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METAL HYDRIDES FOR SHIELDING APPLICATIONS

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ABSTRACT

Tests have been conducted to determine the behavior of lithium hydride and calcium hydride under a variety of conditions.

Metals of interest as container materials were subjected to stress-rupture and tensile tests after undergoing one or more thermal cycles to certain maximum temperatures while in contact with lithium hydride at various lengths of time.

Calcium hydride was produced and fabricated, then tested to determine some of its physical properties.

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INTRODUCTION

During the period April 1957 through July 1959, Y-12 carried out a substantial amount of development work related to light-weight shielding for nuclear reactors. This work supported the program of the General Electric Company pertaining to aircraft nuclear propulsion. Lithium hydride was the material of chief concern. Most of the Y-12 work conducted on lithium hydride has been summarized in a report issued by GE.[1] This report summarizes the LiH work not covered by the GE report and also the limited work done with calcium hydride.

SUMMARY

Prototype shields for the General Electric Aircraft Nuclear Propulsion Project were constructed of lithium hydride embedded in a "honeycomb" of Type 304 stainless steel. Thermal conductivity tests indicated that the presence of the honeycomb made no noticeable difference in values.

A number of tests indicated that no particular hazards are involved when lithium hydride, even in large quantities, comes in contact with water.

Stress-rupture tests were made on various metals which were of interest as container materials. In these tests, specimens were held at elevated temperatures under a stress that would cause a rupture in 1000 hours if no corrosive materials were present. Most samples exceeded the 1000-hour period.

Tensile tests were made on Inconel which had undergone 3000 hours of thermal cycling while filled with lithium hydride. From the results it appears that Inconel is not affected by thermal cycling.

Inconel and Type 301 and 316 stainless steels were subjected to many thermal cycles. Spot corrosion was noted on the Type 301 containers after 230 thermal cycles but none appeared on the Inconel and Type 316 stainless steel even after more than 250 thermal cycles.

Calcium hydride was prepared and fabricated and some of its physical properties determined.

LITHIUM HYDRIDE

THERMAL CONDUCTIVITY

The thermal conductivity was determined for cold-pressed lithium hydride which was reinforced with perforated honeycomb oriented with the axis of the cells normal to the direction of heat flow. Results obtained are given in Table I. The values obtained correspond closely with values obtained on similar material without the metal honeycomb.

HAZARDS TESTING WITH LITHIUM HYDRIDE

A number of tests were run to observe the sort of results which might be expected from the contacting of large quantities of lithium hydride with water. Color movies of these tests were made.[2]

Table I

THERMAL CONDUCTIVITY OF COLD-PRESSED LITHIUM HYDRIDE, REINFORCED WITH PERFORATED HONEYCOMB[1]

Mean Temperature (°C)	Thermal Conductivity (cal/cm-sec-°C)
107	0.036
202	0.023
290	0.017
397	0.016

[1] Type 304 stainless steel honeycomb, 1-inch square cells, foil thickness 0.001 inch, perforated along the cell length with ½-inch diameter holes on ¾-inch centers.

Three, 30-gallon drums filled with salvage hydride and one, 55-gallon drum containing about thirty gallons of salvage hydride, along with an open-top can containing a single massive casting of about twenty-five gallons volume, were used in the first tests. These containers were placed in a large body of water under various conditions. Before being placed in the water, the drums were perforated with an ax to admit water. The most violent reaction was obtained with a 30-gallon drum filled with small pieces of cold-pressed hydride and containing some fines. The open end of the drum was covered with a coarse wire mesh, and the sides and bottom were liberally perforated using a fire ax. This was the only test in which the hydrogen, generated by contact with water, ignited spontaneously. The hydrogen fire was vigorous, with flames about thirty feet in the air, and lasted for over an hour. When enough hydride had reacted that the drums could sink, only a column of bubbles marked the place where they went down.

