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PHASE RELATIONSHIPS IN
THE (α + δ) REGION
OF THE Zr-H SYSTEM

AEC Research and Development Report

ATOMICS INTERNATIONAL

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PHASE RELATIONSHIPS IN
THE ($\alpha + \delta$) REGION
OF THE Zr-H SYSTEM

By

K. E. MOORE

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ABSTRACT

The $(\alpha + \delta) \rightleftharpoons \delta$ phase boundary of the Zr-H system has been defined on the basis of studies performed on zirconium hydrides containing 4 at. % U (SNAP fuel). The methods used include optical hot stage microscopy and room-temperature metallography, dilatometry, and x-ray diffraction. This boundary was found to exist between about 1.33 H/Zr at 1020°F and 1.60 H/Zr at 75°F. A metastable phase, γ' coexisting with α and δ phases, was found to transform to δ at about 560°F between 1.20 H/Zr and the $(\alpha + \delta) \rightleftharpoons \delta$ boundary (1.50 H/Zr).

I. INTRODUCTION

The zirconium hydride - uranium fuel (ZrH_x - 4 at. % U) used in SNAP reactors normally operates at the delta (δ) and epsilon (ϵ) phase region temperatures and compositions of the zirconium-hydrogen system (Figure 1a). However, low-temperature reactor operation could result in the delta $\rightleftharpoons$ (delta + alpha) [$\delta \rightleftharpoons (\delta + \alpha)$] transformation. The purpose of this study was to establish the position of this boundary so that future evaluations of $\alpha \rightleftharpoons \delta$ region reactor operation will be more meaningful.

Relatively few attempts by other investigators have been made to define the position of the $(\alpha + \delta) \rightleftharpoons \delta$ boundary. The data previously obtained are given in Figure 1b. As can be seen, the room-temperature limit of the $(\alpha + \delta)$ field has been reported to exist over a wide range of compositions. The uncertainty surrounding the position of this point can probably be attributed to the nature of the gamma prime (γ') phase which coexists with α and δ phases. The separate investigations of Beck⁽¹⁾ and Sidhu *et al.*⁽²⁾ did much to clarify this uncertainty, resulting from previous work, regarding the existence of γ' . Beck considered most of the earlier studies, in addition to his own, in proposing a model for its formation. In his model, γ' is a metastable phase, of intermediate composition between α and δ , and forms in preference to α as a result of the sluggish $\delta \rightarrow \alpha$ transformation. Moreover, he suggested that γ' is stoichiometric ZrH with hydrogen occupying half of its tetrahedral interstices. The latter contention was later supported in the neutron and x-ray diffraction studies of Sidhu *et al.* Considering material containing γ' and δ phases as existing in the $(\alpha + \delta)$ phase region, Beck found the room-temperature limit to be about 61.4 at. % H_2 (1.59 H/Zr). If only the relative amounts of α and δ phases are observed with increasing hydrogen concentration [α phase exists to about 1.41 H/Zr⁽¹⁾], this point would appear to be at a much lower H/Zr value.

Studies⁽³⁻⁶⁾ at elevated temperature are limited in scope and are in disagreement. Libowitz⁽³⁾ reported a value of 1.31 ± 0.04 H/Zr for the limit of the eutectoid isotherm (1020°F) in PCT (pressure, composition, temperature) studies. This agrees fairly well with the PCT work of LaGrange *et al.*⁽⁴⁾ However, the values obtained by Espagno *et al.*⁽⁵⁾ (dilatometry) and a single value of Erickson⁽⁶⁾ are at considerably lower H/Zr atom ratios.

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a. With SNAP Reactor Operating Range Superimposed

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b. Section Showing Results of Previous $(\alpha + \delta) \rightleftharpoons \delta$ Boundary Determinations

Figure 1. Zr-H Phase Diagram

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The possible influence of 4 at. % U and other impurities, found in the SNAP fuel, on the position of phase boundaries has been covered in an earlier report.⁽¹¹⁾ Briefly, it was found that all are inert with respect to the Zr-H binary system over the range of hydrogen concentrations under investigation.

To define the position of the $(\alpha + \delta) \rightleftharpoons \delta$ boundary with greater certainty, a number of experimental techniques were employed. These techniques include optical hot stage microscopy and room-temperature metallography, dilatometry, x-ray diffraction, and electrical resistance measurements.

II. EXPERIMENTAL

A. MATERIALS

The SNAP fuel alloy (Zr - 4.0 at. % U) selected for this work is representative of that used in SNAP reactors, except that normal uranium was used in place of enriched uranium. The fuel alloy was produced by a triple-arc-melt and double-extrusion process. Through chemical analyses performed prior to hydriding, the fuel was determined to have a maximum impurity content of 2800 ppm. Maximum oxygen and nitrogen concentrations were 1200 to 100 ppm, respectively.

