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HYDROGEN EMBRITTLEMENT OF ZIRCONIUM

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ABSTRACT

The amount of hydrogen normally present in zirconium and zirconium alloys suffices to reduce their ductility greatly in an impact test at room temperature, after slow cooling from 600 F. Quenching from 600 F or above gives high impact strength, as does removal of hydrogen by high-temperature vacuum annealing. This report discusses the evidence on hydrogen embrittlement, the diffusion, solid solubility, and equilibrium pressure of hydrogen in zirconium, the microstructure, and the effects of hydrogen and heat treatment on the mechanical properties of zirconium.

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INTRODUCTION

Recent information obtained at Battelle and at Westinghouse Atomic Power Division shows that a small quantity of hydrogen in zirconium has an embrittling effect, which is primarily noticeable as a decrease of impact strength at room temperature. Currently, these two laboratories are devoting a considerable amount of study to the effects of hydrogen, and to ways of removing it from zirconium. Although this work is far from complete, it appeared desirable to prepare a report on the subject to provide other laboratories with an up-to-date statement of information now available. A report from WAPD on their findings, WAPD-59, has just been issued. Other reports will be issued as more information is obtained.

EVIDENCE FOR HYDROGEN EMBRITTLEMENT OF ZIRCONIUM

Measurements of the impact strength of zirconium and zirconium-tin alloys show a transition at about 400 F, with much higher impact strength above this temperature than below it. Typical results are given in Figure 1.

It always had been assumed that this transition was of the type normally found in metals, and no explanation for it had been sought. However, the Westinghouse Atomic Power Division noticed that the low-temperature ductility of zirconium and its tin alloys was improved considerably if the material was heated to a temperature of 600 F or higher and water quenched. Upon reheating to 600 F, or above, and slow cooling, the impact strengths were again low, showing the process to be reversible. WAPD also noted that the microstructure of brittle specimens showed needles of a second phase, while that of ductile specimens did not. One ingot was non-embrittled upon slow cooling from elevated temperatures and did not show the needles of this phase.

These observations correlated well with some being obtained from work at Battelle. The needlelike phase had been identified as the hydride⁽¹⁾ because it had been shown that, when hydrogen was added to zirconium, more of this phase, which is common in zirconium, was present. The particular hydride had not been identified definitely by electron and X-ray diffraction studies which were in progress.

More important information had been obtained in other studies of titanium. A phase having the same appearance had been found in titanium,

(1) BMI 74, "Metallographic Identification of Non-Metallic Inclusions in Zirconium".

FIGURE I. TYPICAL IMPACT VALUES FOR ZIRCONIUM AND ITS ALLOYS

and, in that work, it had been shown that high-temperature outgassing both removed the phase and gave high room-temperature impact strength. Because of the similarity of titanium and zirconium, it was expected that the same result would be obtained for zirconium.

From these results, it was fairly certain that the phase was a hydride of zirconium and that this hydride phase, precipitated as platelets, was causing the embrittlement of zirconium and its tin alloys. Further work was based, therefore, on the assumption that hydrogen was the cause of brittleness in zirconium.

A single nonembrittleable heat of zirconium (G-570) had been found by WAPD. This was analyzed for hydrogen and compared with other heats in which the precipitate phase was visible in the microstructures and which were embrittleable. The results are given in Table 1.

TABLE 1 COMPARISON OF HYDROGEN ASSAY OF NON-EMBRITTEABLE ZIRCONIUM WITH ZIRCONIUM CONTAINING APPRECIABLE PRECIPITATE PHASE

Heat No	Sample Description	Hydrogen Assay*, ppm $\pm$ 4
G-570	WAPD nonembrittleable	13
168	Arc-melted Foote crystal bar	28
171	Arc-melted Foote, 2.5 per cent Sn	30
Z-1192	Arc-melted WAPD crystal bar	52
--	Foote crystal bar	44
321	Arc-melted WAPD crystal bar	31

* B, vacuum-fusion analysis.

Thus, while most of the samples contain 30 to 50 ppm of hydrogen, the WAPD nonembrittleable heat contained only one-third this amount.

These data, and the lack of conflicting information, seem to establish the fact that precipitation of platelets of a hydride phase makes zirconium brittle. With the amounts of hydrogen normally found in zirconium, such precipitation and brittleness occurs during slow cooling at temperatures below 600 F. Quenching from 600 F promotes ductility. Removal of hydrogen, to less than 10 ppm, reduces brittleness, though zirconium containing even 10 ppm of hydrogen is tougher after quenching than after slow cooling, suggesting that the hydride-solubility limit at room temperature is less than 10 ppm.

