hr-100°C-deg.	carbon tetrachloride	10.14
M-3	MCW (1954)	dried in vacuo- $\frac{1}{2}$ hr-100°C-deg.	ether	10.08
M-3	MCW (1954)	dried in vacuo- $\frac{1}{2}$ hr-100°C-deg.	water	10.10
M-3	MCW (1954)--compacts sintered at 1750°C	degassed for 1 hour	helium	10.44
M-4	MCW (1954)--compacts sintered at 1750°C	degassed	mercury	8.41

TABLE XXXII

<u>No.</u>	<u>UO₂ Source</u>	<u>Enrichment</u>	<u>Method of Fabrication</u>	<u>Density</u>	<u>Flux</u>	<u>Exposure</u>
6	fused MCW	natural	hydrostatically pressed & sintered	95%	3×10^{14} nv	15 wks

The specimens were 0.343 in. OD x $2\frac{1}{2}$ in. long. The center temperature was estimated to be 1,100°C and the Zr-UO₂ interface temperature, 500°C.

TABLE XXXIII

<u>No.</u>	<u>UO₂ Source</u>	<u>Enrichment</u>	<u>Method of Fabrication</u>	<u>Density</u>	<u>Diameter</u>	<u>Burnup</u>
4	MCW	natural	cold pressed	75%	0.576 in OD	1000 MWD/T
4	S.O.	natural	cold pressed	80%	0.460 in OD	1000 MWD/T
4	S.O.	5.5%	cold pressed	80%	0.458 in OD	7000 MWD/T

TABLE XXXIV

<u>No.</u>	<u>UO₂ Source</u>	<u>Enrichment</u>	<u>Method of Fabrication</u>	<u>Density</u>	<u>Diameter</u>	<u>Burnup</u>
4	S. O.	5.5%	cold pressed	80	0.500 in.	
4	MCW	natural	cold pressed	75	0.434 in.	

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TABLE XXXV

<u>No.</u>	<u>UO₂ Source</u>	<u>Method of Fabrication</u>	<u>Density</u>	<u>Diam.</u>	<u>Flux</u>	<u>Exposure</u>	<u>MWD/T Burnup</u>
2	natural MCW	hot pressed	90%	0.400 in.	3×10^{14} nv	50 wks	20,000
2	natural steam ox.	hot pressed	90%	0.400 in.	3×10^{14} nv	50 wks	20,000
2	natural MCW	hot pressed	90%	0.400 in	3×10^{14} nv	15 wks	5,000
2	natural steam ox.	hot pressed	90%	0.400 in	3×10^{14} nv	15 wks	5,000

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TABLE XXXVI

<u>No.</u>	<u>UO₂ Source</u>	<u>Method of Fabrication</u>	<u>Density</u>	<u>Defect Size</u>	<u>Specimen Dimensions</u>	<u>Flux</u>	<u>No. of Cycles</u>
3	MCW	cold pressed and sintered	90%	5 mil	0.344in.OD x 3 in. long	5×10^{13} nv	40
3	MCW	cold pressed and sintered	90%	5 mil	0.344 in.OD x 3 in. long	5×10^{13} nv	40
3	MCW	cold pressed and sintered	90%	10 mil	0.344in.OD x 3 in. long	1×10^{14} nv	40
3	MCW	cold pressed and sintered	90%	10 mil	0.344in.OD x 3 in. long	1×10^{14} nv	40

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TABLE XXXVII

<u>No.</u>	<u>UO₂ Source</u>	<u>Fabrication</u>	<u>Density</u>	<u>Specimen Dimensions</u>	<u>Flux</u>
1	MCW	hot pressed	81%	0.345 in. diam. x 5 in.	3×10^{14} nv
1	MCW	cold pressed and sintered	92%	0.345 in. diam. x 5 in.	3×10^{14} nv
2	steam oxidized				
2	steam oxidized	cold pressed and sintered	90%	0.345 in. diam. x 5 in.	3×10^{14} nv

TABLE XXXVIII

<u>No.</u>	<u>UO₂ Source</u>	<u>Enrichment</u>	<u>Fabrication</u>	<u>Density</u>	<u>Defect</u>	<u>Flux</u>
2	steam oxidized	6.1%	hot pressed	80%	5 mil hole	2×10^{13} nv
2	steam oxidized	6.1%	hot pressed	80%	none	2×10^{13} nv

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TABLE XXXIX

<u>No.</u>	<u>UO₂ Source</u>	<u>Enrichment</u>	<u>Method of Fabrication</u>	<u>Density</u>	<u>Defect</u>
2	MCW	natural	hydrostatically pressed	90%	none
1	steam oxi-dized	4.7%	cold pressed and sintered	89%	5 mil hole
1	steam oxi-dized	natural	cold pressed and sintered	89%	none
2	MCW	natural	cold pressed and sintered	92%	none
2	steam oxi-dized	natural	hot pressed	93%	none
1	steam oxi-dized	4.7%	hot pressed	93%	none
1	steam oxi-dized	4.7%	cold pressed and sintered	89%	none

