Isotopic Exchange of Beryllium Hydride with Deuterium

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Beryllium hydride has been synthesized by Ethyl Corporation workers based upon a modification of the method of Coates (Coates and Glockling, 1954; Banfors and Coates, 1964) and Holley (Head et al., 1957), a method that gives product purities of 90–98 wt. % (Baker et al., 1978). The direct synthesis using beryllium powder and hydrogen has been unsuccessful. Beryllium deuteride can also be prepared by Ethyl Corporation's process using all-deuterated organic reactants. However, it is difficult to replace all deuterium atoms in hydrogenated alkyls, and the procedures are slow and costly.

This note reports a process of producing beryllium deuteride by activating pyrolysis-process beryllium hydride and exchanging the hydride with deuterium gas under pressure and temperature.

Experimental Method

All work was conducted under a moisture-free argon atmosphere. Because of the toxicity of beryllium compounds, a glove box was employed in transferring beryllium hydride and deuteride to and from pressure vessel reactors (Shriver, 1969).

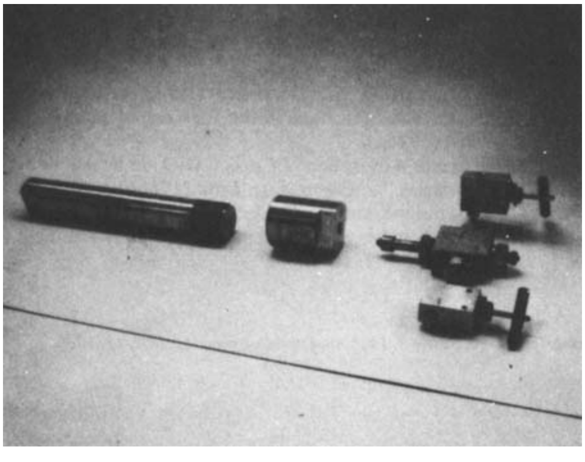

Figure 1. Cold-seal pressure vessel.
Udimet 500 alloy, 0.95 cm ID
Seal section is unheated, hence the designation "cold-seal"

Equipment

The BeH_2-D_2 exchange experiments were carried out using two types of apparatus: an apparatus for parameter studies, and a dynamic scale-up apparatus. The pressure vessel for parameter studies is shown in Figure 1. A 38 mL capacity pressure vessel was fabricated of Udimet 500 alloy and was fitted with 0.15 cm ID type 304L stainless steel tubing, Autoclave Engineering Co. 2 kbar (200 MPa) valves, and a porous 5 μm stainless steel filter. A Marshall Products Co. furnace, 208 V, 15 A capacity, and vertically supported on a drill-press column was used to heat the bottom section of the pressure vessel. The pressure vessel seal (59° angle male, 60° angle female) was unheated. A Leeds and Northrup Co. Speedomax H Recorder, a series 60 control unit, and a Fincor saturable core reactor maintained temperatures automatically. The temperature of samples was measured with stainless steel sheath thermocouples inserted into the sample. Pressures were measured with a Baldwin-Lima-Hamilton SR-4 2 kbar (200 MPa) pressure cell on the reactor and a 3.3 kbar (330 MPa) Heise gauge on the deuterium gas storage

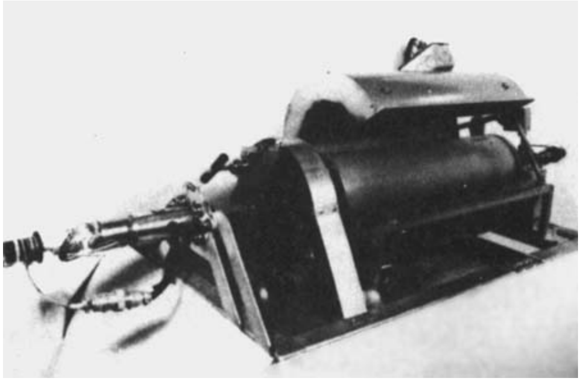

Figure 2. Rotating reactor and heating system.