The embrittling effect which is found is primarily a notch effect and revealed by a notched-bar impact test. Unnotched tensile bars, tested at either low or high strain rates, normally have only slightly less ductility at room temperature than at 600 F. With larger amounts of hydrogen, brittleness in tensile tests might appear.

Assuming that hydrogen is the source of brittleness, several studies of its behavior in zirconium were started. So far, only partially complete data are available, nevertheless, the information is significant enough so that its reporting is justified. The balance of this report is devoted to these studies of the behavior and the effects of hydrogen in zirconium.

BEHAVIOR OF HYDROGEN IN ZIRCONIUM

Solubility of Hydrogen in Zirconium

The work of Hall, Martin, and Rees⁽²⁾ showed that hydrogen is absorbed readily by zirconium in amounts which decrease with increasing temperature at constant pressure. Their data indicate that, at atmospheric pressure, the maximum amount of H_2 absorbed is about 240 cc of hydrogen per gram of zirconium at 20 C. Corresponding values at 400, 800, and 1100 C are approximately 235, 160, and 40 cc per gram, respectively.

The quantity of hydrogen absorbed at low temperatures, 235 to 240 cc per gram, is within 5 per cent of correspondence with the amount contained in ZrH_2 . At least one lower hydride is believed to exist at these temperatures, but the decomposition pressure for it must be very low, since the data of Hall, Martin, and Rees show essentially zero pressure for hydrogen contents corresponding to the lower hydrides.

In the present case, where we are interested in very small hydrogen concentrations of the order of 25 ppm or 0.28 cc per gram of zirconium, the equilibrium between solid solutions of atomic hydrogen in zirconium with some hydride lower than ZrH_2 must be known. In order to determine this, detailed studies of solubility are required, and such studies have not been conducted yet.

The only available information which bears on this point was obtained from reaction rate and diffusion studies. This information may not be especially accurate, but is useful nevertheless.

(2) H. E. Martin and R. A. Rees, *Trans. Faraday Society*, 41, 1111 (1945).

The tentative values obtained from these studies, given below, are based on the assumption that the concentration at the surface of a specimen, calculated from the concentration gradients of diffusion specimens, represents saturation at the temperature of the experiment. Because the mode of diffusion is volume diffusion, this assumption seems to be correct.

<u>Temperature,</u> <u>C</u>	<u>Solubility,</u> <u>weight per cent</u>	<u>Solubility,</u> <u>atomic per cent</u>
400	0.028	2.6
425	0.038	3.5
450	0.041	3.7
475	0.048	4.4
500	0.057	5.2
600	0.066	6.0

The solubility data above represent values within the boundary of the alpha solid-solution region or at the boundary of the alpha-alpha (beta) region. As the transition temperature is approached, the solubility should decrease. This is in agreement with the observation that hydrogen stabilizes the high-temperature beta allotrope of zirconium.

The solubility data are given graphically in Figure 2. In the graph, it can be seen that the value for 600 C does not follow the straight line which can be drawn through the other points. This may indicate experimental error, or that the expected region of decreasing alpha solubility is being approached (solubility of hydrogen in alpha zirconium must be zero at 865 C).

The solubility line has been extrapolated to lower temperatures. Although this line is subject to considerable error, there is remarkably good agreement between it and the qualitative conclusions from other work. Thus, at 600 C, 100 ppm of hydrogen can be dissolved, and, in specimens containing 60 to 70 ppm of hydrogen, quenching from 600 F eliminates hydrides, as shown by microscopic studies and impact tests. Aging generally occurs at temperatures of 300 to 400 F, where the solubility appears to be 15 to 50 ppm. This is the range of actual hydrogen contents for most zirconium. Finally, material with less than 10 ppm is not particularly susceptible to embrittlement. According to Figure 2, precipitation would not be expected until temperatures were less than 150 C, where the precipitation reaction would be expected to be quite sluggish.

Thus, there is some confirmation of these solubility data. Nevertheless, it should be emphasized that the data are incomplete and that much more work at lower temperatures is required to fix the solubility line at these temperatures with reliability.

-14-

FIGURE 2 SOLUBILITIES OF HYDROGEN IN ALPHA ZIRCONIUM
AT VARIOUS TEMPERATURES

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MICROSCOPIC STUDIES

Microscopic studies of brittle zirconium have revealed the presence of a needlelike phase or inclusion, while similar examinations of nonembrittled metal show its absence. Previous work concerned with the identification of nonmetallic inclusions in zirconium⁽¹⁾ has identified this phase as zirconium hydride. The appearance of the hydride inclusion shown at a magnification of 1000 X in Figure 3 is typical.

