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IN REACTOR PERFORMANCE OF DEFECTED ZIRCALOY-CLAD U_3Si FUEL ELEMENTS IN PRESSURIZED AND BOILING WATER COOLANTS

Exp-NRX-61607

by

M. A. FERADAY, G. M. ALLISON, J. F. R. AMBLER,

G. H. CHALDER and J. J. LIPSETT

Chalk River, Ontario

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Performance en réacteur d'éléments combustibles (U_3Si gainé de zircaloy) rendus défectueux et exposés à deux types de caloporteurs (eau pressurisée et eau bouillante)

par M.A. Feraday, G.M. Allison, J.F.R. Ambler, G.H. Chalder et J.J. Lipsett

Résumé - Dans un premier essai un élément précédemment irradié (~ 5300 MWd/tonne U) a été rendu défectueux puis il a été exposé d'abord à de l'eau pressurisée puis à de l'eau bouillante à ~ 270°C. Dans un second essai, un élément non irradié contenant un vide central a été disloqué et saturé avant d'être exposé à de l'eau pressurisée pendant 50 minutes. On a dû mettre rapidement fin aux deux essais par suite de la forte activité décelée dans le caloporteur de la boucle par un détecteur gamma et un détecteur de neutrons retardés.

L'examen post-irradiation a montré que les deux éléments ont subi d'importantes ruptures de gaine expliquées par l'augmentation de volume résultant de la formation de grandes quantités de produits de corrosion. Ces produits sont dus à la réaction de l'eau avec la partie centrale chaude du combustible.

La conclusion est que la résistance à la corrosion de l'U_3Si à 300°C n'est pas sérieusement modifié e par l'irradiation. Cependant, la vitesse de la corrosion augmente rapidement quand la température s'élève.

Chalk River, Ontario
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SYNOPSIS

The results of two in-reactor defect tests of Zircaloy-clad U_3Si are reported.

In the first test, a previously irradiated element (~5300 MWd/tonne U) was defected then exposed to first pressurized water then boiling water at ~270°C. In the second test, an unirradiated element containing a central void was defected, waterlogged, then exposed to pressurized water for 50 minutes. Both tests were terminated because of high activity in the loop coolant detected by both gamma and delayed neutron monitors.

Post-irradiation examination showed that both elements had suffered major sheath failures which were attributed to the volume increase accompanying the formation of large quantities of corrosion product formed by the reaction of water with the hot central part of the fuel.

It was concluded that the corrosion resistance of U_3Si at 300°C is not seriously affected by irradiation, but the corrosion rate increases rapidly with temperature.

Fuel Materials Branch
Chalk River Nuclear Laboratories
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1. INTRODUCTION

The delta phase of the uranium-silicon system (U_3Si) is attractive as a nuclear fuel because of its high uranium density, low parasitic absorption and good aqueous corrosion resistance. U_3Si is being developed for use in CANDU-type reactors fuelled with natural uranium and cooled by pressurized water or boiling water because of expected reductions in unit energy costs[1].

Confidence in the good aqueous corrosion resistance of U_3Si is based on out-reactor tests in 300-350°C water both on unirradiated U_3Si and on specimens irradiated to burnups between 1000-4000 MWd/tonne U[2]. Although no deliberate in-reactor defect tests have previously been done on U_3Si, two Zircaloy clad elements containing solid rods of U_3Si (1200 MWd/tonne U) operated in-reactor for up to three days in 265°C water after splits developed in their sheaths (see section 5)[3]. From these results it was concluded that the corrosion resistance of U_3Si was not seriously affected by irradiation[3].

Recent irradiation tests have shown that provision of an internal void in U_3Si fuel elements was effective in reducing sheath strain, compared to earlier tests[4]. The central void would be progressively filled during irradiation, but in the event of a sheath defect early in the life of the fuel element, the presence of residual voidage in the fuel raises the possibility of coolant reaching the hotter (~500°C) central region of the fuel-causing enhanced corrosion. Alternatively, water-logging (i.e., the central void filling with water) during a shutdown could cause enhanced corrosion and/or high internal pressures as the fuel temperature rises during the subsequent rise to power.

The two phases of the defect test described below were designed to study:

a) Phase I: the corrosion behaviour of previously irradiated (~5300 MWd/tonne U) U_3Si, clad in a defected Zircaloy sheath, in pressurized water and boiling water environments.

b) Phase II: the corrosion behaviour of an unirradiated element containing U_3Si having a central void and clad in a defected Zircaloy sheath; the element would be waterlogged before being installed in the loop.

c) Phases I and II: the type and magnitude of the activity given off by the U_3Si.

2. DESCRIPTION OF THE ELEMENTS

Figure 1 summarizes the data on elements MJK (Phase I) and APZ (Phase II).

Each element was defected with a 0.8 mm diameter hole at the locations shown in Figure 1. During in-cell drilling of the defect in the previously irradiated specimen MJK, two 0.8 mm diameter holes ~0.5 mm apart were accidentally started. The downstream or lower hole was subsequently drilled right through the sheath and into the U_3Si to a total depth of 1.5 mm[5]. The fuel for this element consisted of two enriched U_3Si fuel rods (Figure 1) each of which originally contained a nominal 7 vol% central void; based on destructive examination of similar elements, these voids are assumed to have been filled in by irradiation induced swelling of the U_3Si during the earlier irradiation[4].

No difficulty was experienced in drilling through the sheath of the unirradiated element, APZ. The fuel for this element consisted of two enriched U_3Si rods between two natural U_3Si flux suppressors, all of which contained a nominal 7 vol% central void (Figure 1).

3. IRRADIATION OF THE ELEMENTS

3.1 Phase I

Specimen MJK was irradiated at a calculated power output of 700 W/cm. After 17 equivalent full power days operation

(seven in pressurized water at 260°C and ten in boiling water at 280°C), MJK was removed from the loop for underwater examination of the defect hole. After an 11-day period of underwater storage in the NRX trench, the specimen was re-installed in the loop in pressurized water, but after a further five hours' operation at a fuel power ranging up to 550 W/cm, it was removed because of high gamma and DN monitor signals (Figures 2 and 3).

3.2 Phase II

After defecting and prior to irradiation, element APZ was water-logged by autoclaving for one day in 260°C water. The water content of the element was measured as 2.3 grams indicating that the void was full. The irradiation test in 260°C pressurized water was terminated after about 50 minutes at fuel powers ranging up to 550 W/cm because of high signals in both the gamma and DN monitors (Figure 4).

4. RESULTS

4.1 Power Output

The fuel power outputs shown in Figure 1 for elements MJK and APZ were derived from the measured power output of a similar element previously irradiated in this loop[6].

4.2 Temperature Distribution in the Fuel

The fuel central temperatures shown in Figures 3 and 4 were calculated using:

a) a constant fuel/sheath heat transfer coefficient of 5 $W/cm^2°C$ for previously irradiated element MJK and 1.2 $W/cm^2°C$ for the new element, APZ.

b) a water/sheath film coefficient of 5.5 $W/cm^2°C$

c) an average thermal conductivity of 0.2 W/cm°C for the U_3Si[4]

d) heat generation in the fuel of 182 MeV/fission.

4.3 Monitor Data

Continuous gross gamma and delayed neutron (DN) monitoring of the loop coolant was provided during both phases of the test.

Phase I: During the first period of exposure of pre-irradiated specimen MJK (3-20 March), no significant change in gamma signal from the defect was noted (Table 1); but the DN monitor registered a significant increase during the last two days of the test (Figure 2). The magnitude of the DN signal immediately prior to shutdown was calculated to correspond to the activity released by recoil from 0.23 cm^2 of fuel exposed to the coolant.

Element MJK was re-inserted in the loop for a second period of exposure, but failed during the first reactor startup on March 31. During the first stages of this startup, both monitors indicated signals which were slightly higher (Figure 3) than at the end of the first test of MJK, and these rose slowly during the period 2000 hrs to 2130 hrs. During the subsequent power increase to 30 MW, both monitor signals increased rapidly to values indicating a major failure. The delayed neutron signal at 2400 hrs corresponded to a recoil source equivalent to 25 cm^2 of U_3Si. After the reactor shutdown the gamma activity in the coolant decreased steadily and had returned to background (600 cpm) within six hours, due to decay and clean-up.

Phase II: During the Phase II test on element APZ (21 March) the gamma and DN signals (Figure 4) rose sharply shortly after reactor startup. At about 2129 hours when the power was raised from 13 to 23 MW, the DN monitor signal dropped to the background level, suggesting that the defect hole had become blocked. About 20 minutes later, when the reactor power was raised from 23 to 30 MW, both the gamma and DN monitor signals rose very rapidly, following which the reactor was shut down. The gamma activity fell from a high of 2×10^5 cpm to about 1.4×10^4 cpm eight hours after shutdown, due to decay and clean-up.

The radiation field on the unibolt fitting at the top of the loop test section was as high as 50 Roentgen/hour during both tests, but dropped to less than 5 Roentgen/hour within a few minutes of the reactor being shut down.

4.4 Chemical and Radiochemical Results

Although some difficulty was experienced in maintaining the pH control during the first three days of Phase I (MJK), the prescribed ammonia concentration of 12 mg/kg was maintained for the balance of both phases (Appendix A).

The radiochemical results from both tests are summarized in Table 2 and are discussed in detail in Appendix A. The measured production rate of Kr-88 and I-133 within the test section coolant during the first part of Phase I indicate that the defect in element MJK started to enlarge between 14-16 March. No quantitative radiochemical results were made during the second test on MJK (31 March), but gamma spectra of loop coolant samples indicated that, unlike failures in UO_2 fuel, the fission gases and iodines with half-lives greater than two hours did not dominate the spectra.

No quantitative radiochemical measurements were made during the Phase II of the test (APZ), however the comments regarding the gamma spectra on the loop water in the test on MJK also apply for this test.

Two methods of measuring the uranium released from the defects are discussed in Appendix A. The results are inconclusive in that they cannot be used with any certainty to estimate even minimum amounts of fuel released from the U_3Si failures, but they do indicate that some release did occur. If it is assumed that the uranium which moved was from the U_3Si failures, this would indicate that at least 80 mg of U_3Si had been released. This is a risky assumption since the loop had also been contaminated in the past from UO_2 failures.

4.5 Macro-examination

Phase I

Underwater examination of element MJK after the first three-week exposure (i.e., Part I of Phase I) showed that a slight split and a bulge had formed in the sheath of the original defect hole (Figure 5). Trench examination of MJK following its second period of exposure (i.e., Part 2 of Phase I) which lasted five hours, confirmed the conclusion drawn from the monitor results, that the element had sustained a

major failure (Figure 6). Cell examination of the unpolished cross-sections (Figure 6) showed a quantity of corrosion product in the U_3Si, which decreased in volume in the sections remote from the defect.

Phase II

Underwater examination of element APZ after 50 minutes' irradiation showed that the sheath and one enriched U_3Si rod had split open 180° from the original defect (Figure 7). Cell examination of the cut sections (Figure 7) showed that corrosion product had entirely filled the central void space in the lower of the two enriched rods and the lower half of the central void in the upper enriched rod. Less corrosion product was seen in the top half of the upper enriched rod and in the void of the top end flux suppresor.

Although precise diameter measurements could not be made, measurements taken from photographs indicated diameter increases at the rupture of 4-6 mm in both elements.