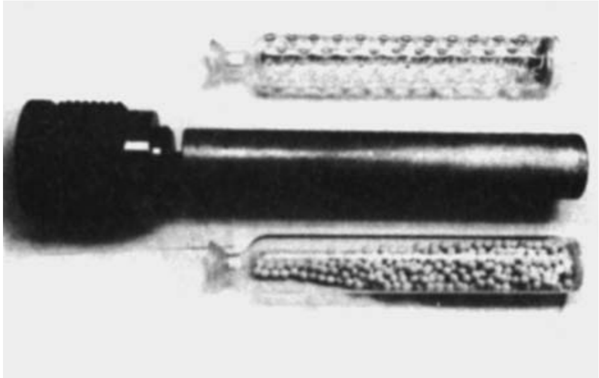

Figure 3. Canisters for hydride containment.

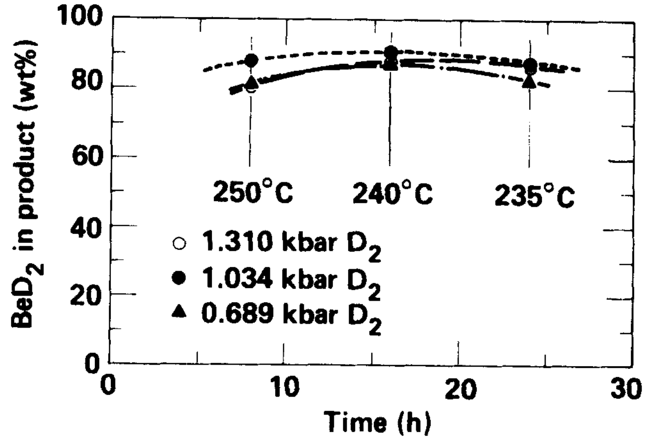

Figure 5. Optimum BeD$_2$ yield is obtained by operating at 1.034 kbar (103.4 MPa) deuterium pressure, 240°C, 16 h.

supply. A Cenco vacuum pump together with a liquid-nitrogen trap served to evacuate the system prior to admitting D_2 gas. Containers for BeH_2 were made of Pyrex with an orifice to admit gas provided in the ground-glass stopper. Beryllium hydride samples for the static system were 40 mg.

The scale-up experiments were done in a rotating reactor shown in Figure 2. Figure 3 shows the dimpled Pyrex canister for BeH_2 and the stainless steel housing used to hold the Pyrex canister on the pressure vessel closure. The canister housings contained porous stainless steel disks on the ends to allow D_2 gas to enter. The Pyrex tube was also fitted with a porous glass frit. D_2 gas was fed to the reactor through a valve, and the gas feed line was disconnected prior to the start of rotation. Pressure Products, Inc. fabricated the reactor from AISI 4340 steel and lined it with type 316 stainless steel. This reactor has a gross volume of 650 mL and a free-gas void volume of 345 mL after the container is installed. The closure seals consist of a wedge ring made of Berylco 25, a Viton O-ring, and a Spirolox retainer ring. The reactor is turned at 4 rpm by a sprocket-chain driven by a Vickers, Inc. hydraulic drive motor, No. MRT 3, and a Vickers pump, No. PTR-3. The vessel was externally heated by ten Chromalox strip heaters made by E. L. Wiegand Co., No. SE 1405 (R69 HKL) each rated at 500 W at 208 V. The housing was 0.635 cm aluminum plate. Temperatures in the reactor were measured by a Chromel-Alumel sheath thermocouple that rotated with the reactor, and the signals were taken off the thermocouple housing by means of gold brushes made by Airflyte Electronics Co., No. 110-2 CAY. Pressure in the reactor was monitored with pressure transducers with signals taken off by Airflyte Electronics Co. No. 110-6 gold brushes in the same manner as for the thermocouples. Beryllium hydride samples for the dynamic system were 8 g.

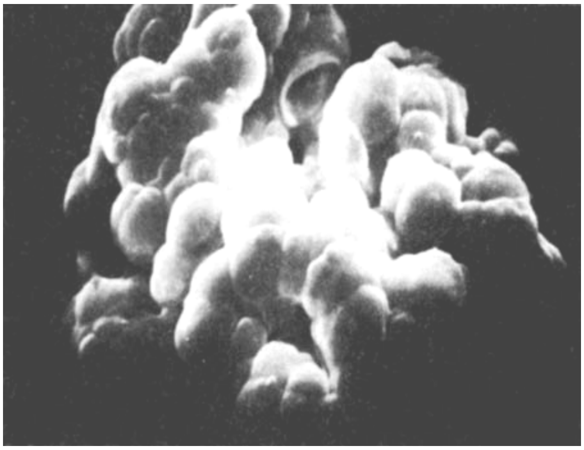

Figure 4. Amorphous beryllium hydride produced by solvent pyrolysis process.