In smaller-scale tests it was demonstrated that massive blocks of lithium hydride, either uncanned or in a can having a single hole about one inch in diameter, reacted quite mildly with water and did not ignite spontaneously. Stainless steel cans, three inches in diameter by six inches long and having a 0.030-inch by 1.5-inch slot in the side of the can and filled with lithium hydride shapes, were heated and then placed in water. In all cases the cans

sank promptly and a small stream of bubbles came to the surface. The most stringent of these small-scale tests was to heat a can containing an undersized piece of cold-pressed and machined lithium hydride, with half the remaining volume filled with minus 100 mesh lithium hydride powder, to 1100° F. There was a slight hissing sound as the can hit the water, but it sank promptly and reacted no differently from the other specimens.

MATERIALS OF CONSTRUCTION

A question arose concerning whether Type 304 stainless steel, which is used for thermocouple sheaths, would be adversely affected by the silver braze alloy used to attach the thermocouples to shield components. To answer this question a band of braze alloy was laid down on a Type 304 stainless steel plate and tensile specimens were cut from the plate so that the braze was in the gage length. The specimens were then subjected to various treatments after which tensile tests were run. Results of these tests are given in Table II.

Table II

EFFECT OF SILVER SOLDER ON TYPE 304 STAINLESS STEEL EXPOSED TO LITHIUM HYDRIDE

Sample Number	Treatment	Yield Strength (psi)	Tensile Strength (psi)	Elongation (%)
1	Silver solder, heat treat,[1] with LiH	56,366	91,512	46
2	Standard, heat treat, with LiH	55,628	90,314	46
3	Silver solder, heat treat, with LiH	56,366	92,838	45
4	Standard, heat treat, with LiH	51,724	93,369	53
5	Standard, heat treat, without LiH	56,728	95,515	48
6	Silver solder, heat treat, without LiH	54,090	92,876	46
7	Silver solder, heat treat, without LiH	55,291	92,857	47
8	Standard, no heat, no LiH	54,642	93,634	50
9	Silver solder, no heat, no LiH	51,451	92,612	54
10	Silver solder, no heat, no LiH	53,525	90,078	51

[1] Heat treatment was at 700°F for 138 hours.

Metals which were of interest as container materials were subjected to stress-rupture tests in contact with lithium hydride. In these tests, the specimens were held at elevated temperature under a stress which should cause rupture in 1000 hours if no corrosive material were present. Results of the tests which did not terminate until after the period covered in the GE report[3] are given in Table III.

Seven tensile test specimens were cut from T-shaped Can PS-10[4] which had undergone 3000 hours of thermal cycling while filled with a cold-pressed shape of lithium hydride. This can was fabricated from 0.037-inch Inconel sheet and had two holes drilled in one face to

Table III

STRESS-RUPTURE TESTING OF ALLOYS IN CONTACT WITH LITHIUM HYDRIDE

Alloy	Temperature (°F)	Stress (psi × 10^{-3})	Time (hrs)	Remarks
316 ELC	900	25	1440	Welded. Terminated without failure.
301 SS ¼ Hard	1000	20	1008	Welded. Terminated without failure.
301 SS ¼ Hard	1000	20	1176	Welded. Terminated without failure.
301 SS ¼ Hard	1000	20	1176	Welded. Terminated without failure.
301 SS ¼ Hard	1000	20	936	Welded. Failed.
301 SS ¼ Hard	1000	20	1008	Welded. Failed.
301 SS ¼ Hard	1000	20	1152	Welded. Failed.
Inconel	900	40	1008	Dead annealed. Terminated without failure.
Inconel	900	40	816	Dead annealed. Failed.
Inconel	900	40	1008	Dead annealed. Failed.
Inconel	900	40	1344	Welded. Terminated without failure.
Inconel	900	40	1344	Welded. Terminated without failure.
Inconel	1000	22	1728	Welded. Terminated without failure.
Inconel	1000	22	384	Welded. Failed.
Inconel	1000	22	648	Welded. Failed.
Inconel	1100	20	300	Welded. Failed. 1 wt % LiF.
Inconel	1100	20	312	Welded. Failed. 1 wt % LiF.
Inconel	1100	20	1176	Welded. Failed. 1 wt % LiF.

observe the effect of air inleakage. The specimens were cut from the face opposite that in which the holes were situated. Three of the specimens had a weld situated in the gage length. From the tensile test results listed in Table IV, it appears that the thermal cycling did not greatly affect the Inconel.