4.6 Metallographic Examination

General

Three transverse sections from element MJK (Phase I) and two from element APZ (Phase II) were prepared and examined in both the etched[7] and unetched conditions. Features observed are shown in Figures 8-19 (MJK) and Figures 20-29 (APZ). No U_3Si grain boundaries could be revealed in any of the five sections examined.

The average hydride content in the Zircaloy sheath from element MJK (Figure 8a) is estimated to be 50-100 ppm and is not much higher than in an unirradiated archive specimen (Figure 8b). Generally the hydride was randomly oriented. There was a small area (from section 2 of Figure 6) where a concentration of radial hydride was seen at the outside diameter together with a possible hydride layer on the inside diameter of the sheath (Figure 8c).

There was no apparent increase in hydrogen content of the Zircaloy sheath of element APZ on irradiation.

U_3Si - Element MJK

Examination of section 1, through the original drilled defect, showed a star-shaped area of corrosion about the center of the fuel (Figure 9). There were cracks from the ends of the star arms to the fuel-sheath interface. The fuel element had split open longitudinally along the arm of the corrosion star immediately under the drilled defect. Corrosion on the fuel periphery was limited to a small area directly under the drilled defect and where the corrosion product was a maximum of 5 microns in thickness (Figure 10). Most of the fuel was in tight contact with the sheath and no corrosion product was seen at the interface (Figure 11).

In section 1, the U_3Si adjacent to the main corrosion fronts was darker in both its as-polished and as-etched condition than the bulk of the U_3Si (Figure 12) and had a "spotty" appearance (Figure 13). For the sake of convenience this constituent was called phase "X". The U_3Si_2 within the "X" phase was heavily cracked. In some areas there were filaments of a white phase (other than U_3Si_2) penetrating into the "X" Phase (Figure 13) while in other areas the same white phase was present as a layer between the "X" phase and the final corrosion product (Figure 14). Remote from the corrosion front, the final corrosion product contained particles consisting of the "X" phase and the white phase (Figure 15). The percentage of the white phase decreased near the corrosion front, while remote from it, at the center of the corroded area, the particles contained no "X" phase (Figure 16).

In section 2 (Figure 17), there was a diametral crack through the fuel from the sheath split, and an area 6.5 mm in diameter in the center of the fuel which etched lighter than the bulk of the U_3Si. As in section 1 the fuel was in tight contact with the sheath. At the center, the U_3Si along the sides of the cracks appeared darker than in the bulk of the fuel (Figure 18). This was similar to the "X" phase seen in section 1, and within it the U_3Si_2 was heavily cracked.

In section 3 (Figure 19) there was a partial diametral crack, and a light etching area similar in appearance and size to that seen in section 2 (Figure 17). There was tight contact between the fuel and the sheath. The appearance of this section was similar to that of undefected fuel elements irradiated to a similar burnup, in which the central void has been completely filled[4].

U_3Si - Element APZ

Examination of section 4 (Figure 20) showed a star-shaped corrosion area similar to that in fuel element MJK, the corrosion product having completely filled in the central void. There was also a corrosion layer on the outer diameter (O.D.) of the U_3Si, the maximum thickness of which was 80 microns (Figure 21).

Under the corrosion product on the O.D. of the fuel, there was a layer of white phase, and some of the U_3Si around the U_3Si_2 particles near the corrosion front was darker than the bulk of the U_3Si (Figure 22).

The same white phase seen in MJK was present as a broken ring within the final corrosion product at the center of the fuel (Figures 20 and 23). From its position, it seems probable that the ring had been formed on the surface of the central void originally present in the fuel, but it is uncertain how the corrosion product got inside the ring without breaking it up. The white phase was also present at the corrosion front (Figure 24). Also present at the corrosion front was a dark band similar in appearance to the "X" phase seen in fuel element MJK. Some of the U_3Si_2 particles ahead of the corrosion front had the dark phase associated with them in a similar manner to those seen near the corrosion front on the fuel O.D. On etching, the dark band was seen to consist of two phases (Figure 25). The darker of the two phases was called "X_1", and the other "X_2". The "X_1" phase was the one associated with the U_3Si_2 particles ahead of the main corrosion front. There were cracks in the "X_2" phase and in the U_2Si_2 in it. Within the final corrosion product there were particles consisting of the white phase and the "X_2" phase (Figure 25).

In section 5 (Figure 26) there was again corrosion both at the center and at the O.D. of the fuel. The corrosion products at the fuel O.D. showed the same features as were seen in section 4. The central corrosion area was circular in shape (Figure 26), and the same phases were present as in section 4. However the "X_2" phase was present as a thick (1.5 mm) layer (Figure 27). There was heavy circumferential cracking of the "X_2" phase itself and of the U_3Si_2 particles within it (Figure 28). At the interface of the "X_2" phase with the main corrosion product there was a layer of the

white phase. Within the main corrosion product there were particles consisting of the white phase and the "X_2" phase (Figure 29).

5. DISCUSSION

At least one of the two ruptured U_3Si elements irradiated by Howe[3] remained at power (750 W/cm length) for about 3 days following the detection of a failure by a rising signal from the gamma monitor. Post-irradiation examination showed that the defects in both his elements had not propagated as much as those in the present test in which the elements were exposed for shorter times following detection. In Howe's elements, which were fabricated by co-extrusion, the Zircaloy cladding was bonded to the solid (i.e. no central void) U_3Si core[3].

Metallographic examination of elements similar to MJK, after irradiations ranging from 1600 to 8400 MWd/tonne U, showed that the central voids were filled in, the U_3Si was cracked, and the fuel and sheath were in intimate contact and probably bonded[4]. Metallographic examination of element MJK after the present test showed that the sheath was bonded to the fuel; we have therefore assumed that MJK was in this condition at the start of the defect test. This fuel sheath bond restricted corrosion at the fuel O.D. to the area immediately under the defect, gross corrosion and swelling only occurred where the coolant gained access to the center of the fuel. In fuel element APZ, where there was no bond between the sheath and fuel, there was considerable corrosion at the O.D. of the fuel.

No comparison in defect behaviour can be made between Howe's elements and the fresh element APZ of the present test since the fuel and sheath of APZ were unbonded, permitting free access of water to the hottest parts of the fuel surrounding the central void. However a valid comparison is possible between Howe's elements and previously irradiated element MJK of the present test since both contained solid U_3Si rods bonded to the Zircaloy sheath[3,4].

Results from the Phase I test are consistent with the following suggested failure mechanism in element MJK. During the first 17 day test, the bonded sheath confined attack to that U_3Si immediately under the sheath defect. Thus the

amount of corrosion product formed was small and little or no activity was released to the loop. The increase in production of I-133 and Kr-88 (Table 2) during the first three-week irradiation of specimen MJK suggests that there was an increase in the surface area of uranium exposed from which fission products could escape to the coolant. This increasing trend from about 14 March was also noted on the DN monitor. At the end of the period, enough corrosion product had formed to cause a small bump and a split in the sheath (Figure 5). During the eleven-day period of under-water storage between the two parts of the test, the element cooled sufficiently for water to be expected to penetrate along cracks in the fuel. No such long shutdown occurred in Howe's elements following the defect. Expansion of this water, or the corrosion product formed from it, caused the sheath to split early in the second part of the test. Penetration of water or steam to the hotter central fuel region then resulted in a high corrosion rate and the large volume increase of the corrosion product caused further crack propagation in the fuel and sheath (Figure 6). The split in the fuel and sheath reached its final size when sufficient water had entered the element to lower the fuel temperature and thus the corrosion rate, leading to the reduced slope of the monitor signals near the end of the test (Figure 3).

New element APZ differed from MJK in that the central void was still present (and filled with water), and the sheath was not in close contact with the fuel. The following suggested failure mechanism of element APZ during Phase II of the test is consistent with the monitor data (Figure 4) and metallographic results. For the first 15 minutes following reactor startup, water was forced out of the defect hole as a result of the change in specific volume of the water and/or the formation of steam. During this period, the calculated central temperature surpassed the saturation temperature of the coolant at the loop pressure of 95 bars ($T_{sat} \approx 308°C$) and all the water inside the central void turned to steam. After about 15 minutes, probably when the reactor power was raised from 13 to 23 MW, the defect hole became blocked and as a result the DN monitor signal dropped to background level. It appears likely that the defect hole was blocked by corrosion product since calculations of differential thermal expansion indicate that the fuel and sheath would not have come into complete contact at this

stage. During the following 20 minutes, the increasingly superheated steam caused considerable further corrosion of the U_3Si. Final failure of the fuel cylinder and sheath resulted either from the build-up of corrosion product and/or high internal pressure of steam in the void. Further corrosion of the U_3Si continued until the reactor was shut down 15 minutes later. It appears possible that corrosion product hydrogen and other gases released as the water in the void flashed to steam were trapped in the upper end of the split element thus preventing water from rising, and may be the cause of the reduced corrosion in this area (see Figure 7).

The major defects which developed in these elements (i.e. part 2 of Phase I and Phase II) were clearly indicated by the gamma and DN monitors shortly after reactor startup. We have estimated from monitoring data that exposure to the coolant of an area of 25 cm^2 of fuel for MJK and 60 cm^2 for APZ had occurred in each element. This was confirmed by examination of photomicrographs of element MJK which indicated that about 17 cm^2 of U_3Si were exposed to the coolant at the end of the test; the remainder of the recoils probably came from the corrosion product surface exposed to the coolant. The calculated free surface of U_3Si in element APZ was about 85 cm^2, indicating that about three-quarters of the surface was freely accessible to the coolant.

Although a recognizable DN monitor signal was obtained in the X-6 loop during the first part of the Phase I test (MJK), such a signal would probably not be recognizable in a power reactor such as BLW-500. We have calculated that a recognizable DN monitor signal (i.e. twice background) should be obtained from about 1.5 cm^2 of exposed natural U_3Si in BLW-500 when the reactor has the minimum surface uranium contamination (1.5×10^{-8} gU/cm^2). This corresponds to a much less severe failure than those experienced in these loop tests (25 & 60 cm^2 exposed fuel). In the X-6 loop, we estimate that 1.5 cm^2 of enriched (1.8 wt% U^{235} in U) fuel exposed should give a DN monitor signal of about 1650 cps. If the DN monitor curve recorded during Phase I had continued on at the same exponential slope, this signal (1650 cps) would have occurred with four more days operation after the shutdown on the 20 March (Figure 2).

In comparison with the defect behaviour of Howe's elements, it appears as if the reactor shutdown after part 1 of Phase I (MJK) occurred at a critical time. The 11 day cooling period for element MJK just prior to part 2 of Phase I appears to be the significant fact in explaining the rapid propagation of the defect during the second startup. Had the prolonged shutdown not occurred, it appears likely that slow propagation of the defect in MJK would have continued, giving an increased and fully recognizable monitor signal, before a major sheath split occurred.

The implication from both phases of this test (and from Howe's earlier results) is that a defect which occurs during irradiation of a U_3Si fuel element will not have serious effects so long as the reactor continues operation. Should an extended shutdown occur, or should a defect be present in a freshly installed fuel element, ingress of water into the element will increase the speed of failure. The amount of water which enters the element will probably dictate the speed of failure, and this can be markedly reduced in fresh fuel by employing a bonded sheath and/or sealing the void volume present in the element. Should extensive cracking of U_3Si under irradiation be inevitable, there would always be the possibility of some water-logging in a defected element subjected to an extended shutdown, even if sheath and fuel were bonded, as in MJK.

