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A. Willis		STATEMENT OF PROBLEM	
J. R. Lewis		ABSTRACT	
D. F. Atkins		Samples taken from acceptable regions of two SNAP-8 fuel rods that had been rejected because of localized surface cracking were irradiated in the shield test reactor to parts-per-million of fuel burnup and then annealed to evaluate fission gas mobility. Modified and unmodified fuel samples were tested. The objectives were, (1) to provide a preliminary evaluation of materials, (2) to demonstrate the feasibility of using existing equipment under pressurized conditions and evaluate the maximum number of potentially troublesome variables, and (3) to define a standard test that could be used to compare different compositions of alloys.	
G. D. Calkins		This report summarizes a series of sequential tests in a qualitative sense. The many changes in variables that were imposed on the system make detailed quantitative conclusions impossible. Tables 1, 2, and 3 summarize the tests that were conducted, the sample appearance after test, and the conclusions that could be drawn from each test.	
L. Maisel		Succinctly, one can conclude that:	
J. R. Miller		1) Differences between the tested modified and unmodified materials were observed.	
L. Lundberg		2) Differences between samples taken from the same rod were observed.	
J. K. Balkwill		3) The occurrence of the δ - β transformation causes bursts of released gas. No similar response is noted for the ϵ - δ transformation.	
E. D. Grazzini		4) A single transformation does not cause 100% gas release and successive transformations cause additional release of fission gases.	
R. Ashley		5) The fission gas mobility is unrelated to hydrogen mobility unless hydrogen loss causes a phase transformation.	
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Introduction: This report reviews the basis for and the current progress in evaluating SNAP Fuel elements by post irradiation annealing of lightly irradiated materials. It is an interim report to disseminate the information that has been obtained from the first irradiation capsule test.

Technological Background: Fuel element swelling (more precisely the tendency of fuel materials to swell) is being studied by an indirect method that provides positive results when viewed within the framework of existing fuel material technology. Fuel material swelling can be defined as "large volume increases due to a mechanical instability phenomenon, resulting from the inability of both the matrix surface tension and mechanical strength forces to resist the internal gas pressure forces that have resulted from the interactions among rare gas atoms to form gas-filled bubbles within the material."

This phenomenon should not be confused with the nominal volume increases that are associated with the creation of two large atoms by each fission. The creation of additional atoms, whose total volume exceeds that of the original fissioned atom, requires a volume increase because of the relative incompressibility of matter. Chemical effects, such as formation of complex oxides, can alter the relative volumes or sizes of the formed atoms. However, the inert gas atoms have the somewhat peculiar attribute of being relatively inert chemically and of being able to magnify their required volume when sufficient numbers of these atoms agglomerate to form gas bubbles.

New atoms are formed by fission and the initial distribution of these newly created atoms is random within a homogeneous fuel material. Atomic mobility is required to cause the associated of gas atoms or the formation and growth of bubbles of troublesome size. It follows then that the determination of the temperature at which gas atoms become mobile provides a measure of the temperature level where fuel element swelling becomes a problem. Rather than to start a long discussion of the factors that influence mobility, accept the fact that the measurement of rare gas atom can provide a clear definition of the troublesome temperature within practical limits, and also recognize that specific situations can exist where further considerations may also be necessary.

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Historically, methods that have been used to evaluate and improve the stability of Uranium alloys^{(1),(2)} at Atomics International are being applied here to evaluate existing fuel materials. A unique interpretation problem has existed because a pressurized rather than a vacuum system had to be tolerated. Thus, this report evolves into a description of the first tests on a new fuel system and the separation of experimental limitations of the technique from the basic system response.

Test Objectives: Two classes of materials were to be investigated in this preliminary test, (a) unmodified materials and (b) modified materials. These two classes of materials differ in additive level, grain size and structure. Unmodified materials have columnar grains that extend to or near to the center of the fuel slug while modified materials have a nearly equiaxed grain structure. These first samples were tested to investigate test procedures as well as material response and exact characterization of material structure was not attempted. The main objectives were to compare materials, to demonstrate feasibility of the test technique and to find out what unique problems might be encountered in tests on these materials. The objectives have been well satisfied.