All fuel material used in this study was hydrided to about 1.40 H/Zr. The actual H/Zr ratio of each fuel rod was established by weight gain, to about ± 0.01 H/Zr. Additional H/Zr levels (viz., 1.10, 1.20, 1.30, 1.45, 1.51, 1.55, 1.58, and 1.60) were obtained by either hydriding or dehydriding 5 to 6 in. sections of fuel to the desired level. Compositions were accurate to ± 0.02 H/Zr.

Samples to be used in hot stage microscopy, dilatometry, and electrical resistance examinations were centerless ground to 0.125 ± 0.001 in. in diameter. Dilatometry and resistance samples were about 2.5 in. long.

B. HOT STAGE MICROSCOPY

A Unitron inverted-stage microscope and vacuum heater attachment were used in hot stage microscopy examinations. The heater element consisted of tungsten windings positioned within a gold foil enclosure (Figure 2). Temperatures were measured with a stainless-steel sheathed Chromel-Alumel thermocouple inserted through the side of the sample holder and in contact with the hydride sample. The sample holder, fabricated from Type 304 stainless steel, was used as a heat sink, sample holder, and thermocouple positioner. Hydride samples, which were 1/8 in. in diameter by 1/16 in. long, were ultrasonically cleaned and rinsed with ethyl alcohol after metallographic preparation, prior to insertion into the sample holder. The "as-polished" surfaces of specimens were examined with polarized light. An ion pumping station was used to maintain a dynamic vacuum in the system of $<10^{-6}$ mm Hg.

Figure 2. Vacuum Heater Attachment for Microscope

C. DILATOMETRY

The quartz dilatometer was described in an earlier report,⁽¹¹⁾ so that only a brief description will be given here. The specimens consisted of 1/8-in. diameter rods about 2.5 in. long. Each specimen was placed in the bottom of a closed-end quartz tube, which was inserted into a massive heat sink surrounded by a furnace. The dilation of the specimen was transmitted to an LVDT (linear variable differential transformer) through a quartz rod, and the output of the LVDT was recorded on a dual-pen chart recorder, together with the temperature of the specimen. The specimen temperature was monitored with Chromel-Alumel thermocouples attached to the outer surface of the quartz tube.

All measurements were made in helium atmosphere, at 800 mm Hg pressure, to minimize temperature differences between the specimen and the quartz tube. The exception was the second run of the first 1.41 H/Zr specimen, which was made in vacuum. In all cases, the system was sufficiently clean, as evidenced by the constancy of specimen weights and the absence of visible oxide or nitride coatings on the specimens after the runs.

D. OTHER METHODS

Electrical resistance of a hydride (1.41 H/Zr) sample was measured by a potentiometric method, in which the voltage drop across a sample due to passage of direct current was compared with that across a standard resistor in series with the sample.

High-temperature x-ray diffraction was also used to a limited extent. This apparatus, as well as the electrical resistance apparatus, has been described in a previous report.⁽¹¹⁾

III. $(\alpha + \delta) \rightleftharpoons \delta$ BOUNDARY

Good agreement was obtained between elevated-temperature microscopy and dilatometry examinations, in which the $(\alpha + \delta) \rightleftharpoons \delta$ boundary was defined between hydride compositions of 1.41 and 1.55 H/Zr and temperatures ranging from 900 to 260°F. The $\gamma' \rightarrow \delta \rightarrow \alpha$ phase transformation was consistently found, by all methods, to occur at about 560°F between 1.20 H/Zr and the $(\alpha + \delta) \rightleftharpoons \delta$ boundary (1.50 H/Zr). The nature of this transformation is discussed in Section IV.

Based on room-temperature metallographic examinations, the room-temperature limit of the $(\alpha + \delta)$ field was found to exist at or close to 1.60 H/Zr. Moreover, the microstructural features of these samples indicated that the eutectoid isotherm exists to at least 1.30 H/Zr. The results of this examination also provided a basis for evaluating elevated-temperature results.

Phase boundary determinations were based on the initial assumption that the temperature at which the solution or precipitation of γ' occurred could be taken as the $(\alpha + \delta) \rightleftharpoons \delta$ boundary [Beck's Model⁽¹⁾]. As will be shown, this assumption was proven to be valid between room temperature and 560°F. Above this temperature (to the eutectoid isotherm), observation of the solution of α phase isolated the position of this boundary.

A. ROOM-TEMPERATURE METALLOGRAPHY

A series of hydride compositions, ranging from 1.10 to 1.60 H/Zr, were examined. Photomicrographs (250X) of their microstructures, and their locations in relation to the phase diagram, are shown in Figure 3. Two forms of eutectoid were found in the 1.10 H/Zr material; one globular shaped, and the other stringer-like. The stringer form, also found in 1.30 H/Zr material, was always enveloped by a rind of γ' . "Metastable" γ' was found in all samples and, with the exception of the γ' rind enveloping eutectoid stringers, formed as platelets. The size and distribution of γ' platelets was clearly composition dependent. The ambient-temperature limit of the $(\alpha + \delta)$ field is predicted to be close to 1.60 H/Zr; α phase was detected only in 1.10 and 1.30 H/Zr material.