Should water-logging of a defected element occur, the extent of failure on subsequent reactor startup can be minimized by reducing the rate of power application to the fuel. A clearly recognizable signal was obtained from the water-logged element APZ in the present test at <15% of full power. The size of the defect corresponding to this signal is not known, but would be significantly less than that which ultimately developed at full power. Thus, immediate shutdown of the reactor and/or removal of fuel defects detected at less than 15% power on startup, would probably avoid serious failure even in water-logged elements.

The test performed on APZ, i.e. deliberate water-logging of a large internal void volume, followed by rapid power application, represents the worst case in regards of possible fuel failures. Although major sheath splits occurred, the activity released to the coolant decreased rapidly following reactor shutdown. While a reliable measurement of uranium release is not possible, for the reasons given in Appendix A, it appears to be of the order of tens to hundreds of milligrams. The quantity of uranium, deposited in the primary

system of a large reactor, which would interfere with monitoring of fresh defects, has been estimated to be of the order of 10 g[8]. Thus the occurrence of an occasional failure corresponding to that in APZ, while inconvenient, would not be a major disaster.

The results of this test show that irradiation does not appreciably affect the corrosion rate of U_3Si at a temperature near 300°C, i.e. at fuel surface, (about 0.2 mg/cm^2 h) but demonstrates, that as expected, the corrosion rate increases with temperature. Using section B of Figure 7 to represent the maximum amount of corrosion found, and assuming that all the U_3Si inside the corrosion front has been consumed, we calculate an average corrosion rate at a mean temperature of 500°C as 6×10^3 mg/cm^2/h. No laboratory results are available under these conditions for comparison. It should be noted that for corrosion at the center of a fuel element the temperature of the corrosion front progressively <u>decreases</u>, since heat is being extracted through the relatively unaffected outer surface.

The metallographic examination of the elements MJK and APZ shows that the corrosion reaction for U_3Si and water, or steam, is a highly complicated one. Although it is impossible to give a detailed explanation of the corrosion mechanism, a number of features are apparent. Firstly, corrosion in both elements involved the formation of intermediate phases before the final corrosion products. Secondly, the number of these phases was not the same in the two fuel elements. One phase which was common to the corroded areas in both fuels was the white phase. This was always seen immediately adjacent to the final corrosion product and also within the final corrosion product. Work by D'Eye and Trowse[9] identified a similar phase seen in U_3Si corroded at 300°C and above in steam and water, as βUSi_2. The other intermediate phase "X", seen in the corroded areas of fuel element MJK was darker and etched more readily than U_3Si. Since the boundary between the "X" phase and the U_3Si is not a distinct line, the "X" phase may not be a separate phase but substoichiometric U_3Si, represented by the formula U_3Si_{1-x}. By similar reasoning it is the "X_1", phase in fuel element APZ which is substoichiometric U_3Si, "X_2", being a distinctly different phase since it has definite boundary with the "X_1" phase. Why this should be the major phase formed by corrosion in the sections of fuel element APZ from positions remote from the defect is not apparent.

Much of the preceding paragraph is supposition and necessarily so since there has been no thorough investigation of the corrosion reactions taking place out-reactor between U_3Si and water or steam at temperatures comparable to those at the center of the fuel during irradiation. Since this information is lacking it is not possible to account for the differences in corrosion behaviour of the two fuel elements.

In none of the specimens examined was there evidence to indicate that corrosion of the U_3Si causes a marked hydrogen pick up by the Zircaloy sheath.

6. CONCLUSIONS

1. The major sheath failures in both elements (MJK and APZ) resulted from internal pressures caused by the build-up of corrosion products in the hottest part of the fuel; build-up of steam pressure in element APZ may also have been a contributing factor in the failure.

2. The ingress of water into cracks in the fuel in element MJK during an 11-day underwater cooling period was the cause of the rapid propagation of the defect in this element on re-irradiation.

3. The corrosion resistance of U_3Si at 300°C is not seriously affected by irradiation but the corrosion rate increases rapidly with temperature.

4. The corrosion reaction for U_3Si and high temperature water/steam is a highly complicated one, in which intermediate corrosion products are formed.

5. U_3Si is capable of giving off strong gamma and DN monitor signals from fission products which have a short half life.

6. These two serious failures did not result in a large release of uranium to the loop.

7. REFERENCES

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7. Etches

   a) Murakami's reagent used to provide contrast between U_3Si and U_3Si_2 - see A. Kaufmann, B. Cullity and G. Bitsianes "Uranium-Silicon Alloys". Trans. AIME 209, p.27. January 1967.

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APPENDIX A

CHEMICAL AND RADIOCHEMICAL RESULTS

G.M. Allison

1. COOLANT CHEMISTRY

1.1 Phase I

The coolant was to contain 10-12 mg NH_3/kg during both phases of the irradiation. However, during the first three days of Phase I, March 4-7, 1967 (element MJK), the ammonia concentration in the pressurized-water coolant varied from 100 to 1800 mg/kg because of a malfunction of the ammonia-addition equipment. Good ammonia control was maintained for the remainder of this phase (March 7-20). During the second period that element MJK was in the loop (five hours on March 31, 1967) the ammonia concentration was the prescribed 12 mg/kg.

For several hours prior to the reactor startup in Phase I (3 March) the loop water was degassed in order that hydrogen production could be followed when the irradiation began. During reactor operation with the loop in the pressurized-water mode degassing cannot be done conveniently or efficiently, so gases produced by radiolysis of ammonia were allowed to build up to an equilibrium level. After four hours' irradiation, the H_2 and N_2 concentrations at the test section inlet had reached 10 and 3 cm^3/kg respectively; the equilibrium concentrations appeared to be 18 cm^3H_2/kg and 6 cm^3N_2/kg. When the loop operated in the boiling mode the steam from the separator was degassed in the degassing condenser giving inlet H_2 concentrations between 0.5 and 1 cm^3/kg.

1.2 Phase II

The ammonia concentration at the beginning of Phase II was 28 mg/kg which would soon have decreased under irradiation to the specified 12 mg/kg. However, the irradiation was terminated after about 50 minutes due to severe failure of the defected element, APZ.

2. FISSION PRODUCT RELEASE

Fission products were present in the coolant from two sources:

1) uranium contamination on the outside of the fuel sheaths and on the pressure tube

2) the defected element itself.

An increasing fission product level would indicate propagation of the defect, i.e., an increase in the area of uranium exposed to the coolant and an easier escape path to the coolant.

2.1 Phase I

During the first part of the Phase I irradiation of element MJK, the fission product gas Kr-88 was measured regularly in the loop coolant to indicate defect propagation. For the pressurized water operation (no degassing) it was assumed that equilibrium conditions prevailed, i.e., the fission gas produced in the coolant in the test section (atoms/s) was equal to loss by radioactive decay (total disintegrations per second in the coolant). For boiling operation with efficient degassing a balance across the test section was made by measuring Kr-88 in water at the test section inlet and in water and steam from the separator at the outlet. From the disintegrations per second per gram of coolant measured and the pertinent flow rate (grams/second), the production of Kr-88 (atoms/s) in the test section coolant was calculated.

The results in Table 2 show that prior to the March 16 samples, the Kr-88 production rate was not increasing and was essentially the same as that found in the previous test without defected fuel. At some time between March 10 and 16 an increase in Kr-88 production occurred.

Radioiodine measurements were also made and a factor of two increase in I-133 production occurred between March 14 and 20. Combined with the Kr-88 data this would indicate the defect started to enlarge between March 14 and 16.

During the short second period of irradiation of element MJK on March 31 when failure occurred, no quantitative radio-

chemical measurements were made. However, gamma spectra of the loop coolant were taken with a Ge(Li) spectrometer which showed a very complex mixture of short-lived γ-emitting nuclides with more than 20 well-defined photopeaks. The very high activity in the coolant and the short irradiation time limited the work done but it was obvious that, unlike failures in UO_2 fuel, the fission gases and iodines with half-lives greater than 2 hours did not dominate the spectra.

2.2 Phase II

Defected element APZ only received about 50 minutes of irradiation before the test was terminated due to high activity release. Again no quantitative radiochemical measurements could be made and the comments regarding the failure of element MJK above also apply here.

3. URANIUM RELEASE FROM THE FAILURES

During the irradiation of the defected elements and during periods between tests when there was no fuel in the loop, the coolant was analyzed for uranium to see if any release was indicated. The uranium was determined by a fluorimetric method and the limit of detection was 2 μgU/kg of coolant. Results are given in Table 2. Significant amounts were only found after the Phase II failure. Assuming the mass of flowing water in the loop to be 110 kg, the maximum uranium indicated in the coolant was $\frac{120 \times 110}{10^3}$ or 13 mg.

Another indication of uranium release is obtained by measuring Kr-88 in the coolant during the periods after the failures when there was no fuel in the loop. Some fraction of any uranium released to the coolant will deposit on the walls of the test section and, when irradiated, will produce fission products. Kr-88 was used as a measure of this deposited uranium based on the following assumptions:

a) the uranium was spread evenly and thinly over the surface of the test section

b) one-half of the fission recoils entered the coolant

c) average thermal neutron flux = 4.5×10^{13} n/cm^2-s.

Results expressed as mg U-235 are given in Table 2. It can be seen that in subsequent fuel tests under different chemistry conditions the amount of contamination in the test section rose greatly. This was probably due to movement of uranium from out-reactor to in-reactor surfaces because of the disturbance caused by the changing chemistry. If one assumes that the uranium moved was from the U_3Si failures this would indicate that at least 80 mg of U_3Si had been released. However, this is a risky assumption since the loop had also been contaminated in the past from UO_2 failures.

These results cannot be used with any certainty to estimate even minimum amounts of fuel released from the U_3Si failures. However, they do indicate that some release did occur.

TABLE 1

GAMMA MONITOR DATA

Date	Monitor Level Gamma (cpm)	Remarks
23 February 1967	625	X-610 test in loop
3 March 1967	550	Specimen MJK (Part 1) installed
6 March 1967	600	
9 March 1967	700	
12 March 1967	650	
15 March 1967	680	
18 March 1967	650	
19 March 1967	680	
20 March 1967	680	Scheduled removal of MJK
21 March 1967	See Figure 4	Specimen APZ
31 March 1967	See Figure 3	Specimen MJK (Part 2)