Since a large number of small bubbles, in contrast to a few large bubbles, are needed to minimize mechanical instability problems at high burnups, interest arises not only in evaluation of the modifier level that is used but also in the size distribution of this modifier--if modifier level rather than grain size is to be an important variable. Accordingly the samples were examined by electron microscopy replica techniques to evaluate whether such differences between materials did exist. Unmodified materials were readily replicated by simple stripping techniques. Even the more sensitive floating techniques did not provide suitable replicas on the examined modified sample. Thus some unknown difference between the two examined materials did exist. The effort required to pursue this difference went beyond the scope of this program. A more complete evaluation of these materials program has been initiated. The difference in material response suggested by these tests does not permit conclusions concerning whether the difference arises between the batches of different materials, differences in composition, or differences in structure.

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Description of the System: The phase diagram for this system⁽⁴⁾ is shown in Figure 1. At high hydrogen contents, which are of interest here, an $\epsilon - \delta$ transformation occurs. According to Chang⁽³⁾ this is a shear type transformation which is caused by twinning of the lattice on cooling. At higher temperatures a structural change from face centered cubic, δ , to body centered cubic, β , occurs, this latter process involves a second order transformation that requires moving boundaries, or lattice disregistry, and it is quite different from the $\epsilon - \delta$ transformation. Finally we have the hexagonal α -phase which can be formed from the β with large losses of hydrogen and this transformation is similar to the $\delta - \beta$ transformation in character.

The $\epsilon - \delta$ transformation requires only a subtle shift in the placement of atoms and no large fission gas release should be expected. The other two transformations require disregistry between phases and can cause volume instability due to the sweeping or motion of boundaries. For example:

(1) Reynolds showed that no nucleation of ferrite occurred in cold worked austenite during irradiation but that the existing ferrite nuclei formed by cold work did grow during irradiation.⁽⁵⁾

(2) Rothwell indicates that phase transformations in UO_2 cause bursts of gas release.⁽⁶⁾

(3) Willis reported that the volume instability of zirconium base uranium alloys was much more severe during temperature cycling through phase changes than might be expected due to high temperatures alone.⁽⁷⁾

(4) Brinkman,⁽⁸⁾ Konobeevsky,⁽⁹⁾ and Bleiberg⁽¹⁰⁾ have demonstrated or predicted from various approaches that phase transformations requiring a readjustment of crystal structure can cause volume instability.

(5) Other investigators have made the same or similar technical points.

Therefore, initially one would expect no instability due to the $\epsilon - \delta$ transformation but a major gas release from the other transformations would be expected.

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Test Techniques: Samples taken from various regions in the cross sections of two SNAP 8 fuel rods were thinned to 0.004 to 0.006" plates by grinding. Each sample weighed approximately 0.020 grams and contained a nominal 10% of uranium - 235 by wt. Five of these platelets were sandwiched between Aluminum "D" blocks which promote heat loss and this assembly was sealed in a helium-filled, aluminum capsule. The irradiation at 10^{12} nv for 20 hours in the Shield Test reactor involved little heat generation and little temperature rise occurred in the samples. Chemical analyses were used to demonstrate that no hydrogen was lost during thinning operations. Burnup levels were determined by radiochemical analysis.

The samples were irradiated at the ambient temperature in the shield test reactor of Atomics International, which was the most readily obtainable irradiation source. The samples were allowed to decay for several days and then the release of the short lived Xenon-133 isotope (5.27 day half-life) was measured on heating to several temperatures for various lengths of time.