Table IV

TENSILE TESTS ON INCONEL AFTER 3000 HOURS OF THERMAL CYCLING IN CONTACT WITH LITHIUM HYDRIDE

Type Specimen	Ultimate Tensile Strength (psi)	Yield Strength 2% Offset (psi)	Elongation (%)	Hardness (R_B)
Parent Metal	95,500	39,000	39	56
Parent Metal	93,750	37,500	39.5	66
Parent Metal	94,850	36,000	38.5	50
Parent Metal	93,500	36,700	38.5	56
Welded[1]	83,900	41,650	22	66
Welded[1]	91,350	46,350	29	47
Welded[1]	84,450	40,850	24	56

[1] Specimen broke in the weld.

Thermal cycling tests were conducted on six, short, prototype shield cans filled with lithium hydride. These cans were of a T-shape, 12 inches wide on the broad face, 8.5 inches wide on the narrow face, 6 inches thick, and 6 inches long. Each can was filled with a cold-pressed and machined shape of lithium hydride. There were two cans each of Inconel, low-carbon Type 316 stainless steel, and one-quarter hard Type 301 stainless steel. The thermal cycling procedure consisted of lowering the cans into a furnace held at 900° F. After the can temperature rose to ~ 890° F, the can was held at temperature for four hours. The can was then removed from the furnace and allowed to cool to about 210° F in still air before repetition of the cycle. Results are given in Table V.

Table V

RESULTS OF THERMAL CYCLING "T" CANS FILLED WITH LiH

Container Material	Metal Thickness (inch)	Cycles Before Spot Corrosion	Total Cycles	Remarks
301 SS	0.037	230	253	
301 SS	0.037	230	253	
Inconel	0.037	--(1)	253	
Inconel	0.037	--	253	
316 SS	0.037	5	155	Bad weld at start. Leaked.
316 SS	0.037	--	253	
316 SS	0.037	--	199	This can was prepared to replace the one that leaked.

(1) No spot corrosion noted unless indicated.

CALCIUM HYDRIDE

INTRODUCTION

Reference is made to a survey report by Kilb[5] concerning calcium hydride. The following covers all work done at Y-12 on the preparation, fabrication, and properties of this material.

PRODUCTION

One production run of about twenty-two kilograms of CaH_2 was made using pellets of calcium metal approximately one-quarter inch in diameter. Control of the reaction rate was accomplished using the same technique as in laboratory runs; i e, by partially pressurizing the reactor with argon to dilute the hydrogen. Gases were purified by passing over uranium chips at about 600° C. Total run time including heatup was 36 hours, but it is believed that this time could have been reduced substantially by increasing the partial pressure of the hydrogen at the time the reaction approached completion and the rate decreased. The bulk of the batch appeared to be high-grade hydride and was found by the hydrogen evolution analysis to be 98.13% CaH_2. A top layer (about one pellet thick) of darker material analyzed 89.74% CaH_2. The bottom of the vessel had become somewhat overheated resulting in a layer of unreacted and fused calcium metal about three-quarters of an inch thick, covered by about one inch of partially fused hydride. This fused hydride analyzed 96.63% CaH_2.

