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COMPATIBILITY OF ZIRCONIUM HYDRIDE
AND CARBON DIOXIDE

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ABSTRACT

The purpose of the investigation was to study the stability of unclad zirconium hydride as a reactor moderator in carbon dioxide coolant. This investigation was carried out as part of a program to evaluate various moderator-coolant combinations for the Maritime Gas-cooled Reactor (MGCR) Program. Particular emphasis was placed on rates of corrosion, retention of hydrogen, and dimensional stability.

Two ranges of hydride were tested--alpha- plus delta-phase hydride ($\text{ZrH}_{0.9 \pm 0.2}$) and delta-phase hydride ($\text{ZrH}_{1.5}$). The delta-phase hydride had excellent dimensional stability, but suffered as great as 20% hydrogen loss at 1200°F , together with severe corrosion. The alpha- plus delta-phase hydride swelled and warped in a temperature gradient but did not lose much hydrogen and did not corrode severely even at 1200°F . The results indicated that zirconium hydride could not be used as unclad moderator in a carbon dioxide atmosphere in the temperature range desired for the MGCR.

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COMPATIBILITY OF ZIRCONIUM HYDRIDE AND CARBON DIOXIDE

INTRODUCTION

This work was performed during the first six months of the Maritime Gas-cooled Reactor (MGCR) Program when the zirconium-hydride-CO₂ reactor system, using zirconium hydride as either clad or unclad moderator, was being considered. The purpose of the investigation was to study the stability of unclad zirconium hydride in CO₂. The objectives of the test were to determine the type, rate, and extent of corrosion of zirconium hydride at 800°F to 1200°F in CO₂, the loss of hydrogen to the atmosphere, and the migration of hydrogen in samples in a temperature gradient. It was hoped that mild surface oxidation would occur to form a barrier which would not only prevent further oxidation, but also inhibit hydrogen migration to the surface where it could be lost to the CO₂ atmosphere.

MATERIALS

The hydride was prepared at General Atomic by hydriding reactor-grade zirconium. The hydride was then homogenized for 40 hr at 700°F to assure uniform hydrogen distribution. Two plates of delta-phase hydride containing ZrH_{1.49} (60 atomic-% H) were prepared. This composition was determined from the hydrogen consumption and the weight gain of the metal after hydriding. Chemical analysis confirmed the composition to be ZrH_{1.48±0.02}. Two rods were prepared in the alpha- plus delta-phase. Chemical analysis of rod No. 1 showed an average of ZrH_{1.19±0.07} (55 atomic-% H) and rod No. 2 showed ZrH_{0.69±0.01} (41 atomic-% H). The deviations indicated above are average from the mean. The phases are indicated in Fig. 1. (There are discrepancies in the phase terminology in the literature: D. A. Vaughan^{(1)*} calls the tetragonal hydride phase gamma, although previously this has been called delta. However, the phase in question is called delta in this report, which is the terminology used by Ells and McQuillan.⁽²⁾) Welding-grade CO₂ was used and maintained at a dew point of -60°F; it proved to be 99.9% pure.

*References are listed on page 17.

Fig. 1--Zirconium-hydride system

APPARATUS

The apparatus for this experiment was a modification of the apparatus described by Merten, Stone, and Wallace⁽³⁾ for the production of uranium-zirconium-hydride fuel elements. The experiment was conducted in "Mullite" tubes, which were placed in furnaces containing three separate heating elements (see Fig. 2). The temperature of each element was regulated by a controller using a thermocouple placed between the element and the Mullite tube. The furnaces were 25 in. long and were controlled so that the temperature variation in the central 6-in. zone would be less than 5°F . The tubes were equipped to permit evacuation of atmospheric gases, after which CO_2 could be injected into the tube and exhausted through a mercury bubble trap.

1. CONSTANT-TEMPERATURE ZONE	5. CO ₂ OUTLET
2. TEMPERATURE-GRADIENT ZONE	6. VACUUM LINES
3. CO ₂ INLET	7. HEATER
4. THERMOCOUPLE INLET	8. HEATER

Fig. 2--Schematic diagram of carbon-dioxide testing apparatus

EXPERIMENTAL PROCEDURE

The samples were prepared from each of the hydride plates and rods described above under "Materials." Sections were cut from the ends of each rod and each plate for analysis and constant-temperature corrosion tests. These sections were divided into 12 samples each and split, so for each sample tested there was a duplicate for control analysis. The remaining portions of the rods and plates were split lengthwise and one half of each was tested in a temperature gradient and the other half was retained as a standard.