TABLE 2

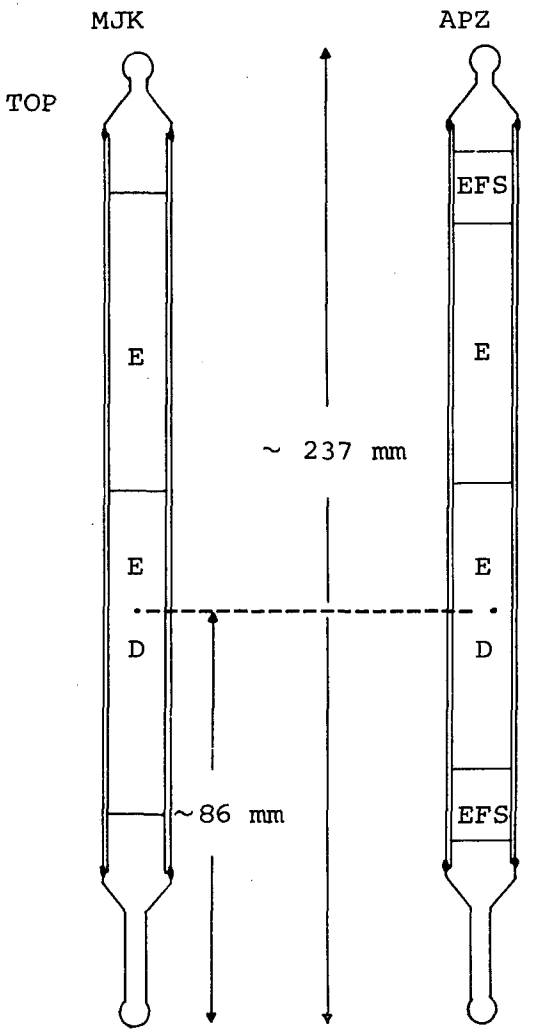
SUMMARY OF CHEMICAL AND RADIOCHEMICAL RESULTS FOR PHASES I AND II OF X-616 TEST

Date (Time)	Test	Operation Mode	Kr-88 Production Rate (atoms/sec)	Uranium Conc. in Loop Water (μg U/kg coolant)	U-235 Contamination on Test Section (mg U-235)	I-133 Production Rate (atoms/sec)
21 February	X-610	BW	2.3×10^7	--	0.02	--
3 March	X-616 Ph. I (MJK) installed	PW	--	↑	--	--
9 March	X-616 Ph. I (MJK)	PW	2.8×10^7	↑	--	--
10 March	X-616 Ph. I (MJK)	BW	2.1×10^7	<2	--	--
14 March	X-616 Ph. I (MJK)	BW	--	(six samples)	--	1.3×10^8
16 March	X-616 Ph. I (MJK)	BW	6.0×10^7	↓	--	--
20 March	X-616 Ph. I (MJK) removed	BW	6.7×10^7	↓	--	2.5×10^8
21 March	X-616 Ph. II (APZ) installed & removed	PW	--	--	--	--
21 March	No fuel	--	--	68	--	--
22 March	No fuel	--	--	120	--	--
23 March	No fuel	--	--	--	0.06	--
28 March	No fuel	--	--	<2	0.04	--
30 March	No fuel	--	--	<2	--	--
31 March (2245 hrs)	X-616 Ph. I (MJK) re-installed	PW	--	3	--	--
1 April (0108 hrs)	X-616 Ph. I (MJK)	PW	--	<2	--	--
1 April	X-616 Ph. I (MJK) removed	--	--	--	--	--
3 April	No fuel	--	--	<2	0.07	--
5 April	No fuel	--	--	<2	--	--
7 April	No fuel	--	--	--	0.05	--
17 April	X-639	PW neutral coolant	--	--	0.11	--
12 May	X-610 Ph. II	BW neutral coolant	--	--	1.5	--

BW = boiling water PW = pressurized water

Figure 1

Details of Elements MJK (Phase I) and APZ (Phase II) for X-616



		MJK	APZ
Sheath	- material	Zircaloy-2	Zircaloy-4
	- OD (mm)	15.2	15.2
	- thickness (mm)	0.72	0.63
U_3Si	- OD (mm)	13.72	13.80
	- ID (mm)	nil*	3.7
	- length (mm)	130.4	129.5
	- length with EFS (mm)	-	157.0
	- Si (wt%)	4.0	4.0
	- Carbon (ppm)	400	375
	- wt% U^{235} in U	1.8	1.8
	- Heat treatment	800°C - 3 days	800°C - 3 days
Power Output at 42 MW Reactor Power (W/cm)		700	770
Burnup (MWd/tonne U)			
	- start of test	5320	new element
	- end of test	5920	~0
Defect diameter (mm)		0.8	0.8

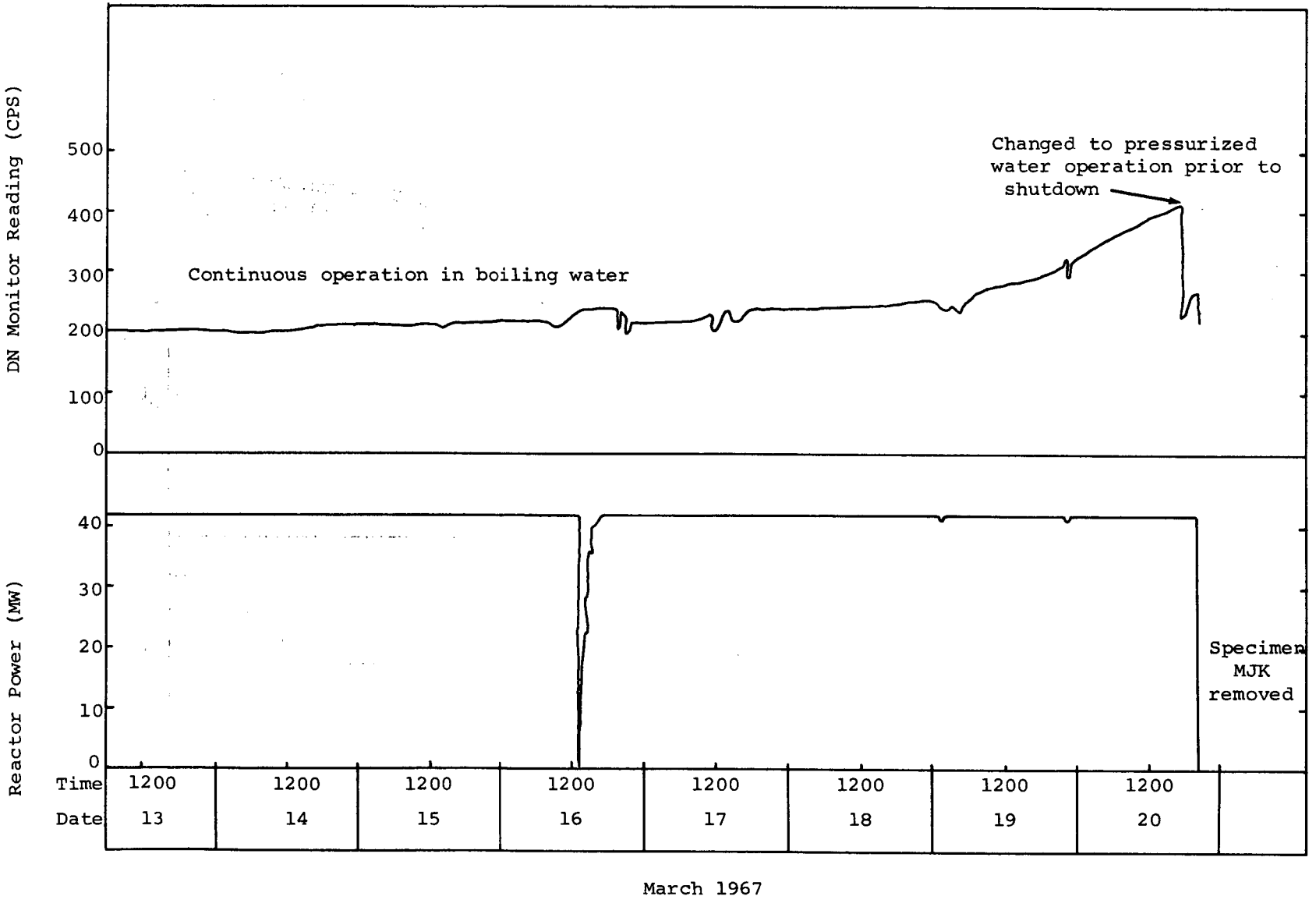
EFS = end flux suppressor of natural U_3Si

E = enriched U_3Si slug

* original void (3.5 mm dia.) entirely filled in during previous irradiation

D = defect hole

Figure 2 - NRX reactor power record and X-6 delayed neutron monitor record for 13-20 March, 1967 - Element MJK (Phase I - Part I)



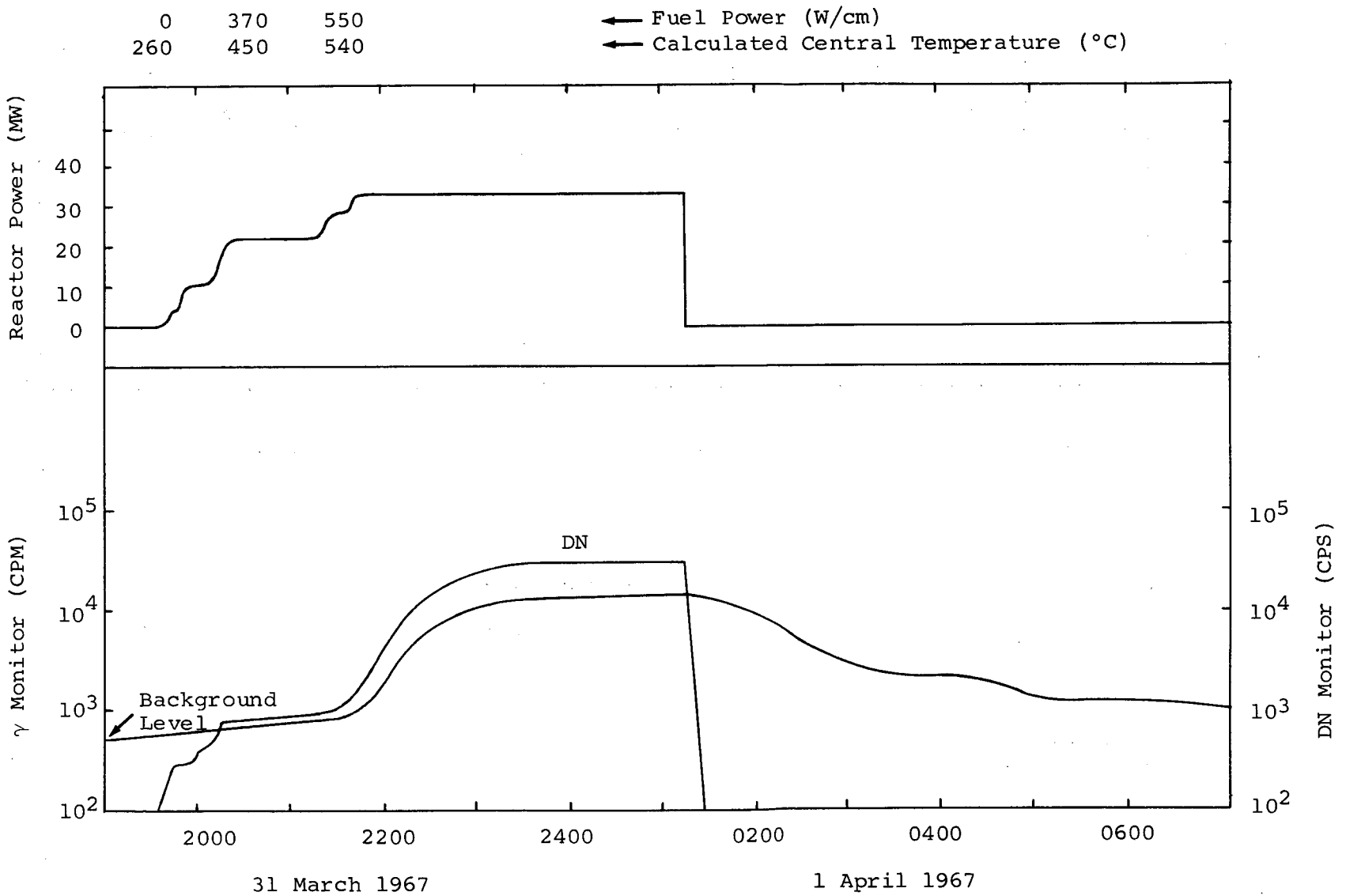


Figure 3 - Reactor power, delayed neutron and gamma monitor recordings for element MJK (Phase I, Part 2)