1,000X; small particle size range, 5–20 μ.
ρ = 0.62–0.65 g/cm^3

Preparation of Beh$_2$

Amorphous beryllium hydride as prepared by the pyrolysis of di-t-butylberyllium etherate (Baker et al., 1978) does not isotopically exchange unless it is further activated by milling. Figure 4 shows 95 wt. % amorphous BeH_2. The milling is done in a 1.1 L Abbe ball mill lined with tungsten carbide using 1.27 cm dia. tungsten carbide balls to avoid contaminating the hydride, although Burundum cylinders, 1.27 cm × 1.27 cm, were also used successfully. The grinding media occupied 30% of the total volume of the mill. About 10 g of BeH_2 were ground at one time

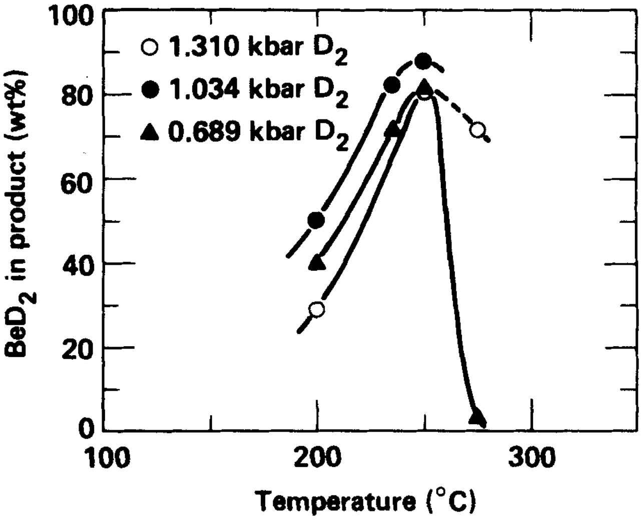

Figure 6. Wt. % BeD$_2$ in product as a function of temperature for 8 h contact time.

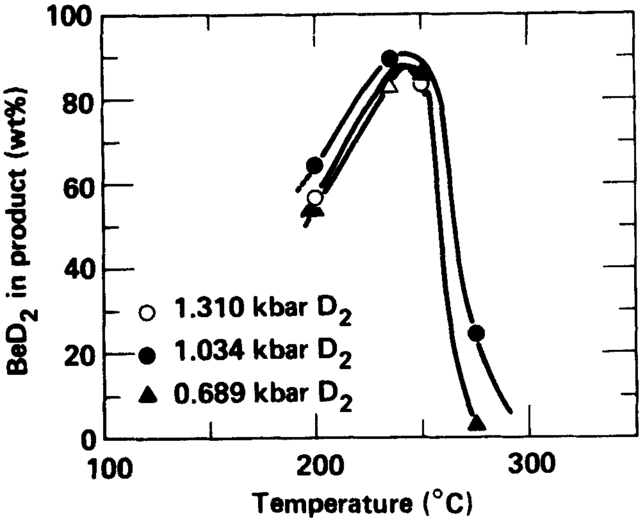

Figure 7. Wt. % BeD_2 in product as a function of temperature for 16 h contact time.

to <22 µm. Grinding time was 3 h at 125 rpm. A pressure gauge was attached to the ball mill to measure any pressure changes during milling. By knowing the pressure, volume, and gas analysis, we determined the number of moles of each constituent released upon milling.

An alternate activation procedure is to densify the amorphous BeH_2 at 8 kbar (800 MPa) at 180–200°C for 1 h in a piston-mold unit and then pulverize the compact to approximately 3.5 µm.

Analytical measurements

Methods for determination of hydride hydrogen, beryllium alkyls, alkoxides, and chlorides are described in earlier papers (Baker et al., 1978; Bucholz and Fraser, 1964). Gas atmosphere compositions were done by mass spectrometry analysis.