The small samples were placed in stainless-steel trays which were placed in stainless-steel tubes and put into the constant-temperature zones of the Mullite tubes. These samples were tested at 800°F, 1000°F, and 1200°F, respectively, for 1000 hr in a flow of CO₂. The remaining pieces of the rods

and plates were tested in the temperature-gradient section of the 1200°F tube. These samples were placed in a stainless-steel tray with six thermocouples fastened in holes at 1-in. intervals along one of the rods. The thermocouples gave the temperature gradient in one sample and it was assumed that the duplicate samples had the same gradient. These specimens were adjusted so that the cool end was at 800°F $\pm$ 5°F and the hot end was at 1165°F $\pm$ 5°F.

The samples were placed in their respective tubes and the system was evacuated to below 100 microns and flushed several times with CO₂. The chambers were then filled to 1-atm pressure and heated under a slightly positive pressure. The system was cooled and opened at 250, 500, and 1000 hr. At these times the samples were examined visually and weighed, and one sample of each material at each temperature was retained for chemical analysis and metallographic observation. The samples placed in the temperature gradient were examined before and after 1000 hr. During the 1000-hr period, the only examination was visual.

VISUAL RESULTS

After 250 hr at test temperature, all of the samples were dark with some white material in the fine cracks and on the surfaces which were machined prior to testing. The oxide coating appeared uniform and adherent, particularly on the delta-phase hydride (ZrH_{1.5}).

After 500 hr, the oxidation appeared to be more extensive. The oxide penetration was extensive in the cracks, particularly in the ZrH_{1.5} specimens. One delta-phase sample at 1200°F had shattered.

The visual effects of corrosion after 1000 hr at test temperature are shown in Figs. 3, 4, and 5. The acceleration of oxidation with temperature seemed much more severe in the case of the delta-phase hydride than in the alpha- plus delta-phase samples in Fig. 3. This accelerated corrosion, however, may not be a true characteristic of delta-phase hydride, but may be the result of undetermined trace impurities or of many microscopic fractures throughout the samples tested. Fig. 5 shows the two alpha- plus delta-phase rods, (a) ZrH_{1.1} and (c) ZrH_{0.75}, tested in the same temperature gradient. Initially, rod (a) was cracked more than rod (c) and had correspondingly

Fig. 3--Hydride samples after 1000 hr at constant temperature: $\text{ZrH}_{1.5}$ (7a) at 1200°F ; (8a) at 1000°F ; (9a) at 800°F $\text{ZrH}_{0.75}$ (7b) at 1200°F ; (8b) at 1000°F ; (9b) at 800°F

Fig. 4--Temperature gradient samples: (a) and (c) tested delta-phase hydride; (b) and (d) standards.
High temperature at top of figure

Fig. 5--Temperature gradient samples: (a) and (c) tested alpha- plus delta- phase hydride; (b) and (d) standards. High temperature at top for (c), at bottom for (a)

more corrosion. Rod (a) lengthened $3/64$ in. and rod (c) $4/64$ in. in the 1000-hr test. Rod (c) developed a considerable bend during the 1000-hr test, possibly caused by oxide penetration. This rod was the sample to which the monitoring thermocouples were attached. Figure 4 shows the difference in corrosion of two plates (a) and (c) of the same delta-phase hydride in the same temperature gradient; plates (c) and (d) were brittle and contained fine microscopic cracks; plate (c) corroded extensively; plates (a) and (b) were sound and solid; plate (a) scaled and corroded only slightly in 1000 hr at the high-temperature end. The oxide on plate (a) appeared to be uniform and protective, although slight cracking and scaling had started in the high-temperature region.

CHEMICAL ANALYSIS

The hydrogen analysis was performed by burning the samples at 900° to 1000°C in a flow of dry oxygen. The water produced was then collected in a magnesium perchlorate trap and weighed to determine the hydrogen content of the sample.