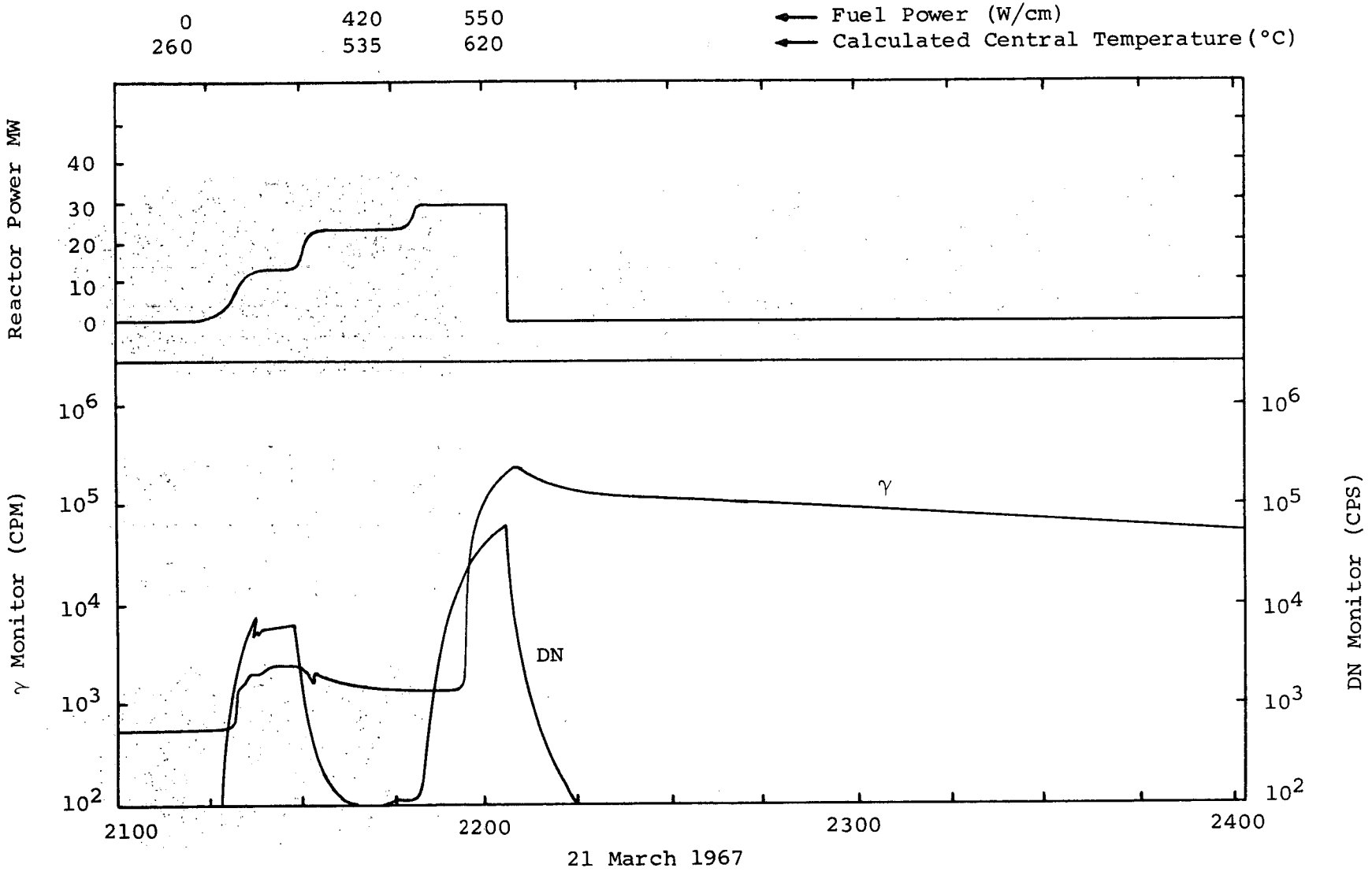
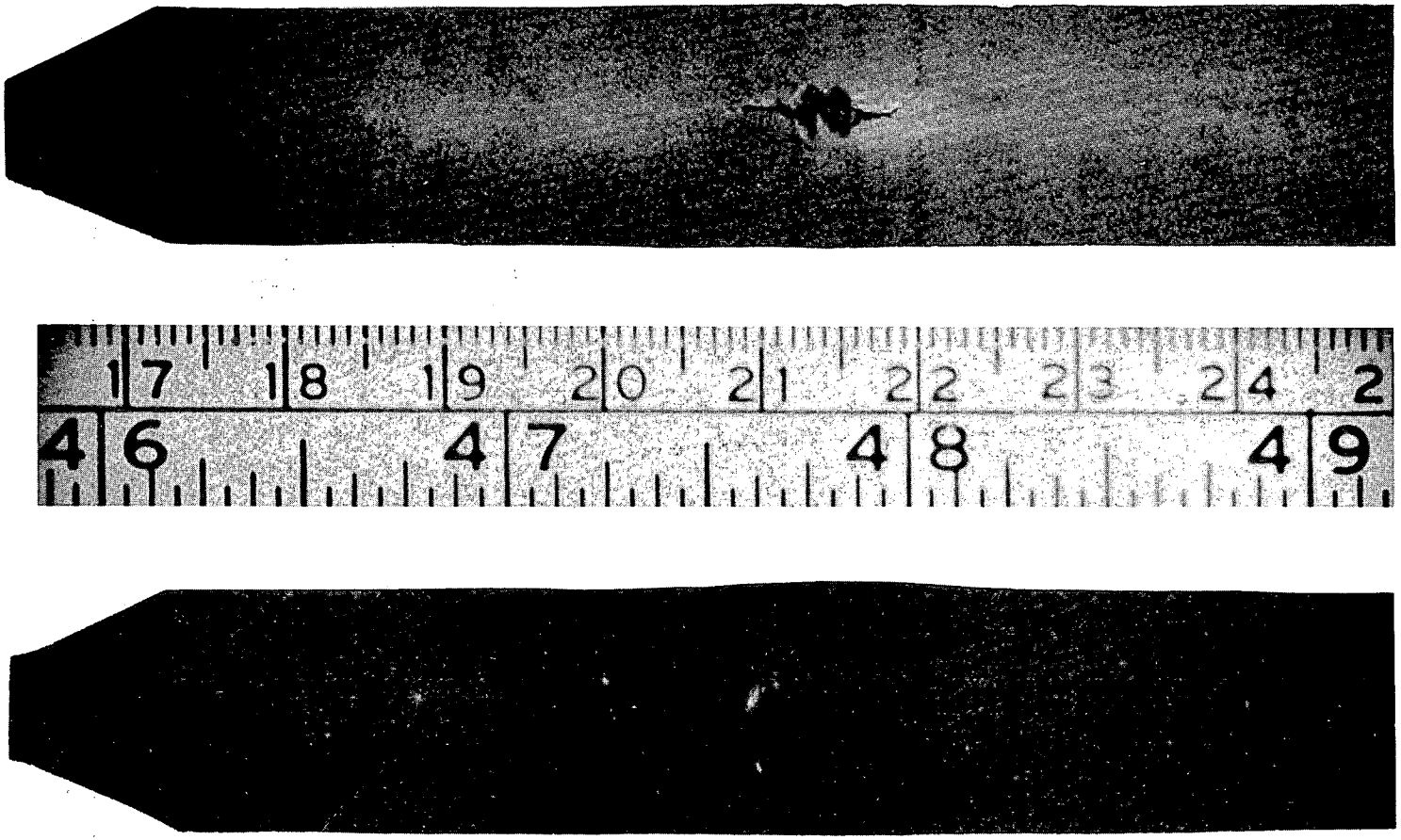


Figure 4 - Reactor power, delayed neutron and gamma monitor recordings for Element APZ.



Bottom end

Figure 5 - Defect after 17 days irradiation, showing split in sheath (0°) and bulge (90°). Specimen MJK.