The after irradiation heating is accomplished within an evacuated ceramic tube with the sample sandwiched vertically between two massive pieces of material that were obtained from the same source material. These massive pieces, which will henceforth be called "buffer" slugs, provide hydrogen but no fission products to the 80 cc system volume, and thereby minimize the degree of dehydriding of the test sample. This procedure partially obviates the need for complicated programming of temperature and hydrogen pressure during the heating and cooling cycles.

A schematic diagram of the test container is presented in Figure 2. Important points are that the thermocouple is located to the side of the sample and buffer slugs, which are contained in a molybdenum boat that touches the sides of the ceramic tube in nearly line contact. The ceramic tube (Zircofrax) is impervious to hydrogen at test temperatures and it is joined to a graded seal which reaches only 70°C and is also impervious to Hydrogen. The graded seal is joined to a metal header. An "O" ring seal provides leak tightness for the reusable, assembled unit. The metal header has attached to it a pressure gauge (0-200 psi), a vacuum or prefill tube, and a stainless steel counting tube. The entire device is evacuated; or evacuated and prefilled with Argon; or evacuated and prefilled with Argon

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and hydrogen-depending upon the specific scoping test that one wishes to consider.

The stainless counting tube is inserted into a well-type scintillation counter and the ceramic tube into the center of a horizontally mounted resistance furnace. A single channel, gamma ray spectrometer is used to monitor the released fission gas that is contained within the counter well. The counting system can scan selected energies ranging from 0-100 kev to 3 mev and can thus detect the presence of a variety of fission products, most of which would be considered contaminants, if they did appear.

The fission gas release measurements concentrate on the short-lived Xe-133 isotope that has photopeaks at 81 and 52 kev. A thulium-170 source of known disintegration rate which has a photopeak at 84 kev is used to calibrate and to evaluate the efficiency of the counting system.

Calculations concerning the importance of dehydriding samples during heating tests have been provided in Appendix 1.

No standard test which would permit detailed comparisons among samples existed during this series of preliminary tests. The sequence was by its very nature exploratory and sequential with new cycles being generated by each novel test result. An attempt was made to vary the test conditions as much as possible to insure that the additional tests (which are now in progress) would encounter a minimum number of new problem areas but, at the same time, the maximum amount of technical data was sought.

Results:

The test programs for the various samples are presented in Table 1 and the final appearance of the samples is described in Table 2. The general observations and evolved hypotheses are presented in Table 3.

The vacuum was inadequate (10^{-4} torr) in test 1 and possibly in test 2. The final test devices had better than 10^{-6} torr for the starting vacuum.

No attempt will be made to compute diffusion rates at different temperatures because of the multitude of test variables that were used. Such rates have been computed and have some general trends but they are also rather inconclusive with respect to the controlled variables.

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A most pertinent result is obtained when the temperature and pressure data obtained from these tests is, in retrospect, plotted on the phase relationship curves that have been generated by J. Raymond.⁽¹¹⁾ Usually, the bursts of gas could be correlated in terms of measured temperature and pressure with the δ - β boundary line. The fast transient responses that our test procedures have created suggest that the large surface-to-volume samples could contribute substantially larger fractions of their hydrogen to the system in comparison to the adjacent buffer slugs. Actually this does not appear to be true.

A bias in the test procedure does exist. The "buffer" slugs were obtained from the existing SNAP 8 rods. The unmodified rod diameter was smaller than that of the modified rod and consequently more inert or "buffer" material was used in testing the modified material (Table 2). This provides lower hydrogen pressures and consequently the phase transformations can occur earlier.

Conclusions:

1) The tests on modified and unmodified samples differed in two respects. In one sense they had different metallurgical structures. In another sense, a bias in the test procedure did exist as is shown in Table 2. In all cases the modified materials had more massive volumes of "buffer" slugs than unmodified test materials. This differences in "buffer" slug weights was not fully appreciated during these sequential tests where predictions of expected material behavior guided the future test sequence.