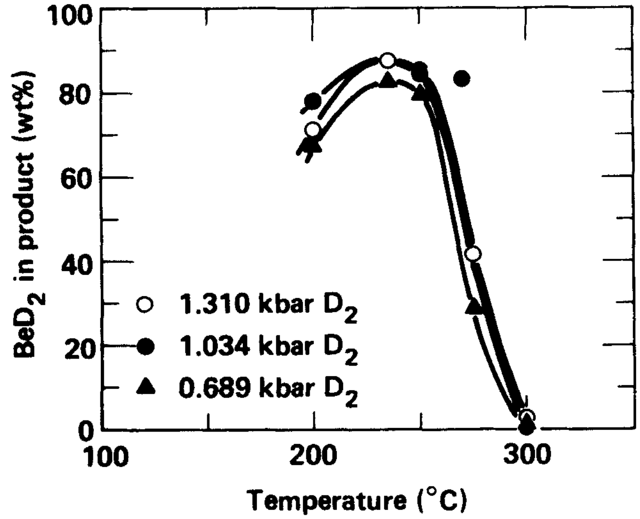

Figure 8. Wt. % BeD_2 in product as a function of temperature for 24 h contact time.

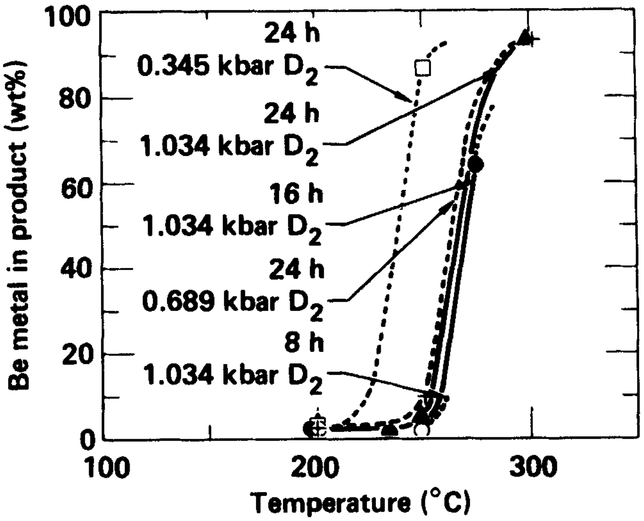

Figure 9. Free beryllium metal in product as a function of temperature at various times and pressures.

Deuterium-hydrogen ratio

The yield of BeD_2 is partially dependent upon the D/H ratio used per exchange cycle. In experiments with 40 mg samples, a 1,000:1 ratio was used at the highest pressure. In scale-up experiments, the proportion of deuterium to hydrogen was substantially reduced, to 12:1.

Deuterium gas was pumped into 1.72 kbar (172 MPa) storage cylinders using a Pressure Products diaphragm compressor. The reactors were charged from the storage cylinders.

Isotopic exchange

Both types of reactors were loaded with BeH_2 in an argon-filled glove box and transferred to a gas manifold for evacuation of the argon with a vacuum pump and subsequent charging with deuterium. The charging pressure was selected so that after

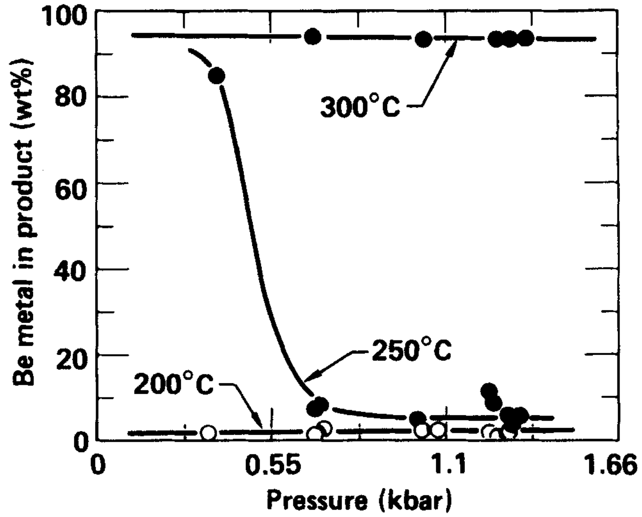

Figure 10. Free beryllium in product as a function of pressure for three temperatures and 24 h contact time.