The microstructures of the 1.10 and 1.30 H/Zr material consisted of $(\alpha + \delta)$ eutectoid and γ' phase in a δ -phase matrix (Figures 3b and 3c). The

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a. Phase Diagram, Showing Position of Samples

b. Sample 1 (1.10 H/Zr)

c. Sample 2 (1.30 H/Zr)

d. Sample 3 (1.41 H/Zr)

e. Sample 4 (1.45 H/Zr)

f. Sample 5 (1.51 H/Zr)

g. Sample 6 (1.55 H/Zr)

h. Sample 7 (1.58 H/Zr)

i. Sample 8 (1.60 H/Zr)

Figure 3. $(\alpha + \delta)$ Region Room-Temperature Microstructures

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($\alpha + \delta$) eutectoid mixture was present in the 1.10 H/Zr sample in the form of globular shaped islands and elongated stringers enveloped by a rind of γ' . Only the elongated form was present in the 1.30 H/Zr sample. The eutectoid islands (in 1.10 H/Zr material) probably occupied regions corresponding to the position and shape of β grains existing at the end of the isothermal portion of the hydriding process. As this material was cooled, at constant composition, through the ($\beta + \delta$) region, much of the β phase was transformed to δ . Considering the phase diagram, it can be seen that the amount of δ in 1.10 H/Zr material increases from about 25% at 1500°F to 70% at the eutectoid temperature under equilibrium conditions. The elongated form, which in the past has been considered an unidentified phase,⁽⁹⁾ represents the final shape of partially consumed β islands, under the nonequilibrium conditions of furnace cooling, prior to eutectoid formation. The tendency of this form to agglomerate under near-equilibrium conditions was demonstrated by reheating this material to 1560°F, followed by cooling at 10°F/hr through the ($\beta + \delta$) region. The microstructure of this sample (Figure 4a) revealed that most of the stringers of eutectoid thickened, and some cases spheroidized.

The small amount of eutectoid present in the 1.30 H/Zr material indicates that the limit of the eutectoid composition is slightly greater than 1.30 H/Zr.

Gamma prime platelets can be seen in the dark grey δ -phase matrix. As can be seen in the series of photomicrographs in Figure 3, the γ' has the general appearance of a needle-shaped phase; however, closer examination (1200X) reveals the true plate shape of this phase (Figure 4b). This figure also shows the fine twinned structure of these plates. This phase also envelopes and appears to have nucleated at the eutectoid stringers. In many cases, the γ' platelets have the appearance of spines growing out from the γ' rind, enveloping eutectoid stringers, extending into the δ -phase matrix (Figures 3b and 3c). These spines appear to be continuous at their base with the γ' rind; however, examination at higher magnification (Figure 4c) shows a definite interface at the base of the γ' spines.

The platelets of γ' , present in all of the microstructures to 1.60 H/Zr, appear to have formed on preferred crystallographic planes of the δ -phase matrix in a Widmanstätten pattern; and, in many cases, within δ grain boundaries. The number of γ' platelets formed in δ grain boundaries increases with increasing hydrogen concentration.

a. Slow Cooled (10°F/hr)
From 1560°F

b. Showing γ' Platelets

c. Showing Eutectoid Enveloped
by γ'

Figure 4. 1.10 H/Zr Fuel Material

Alpha phase was not detected in either x-ray diffraction or metallographic examinations of samples between 1.41 and 1.60 H/Zr. This was also the case in the work of Beck performed on samples with a similar range of composition. This strongly suggests that, with the cooling rates used in these examinations, α is present only in those compositions where the $(\alpha + \delta)$ eutectoid formation occurs (≤ 1.30 H/Zr). The presence of γ' in the 1.60 H/Zr, although small sized and finely distributed, indicates that the room-temperature limit of the $(\alpha + \delta)$ phase field lies close to 1.60 H/Zr.

B. HOT STAGE MICROSCOPY

Five hydride compositions (1.51, 1.50, 1.45, 1.41, and 1.20 H/Zr) were examined in the hot stage microscope. Both photographic stills and 16 mm motion pictures, at magnifications of 520X and 120X respectively, were obtained to record microstructural changes occurring at elevated temperatures. Phase transformation temperatures are given in Table 1.

TABLE 1
PHASE TRANSFORMATION TEMPERATURE RANGES

Method	Transformation	Transformation Temperatures (°F)					
		H/Zr Atom Ratio					
		1.20	1.41	1.45	1.50	1.51	1.55
Hot Stage Microscopy	$\gamma' \rightarrow \delta \rightarrow \alpha$	540-570	540-570	540-570			
	$(\alpha + \delta) \rightarrow \delta$		860-900	780-820			
	$\gamma' \nrightarrow \delta$				480-510	470-500	
	$[(\alpha + \delta) \nrightarrow \delta \text{ boundary}]$						
Dilatometry	$\gamma' \rightarrow \delta \rightarrow \alpha$		535-590				
	$(\alpha + \delta) \rightarrow \delta$		885-905				
	$\gamma' \nrightarrow \delta$					470-490	250-285
Resistance	$\gamma' \rightarrow \delta \rightarrow \alpha$		550