2) For some undefined reasons, differences in the rate of gas release from different batches of unmodified materials, and between modified and unmodified materials did exist. The first sample tested showed the maximum gas release rate, the highest "buffer" slug weight and the poorest initial vacuum for this class of materials. Surface oxide or nitride formation did exist in this test and gas release was observed in the temperature range where one might solution treat the material to diffuse these components (700°C).

3) There is no relationship between hydrogen mobility and rare gas atom mobility, unless changes in hydrogen content provide second order phase changes. Accordingly, one can decide that hydrogen migrates as an

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interstitial component in Zr-U-H alloys of H/Zr ratio of 1.70 to 1.55, the limits studied in these tests.

4) The occurrence of the ϵ - δ phase transformation has caused no gas release.

5) The δ - β transformation provides gas release and should cause catastrophic fuel element instability based on existing technology. Avoid this transformation in practical applications!

6) There appears to be a rate effect on quenching with respect to fission gas release. More study is needed to define why quenching is not as efficient as rapid heating with respect to fission gas release.

7) One cycle of phase transformation, without assurance of a full transformation cycle, does not release all of the available fission gases.

8) Previous results obtained by Johnston and Savage indicate the present burnup levels may be too high to yield the best data and the exposure for the next series of tests will be reduced by a factor of four, which will permit measurements over a shorter cooling time period but will provide better irradiation scheduling.

Table 1. Summary of the individual test objectives as they developed during investigation.

TEST

OBJECTIVES AND TEST DESCRIPTIONS

- 1 The objective was to evaluate the temperature required to promote fission gas release in unmodified materials. The sample was heated to progressively higher temperatures for various lengths of time. Gas was released at 700°C. A burst of gas release occurred at 969°C and the sample was cooled and heated through this temperature range to evaluate the consequence of this treatment. No significant increase in counting rate was observed.
- 2 The objective was to evaluate the temperature required to promote fission gas release in modified material. Little fission gas was released at 710°C in 16 hours or upon heating to 980°C. Bleeding hydrogen from the system caused fission gas release and the material then released additional gas when heated and cooled.
- 3 The objective was to repeat Test 1 on another sample of unmodified material. The release rate was markedly lower at 700°C. A burst of gas was obtained at 920-925°C and additional gas was released on heating and cooling the sample. The container was evacuated and annealed at a later date. A large burst of gas was obtained on heating to 950°C showing that all of the gas was not released on one heating cycle. Quenching caused a decrease in activity as might be expected as a consequence of lower pressures at the lower temperatures. Reheating to 950°C caused another burst of gas release. The system was bled of H₂ gas and quenched with no great change in activity. Reheating to 950°C caused another burst of gas release. Cooling in the furnace from 950 to 850°C resulted in additional gas release, much more than was obtained during previous quenching tests.

Table 1 (continued)

<u>TEST</u>	<u>OBJECTIVES</u>
3 (continued)	One half-life later this sample was again evacuated and filled with Argon. Heating to 940°C caused gas release. Quenching to room temperature caused no gas release but reheating caused some additional increase in activity. Bleeding additional gas and quenching had no great effect and the activity drop normally observed on quenching was not observed in these tests. This sample was, by now, quite old and low on Xe ¹³³ and remaining tests were inconclusive.
4	Another unmodified sample was heated. The prefill gas contained a few millimeters of Argon and 7 psi of Hydrogen measured at room temperature. The objective was to evaluate the consequence of hydriding an irradiated sample. Hydrogen was absorbed at 500-600°C and heating between 725 and 860°C caused no large activity release. A minor burst of activity occurred at 850-882°C and quenching and heating gave further small activity increases. Heating from 978°C to 992°C gave a large burst but one hour's additional heating provided no additional gas release. The following day the sample was heated from room temperature to 550°C in 3 hours with no real change in activity level.
5	This sequence was designed to test all of the previously developed hypotheses. The sample prefilled with H ₂ and A and was heated to 600, 650, 700, and 750, 800, 850, 870, 900, 920, 950, and 970°C and some Xenon was released, but this was interpreted as potential surface release, perhaps due to slight oxidation because the Xenon activity level was so low (100 cpm). Sixteen hours at 690°C gave negligible increase in counting rate. The sample was heated to 770°C at 14 psi pressure, and hydrogen was bled from the system with no subsequent increase in activity. Heating to 990°C