CHEMICAL RESULTS

The chemical analysis of the samples, as given in Table 1, is considered accurate to within 1% of the values given. In the constant-temperature tests, the delta-phase ($\text{ZrH}_{1.5}$) showed a hydrogen loss in 1000 hr of 20% at 1200°F , 10% at 1000°F , and 3% at 800°F . For the alpha- plus delta-phase ($\text{ZrH}_{0.9\pm0.2}$), there was less than 3% hydrogen loss in 1000 hr at 1200°F with no detectable loss at lower temperatures. The initial and final hydrogen content of the samples in the temperature gradient is plotted in Figs. 6 and 7. Graph (b) of Fig. 6 shows considerable scatter in the hydrogen content at the high-temperature end of the plate because of the severe oxidation and cracks in the plate which prevented hydrogen migration. The peculiar hydrogen migration exhibited in graph (a) of Fig. 7 cannot be explained unless it is assumed that the rod shifted from the temperature gradient during the test. The hydrogen content does not correspond to the uniform gradient in the observed surface corrosion. A log plot of weight gain versus time for the samples tested in the constant-temperature zone is given in Fig. 8. Much of

Table 1

ANALYTIC RESULTS OF SAMPLES UNDER TEST

Sample No.	Condition		Chemical Analysis of H/Zr		Diffusion Layer (mil)	Oxide Layer (mil)	Remarks
	hr	°F	Before test	After test			
SHE-1-8-1	250	1200	1.4	1.4	None	1.1	Oxide uniform with localized heavy areas
SHE-1-9-1	250	1200	1.1	1.1	1.1	1.2	Oxide uniform but irregular apparently owing to basic material condition
SHE-1-8-4	500	1200	1.5	1.3	None	0.7-1.9	Oxide very heavy at fractured areas; <u>spec. extremely fractured</u>
SHE-1-9-4	500	1200	1.1	1.1	1.4	1.0-3.1	Oxide uniform but surface irregular
SHE-1-8-10	500	1200	1.5	1.2	None	1.3-5.5	Oxide heavy at fractured areas; <u>spec. extremely fractured</u>
SHE-1-8-7	1000	1200	1.5	1.2	None	1.5	Oxide heavy at fractured areas; <u>spec. extremely fractured</u>
SHE-1-9-7	1000	1200	0.77	0.74	None	1.2-1.7	Heavy irregular oxide
SHE-1-9-10	1000	1200	0.74	0.72	0.8-1.9	1.0-4.5	Layers nonuniform and irregular
SHE-1-8-2	250	1000	1.5	1.5	None	2.5	Oxide appears uniform; <u>spec. slightly fractured</u>
SHE-1-9-2	250	1000	1.1	1.1	0.3	0.2	Oxide layer is nonuniform; average value given
SHE-1-8-5	500	1000	1.5	1.5	None	0.8-3.2	Oxide nonuniform; heavy in fractured area; <u>spec. slightly fractured</u>
SHE-1-9-5	500	1000	1.1	1.1	0.4	0.2-3.3	Oxide irregular and intermittent
SHE-1-8-8	1000	1000	1.5	1.3	None	0.7	
SHE-1-8-11	1000	1000	1.5	1.4	None	1.2	Oxide heavy at fractured areas; <u>spec. extremely fractured</u>
SHE-1-9-8	1000	1000	0.74	0.74	2.5	7.5	
SHE-1-9-11	1000	1000	0.71	0.73	0.3	0.7-1.8	

Table 1--continued

Sample No.	Condition		Chemical Analysis of H/Zr		Diffusion Layer (mil)	Oxide Layer (mil)	Remarks
	hr	°F	Before test	After test			
SHE-1-8-3	250	800	1.5	1.5	None	None	Diffusion band and oxide too thin to measure; <u>spec. fractured</u>
SHE-1-9-3	250	800	1.1	1.1	Noted	Noted	
SHE-1-8-6	500	800	1.5	1.5	None	None	Slight diffusion band too thin to measure
SHE-1-9-6	500	800	1.1	1.1	Noted	None	
SHE-1-8-9	1000	800	1.5	1.4	Noted	Noted	Thin intermittent oxide; <u>spec. extremely fractured</u>
SHE-1-8-12	1000	800	1.5	1.5	None	Noted	Thin intermittent oxide; <u>spec. extremely fractured</u>
SHE-1-9-9	1000	800	0.74	0.75	Noted	Noted	Layers too thin to measure
SHE-1-9-12	1000	800	0.71	0.71	0.1	Noted	Layers too thin to measure