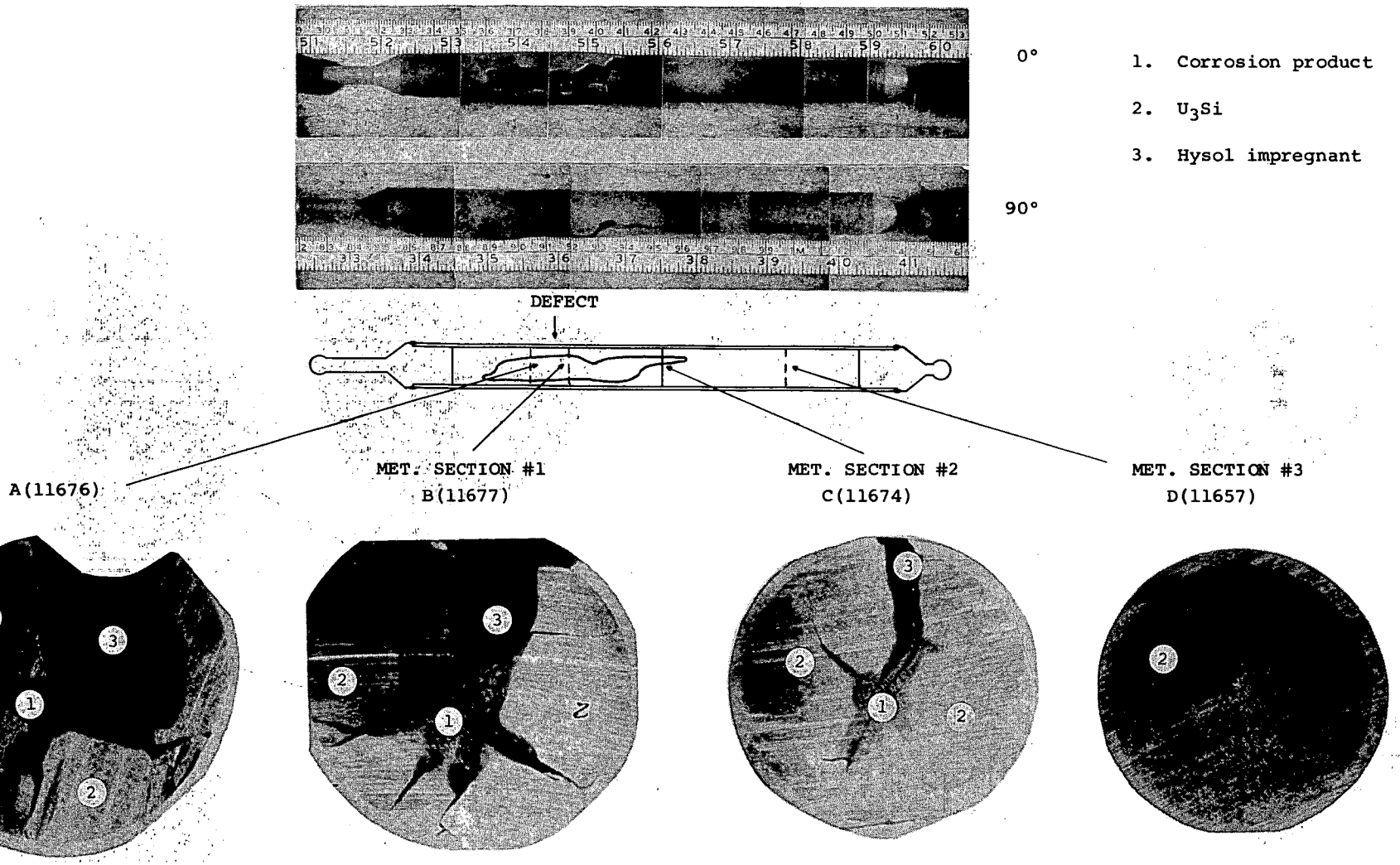


Figure 6

Unpolished Sections of Specimen MJK After Major Rupture

Approx. Scale 5 mm

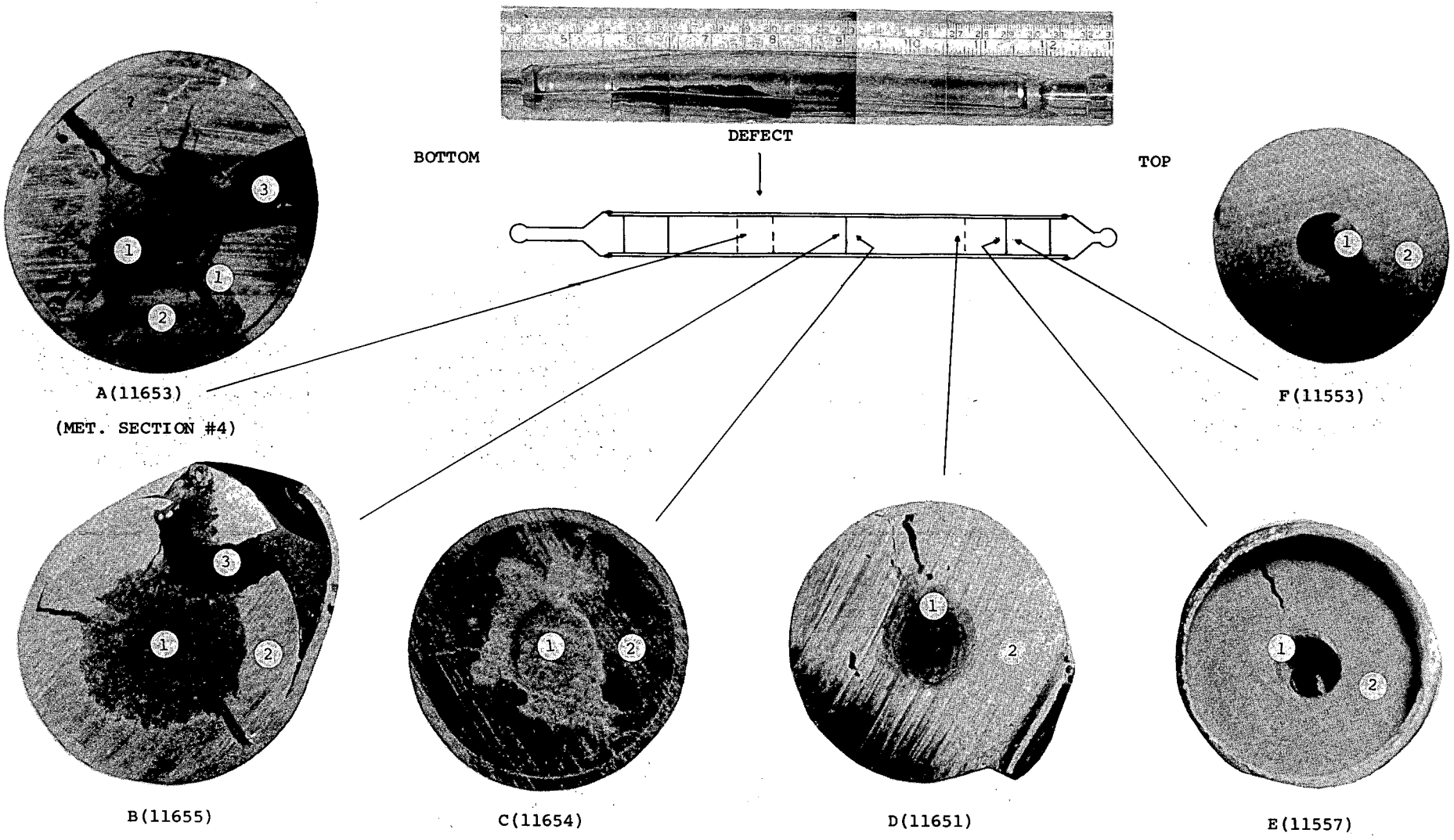


FIGURE 7

Unpolished Cross-Sections of Element APZ After a Short In-Reactor Defect Test

Approx. Scale 5 mm

1. Corrosion product
2. U_3Si
3. Hysol impregnant

NOTE: Sections A, B, C & D are cut faces. Sections E & F are ends of rods

Figure 8 HYDRIDE DISTRIBUTION IN THE ZIRCALOY SHEATH FROM ELEMENT MJK

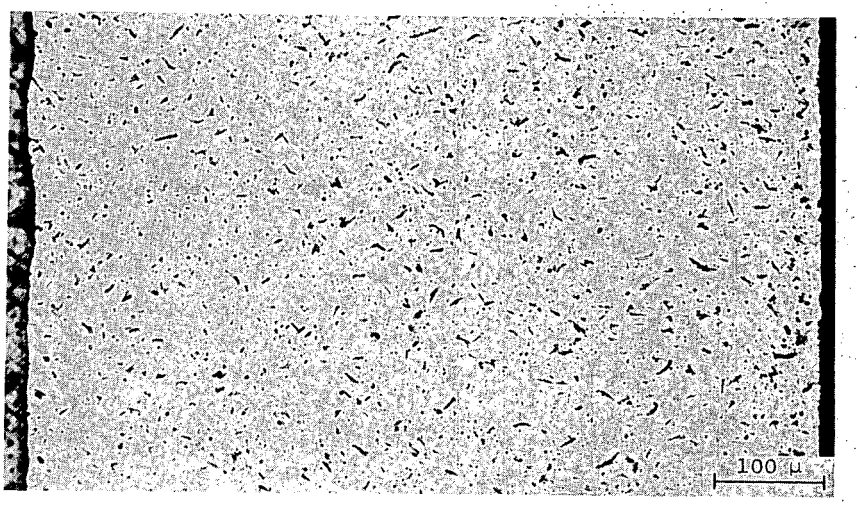


Figure 8A (R-28-B8)

Typical hydride distribution after defect test.

(Chem. polished)

O.D.

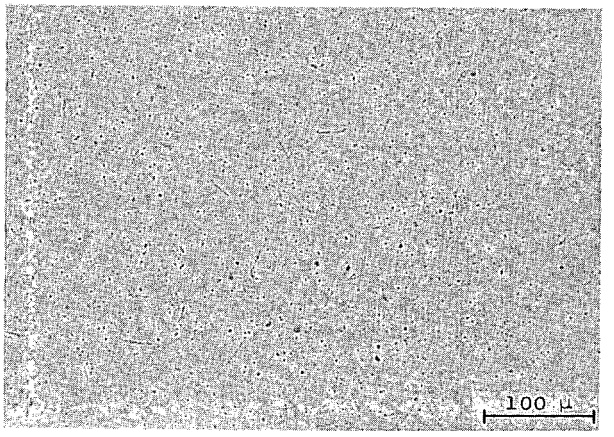


Figure 8B (K-56-A1)

Typical hydride distribution in unirradiated sheath.

(chem. polished)

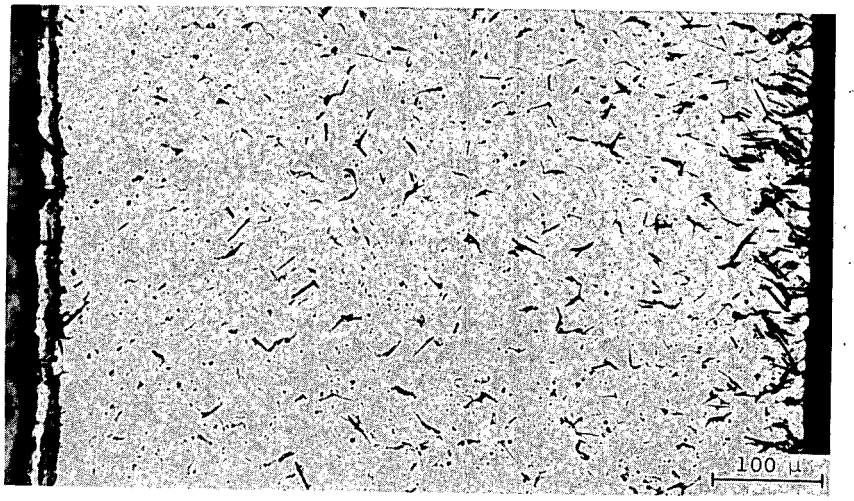


Figure 8C (R-28-B9)

Local area of radial hydride on O.D. and possible layer on I.D.

(Chem. polished)

O.D.

SECTION #1 ELEMENT MJK

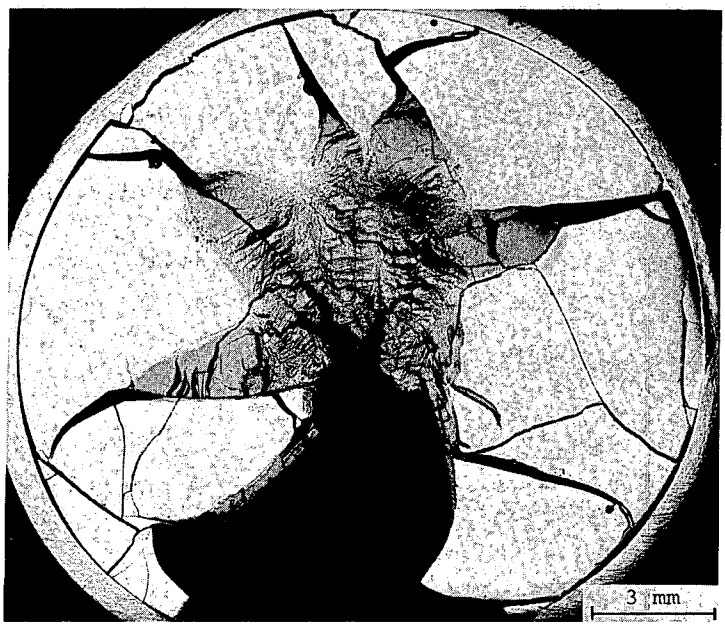


Figure 9 (R-28-C1) As Polished

Corrosion area near the original defect.

Figure 10 (R-28-C2) As Polished

Corrosion layer on the U_3Si periphery directly under the drilled defect.

← U_3Si

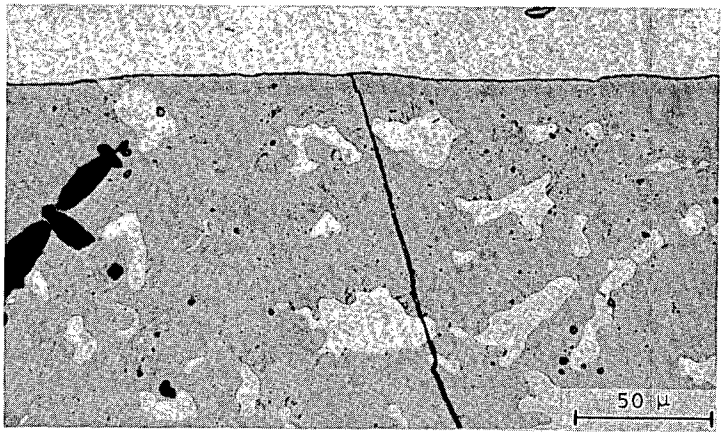


Figure 11 (R-28-C13) Etched

Tight contact between the U_3Si fuel and Zircaloy sheath.