Table 1 (continued)

TESTOBJECTIVES

5 (continued) provided no additional gas release. Cooling to 810°C had no effect and reheating to 920°C would not make the sample give up its fission gases. Cooling to 800 and another 17 hours of heating provided no gas release. Venting gas at 24 psig and 900°C produced no burst, but subsequent heating from 900 to 920°C provided a small burst which was clearly identified as Xenon-133. Another venting at 920°C caused no burst of gas release! Furnace cooling to 650°C caused additional gas release and heating up to 950°C caused additional gas release. Quenching to room temperature had little effect on gas release but reheating caused a large burst. A heating rate effect on gas release seems to exist!

6 The last test involved heating unmodified material without companion, buffer slugs to 800°C for long times, anticipating one large burst of activity release. In contrast, a slow rate of gas release over a 16 hour time period was obtained, but no burst was observed.

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Table 2

Description of Annealing Test Materials

Test	Sample	Weight of Sample, mg.	Weight of Buffer Slugs, g.	Condition of Materials at End of Test
1	Unmodified	16.87	6.751	Heavy Yellow discoloration. 30 psig pressure at end of test.
2	Modified	19.70	12.57	Slate grey color. 2 psig pressure at end of test.
3	Unmodified	21.0	4.873	Light straw yellow color. No pressure at end of test.
4	Unmodified	15.18	4.55	Grey color. One slug cracked. No pressure at end of test.
5	Modified	24.75	12.76	Grey color. One slug dark purple on one end. Slugs cracked.
6	Unmodified	19.37	None	Dark Purple

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Table 3 Summary of Sequential Test Results

Test	General Observations	Future Objectives or Hypotheses
1	Gas release occurred at 700°C. This observation should be repeated and the modified materials should be re-examined with a good vacuum. The burst at 969°C may indicate the presence of a phase change (δ - β). The poorly defined, but existing ϵ - δ transformation was not detected.	<ol style="list-style-type: none"> 1. Prove phase transformation hypothesis, δ-β. 2. Check modified material. 3. Consider whether initial vacuum was adequate. 4. Evaluate why was no burst of gas obtained on cooling.
2	Gas release did not occur at 710°C and heating to 980°C promoted no great gas release. Removing hydrogen caused gas release and subsequent heating and cooling caused further gas release.	<ol style="list-style-type: none"> 1. Modified materials are decidedly different from unmodified materials. 2. The phase transformation hypothesis seems quite tenable. 3. The ϵ-δ transformation seems to be innocuous. 4. A single phase transformation does not result in 100% gas release.
3	Samples taken from a given SNAP 8 rod, cross section can be decidedly different, or the test techniques require more attention. The release of fission gas on heating and cooling are not consistent.	<ol style="list-style-type: none"> 1. Better environmental control may be needed. 2. All of the gas is not released on one test cycle. 3. Heating or cooling rate effects may exist.

Table 3 (continued)

Test	General Observations	Future Objectives or Hypothesis
4	<p>The prefill hydrogen was absorbed at 500°C with no gas release.</p> <p>An unexpected burst of gas at 800-882 was obtained. The One hour of temperature caused no additional gas release. Thus transient heating tests can provide fission gas release where none is expected at constant temperature.</p> <p>Transient phenomena associated with heating and cooling were studied (i.e., Appendix 2)</p>	<ol style="list-style-type: none"> 1. Hydrogen mobility is not the source of fission gas release. 2. Transients are a true source of gas release; in contrast to long term heating tests at constant temperature. 3. Equipment response can limit short term test evaluations.
5	<p>Modified fuel seems to be superior to unmodified fuel (for these two sample sources; the effect of buffer weight was not yet appreciated).</p> <p>Bleeding hydrogen caused no release of gas on the first or second cycle or during intermediate heating. A third hydrogen bleed plus heating caused a burst of gas to be released. No further gas release occurred during a fourth bleed at temperature, but temperature cycles caused additional gas release.</p> <p>There seems to be a difference in gas release on rapid heating and cooling.</p>	<ol style="list-style-type: none"> 1. This modified fuel sample looks stable to 900°C. 2. Surface oxidation during initial heating tests may present some problem. 3. Accept transformation hypothesis, but verify further in future test sequences. 4. A rate sensitivity on heating and cooling seems to exist with respect to gas release.