Another production-size batch (27 kgs) of calcium hydride was made. A thermocouple was placed in the bottom of the reacting mass to guard against overheating. Due to difficulty with furnace controls, the run required about sixty-two hours for completion. In this run the product appeared to be a good grade of hydride and analyzed 98% pure. The central portion of the reaction mass sintered to a fairly hard, spongy cake. Microscopic examination of the material from the sintered portion revealed crystals of considerable size, indicating that calcium hydride, like lithium hydride, undergoes rapid crystal growth at high temperature.

Hydriding of massive calcium metal of suitable dimensions to produce desired shapes directly was also investigated. This procedure may be accomplished easily with barium metal, but it has been found to be more difficult with calcium. The procedure for hydriding calcium pellets also applies to massive calcium; the rate of hydrogen addition must be carefully controlled. With such control, pieces of calcium metal one inch in diameter have been hydrided through to the center, but pockets of metal remained at various locations within the cylinders. Complete hydriding may be simply a matter of sufficient time and proper hydrogen pressure.

FABRICATION OF CALCIUM HYDRIDE

A series of cold pressings of calcium hydride were made at pressures from 15,000 to 50,000 psi using a die and ram. The densities obtained are given in Table VI.

Table VI

DENSITY OF COLD-PRESSED CALCIUM HYDRIDE COMPACTS PRESSED AT VARIOUS PRESSURES

Pressing Pressure (psi × 10^{-3})	Density (g/cc)
15	1.46
20	1.54
25	1.55
30	1.56
35	1.60
40	1.60
45	1.62
50	1.63

One possible explanation for the failure to achieve high-density calcium hydride compacts is that there is normally a micro porosity in grains of calcium hydride. If this were so, sintering or fusing might largely remove this porosity and make possible the preparation of high-density compacts by standard cold-pressing techniques. A sample of minus 80 mesh calcium hydride was, therefore, heated under an atmosphere of hydrogen to almost 1000° C. During the heating, the pressure in the reactor rose to 25 psig at one time due to outgassing. This action is similar to that which occurs when heating lithium hydride which has been previously exposed to air containing even traces of moisture. The hydrogen evolved was repeatedly vented until outgassing was complete. It was noted, at the high temperature, that the dissociation pressure was about 15 psig. When the reactor was opened, three distinct layers were found. The top portion was sintered to a hard porous mass and analyzed 96.84% CaH_2. The lower portion was a hard dense mass which showed some evidence of fusion and analyzed 98.10% CaH_2. In the very bottom was a thin layer of material which had definitely fused and analyzed 97.89% CaH_2. Since the fused portion of the charge was well below the thermocouple and a decided temperature gradient existed in the furnace, it appears that the melting point of calcium hydride is somewhat over 1000° C.

A much larger charge of calcium hydride was next loaded into a reactor and thermally cycled three times to about 960° C under an atmosphere of hydrogen. Outgassing was noted only on the first thermal cycle, indicating that, at high temperature, the reaction goes rapidly to completion. The shape of the heating and cooling curves indicated that there is a phase change at about 815° C with heat being absorbed during heating and liberated during cooling. The melting point of calcium metal is somewhat above this temperature (842 - 848° C) so it might be suspected that the phase change is the melting of a calcium-calcium hydride eutectic. However, the purity of the hydride (~98%) would almost preclude the possibility of the presence of sufficient metal to account for the large effect observed.

After this sample had been thermally cycled three times, the temperature was raised to 1010° C (the maximum furnace temperature) in an effort to fuse it. As the temperature was

Table VII

DISSOCIATION PRESSURE-TEMPERATURE RELATIONSHIP FOR CALCIUM HYDRIDE

Temperature (°C)	Dissociation Pressure (psig)
800	4
850	7
900	9
1010	22

Table VIII

DISSOCIATION PRESSURE-TEMPERATURE RELATIONSHIP FOR CaH_2[1]

Temperature (°C)	Dissociation Pressure (mm Hg)
765	37.5
792	56.4
840	116.3
870	181.0
884	217.1
894	253.1

[1] From J Am Chem Soc 61, 318 (1939).

raised slowly, the pressure above atmospheric, as indicated by a calibrated pressure gauge, was recorded. The dissociation pressure-temperature relationship obtained is given in Table VII.