← U_3Si

SECTION #1 ELEMENT MJK

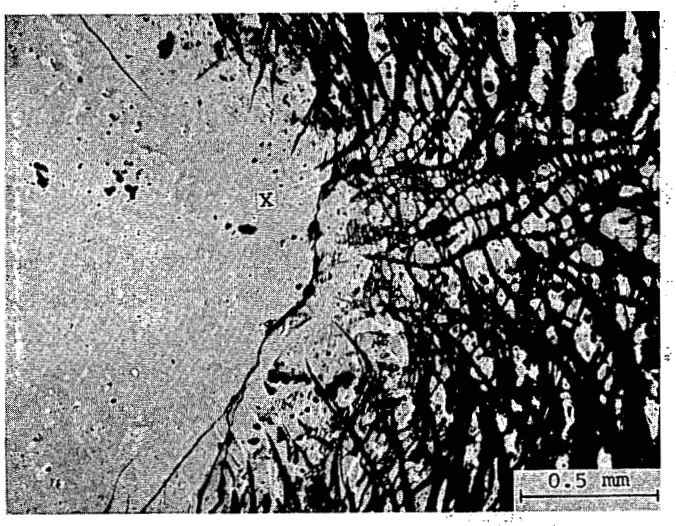


Figure 12 (R-28-C7) As Polished

Corrosion front area - grey band (X phase) between U_3Si and dark corrosion product.

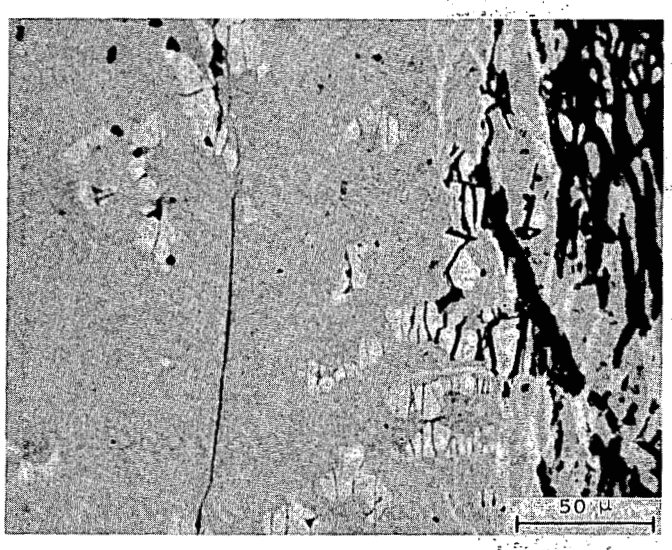


Figure 13 (R-28-C11) As Polished

Cracked U_3Si_2 particles in the X phase and white filament phase at the corrosion front.

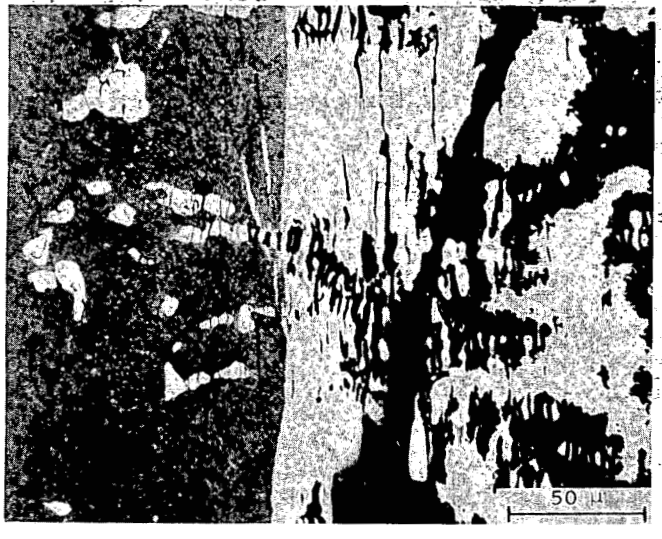


Figure 14 (R-28-C6) Etched

Similar area to Figure 13. White phase present as a band.

SECTION #1 ELEMENT MJK

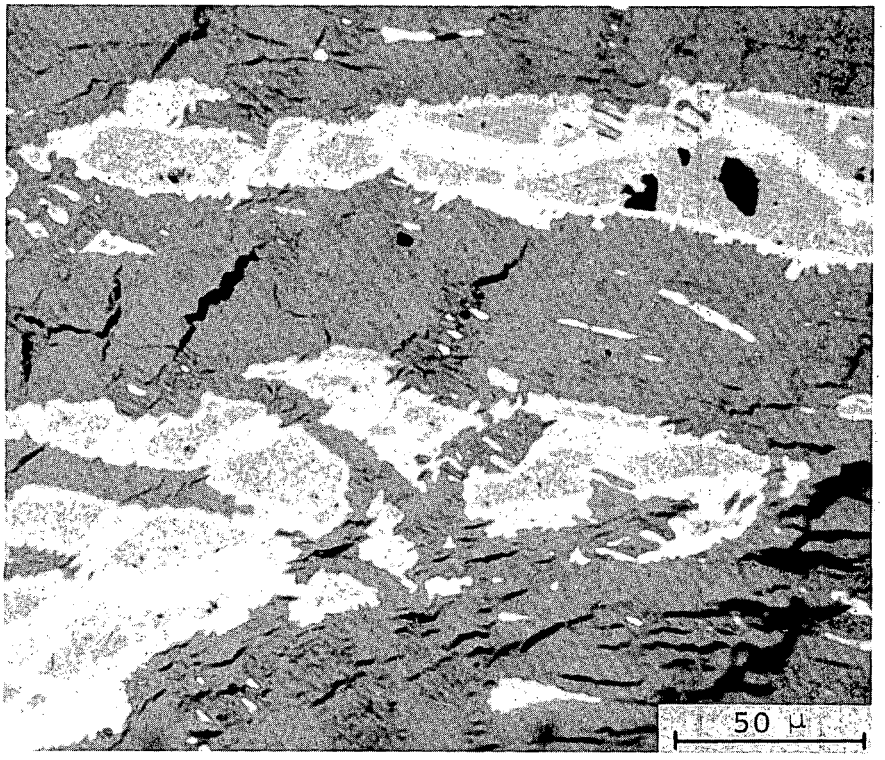


Figure 15 (R-28-C10)
- As Polished

Particles consisting of the white phase and the X phase in outer portion of main corrosion product.

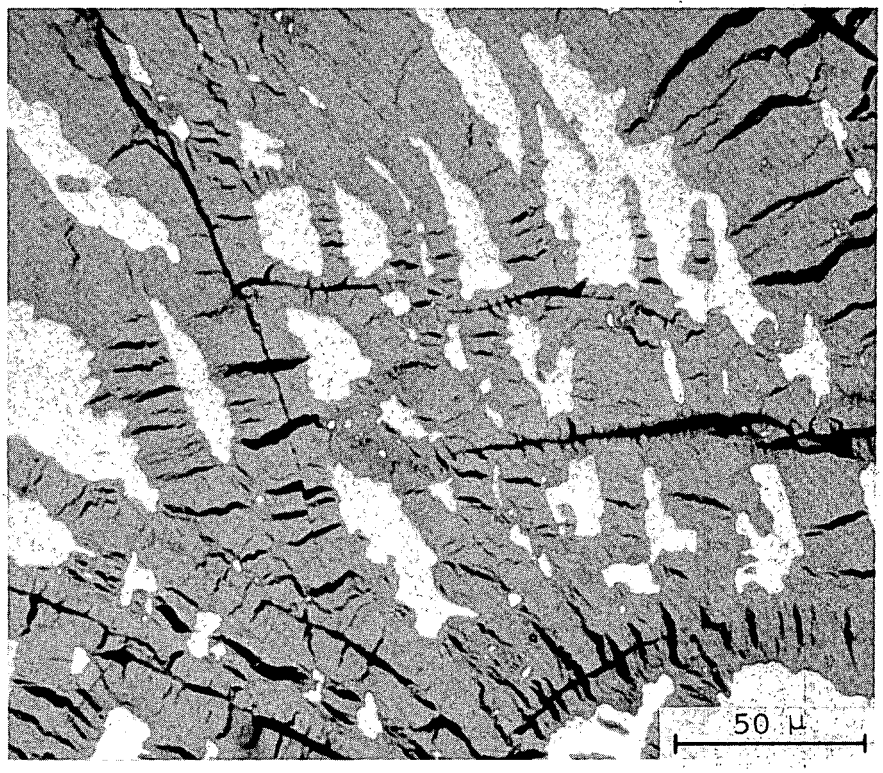


Figure 16 (R-28-C9)
- As Polished

Particles consisting of white phase only in the center of the main corrosion product.

SECTIONS #2 & 3 ELEMENT MJK

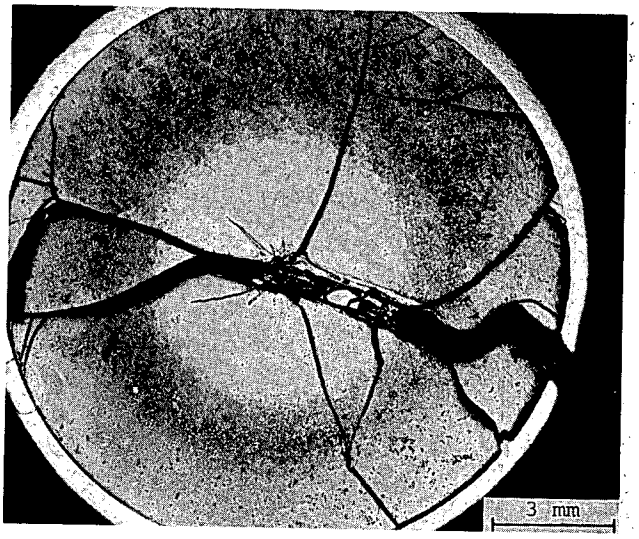


Figure 17 (R-28-B1)

Section 2 (Etched)

Cracking and light etching zone.

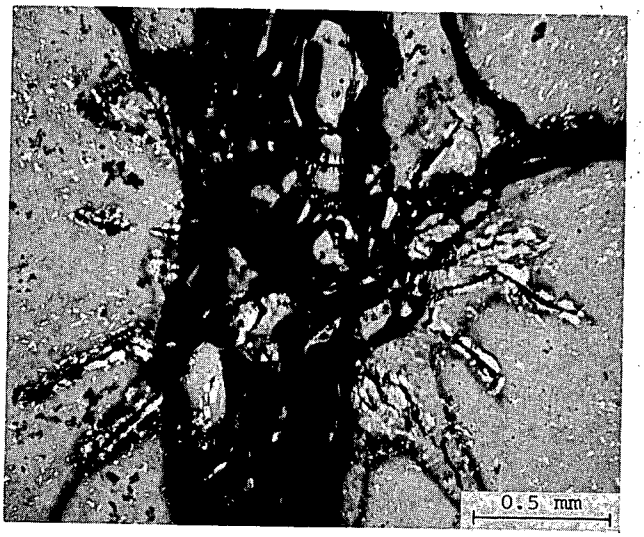


Figure 18 (R-28-B4) Etched

Section #2 - Dark band along the sides of cracks in the U_3Si.