Beta-quenched zirconium retains the hydrogen in solution and consequently is relatively ductile. The effect of quenching on the amount of visible hydride is illustrated in the microstructures reproduced as Figures 4 and 5. The large amounts of needlelike hydride which may be present in "as-deposited" iodide zirconium are shown in Figure 4. Figure 5 is a photomicrograph of the same specimen after water quenching from 1832 F (1000 C). An examination of this photograph reveals the typical structure of beta-quenched zirconium with no evidence of the hydride precipitate.

Figures 6 and 7 illustrate the relation between the microstructure and the ductility. Figure 6 shows the structure of a specimen of iodide zirconium, water quenched from 1525 F, containing 67 ppm of hydrogen. The impact strength of this material was 52 to 54 foot-pounds. Figure 7 illustrates the structure of a sample of the same zirconium stock after water quenching from 1525 F and furnace cooling from a two-hour anneal at 600 F. The impact strength was then 7.5 to 8 foot-pounds. As this correlation between visible hydride and brittleness has been repeated consistently, it is felt that metallographic examination of zirconium can be relied upon to determine relative ductility of the material.

Because of the fact that precipitation of hydride appears to be a principal cause of embrittlement, the mechanism and temperature of precipitation become important factors in future uses of zirconium. In order that these points might be studied metallographically, the actual changes in specimen surface have been observed by using the microscope "vacuum hot stage". With this equipment, beta-quenched zirconium was observed and photographed throughout different heating and cooling cycles. Preliminary results of this work seem to indicate that (a) the hydride appears on the surface of the specimen during a slow cool at about 320 F (160 C), (b) an isothermal treatment at 320 F will precipitate visible hydride on the surface, and (c) the inclusions do not appear during isothermal treatment at 450 F (230 C), but do occur on the surface upon cooling through the 320 F region after such a treatment.

(1) Previously cited.

Identification of Hydride Phase

Attempts are being made to identify the hydride seen in the microstructure of nominally pure zirconium. Etched specimens, in which the needles appear slightly in relief, give an electron-diffraction pattern of a face-centered cubic phase which was identified originally as Zr_4H . Attempts to confirm the identity of this phase by X-ray diffraction have been unsuccessful, as yet. Several faint diffraction lines were observed in addition to those of zirconium, these can be attributed only in part to hydride and do not provide satisfactory confirmation.

Unfortunately, the electron-diffraction technique used, while extremely sensitive to the presence of a minor phase present on the surface of a specimen, is not capable of providing accurate values of the lattice constant. This presents a problem in distinguishing between ZrH and Zr_4H , since these are both face-centered cubic, giving similar diffraction patterns, and differing in lattice constant by only about 2 per cent. Because of geometric and instrumental variations, an accuracy of better than 2 per cent in the lattice-constant data is difficult to achieve. To make matters worse, the nature of the precipitate and its somewhat oriented distribution in the matrix results in the production of a diffraction pattern of spots, rather than continuous Debye rings, from the usual heat-treated specimens. This further tends to reduce the attainable precision.

In an attempt to obtain a more precise lattice constant, a sheet specimen was used in the as-rolled condition, which gave a continuous ring pattern. After suitable etching, a little MgO smoke was caught upon the etched surface, and an electron-diffraction photogram was obtained in which the pattern of MgO was superimposed on that of the hydride. Using the known interplanar spacings of MgO for calibration, the lattice constant of the hydride was determined as $a_0 = 4.79 \pm 0.03$ A. This value is in agreement with the literature value, $a_0 = 4.77$ A for face-centered cubic ZrH , rather than with the value $a_0 = 4.66$ A for Zr_4H .

In this specimen, therefore, the hydride appears to be ZrH . However, the temperature at which precipitation occurred in this case was not well defined, and it must not be construed that Zr_4H cannot form under other conditions.