POLARIZED LIGHT

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a. 260°F

POLARIZED LIGHT

8096-14-1

b. 475°F

POLARIZED LIGHT

8096-15-1

c. 520°F

POLARIZED LIGHT

8096-16-1

d. 380°F (Cooling)

Figure 5. 1.50 H/Zr Fuel Material, Showing Solution and Reappearance of γ' Needles in δ Matrix

The $\delta \rightleftharpoons \gamma'$ phase transformation, corresponding to the $(\alpha + \delta) \rightleftharpoons \delta$ boundary, was observed in 1.50 and 1.51 H/Zr material at about 495 and 485°F, respectively. Based on these observations, it seems apparent that γ' is a transformation product of δ phase. Gamma prime was also observed to go into solution in the 1.45, 1.41, and 1.20 H/Zr material; but, in these cases, the transformation occurred at a constant temperature ($\sim 560^\circ\text{F}$). The simultaneous formation of α phase was observed with the solution of γ' . This transformation is believed to be $\gamma' \rightarrow \delta \rightarrow \alpha$. Results of these examinations suggest that the formation of α phase is related to surface effects, and is not representative of what occurs in the bulk material. Further heating of 1.41 and 1.45 H/Zr material resulted in the solution of "surface" α phase, which corresponds to crossing the $(\alpha + \delta) \rightleftharpoons \delta$ boundary. A detailed account, by composition, of these examinations follows.

1. 1.50 and 1.51 H/Zr

Figure 3f shows the room-temperature microstructure of the 1.51 H/Zr material, which consists of γ' in a δ matrix (the features of 1.50 and 1.51 H/Zr compositions are identical). Figures 5a, b, c, and d are photomicrographs obtained during elevated-temperature examination of a 1.50 H/Zr specimen. Visual observations were made on a 1.51 specimen during a similar thermal cycle.

In both tests, γ' platelets were observed to diminish in number and clarity (resolution) with increasing temperature, to within about 100°F of the temperature where they vanished entirely. The point at which the γ' platelets were no longer visible was taken as the $(\alpha + \delta) \rightleftharpoons \delta$ transformation temperature. The γ' is a transformation product of δ phase, as originally presumed by Beck.

2. 1.45 H/Zr

Two examinations were made on 1.45 H/Zr material. The photomicrographs obtained during the first run are shown in Figure 6. The room-temperature microstructure consists of γ' in a δ matrix (Figure 3e). Little or no change in the "presence" of γ' occurred until the temperature of the specimen reached 500°F. Resolution of γ' platelets decreased on heating from 500 to 560°F. At this point, γ' began to disappear (dissolving into the δ matrix), with the simultaneous growth of primary α phase in isolated areas. This transformation seems most probably to be $\gamma' \rightarrow \delta$, followed by the precipitation of primary α from δ

a. 75°F

b. 550°F

c. 580°F

d. 820°F

Figure 6. 1.45 H/Zr Fuel Material, Showing Solution of γ' , and Formation and Subsequent Solution of α in δ Matrix

phase. Figure 6b is a photomicrograph taken while this transformation was occurring; primary α is indicated by the arrows. The extent of the α -phase growth, in the particular area observed and photographed, is shown in Figure 6c. These islands of α phase have formed above the plane of the δ matrix. Solution of α phase into the δ matrix was affected by heating to about 800°F. The photomicrograph taken at 820°F shows this area after solution has occurred. This undoubtedly corresponds to crossing the $(\alpha + \delta) \rightleftharpoons \delta$ boundary, at or near 800°F.

A second sample was prepared for a similar run. In this case, a movie was used to record this phase transformation.

The course of solution of γ' platelets in the δ matrix can be seen in frames taken from the movie (Figure 7). This transformation was nearly complete at the end of the 560°F isotherm; however, γ' did not completely vanish until the temperature exceeded 600°F.

The growth of primary α phase can be followed in a very small area in Figures 7c through 7f. The small impurity particles indicated in Figure 7a appear to have acted as nucleation sites for the growth of this phase. Further heating resulted in solution of the α -phase island, which agrees with the observations made on the first 1.45 H/Zr sample.

Meaningful observations were limited to heating cycles for samples at 1.45 H/Zr, since considerable surface distortion occurred in cooling cycles. However, post-test metallography was performed, in which it was found that no observable microstructural changes occurred as a result of the thermal cycles used in hot stage microscope runs. This also suggests that the amount of hydrogen loss was small.

3. 1.41 H/Zr

Four runs were made, using this material. Photomicrographs from two of these were selected to depict the phase transformations that occur in this material within the temperature range investigated.

The photomicrograph of Figure 8b shows the extent of α phase forming at the surface of this material upon the solution of γ' at about 560°F. Figure 9 shows selected frames from a movie showing the solution of a particular α -phase island at the $(\alpha + \delta) \rightleftharpoons \delta$ boundary.