Fig. 6--Hydrogen migration in delta-phase zirconium hydride;
(a) and (b) in temperature gradient, (c) for 1000 hr in 1 atm
flowing CO_2

Fig. 7--Hydrogen migration in alpha- plus delta-phase zirconium-hydride gradient; (a) and (b) in temperature gradient, (c) for 1000 hr in 1 atm flowing CO_2

Fig. 8--Log weight gain versus time plot; (a) delta $\text{ZrH}_{1.5}$, (b) alpha plus delta $\text{ZrH}_{0.9 \pm 0.2}$

the scatter of data is due to lack of really accurate measurement of surface area since the increased area due to cracks was ignored in this plot.

METALLOGRAPHIC RESULTS

The metallographic observations are tabulated in Table 1 and are illustrated in Figs. 9 through 16. The corrosion samples used for these photomicrographs are the same as those used for Fig. 3. The observations of the samples in the temperature gradient are not included since the various sections correspond very closely to the observations of constant-temperature samples at corresponding temperatures. The oxide coating for plate (a) of Fig. 4 was very thin and uniform at the cool end, but the coating grew increasingly thicker as the high-temperature end was approached.

A complete set of hardness readings was taken, but the information obtained was of negligible value. The hardness along the plates in the temperature gradient seemed to be more uniform along the samples after corrosion testing than before. Oxygen content was the only thing indicated by the hardness tests. A typical sample gave DPH readings of 180 in the hydride, 743 in the diffusion band, and 1174 in the surface-corrosion product. The corrosion product was not identified but it appeared to be ZrO_2 .

CONCLUSIONS

The major conclusions drawn from the results of this investigation may be summarized as follows:

Material fracture and oxide breakaway gave disastrous results in 1000 hr at temperatures as high as 1200°F. The most damaging effects seemed to be facilitated by microscopic cracks which were propagated by the oxidation.

The surface oxidation proved to be fairly satisfactory as a barrier to prevent hydrogen loss. Although some loss was observed at 1000 hr, as shown in Table 1, the loss was mainly in the samples where excessive oxide breakaway coupled with high internal hydrogen pressure occurred. The temperature-gradient hydrogen redistribution represented in Figs. 7 and 8 shows that the hydrogen migrated from the high-temperature region to the low-temperature region. This indicated that the hydrogen was unable to diffuse through the surface oxide to come to equilibrium with the atmosphere and therefore

Fig. 9--Alpha- plus delta-phase
hydride as received

Fig. 10--Alpha- plus delta-phase
hydride after 1000 hr at 800°F
in CO₂

Fig. 11--Alpha- plus delta-phase
hydride after 1000 hr at 1000°F
in CO₂

Fig. 12--Alpha- plus delta-phase
hydride after 1000 hr at 1200°F
in CO₂

Fig. 13--Delta-phase hydride
as received

Fig. 14--Delta-phase hydride after
1000 hr at 800°F in CO₂

Fig. 15--Delta-phase hydride after
1000 hr at 1000°F in CO₂

Fig. 16--Delta-phase hydride after
1000 hr at 1200°F in CO₂

redistributed to equalize the hydrogen fugacity in each plate.

The delta-phase hydride had much greater dimensional stability than the two-phase alpha- plus delta-phase hydride. This was particularly evident with the growth and warpage of the lower hydride specimens (shown in Fig. 5) in the 800° to 1165°F temperature gradient.

The MGCR requires a moderator which is good to at least 1200°F with a lifetime of at least three years. Because of the scaling and cracking of the delta-phase hydride at 1200°F and the dimensional instability of the alpha-plus delta-phase hydride in a temperature gradient, the use of zirconium hydride as an unclad moderator in CO₂ was considered undesirable.

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