Fig. 1 J 875
Extruded clad at 1600°F

Fig. 2 J 875
Extruded Unclad at 1900°F

Fig. 3 Mo2Cl-16
Extruded clad at 1585°F

Fig. 4 MM431
Extruded Unclad at 1935°F

Effect of Extrusion Temperature on Homogeneity of U-12 Mo Extrusions

Fig. 5 Total Hydrogen as a Function of Total Corrosion for Various Induction Melted Chill Cast Alloys

Diamond Pyramid Hardness - 30 kg Load

Fig. 6 Hardness As a Function of Total Corrosion for Various Induction Melted Chill Cast Alloys

a. As cast
250X

b. 7 days
650°F Water
250X

Fig. 7 Induction Melted Chill Cast U-12 w/o Mo
a. As cast and b. after 7 days in 650°F water

a. As homogenized
250X

b. Homogenized
plus 7 days
in 650°F Water
250X

Fig. 8 Induction Melted chill cast U-12 w/o Mo a. As homogenized
and b. Homogenized and corrosion tested 7 days in 650°F water

- a. Extruded, annealed at 900°C
 -24 hr-W.Q., then 28 days
 corrosion in 650°F water.
 Pre-Corrosion DPH - 318
 Post-Corrosion DPH - 396
 Corrosion (mg/cm²) - 290

250X

- b. Extruded, annealed at
 900 C-24 hr-W.Q. + 400°C
 - 5 wks-W.Q., then 28 days
 corrosion in 650°F water
 Pre-Corrosion DPH - 458
 Post-Corrosion DPH - 491
 Corrosion (mg/cm²) - 55

250X

Fig. 9 Hydride Formation in Unclad Corrosion Samples of U-12 Mo
 Annealed at Low Temperatures

a. Transverse cross-section
of stress sample

20X

b. Compression side
hydride formation

150X

c. Tension side
hydride formation

150X

Fig. 10 Microstructure of fractured stress specimen after 5 days corrosion at 650°F water

THE INFLUENCE OF ADDITIONS TO THE WATER ON THE
CORROSION PROPERTIES OF U-12 MO IN 650°F DE-
GASSED WATER

Fig. 11

The Influence of Additions to the Water on the
Hydrogen Content of U-12 Mo in 650°F Degassed Water

Fig. 12

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The Influence of Additions to the Water on
the Hardness Properties of U-12 Mo in
650°F Degassed Water.

Fig. 13

Fig. 15 Cathodic Polarization Curves for Unalloyed Uranium in Buffered Phosphate Solution

Back-up material oxide

U-Mo sample

500X

Fig. 14 An as-mechanically polished section of a corrosion tested specimen showing an oxide finger penetrating in from the surface.

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Fig. 15 Cathodic Polarization Curves for Unalloyed Uranium in Buffered Phosphate Solution

Potential - Volts vs. S.C.E.

Fig. 16 Cathodic Polarization Curves for U-12 w/o Mo as a Function of pH and surface condition.

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Fig. 17 Cathodic Polarization curves for an Induction Melted Chill Cast U-12 w/o Mo Alloy in a Buffered Phosphate Solution

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Fig. 18 Cathodic Polarization Curves for Various Uranium Alloys in Buffered Phosphate Solution

Fig. 19 Cathodic Polarization Curves for a Platinized U-12 w/o Mo Alloy
in Buffered Phosphate Solution

URANIUM-MOLYBDENUM

Fig. 20

Δ = ALPHA + EPSILON
 ▽ = ALPHA + GAMMA
 ○ = GAMMA
 □ = EPSILON

+ = GAMMA + EPSILON
 ◇ = EPSILON + MOLYBDENUM
 ⊙ = GAMMA + MOLYBDENUM

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1634B-1-1

Mo3a2-4-A

Fig. 21 a. As-extruded U-10 Nb Longitudinal view
250X

1634B-1-2

Fig. 21 b. Transverse view
250X

1634B-2-1

Fig. 22 a. Extruded plus gamma quenched U-10 Nb
Longitudinal view
250X

1634B-2-2

Fig. 22 b. S
250X polarized light

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WAPD-PMM-238

1634B-3-1

Fig. 22 c. 400°C for 7 days

250X

1634B-4-1

Fig. 22 d. 400°C for 21 days

250X

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1635B-1-2

Fig. 22 e. 500°C for 2 days
250X polarized light

1635B-2-1

Fig. 22 f. 500°C for 7 days
250X

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Mo3A2-1-14 A(3)

Fig. 23 Cold drawn U-10 Nb corrosion
tested for one day in 650°F H₂O
250X

a. Corrosion at Defect
75X

b. Diffusion Zone
Corrosion
250X

c. Diffusion Zone
Corrosion
250X

Fig. 24 Microstructure of Heat Treated 10 Nb Alloy at the Clad Defect after 28 days of Corrosion in 650°F Water

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Fig. 25 - Total Corrosion vs Test Time for Cold Drawn U-12Mo Bare Samples Annealed at 900°C for Various Times.

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