7759-5108

a. 500°F, 0 min b. 540°F, 17 min c. 550°F, 21.5 min d. 560°F, 26 min e. 560°F, 29 min

7759-5109

f. 560°F, 34 min g. 610°F, 38 min h. 655°F, 42 min i. 800°F, 54 min j. 830°F, 58 min

Figure 7. 1.45 H/Zr Fuel Material (Photographed at 120X, enlarged to 600X)

a. 75°F

POLARIZED LIGHT

7759-5110

b. 555°F

POLARIZED LIGHT

7759-5111

Figure 8. 1.41 H/Zr Fuel Material, Showing Solution of γ' and Formation of α Phase

7759-5112

a.
650°F, 0 min

b.
770°F, 14 min

c.
780°F, 16 min

7759-5113

d.
795°F, 18 min

e.
830°F, 20 min

f.
860°F, 24 min

Figure 9. 1.41 H/Zr Fuel Material, Showing Solution of α Phase in Selected Zone (Photographed at 120X, enlarged to 600X)

4. 1.20 H/Zr

Two samples of this material were examined. Both samples were heated to about 700°F, followed by furnace cooling to room temperature. Photomicrographs obtained in the second run shows the $\gamma \rightarrow \delta$ phase transformation that occurs at about 560°F. The pre-test microstructure of this sample (Figure 10a), in the field of view observed, consisted of a eutectoid stringer (upper left) surrounded by γ' , and γ' platelets in a δ matrix. Gamma prime was distinct, and little or no change occurred in the microstructure until the sample temperature reached about 500°F. As in runs on 1.41 and 1.45 H/Zr material, γ' platelets became less distinct and fewer in number between 500 and 560°F. Figure 10b shows the effects of the transformation occurring at this temperature. The surface of these samples became distorted, with the disappearance of γ' and apparently simultaneous formation of primary α . In Figure 10c, bright field illumination of the same area shows α phase in the upper left hand corner of the photograph.

The formation of large amounts of primary α , at or above 560°F, cannot be representative of what occurs in the bulk material, since this material existed for a relatively long period of time between 560 and 1020°F during cooling from the hydriding temperature; as can be seen in Figures 3b and 3e, no primary α was observed in 1.10 and 1.30 H/Zr samples. Moreover, metallographic examination (which required removal of a few microns of surface material during metallographic sample preparation) performed after each run revealed that no change had occurred in the microstructure. The rapid formation of primary α must be associated with preferential nucleation and growth at the surface.

C. DILATOMETRY

Thermal expansion measurements were made on three hydride compositions. In general, precise measurements were taken only in temperature intervals where phase transformations were anticipated from hot stage microscopy results, using low heating and cooling rates. These rates are given in Table 2. Outside these temperature intervals, specimens were heated or cooled at about 5°F/min.

Manifestations of phase transformations were rather small in all runs; but the results were, nevertheless, quite convincing. Curves of expansion vs

a. 75°F

b. 575°F

c. 585°F

Figure 10. 1.20 H/Zr Fuel Material, Showing Solution of γ' and Formation of α Phase

TABLE 2
HEATING AND COOLING RATES USED DURING
EXPANSION MEASUREMENTS

H/Zr Atom Ratio	Run No.	Rate of Heating or Cooling	
		+(°F/hr)	-(°F/hr)
1.41	1a	55	
	1b	100	
	2a	55	
	2b		40
	3*		≤6
1.51	1		70
1.55	1a	80	
	1b		55

*Sample was intermittently aged at constant temperature during course of run (as shown in Figure 16)

TABLE 3
RESULTS OF HIGH-TEMPERATURE X-RAY
DIFFRACTION EXAMINATION

H/Zr Atom ratio	Temperature (°F)	Relative Intensity of Strongest Reflection from Each Phase		
		δ	α	γ'
1.41	75	Strong	Masked by uranium	Weak
	600	Strong	?	Absent
	75	Strong	Masked by uranium	Faint
1.20	75	Strong	Very weak	Medium
	600	Strong	Very weak	Absent
	75	Strong	Very weak	Faint
	75, after heating to eutectoid temperature, furnace cooled	Strong	Medium	Absent

temperature obtained in the various runs are shown in Figures 11 through 13. The results of the expansion measurements, as related to phase transformation, are summarized in Table 3. A detailed description, by composition, of dilatometry runs follows.

1. 1.41 H/Zr

Figure 11a shows the expansion curves obtained from a 1.41 H/Zr specimen in the first run. Inflections in the curve exist at about 565°F and 886 to 906°F. These temperatures are in excellent agreement with the observations made on the hot stage microscope. In the region just below 565°F, the average linear coefficient of thermal expansion is 16.2×10^{-6} in./in.-°C; whereas, above this temperature, the coefficient is 10.0×10^{-6} in./in.-°C. Micrometer length measurements, before and after this run, revealed that the length of the specimen had increased 0.6 mil (+0.024%), although the mass remained effectively unchanged.