Owing to the extreme sensitivity of electron diffraction for detection of a minor phase, it is difficult to obtain quantitative estimates of the relative amounts present. However, an attempt was made to correlate the intensity of the hydride pattern with the hydrogen content. WAPD Specimen G-570-42, analyzing 13 ppm hydrogen and not embrittled, was selected on the basis of the reported absence of needles(3). It was compared with a

(3) WAPD MR-29 for May, 1962

FIGURE 3. HYDRIDE INCLUSION IN ZIRCONIUM

1111

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FIGURE 4. LARGE AMOUNT OF HYDRIDE
IN CRYSTAL BAR

FIGURE 5. SPECIMEN OF FIGURE 4, WATER
QUENCHED FROM 1000 C.
HYDRIDE IS IN SOLUTION

100X

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FIGURE 6. ZIRCONIUM CONTAINING 67
PPM HYDROGEN, WATER
QUENCHED FROM 1525 F.
NO HYDRIDE NEEDLES, IMPACT
STRENGTH 52-54 FOOT-POUNDS

100X

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FIGURE 7. SAME MATERIAL AS IN FIGURE 6,
ALSO WATER QUENCHED FROM
1525 F. SUBSEQUENTLY HEATED
TO 600 F. AND FURNACE COOLED.
MANY HYDRIDE NEEDLES, IMPACT
STRENGTH 7.5-8 FOOT-POUNDS

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specimen of crystal bar known to have considerable precipitate. The hydride patterns were obtained from both samples, but the pattern was much weaker in the case of the nonembrittled sample. Careful metallographic examination of this specimen showed that the needles, though few in number, were not entirely absent. This finding is not inconsistent with the residual hydrogen content of the specimen.

Failure to obtain X-ray diffraction proof of the presence of hydride might be anticipated, in view of the well-known insensitivity of this method to detect minor phases. Assuming 0.003 weight per cent hydrogen in zirconium, if present as ZrH, there would be a total of less than 0.3 per cent hydride. In general, this is too low a concentration for detection by X-ray diffraction.

Diffusion Rates of Hydrogen in Zirconium

Diffusion coefficients for alpha zirconium determined for three different temperatures are listed below. The values are tentative and subject to possible error because of approximations necessary in treating the data.

<u>Temperature,</u> <u>C</u>	<u>$D \times 10^{-6}(\text{cm}^2/\text{sec})$</u>
400	6
500	10
600	16

From a plot of the experimentally determined diffusion rates versus reciprocal temperature, diffusion rates were predicted for 316 to 538 C (600 and 1000 F) by extrapolation. From these data, it was found that a cylinder 1/8 inch in diameter (infinite length) could be saturated to 99 per cent with hydrogen at 600 F in 120 minutes. This result and other data are tabulated below.

<u>Temperature,</u> <u>C</u>	<u>Diameter of Cylinder,</u> <u>inches</u>	<u>Time to Saturate</u> <u>(99%) With Hydro-</u> <u>gen, minutes</u>
316 (600 F)	1/8	120
500	1/8	40
600	1/8	25
316 (600 F)	1/2	1900

The diffusion rates for hydrogen in zirconium are seen to be extremely high and do not decrease rapidly as temperature is lowered. This fact

explains the high speed of hydride precipitation and solution at low temperatures. Thus, air cooling at temperatures below 500 F can cause hydride precipitation and brittleness, and a one-minute treatment at 600 F suffices to redissolve the hydride.

If the rate of diffusion were the controlling factor, the complete removal of hydrogen from specimens with the dimensions of the usual impact-test bars should present no problems. This is not the case, however, since it has been found that the equilibrium pressure of hydrogen over zirconium containing small amounts of hydrogen is extremely low and is the dominant factor in hydrogen removal.

Equilibrium Pressure and Hydrogen Removal

If removal of hydrogen from zirconium is to proceed at the rate allowed by diffusion, the ambient atmosphere must have a partial pressure of hydrogen lower than the equilibrium pressure of the hydrogen solution. Theoretically, in an atmosphere consisting of a hydrogen-free inert gas, degassing could take place. However, the evolution of hydrogen from the specimen would be impeded by stagnation of the hydrogen molecules at the metal surface. This effect is overcome by using the best vacuum obtainable. It has been our experience that the gases present in a vacuum system containing metal specimens at elevated temperatures analyze about 50 per cent hydrogen. In order to estimate the degree of vacuum necessary to produce a selected residual hydrogen concentration in zirconium, the gas pressure in a vacuum may be considered as 100 per cent hydrogen.