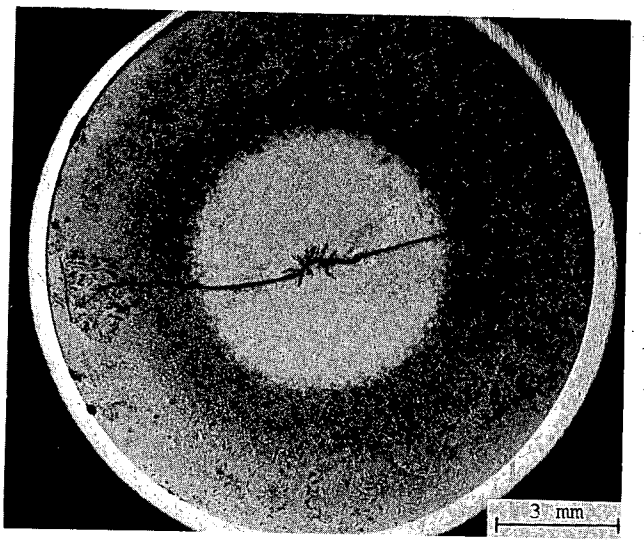


Figure 19 (R-28-A1)

Section 3 (Etched)

Cracking and light etching zone.

SECTION #4 ELEMENT APZ

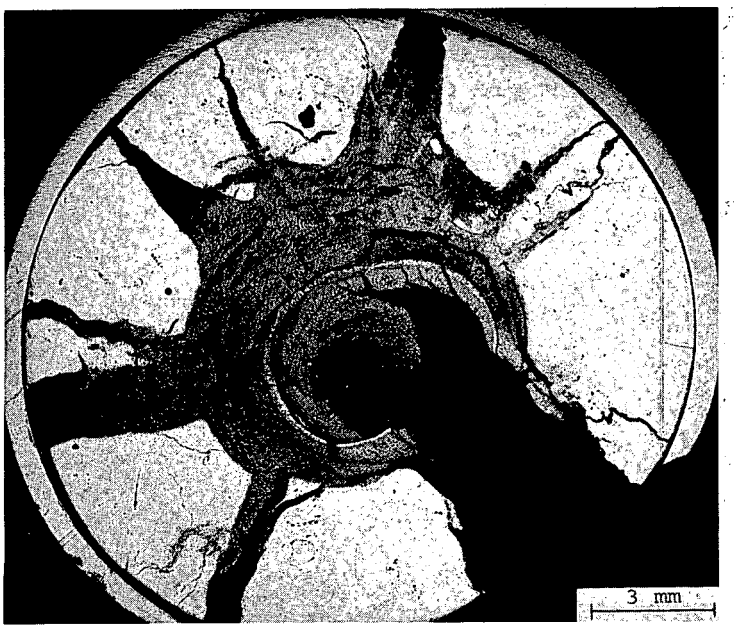


Figure 20 (R-27-A1) As Polished

Section near the drilled defect hole showing star shaped corrosion area and circular band of white phase.

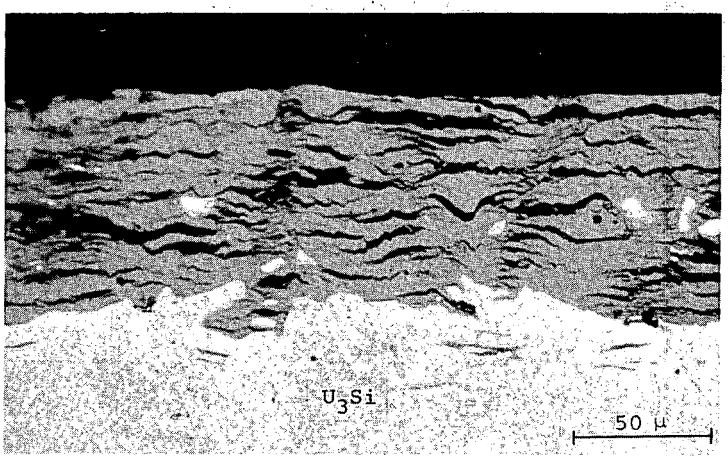


Figure 21 (R-27-A2) As Polished

Corrosion layer on the outside diameter of the U_3Si.

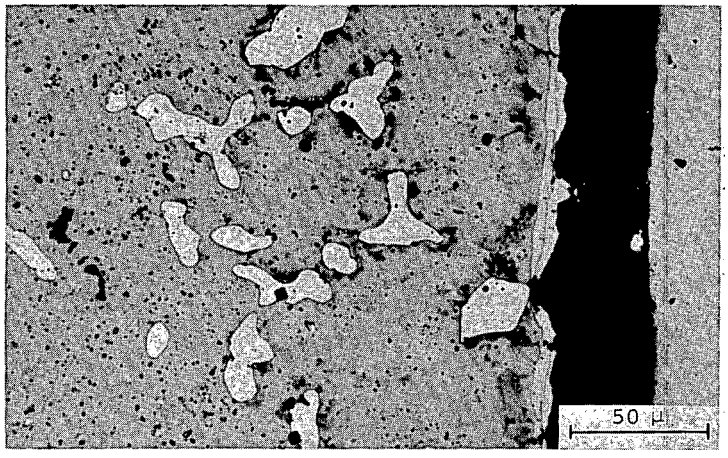


Figure 22 (R-27-A4) Etched

White phase layer at the interface between the main corrosion product and the U_3Si. Some darkening of the U_3Si around the U_3Si_2 particles.

SECTION #4 ELEMENT APZ

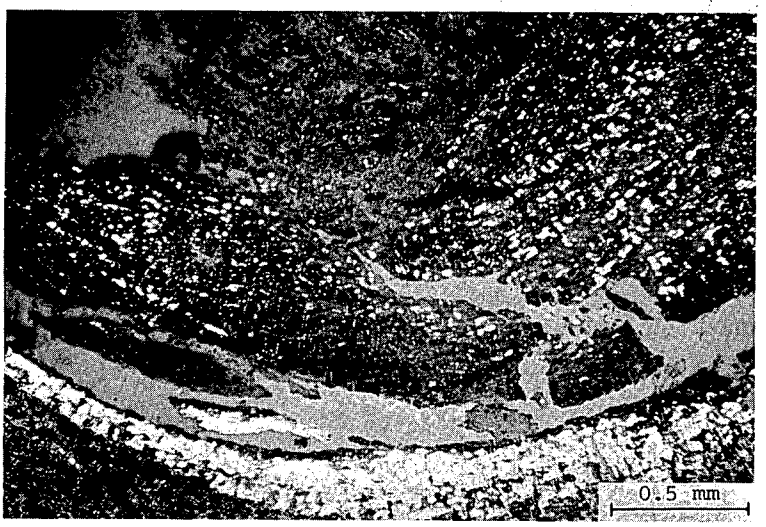


Figure 23 (R-27-A10) Etched

Broken ring of white phase in the center of the final corrosion product.

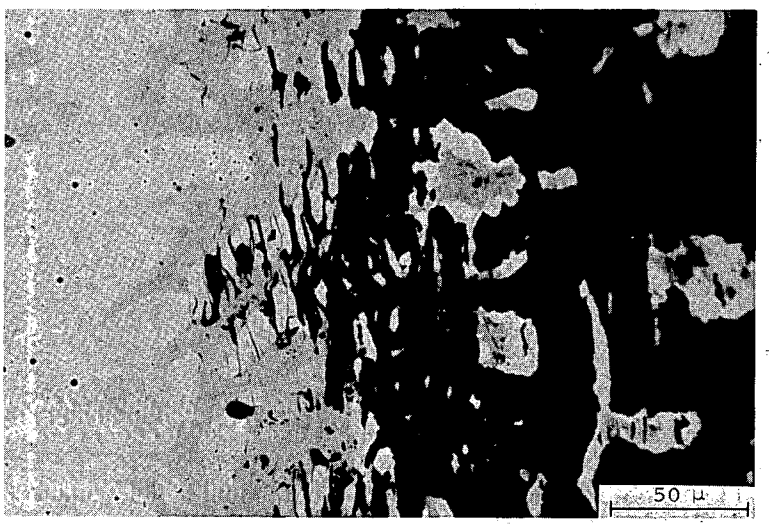


Figure 24 (R-27-A12) As Polished

Dark phase and some white phase at the main corrosion front.

Figure 25 (R-27-A7) Etched

White phase and two dark phase (X_1 and X_2) layers at the main corrosion front.

SECTION #5 ELEMENT APZ

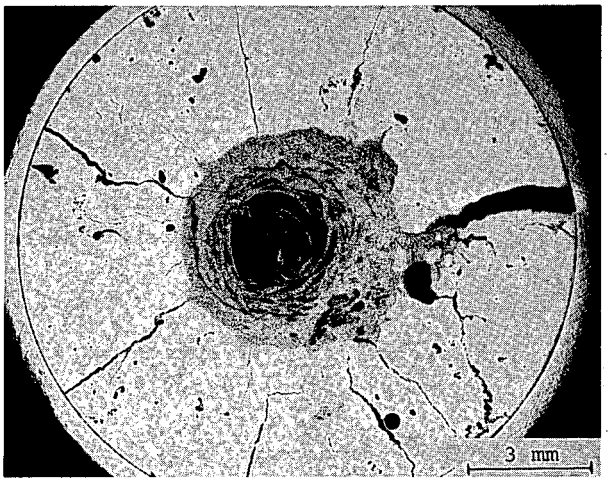


Figure 26 (R-27-B1) As Polished

Central corrosion and cracks in section away from the defect.

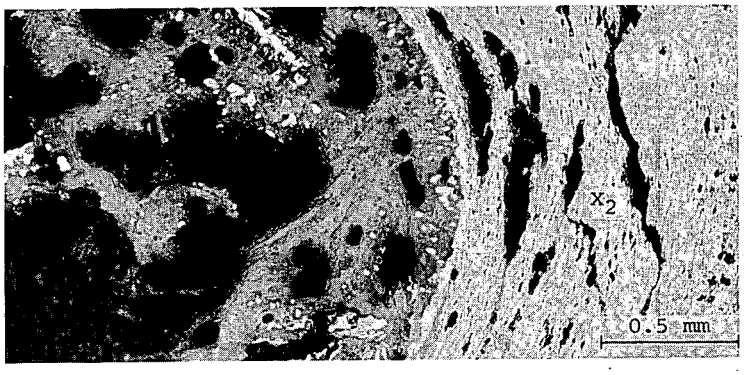


Figure 27 (R-27-B4) Etched

Thick layer of X_2 phase in central corrosion area.

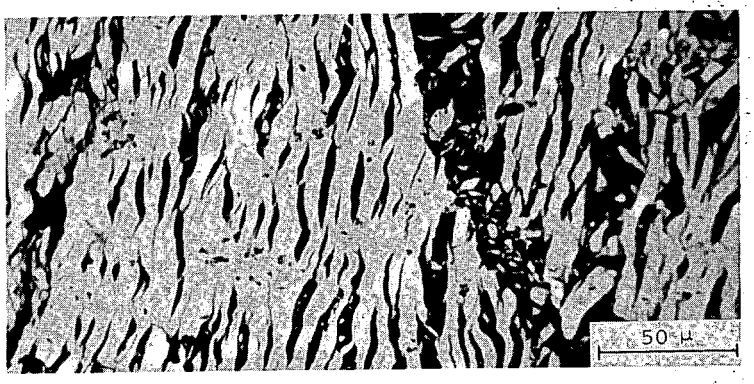


Figure 28 (R-27-B9) As Polished

Cracked X_2 phase containing some U_3Si_2 particles.

Figure 29 (R-27-B8) As Polished

X_2 phase and white phase layer at the center of the fuel. Dark final corrosion product containing particles of the white phase and X_2 phase.

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