An inflection can be seen in the curve obtained in the second run, again at about 565°F; and the corresponding break in the cooling curve exists at about 535°F (Figure 11b), which indicates the reversibility of this transformation. A closer look at the curves indicates that there may be a narrow region (562 to 590°F in the heating curve, and 536 to 547°F for the cooling curve) where the coefficient of expansion is intermediate to those above and below this region. This effect is quite small, and might be easily ascribed to noise in instrumentation; however, since the result was reproducible in all runs, it is believed to be real. Conversely, the expansion rate was slightly greater during the $(\alpha + \delta) \rightarrow \delta$ transformation range (886 to 906°F). Detection of phase transformations in $\delta \rightleftharpoons \epsilon$ region studies also occurred over a range of temperatures.^(11,12) The coefficient of expansion above the $\gamma' \rightarrow \delta \rightarrow \alpha$ phase transformation temperature range is very nearly 10×10^{-6} in./in., in both heating and cooling, in good agreement with the results of the first run.

Neither the specimen length nor weight changed during the second run, which supports the belief that the increase in length of the specimen during the first run was not due to change in composition, but to stress relief effects.

a. Run No. 1

b. Run No. 2

Figure 11. Thermal Expansion of 1.41 H/Zr Fuel Material

Figure 12. Thermal Expansion (Run No. 1)
of 1.51 H/Zr Fuel Material

Figure 13. Thermal Expansion (Runs No. 1a and 1b) of 1.55 H/Zr
Fuel Material

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2. 1.51 and 1.55 H/Zr

The cooling curve obtained from the 1.51 H/Zr sample is shown in Figure 12. An inflection in the curve occurs in the region of 470 to 490°F, which corresponds well with the hot stage microscope observation of the $\gamma' \rightarrow \delta$ phase transformation and the $(\alpha + \delta) \rightleftharpoons \delta$ boundary. The fluctuations, in the region of 500 to 536°F, are believed to be due to more than instrument noise; it appears that this behavior is characteristic of the SNAP fuel material, since it was also observed in previous measurements.⁽¹¹⁾

The heating and cooling curves of the 1.55 H/Zr specimen showed fluctuations in the 250 to 285°F region, as shown in Figure 13. It appears that the slope of the heating curve changes at about 285°F and that of the cooling curve occurs at about 260°F, so that the $(\alpha + \delta) \rightleftharpoons \delta$ phase boundary probably lies near these temperatures.

D. ELECTRICAL RESISTANCE

Figure 14 shows a curve of resistance vs temperature data obtained from a 1.41 H/Zr specimen. This curve clearly shows the $\gamma' \rightarrow \delta$ transformation at 550°F upon heating. The $(\alpha + \delta) \rightarrow \delta$ transformation found, using the other techniques, was not detected with this method.

E. REVIEW OF $(\alpha + \delta) \rightleftharpoons \delta$ BOUNDARY RESULTS

Phase transformation temperature ranges, obtained with the various techniques, are given in Table 1, and are plotted in Figure 15. As can be seen, the results of hot stage microscopy and dilatometry examinations agreed very well. Extrapolation of the $(\alpha + \delta) \rightleftharpoons \delta$ boundary defined in elevated-temperature studies agrees with the findings of the room-temperature metallographic examination.

The $\gamma' \rightleftharpoons \delta$ transformation was found to occur, in all cases, at constant temperature (about 560°F) in hydride compositions between 1.50 and 1.20 H/Zr. The observed reversibility of this transformation would seem to indicate that γ' is an equilibrium phase, and that either δ or α is metastable below 560°F. However, additional experiments (described in the following section) show that γ' is metastable, in agreement with Beck's suggestion.

Figure 14. Resistance vs Temperature
for 1.41 H/Zr Fuel Material

7-30-68 UNCL

7759-5101C

a. Phase Diagram, Showing Boundary Determination

8-21-68 UNCL

7759-5119

b. Enlargement of Area Under Study

Figure 15. Zr-H Phase Diagram, Showing Data Used to Define Position of $(\alpha + \delta) \neq \delta$ Boundary

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IV. $\delta \rightleftharpoons \gamma'$ TRANSFORMATION

The nature of the $\delta \rightleftharpoons \gamma'$ transformation must be understood before a complete picture of α and δ region phase relationships can be obtained. To accomplish this, a detailed examination (metallography and x-ray diffraction) was made, using hydrides subjected to various thermal cycles. Preceding the results of this examination, a discussion is given of those observations made during the phase boundary determinations which are relevant to $\delta \rightleftharpoons \gamma'$ transformation kinetics.

A. INITIAL OBSERVATIONS

The fact that γ' goes into solution at 560°F (at ≤ 1.50 H/Zr), and has been predicted to be a metastable phase forming in preference to the equilibrium phase α , suggests that heating the fuel above 560°F would result in the formation of primary α . At room temperature, the amount of γ' would be reduced, although not eliminated,* and the primary α formed would be retained. However, after heating hot stage microscope samples into the ($\alpha + \delta$) region (650 to 750°F), it was found that the amount of γ' did not change measurably, as evidenced by metallography and x-ray diffraction. It might be surmised that the $\delta \rightarrow \alpha$ transformation did not have sufficient time to go to completion, and hydrogen-deficient δ precipitates γ' on cooling. An alternative explanation is that the $\delta \rightleftharpoons \gamma'$ transformation (followed or preceded by the $\delta \rightarrow \alpha$ transformation during heating or cooling) is reversible, and that α phase is metastable below the $\delta \rightleftharpoons \gamma'$ transus.