Table VIII gives the values Johnson and co-workers[6] obtained for the dissociation pressure of calcium hydride from which they derived the equation:

$$\log p_{cm} = -7782/T + 8.070$$

Samples of both sintered and fused calcium hydride obtained in the experiments just described were crushed, ground, and cold pressed at 30,000 psi. The density of these compacts was only about 2% higher than the density of compacts prepared from other calcium hydride.

A 3/4-inch-diameter cylinder of calcium hydride was made by hot pressing at a temperature of 820 - 850° C and a pressure of 2000 psi. The compact was hard and strong but the bulk density was only 1.62 g/cc. Helium displacement gave a density of 1.89 g/cc on this specimen.

A pressure of 22,500 psi was not sufficient to produce satisfactory pressings of calcium hydride by cold isostatic pressing. Pressings made at 30,000 psi were generally satisfactory; however, some pieces pressed at this value cracked after removal from the pressure vessel but before machining. Exact cause of this failure was not determined, but it was believed that it may have been related to the impurity (hydroxide) content in some instances and to improper bag design in other cases.

General Electric reported that a density of 95% of the theoretical value has been attained by hot pressing at 1500° F with the pressure maintained at 2000 psi for thirty minutes.

PHYSICAL PROPERTIES

Rate of Creep

Calcium hydride specimens prepared by cold isostatic pressing at 22,500 psi were sintered

at 900° C and used to determine rate of creep at elevated temperatures. The rate of creep, under a load of 350 psi, was about 10% in 100 hours at 1000° F. At 950° F, under a load of 350 psi, the rate of creep was 2.1% in 100 hours, but at 850° F with this loading, no creep was noted in 150 hours.

Mechanical Strength of Calcium Hydride

Six specimens of calcium hydride, isostatically cold pressed at 30,000 psi, were broken. The compressive strength for the 95% confidence interval was 3850 ± 540 psi. It has been noted that cold-pressed calcium hydride becomes very much stronger when sintered at about 800° C. It is also believed that some densification may occur on sintering. Sufficiently good specimens to determine the compressive strength were not obtained due to spalling of the specimen on sintering, but no appreciable cracking was noted.

Density

The lattice constants for calcium hydride were redetermined by the ORNL using X-ray diffraction. The constants differ slightly from those reported in the literature but the calculated density was given as 1.92 g/cc compared to the literature value of 1.91 g/cc.

Stress-Rupture Tests of Metals in Contact with CaH_2

Specimens of several metals were stressed, with the stress reported to cause rupture in 1000 hours in air at the test temperature, while in contact with calcium hydride. The procedural and equipment details were identical to those used for lithium hydride.[7] Results obtained are given in Table IX.

Table IX

STRESS-RUPTURE LIFE OF MATERIALS OF CONSTRUCTION IN CONTACT WITH CALCIUM HYDRIDE

Material	Temperature (°F)	Stress (psi × 10^{-3})	Time (hrs)	Remarks
Hastelloy C	1500	11	1560	Blank. Terminated without failure.
Hastelloy C	1500	11	1560	CaH_2. Terminated without failure.[1]
Hastelloy C	1500	11	1320	CaH_2. Failed.
SS 304L	1500	3.1	1344	CaH_2. Terminated without failure.
SS 316	1500	5	1707	Blank. Terminated without failure.
SS 316	1500	5	1707	CaH_2. Terminated without failure.
SS 316	1500	5	1707	CaH_2. Terminated without failure.
Hastelloy B	1500	10	762	Blank. Failed.
Hastelloy B	1500	10	288	CaH_2. Failed.
Hastelloy B	1500	10	767	CaH_2. Failed.

[1] Subsequent tensile testing of this specimen showed an ultimate tensile strength at room temperature of 52,200 psi with an elongation of ½%.

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