In order to obtain solubility values, the Hall, Martin, and Rees(2) data were inspected. In spite of the allotropic transition of the metal, the logarithm of the hydrogen pressure plotted against $1/T$ gave a straight line for the concentration 50 cc hydrogen per gram of zirconium in the transition range. Using Sieverts law, the line for 75 cc of hydrogen per gram of zirconium was calculated. The calculated line agreed with a line derived directly from the experimental data in this concentration. At higher concentrations, the extrapolation by Sieverts law did not hold. This was probably because of crossing into a two-phase region. On the other hand, it appears reasonably safe to extrapolate to rather low concentrations by this method. Accordingly, the data at 50 cc per gram were extrapolated from the experimental region of 850 to 950 C to values as low as 316 C and as high as 1400 C. It is recognized that these are long and questionable extrapolations. Calculations for low hydrogen concentrations were all based on the 50-cc per gram line. The results of the calculations are given in Figure 8.

(2) Previously cited.

[REDACTED]

FIGURE 8. EQUILIBRIUM PRESSURE OF HYDROGEN OVER ZIRCONIUM CONTAINING VARIOUS AMOUNTS OF DISSOLVED HYDROGEN

Study of these data shows that high-temperature treatment, in extremely good vacuum systems, is required for effective hydrogen removal. For temperatures below 800 C, a vacuum better than 0.04 micron would be required to reduce the hydrogen to 10 ppm. Since even lower hydrogen contents may be desired, higher temperatures or a better vacuum would be required, with the former a more practical solution.

Experimental studies were begun of the removal of hydrogen at various temperatures and for various times. The data given in Table 2 were obtained in the first part of this work.

TABLE 2. HEAT TREATMENTS OF ZIRCONIUM AND VACUUM-FUSION ANALYSIS FOR HYDROGEN IN ZIRCONIUM

Vacuum Heat Treatment		Hydrogen by Vacuum-Fusion Analysis, ppm
Time, hours	Temperature, C	
8	700	28
8	700	29
4	800	10
8	925	12
8	925	12
4	1190-1336	4
2	1314-1400	6

These data show that, for this vacuum system, temperatures of 800 C or higher were required for useful hydrogen removal. However, much better results were obtained at temperatures in excess of 1200 C.

Additional data, reported in Table 3, were obtained in a vacuum system equipped with high-speed pumps. The system also included a DPI ionization gage, though the readings should not be considered to be highly accurate.

From the data in Table 3, it is apparent that efficient hydrogen removal is possible at temperatures of 830 C or more, in a very good vacuum. The results given in this table agree surprisingly well with the calculated hydrogen pressures given in Figure 8.

These results were confirmed further in other apparatus. There, a 13-hour treatment at 800 C was sufficient to reduce the hydrogen content to 6 to 7 ppm.

The requirements of a dehydriding system will be a high-speed pumping system, capable of attaining pressures of 0.05 micron, or less if possible.

TABLE 3. EFFECT OF VACUUM ANNEALING OF ZIRCONIUM ON HYDROGEN CONTENT

Composition, weight % (Nominal)	Annealing Treatment	Hydrogen Content, ppm*	
		Before Annealing	After Annealing
Zirconium	1525 F, (830 C), 5 hr, 0.05 μ , FC**	67	12
"	1525 F, 26 hr, 0.035 μ , FC	"	5
"	1950 F, (1066C), 3 hr, 0.06 μ , FC	"	7
"	1950 F, 23 hr, 0.02 μ , FC	"	6
Zr + 0.5 Sn	1525 F, 6 hr, 0.04 μ , FC	42	8
Ditto	1525 F, 22 hr, 0.025 μ , FC	"	5
"	1950 F, 5 hr, 0.05 μ , FC	"	5
"	1950 F, 20 hr, 0.04 μ , FC	"	5
Zr + 1.5 Sn	1525 F, 6 hr, 0.04 μ , FC	45	6
Ditto	1525 F, 22 hr, 0.025 μ , FC	"	5
"	1950 F, 5 hr, 0.05 μ , FC	"	5
"	1950 F, 20 hr, 0.04 μ , FC	"	2
Zr + 2.0 Sn	1525 F, 6 hr, 0.04 μ , FC	37	7
Ditto	1525 F, 22 hr, 0.025 μ , FC	"	4
"	1950 F, 5 hr, 0.05 μ , FC	"	4
"	1950 F, 20 hr, 0.04 μ , FC	"	3
Zr + 2.5 Sn	1525 F, 5 hr, 0.05 μ , FC	39	11
Ditto	1525 F, 26 hr, 0.035 μ , FC	"	6
"	1950 F, 3 hr, 0.06 μ , FC	"	4
"	1950 F, 23 hr, 0.02 μ , FC	"	2

* Hydrogen analyses are accurate to ± 2 ppm.