Table 3 (continued)

Test	General Observations	Future Objectives or Hypothesis
6	A single cycle of transformation need cause no burst of gas release but instead can result in a slow and continuous release of gas.	1. Hydrogen may reduce lattice mobility. A single transformation need not cause catastrophic gas release.
7-15	Anomalous heating and cooling rate effects were reproduced with Zr-U-H samples contained in a system doped with fission gases (Kr ⁸⁵). Calibration tests were conducted.	1. The heating and cooling rates are system characteristics. 2. 100% gas release on repeated testing is possible.

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Appendix 1

Estimates of the Degree of Dehydridding During Heating

No two tests contained the same quantity of fuel material but some approximations of the influence of dehydridding during the tests are instructive.

Consider: 9.2 grams of Zr, hydrided to $\frac{H}{Zr} = 1.65$
80 cc system volume
1000°C temperature (uniform)
100 psia system pressure.

Problem: What is the hydrogen content of the sample material?

Solution: The system contains $\frac{9.2}{92}$ or 0.1 mole of Zirconium and $\frac{1.65}{2} \times 0.1 = 0.0825$ moles of Hydrogen (H_2). In the gas phase there is

$$n = \frac{Pv}{Rt} = \frac{100(80)}{(1208) 1273} = 5.2 \times 10^{-3} \text{ moles}$$

Thus the sample has an H/Zr ratio of $\frac{2(0.0825 - 0.0052)}{0.1}$ or 1.56 at temperature.

A sample containing W grams of material under conditions of complete dehydridding of the sample would then generate a pressure of

$$\frac{p \times 5.2 \times 10^{-3}}{100} = \frac{W}{92} \times \frac{1.85}{2}$$

$$\text{and } W_p = 52.1$$

so that for 100 psi pressure we require at least 0.521 grams of material.

One can be concerned further with rate effects on rapid heating or cooling because the test sample, 0.020 g and 0.005" thick, has a larger surface-to-volume ratio than the buffer slugs, 6 grams and 1/4" equivalent diameter. Rapid temperature transients could cause disproportionately large quantities of hydrogen to be released from the small sample.

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Appendix 2

Transient Counting Rate Changes on Heating and Cooling

The tests described in this report have a unique experimental feature which is caused by the release or adsorption of hydrogen during heating or cooling. These phenomena give rise to spurious, but temporary, counting rate effects during rapid heating or cooling and they must be explained satisfactorily because the effect is large.

Upon changing temperature, the counting rate will change because the distribution of rare gas atoms within the partially heated system changes. For example, when the ceramic tube is heated, a larger fraction of the rare gas atoms migrate to the cold end of the system. The act of heating can also cause additional rare gas atoms to be released for counting. Although these atoms are not readsorbed on cooling, a change in activity can occur where cooling promotes gas release - as it does in the described tests. A third, transient, effect occurs on heating and cooling as a consequence of hydrogen redistribution. The measured effects are presented in Figure 3 as they are obtained on the recorder strip charts and some derived results that were obtained in test 3 are presented in Figure 4. The hydrogen release on rapid heating causes a peak counting rate to occur while quenching provides an anomalous decrease in counting rate.