The results obtained in dilatometry examinations, shown graphically in Figure 11b, also suggest reversibility of this transformation. Figure 11b shows that the coefficient of expansion remained the same below 550°F, which suggests that the relative proportions of the phases remained the same, before and after the $\delta \rightleftharpoons \gamma'$ transformation.

*Referring to the phase diagram, the hydrogen concentration in δ phase increases with decreasing temperature; the amount of low-hydrogen phase must increase. Since it is anticipated that γ' originally forms during furnace cooling, it would be expected to be present at room temperature.

Figure 16. Thermal Expansion (Run 3) of 1.41 H/Zr Fuel Material

A limited number of high-temperature x-ray diffraction examinations were performed in the phase boundary determinations. However, resolution of minor phases (α and/or γ') was difficult, particularly with α phase, since α -uranium (110) and (002) lines coincide with the (002) and (101) α -phase (major) lines. But, in an examination of 1.41 H/Zr material (results given in Table 3) in the form of -325, +400 mesh powder, it was noted that the amount of γ' phase was greatly reduced, following heating to 600°F.

Similarly, examination of 1.20 H/Zr material (chosen to follow up on the observation made on 1.41 H/Zr material, because the relative intensities of α and γ' would be easier to resolve) revealed that the intensity of γ' had again decreased after heating to 600°F. In this case, the sample was cooled very slowly to about 300°F. The results of this test are given in Table 3. Unlike the 1.41 H/Zr material, an increase in the intensity of α -phase reflections was resolved. The same sample was then reheated to the eutectoid temperature for about 15 min, followed by furnace cooling to room temperature. The powder pattern obtained revealed the γ' reflections were absent, and the relative proportions of α and δ were about 30 and 70%, respectively.

Since the observations made in high-temperature x-ray diffraction examinations and during phase boundary determinations were apparently contradictory, additional hydride samples were subjected to series of heat treatments, and a special dilatometry run was performed.

B. THERMAL TESTS

A series of hydride samples were subjected to a spectrum of thermal cycles, including the very slow cool used in a dilatometry run. The results were consistently the same; the $\delta \rightleftharpoons \gamma'$ transformation was found to be reversible in solid specimens, while the amount of γ' could be greatly reduced in finely divided hydrides, with a corresponding increase in the amount of α .

Dilatometry Run 3b was performed to investigate the effect of aging 1.41 H/Zr material above the $\delta \rightleftharpoons \gamma'$ transus, followed by very slow cooling through this region. The specimen was cooled at 6°F/hr (max) during the day and soaked at temperature overnight, as indicated in Figure 16. As can be seen, an inflection was again obtained at about 550°F, although the definition is not as good as was obtained in continuous cooling runs. The coefficient of expansion

TABLE 4
AGING TESTS

H/Zr Atom Ratio	Type of Sample	Thermal Cycle	Relative Intensity of Strongest Reflection from Each Phase		
			δ	α	γ'
1.10	Solid	As-hydrided - furnace cooled	Strong	Weak	Medium
1.10	Solid	Aged 3 days, 650°F, cooled 10°F/hr	Strong	Weak	Medium
1.20	Solid	As-hydrided - furnace cooled	Strong	Weak	Medium
1.20	Solid (1/8 in. diameter)	Aged 3 hr. 650°F, quenched in liquid nitrogen	Strong	Weak	Medium
1.20	Solid (1/8 in. diameter)	Aged 3 hr. 800°F, air cooled	Strong	Weak	Medium
1.20	Granules (-10, +100 mesh)	Aged 3 hr. 800°F, air cooled	Strong	Medium	Faint
1.20	Solid (1/8 in. diameter)	Aged 3 hr. 800°F, furnace cooled	Strong	Weak	Medium
1.20	Granules (-10, +100 mesh)	Aged 3 hr. 800°F, furnace cooled	Strong	Medium	Faint

below 550°F is roughly 16×10^{-6} in./in.-°C, as was found in previous runs. This sample was examined metallographically and found to contain the "normal" amount of γ' .

Results of the various heat treat cycle tests are given in Table 4. This table, together with previous observations, indicates the insensitivity of massive samples to a spectrum of cooling rates (10°F/hr to a rapid quench). The only significant change in the microstructure of a solid sample was that shown

in Figure 17, for the quenched 1.20 H/Zr material. The γ' has precipitated out of solution as very fine platelets (~ 2 to 6μ in length) along particular crystallographic planes. Moreover, the γ' did not have sufficient time to form around the elongated form of eutectoid, as was seen in the 1.10 H/Zr furnace-cooled specimen (Figure 3b). These observations strongly suggest this phase forms by a nucleation and growth process.