** FC = furnace cooled.

a nearly leak-proof system, to avoid contamination by nitrogen and oxygen, and means for heating to 800 C or higher.

The high temperatures required probably will not permit dehydriding of finished parts made of zirconium, like STR fuel assemblies. If hydrogen removal ever is considered to be necessary, the sponge or crystal-bar must be dehydrided, and kept hydrogen free in subsequent processing. Considering the success which has been attained in avoiding nitrogen contamination of zirconium, avoiding hydrogen contamination is considered to be relatively simple. However, the possible sources of hydrogen contamination must be considered carefully, because diffusion of hydrogen in zirconium is so rapid that any contamination will penetrate the whole cross section of pieces of normal size. This is far different from the situation with oxygen or nitrogen, which diffuse so slowly in alpha zirconium that any contamination is confined to the surface.

However, there is a possibility that hydrogen can be removed at lower temperatures by a better "getter" for hydrogen than zirconium, or by zirconium itself at a lower temperature than the part to be dehydrided.

Source of Hydrogen in Zirconium

No analyses have been made yet of the hydrogen content of sponge zirconium. However, it seems probable that hydrogen originates with the sponge, since there seemed to be no other logical source. The hydrogen may not be formed actually with the sponge, but may come from water which is picked up by magnesium chloride from the atmosphere. In later operations in which the sponge is heated, the zirconium may decompose the water and pick up both oxygen and hydrogen. Then the hydrogen would be expected to remain through subsequent processing operations.

Several analyses have been made of the hydrogen content of crystal bar. The hydrogen content appears to be extremely variable; it may be as low as 10 ppm or as high as 110 ppm. The average content for seven determinations was 60 ppm.

There does not appear to be much change in the hydrogen content during arc melting. These conclusions are borne out by the fact that hydrogen contents of arc-melted materials have been in the range of 10 to 70 ppm, with an average of 40 ppm, in 16 determinations. For all practical purposes, this hydrogen content is as great as that found in crystal-bar samples. Similarly, it is not likely that hydrogen is increased during arc melting, since there is no significant source of hydrogen. Only in the case of vacuum melting, or in the case of a flowing atmosphere of inert gas over the melt, would a significant decrease of hydrogen content be expected.

[REDACTED]

[REDACTED]

It is equally unlikely that there will be any significant change of hydrogen content in rolling or forging operations. The atmosphere used in this work, air or an inert atmosphere, contains very small amounts of hydrogen or water vapor, and it is unlikely that there will be sufficient hydrogen to produce a change in hydrogen content. Furthermore, the reaction of hydrogen with zirconium appears to be impeded very much by a surface layer of oxide. In experiments on the determination of the reaction rate of hydrogen with zirconium, it has been concluded that the oxide layers originally present on a piece of zirconium prevent the reaction from occurring until the diffusion of this oxide layer permits hydrogen to enter the metal.

It is true that these reaction-rate experiments were performed at much lower temperatures than those used for forging or rolling, that is, 375 to 450 C, instead of 800 C. Whether the same conclusion would apply to zirconium heated to 800 C is not known. It may be that under these conditions the oxide layer would be permeable to small amounts of hydrogen which might be present in the atmosphere. Again, however, analyses which have been made on zirconium and alloys after forging and rolling seem to show that the hydrogen content of these materials is normal.

Under very carefully controlled conditions, the reaction of hydrogen with zirconium will proceed rapidly. The reaction is sometimes slow to begin, presumably because of the protective effect of the surface films normally present on zirconium. After reaction begins, the rate of reaction is $2 \text{ to } 4 \times 10^{-3} \text{ ml/cm}^2/\text{sec}$, at temperatures of 375 to 450 C. Heating in hydrogen certainly must be avoided.

It was possible that hydrogen contamination could occur during corrosion testing. To determine whether very large amounts of hydrogen would be picked up in this manner, samples which had been corrosion tested for as long a time as 7000 hours were assayed. Hydrogen contents of up to 140 ppm were found. These appeared a little high, but since no assays had been made before corrosion testing, it was not known whether corrosion testing had caused an increase of hydrogen content.

WAPD has recently corrosion tested degassed samples of both zirconium and zirconium-tin alloy. In either 650 F water or hydrogenated 600 F water for 14 days, the hydrogen content of the zirconium samples increased from 6-7 ppm to 130-150 ppm. The hydrogen content of the 2.5 per cent tin-zirconium samples increased from 5-8 ppm to 39 ppm during 14 days in 650 F water. During the corrosion testing, the samples gained about 0.15 mg/cm^2 by corroding. From their data, WAPD concluded that the only hydrogen picked up by zirconium was that released during corrosion. The zirconium picked up 60 per cent, the zirconium-tin 15 per cent, of the amount of hydrogen theoretically available from the corrosion reaction.