Table 1. Experimental Results from 8g Scale-up Experiment of 95 wt. % BeH_2 with Deuterium Gas

	Cycle			
	1	2	3	4*
Temp., start, °C††	RT	RT	RT	RT
Temp., max., °C	234	233	234	234
Press., charge, kbar	0.993	0.965	0.889	0.883
Press. at max. T, kbar**	1.424	1.413	1.434	1.413
Time, RT to shut down, h (hold time, 16 h)	32.2	33.1	25	28
D/H ratio	12/1	12/1	12/1	12/1
Solid Analysis				
BeD_2, wt. %	88.3	90.5	89.3	93.9
BeH_2 wt. %	8.7	7.6	7.0	3.2
Be, free, wt. %†	−0.38	1.83	−1.89	−1.34

*Sample from the 3rd cycle was reground and returned to the reactor.

**There were pressure drops due to gas sampling.

†Often the hydrolysis-deuterolysis method for free Be analysis produces negative values. The inconsistency was found to be due to excess H_2 or D_2 gas either trapped within or adsorbed onto the particles of BeD_2.

††Room temperature.

heating we would reach the pressures utilized in isotopic exchange study. Sampling of the pressure vessel atmosphere and aliquots of samples were taken for analysis. Analysis was made for BeD_2, BeH_2, Be metal, H_2, HD, and D_2 from which the percent exchange could be calculated.

RESULTS

Maximum yield of BeD_2

The conditions for the maximum conversion of BeH_2 to BeD_2 are summarized in Figures 5–8. Figure 5 was plotted using the peak values in Figures 6, 7, and 8. Since yield experiments were performed with a restricted number of points, sections of some curves were estimated by drawing the curve parallel to one that contained sufficient data. Operating at 1.034 kbar (103.4 MPa) and 240°C for 16 h produced optimum conversion of 91 wt. % BeD_2 from 95 wt. % BeH_2 in one cycle. This represents a conversion of 94% to the deuteride. During exchange, the free Be metal content increased from 2 to 3 wt. %. Since the 1.034 kbar curve is practically flat, slight deviation in time is not critical. Decreasing the time to 8 h at 1.034 kbar while maintaining a temperature of 250°C would decrease the BeD_2 content by 3 wt. %. Any decomposition of the hydride to Be decreases the amount of hydride available for conversion to deuteride. The decomposition reaction is not reversible.

Figure 6 shows plots of wt. % BeD_2 in the product as a function of temperature for an 8 h contact time, and Figures 7 and 8 show the results of 16 and 24 h contact times, respectively. We believe that greater pressures, e.g., 1.31 kbar (131 MPa), would provide a larger driving force for exchange but there may be a barrier to exchange if the released H_2 remains stagnant in the static system.

Figure 9 shows the increase in free Be metal during 8, 16, and 24 h runs for 0.345, 0.689, and 1.034 kbar (34.5, 68.9, 103.4 MPa) in a static system. For the 1.034 kbar pressure, decomposition of BeH_2 starts at 250°C and is completed at 300°C for all times. Figure 10 shows a plot of free Be in the product as a function of pressure for temperatures of 200, 250, and 300°C and 24 h contact time. At 200°C the BeH_2 is fairly stable.

Table 2. Typical Analysis of Gas Atmosphere in Ball Mill after Grinding BeH_2*

Constituted Gas	Volume %
N_2	1.86
H_2	94
CH_4	0.33
C_2H_6	3.21

*BeH_2 95 wt. % pure; grinding time 3 h at RT

Scale-up

Limited studies conducted in static apparatus allowed scale-up of the exchange process. Conditions in scale-up approximated the optimum operating values determined in the parameter study, namely, 1.378 kbar (137.8 MPa), 234°C and 16 h hold time. The higher pressure and lower temperature were chosen to lessen hydride decomposition. The results of a typical experiment are shown in Table 1.

Effluent gas from milling

Milling of BeH_2 releases organic gases. A typical sampling of the ball mill atmosphere produced the analysis shown in Table 2. The analysis was made on an argon-free basis. N_2 is used in the synthesis of BeH_2 as a gas blanket. C_3H_8, C_4H_{10}, and C_5H_{12} are also often found in small amounts. Degradation of the hydride amounts to about 1–2 wt. % during a 3 h period. It has been suggested that BeH_2 is a polymer, (DTB) · $(BeH_2)_x$ · (DTB), $x = 69.29$, with the term DTB at the end of the chain (Mounier, 1967). The grinding process is thought to break this chain, release organic components, and create fresh, active surfaces. The surface area for a 3 h grind is 3.1 m^2/g as determined by BET using krypton gas.

Acknowledgement

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