These peaks and dips have been re-created in systems that contained unirradiated fuel, argon and fission gases from irradiated fuel elements that have measurable quantities of krypton-85 present. Thus we assign the following interpretation to the curves presented in Figure 3:

- 1) Heating to high temperature causes hydrogen release from the sample and the buffer slugs. The newly released hydrogen contains lower than average quantities of the measured fission gas, xenon-133, and it compresses the existing gas thereby forcing additional quantities of these gases into the counting tube. This disproportionately large amount of fission gas redistributes itself as a consequence of thermal migration and the activity subsequently decreases.

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Appendix 2 (continued)

2) The decrease in activity on cooling arises because the rapid removal of hydrogen from the system volume sweeps fission gases from the counter tube. The removed atoms eventually return due to thermal migration and the counting rate increases. This hypothesis has been examined by quenching from various temperatures and below a certain temperature (pressure) level, no dip is obtained.

The heating curve of Figure 3 assumes that additional gas is released on heating. The cooling curve assumes no gas release.

Close examination of Figure 4 will show that the rise in activity precedes the pressure rise. This may be due to the fact that only gage pressure, 14.7 psi, has been measured. In examining the cooling curve, observe that hydrogen adsorption does not occur below 520°C during long heating times at this temperature. The decrease in activity on heating may reflect the existence of a phase transformation. These results represent two successive cycles in test number 3 with an intermediate removal of hydrogen.

Because these curves could be obtained with non-irradiated fuel surrounded by krypton-85 obtained from highly irradiated fuel, they are presented as artifacts or a response of the system rather than a characteristic of the sample material.

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References

1. Johnston, W. V., et al, "Annual Technical Progress Report, AEC unclassified programs," NAA-SR-7400, p. VII-15 (1962)
2. Johnston, W. V., et al, "Quarterly Technical Progress Report, AEC Unclassified Programs," July-Sept. 1962, p. VI-4, 1962
3. Chang, R., "Phase Transfer Motion Twinning and Anelastic Phenomena Associated with Zirconium Hydride," NAA-SR-5537
4. Libowitz, G. G., "The Zirconium Hydrogen System at High Hydrogen Contents," NAA-SR-5015
5. Reynolds, M. B., "A Study of the Radiation Stability of Austenitic Type 347 Stainless Steel," TID 2504.
6. E. Rothwell, "The Release of Kr⁸⁵ from Irradiated UO₂ on post Irradiation Annealing," J. Nucl. Mat. 5, No. 2, 1962
7. Willis, A. H., "The Irradiation Stability of Low Wt Pct Uranium Zirconium Alloys," Trans AIME Vol 215 p 245 (1959)
8. Brinkman, J. A., "Fundamentals of Fission Damage," NAA-SR-4164.
9. Bleiberg, M. L., "Irradiation Induced Phase Changes in Uranium Base Alloys," 2nd Geneva Conf. A/Conf 15 p/619.
10. Konobeevsky, S. T., "On the Nature of Radiation Damage in Fissile Materials," J. Nucl. Mat. Vol 3 p 356-365 (1956)
11. Raymond, J., "Equilibrium Dissociation Pressures of the Zirconium-Hydrogen Binary in the Delta Epsilon Phase Regions," NASA 8331

Figure 1 Modified Zirconium-Hydrogen Phase Diagram

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FIGURE 2

SAMPLE CONFIGURATION - PLAN VIEW

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FIGURE 3

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FIG 4: TRANSIENT ACTIVITY CHANGES ON HEATING OR QUENCHING

- FIRST HEATING
- HYDROGEN WAS REMOVED FROM SYSTEM AND A QUENCH FOLLOWED BY A HEATING CYCLE ENSUED
- (7) NUMBERS DENOTE P.S.I.G. PRESSURE AT CORRESPONDING TEMPERATURE.

ACTIVITY BUILDUP AS A FUNCTION OF TEMPERATURE

COUNTING RATE, 10³ CPM

LOSS OF ACTIVITY AT CONSTANT TEMPERATURE