These data show that, unless means for avoiding hydrogen pickup are found, the zirconium in a reactor will be notch brittle after use, when the reactor is cold. At operating temperature, the material would be more ductile.

THE EFFECTS OF HYDROGEN EMBRITTLEMENT
ON MECHANICAL PROPERTIES

Hydrogen, when present as a hydride in zirconium in amounts greater than 20 ppm, has a large effect on the impact strength and the impact transition temperature, may increase the yield and ultimate tensile strengths, and may affect the creep and fatigue properties. Even smaller amounts are expected to have a noticeable effect.

The effects of various hydrogen contents in zirconium on the impact strength at 0 C (32 F) and on the hardness are given in Table 4. The various hydrogen contents were obtained by vacuum annealing at 1525 F (830 C). All specimens were from the same ingot (No. 308) and were furnace cooled from 1525 F (embrittled condition) after at least 2 hours at temperature.

TABLE 4. EFFECT OF HYDROGEN CONTENT ON IMPACT STRENGTH OF ZIRCONIUM FURNACE COOLED FROM 1525 F (830 C)

Hydrogen Content, ppm	Impact Strength at 0 C, foot pounds	Hardness, Rockwell "B"
67	14	17
20	32	16
5	73	17

Hydrogen content does not change hardness, but does have a large effect on the impact strength at 0 C (32 F). The appearance of the relative amounts of hydrides in these specimens is shown in Figures 9, 10, and 11.

The effect of hydrogen, when precipitated as the hydride, on the temperature of transition from brittle to ductile failure can be illustrated best by the curves of impact strength versus temperature. Two such curves are shown in Figure 12 for zirconium containing 31 ppm of hydrogen and for zirconium containing 9 ppm of hydrogen.

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FIGURE 9. ZIRCONIUM CONTAINING 67-ppm HYDROGEN, FURNACE COOLED FROM 1525 F. MANY VISIBLE HYDRIDE NEEDLES, IMPACT STRENGTH 14 FOOT-POUNDS

100X 93660
FIGURE 10. ZIRCONIUM CONTAINING 20-ppm HYDROGEN, FURNACE COOLED FROM 1525 F. FEW VISIBLE HYDRIDE NEEDLES. IMPACT STRENGTH 32 FOOT-POUNDS

100X 93656
FIGURE 11. ZIRCONIUM CONTAINING 5-ppm HYDROGEN, FURNACE COOLED FROM 1525 F. IMPACT STRENGTH 73 FOOT-POUNDS

100

1

2

3

4

5

6

100

FIGURE 12. EFFECT OF HYDROGEN CONTENT ON IMPACT STRENGTH OF ZIRCONIUM AT VARIOUS TEMPERATURES

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Two other curves for a zirconium + 2-1/2 per cent tin alloy containing 32 ppm of hydrogen and <10 ppm of hydrogen are shown in Figure 13. From these two figures, it is evident that the presence of 2.5 per cent tin increases the impact strength of both the hydrogen-free and the hydrogen-contaminated zirconium.

From the data given in Figures 12 and 13, it is apparent that, as the hydride dissolves at the higher temperature, the impact strength increases until the materials with high hydrogen contents have an impact strength as great as that of the materials with low hydrogen contents. Incidentally, the conclusions which would be drawn from these data about solubility at various temperatures agree moderately well with the extrapolation given in Figure 2.

The tensile properties may be increased by increasing amounts of hydrides present in zirconium, as evidenced by room-temperature tensile tests on a zirconium + 2-1/2 per cent tin alloy. These tensile properties are given in Table 5. The hydrogen contents before and after vacuum

TABLE 5. EFFECT OF HYDROGEN CONTENT ON THE ROOM-TEMPERATURE TENSILE PROPERTIES OF A ZIRCONIUM + 2-1/2 PER CENT TIN ALLOY IN THE EMBRITTLED CONDITION

	Annealed at 1300 F and Furnace Cooled	Annealed at 1525 F in Vacuum of 0.03 μ and Furnace Cooled
Upper yield point, psi	39,400	31,900
Yield strength, 0.2 % offset, psi	38,900	32,600
Ultimate tensile strength, psi	50,300	44,000
Elongation in 2 inches, %	43	36.7
Reduction in area, %	61	55.4
Hydrogen content, ppm, estimated	> 30	< 10
Grain size, mm	0.025	0.060

annealing are being determined, but it probably is safe to state that the hydrogen content was > 30 ppm before and < 10 ppm after vacuum annealing, on the basis of other analyses made on specimens given the same treatment. The grain size was increased from 0.025 mm for specimens annealed at 1300 F (704 C) to approximately 0.060 mm by vacuum annealing at 1525 F (830 C). The increased grain size would lower the tensile properties, but to what extent is not known.