Figure 4b, a photomicrograph of 1.10 material, shows the fine twins bands within γ' platelets. This structure led Beck⁽¹⁾ to postulate that γ' forms by a "diffusion-controlled twinning process." However, from the fact that he and Sidhu *et al*⁽²⁾ have reported γ' to have a composition of 1.00 H/Zr, it seems unlikely that a twinning process could account for the shift in concentration from δ phase (1.50 to 1.60 H/Zr), since only small displacements of atoms occur during twinning. An alternate explanation for the twinning is that it occurs upon cooling, subsequent to formation of the phase. Further work is needed to investigate this phenomenon.

Of greatest significance is the comparison of relative proportions of α and γ' phases in granule and massive samples obtained in two identical thermal cycles — solid and granule samples aged at 800°F, then air and furnace cooled (Table 4). The amount of γ' was reduced considerably in small particles of hydride, and was independent of the cooling rates used; whereas the relative amounts of α and γ' did not change in companion solid samples. This result is in accord with previous observations. Only in the high-temperature x-ray diffraction tests, using 1.20 H/Zr material (-325, +400 mesh powder), was it possible to form the maximum amount of α phase with the corresponding elimination of γ' . However, it seems likely that the same result would be obtained with -20, +100 mesh granules, if given sufficient aging time at temperature and a very slow cool to room temperature.

Hot stage microscope runs revealed that α phase readily formed at the viewing surface at the $\gamma' \rightleftharpoons \delta$ transformation isotherm. However, in this situation, the free surface may have acted as a preferential nucleation site. Moreover, the growth of this phase is unrestrained over one hemisphere; as previously pointed out, α phase, in all cases observed, grew out above the plane of the δ -phase matrix.

a. 250X

BRIGHT FIELD

8193-1-3

b. 1000X

BRIGHT FIELD

8193-1-6

Figure 17. 1.20 H/Zr Fuel Material, Quenched From 650°F,
Showing Widmanstätten Pattern Formed by γ' Platelets

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The diffusion rate is quite high in the $(\alpha + \delta)$ region — above the $\gamma' \rightleftharpoons \delta$ transus (e. g., $D \cong 10^{-7}$ cm²/sec for hydrogen diffusion in δ hydride at 600°F).⁽¹³⁾ As evidenced in hot stage microscopy examinations and in the case of heat treated particles of hydride samples, α phase was shown to form readily, at or above 560°F, and was retained in particle samples upon cooling to room temperature. Conversely, in Dilatometry Run 3b, the reversibility of the $\gamma' \rightleftharpoons \delta$ transformation, in a solid sample, was demonstrated after very slow cooling (also in the solid sample cooled at 10°F/hr from 650°F). Since the Dilatometry Run 3b and furnace cooling of small particles of hydrides probably approach equilibrium conditions, something other than hydrogen diffusion must be considered as the rate controlling step in the $\gamma' \rightarrow \delta$ and $\delta \rightarrow \alpha$ transformations.

Significant amounts of primary α phase were formed only in cases where strain energy would be lowered, at the surface of hot stage microscope samples and in powder or granule hydride samples. It should also be recalled that, in instances where primary α was observed in solid samples, impurity particles also acted as nucleation sites. In all cases, an increase in the amount of α phase corresponded to a decrease in the amount of γ' phase. This point particularly supports the contention of Beck that γ' forms in preference to α , owing to kinetics of the $\delta \rightarrow \gamma'$ and $\delta \rightarrow \alpha$ transformations. The probable source of the strain energy necessary to inhibit the formation of primary α is the large volume ($\sim 13\%$) contraction accompanying the $\delta \rightarrow \alpha$ transformation; whereas, in the α (fcc) $\rightarrow \gamma'$ (fct) transformation, only $\sim 3\%$ volume contraction occurs. The existence of γ' with α and δ phases is postulated to be a metastable equilibrium condition, and the $\delta \rightleftharpoons \gamma'$ transformation is strain induced.

C. REVIEW OF $\delta \rightleftharpoons \gamma'$ TRANSFORMATION RESULTS

The kinetics of the $\delta \rightleftharpoons \gamma'$ and $\delta \rightarrow \alpha$ transformations were found to differ markedly, depending on the physical size of hydride samples. The $\delta \rightarrow \alpha$ transformation was found to be very sluggish in solid samples, whereas large amounts of primary α were formed in finely divided material. Moreover, the amount of γ' contained in solid samples was found to be virtually independent of cooling rate.

V. CONCLUSIONS

The following conclusions can be made as a result of this work:

- 1) The position of the $(\alpha + \delta) \rightleftharpoons \delta$ phase boundary has been defined.
- 2) Gamma prime appears to be a metastable, strain induced transformation product of δ phase; and, as originally contended by Beck,⁽¹⁾ it forms in preference to α phase.
- 3) The amount of γ' contained in fuel material cannot be altered in thermal cycles anticipated during SNAP reactor operation.

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