It is entirely possible that all of the differences in properties are due to the difference in grain sizes, rather than to the difference in hydrogen content. Evidence obtained at MIT on hydrogen alloys supports the first of

FIGURE 13. EFFECT OF HYDROGEN CONTENT ON IMPACT STRENGTH OF ZIRCONIUM + 2 1/2 PERCENT TIN ALLOY AT VARIOUS TEMPERATURES

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these possibilities. In their work on unalloyed zirconium, an increase from 204 ppm to 415 ppm caused an increase of only 4000 psi in yield strength and only 2000 psi in tensile strength. Thus, it might be expected that 30 to 50 ppm of hydrogen would have an insignificant effect. Of course, there is the possibility that the first small amount of hydrogen will have a larger effect than subsequent additions.

In any event, it is certain that hydrogen has only a small effect on tensile properties, in the range where it is important for its embrittling effect on impact strength. Its effect on ductility may be important, but is unknown; the lower ductility of the dehydrided sample of Table 5 must be attributed to its larger grain size.

The effect of hydrogen content alone is being checked on other specimens of comparable grain size of nominally pure zirconium. There may be an effect of hydrogen content on these properties.

A series of heat treatments were performed on impact-specimen blanks of arc-melted crystal-bar zirconium containing 67 ppm of hydrogen (Ingot 308). All specimens were notched after heat treatment. The results of these treatments on the impact strengths are given in Table 6, and in Figure 14.

These data show that hydride precipitation which causes brittleness occurs during slow cooling below 700 F, for these specimens containing 67 ppm of hydrogen. Water quenching from any temperature above 700 F provides ductility. Slow cooling below this temperature, down to 450 F, increases brittleness. Slow cooling to still lower temperature does not seem to increase brittleness further.

Similar data have been obtained on zirconium-tin alloys, and there does not seem to be any significant difference in the two materials. However, this subject is being investigated further.

In titanium samples subject to hydrogen embrittlement, it has been found that the increased ductility of quenched samples is lost slowly with time. A considerable decrease of strength occurs in a month. The possibility that this effect occurs in zirconium is being investigated.

RWD:ADS:GTM:HAS:RFD:CMS:MWM/mpm
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TABLE 6. EFFECT OF VARIOUS HEAT TREATMENTS ON THE
IMPACT STRENGTH OF ZIRCONIUM CONTAINING
67 PPM HYDROGEN

Treatment	Impact Strength at 0 C, foot-pounds
1500 F (816 C), 2 hours, furnace cooled	14-15
1500 F (816 C), 2 hours, water quenched	52-54
1500 F (816 C), 2 hours, water quenched + 600 F (316 C), 2 hours, furnace cooled	7.5-8
<u>Specimens Annealed First at 1120 F, 2 Hours, Furnace Cooled</u>	
300 F (149 C), 1 hour, water quenched	11-12
350 F (177 C) Ditto	10-11
400 F (205 C) "	12-13
450 F (232 C) "	10-13
500 F (260 C) "	15-16
550 F (288 C) "	20-20.5
600 F (316 C) "	44-48
700 F (371 C) "	60-64
600 F (316 C), 1 hour, furnace cooled to 500 F (260 C), 1 hour, water quenched	16-20
600 F (316 C), 1 hour, furnace cooled to 450 F (232 C), 1 hour, water quenched	16-16.5
600 F (316 C), 1 hour, furnace cooled to 400 F (205 C), 1 hour, water quenched	15-19.5
600 F (316 C), 1 hour, furnace cooled to 350 F (177 C), 1 hour, water quenched	11.5-13
600 F (316 C), 1 hour, furnace cooled to 300 F (149 C), 1 hour, water quenched	15-15.5

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FIGURE 14. EFFECT OF VARIOUS HEAT TREATMENTS ON IMPACT STRENGTH OF NOMINALLY PURE ZIRCONIUM CONTAINING 67ppm OF HYDROGEN

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