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UCRL-51375

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April 12, 1973

Prepared for U.S. Atomic Energy Commission under contract No. W-7405-Eng-48

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Printed in the United States of America

Available from

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Springfield, Virginia 22151

Price: Printed Copy \$ *; Microfiche \$0.95

<u>* Pages</u>	<u>NTIS Selling Price</u>
1-50	\$4.00
51-150	\$5.45
151-325	\$7.60
326-500	\$10.60
501-1000	\$13.60

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109

THERMAL ANNEALING OF IRRADIATED LiH

Abstract

The effects of thermal annealing of irradiated LiH on density, bubble size, and bubble size distribution are presented for materials subjected to a wide range of irradiation conditions.

* * *

Heating of irradiated LiH is known to cause back-reaction of the free hydrogen and lithium present^{1,2} as well as to produce changes in density.³ A correlation was previously made between the Li-metal/H₂-gas ratio and the change in density after annealing.³ It was found that when this ratio was small, i. e., most of the expected metallic lithium was undetected by pulsed nuclear magnetic resonance (NMR), the material recovered much of the swelling produced by irradiation. Several annealed samples were examined by electron microscopy, and it was observed that fairly small changes in bubble size resulted. These findings were cited to support the conclusion that the back-reaction mechanism does not involve migration of bubbles.² The present results show that, in general, bubble sizes increase substantially under some annealing conditions and, therefore, the back-reaction model must be re-examined.

A miscellany of annealing results are presented here, partly simply to record the experiments. Differential thermal

analysis (DTA) showed that the back reaction of lithium and hydrogen in irradiated LiH becomes rapid between 350 and 450°C. Most of the annealing studies were done on samples in which the back-reaction was completed. Some anneals had been attempted at lower temperatures, particularly around 200°C where the "missing" lithium metal (to NMR) was known to precipitate.¹ Very little change in density or internal decomposition was found in samples annealed between 200 and 250°C even for heating times as long as 20 hours. No electron microscopy was done at or on these samples. Consequently, subsequent thermal annealing was done at or above 400°C where the back-reaction occurs rapidly. Three different modes of annealing were used, all of which are illustrated in Fig. 1. These are:

1. "Fast" heating, designated as F. An encapsulated sample was immersed in a furnace at 400°C and held there for times ranging from 5 min to 1 hr. Back-reaction was always complete after 5 min, and time at 400°C did not seem to change

Fig. 1. Temperature-time curves for the various thermal annealing conditions.

the properties. The initial heating rate was $>100^{\circ}\text{C}/\text{min}$.

2. "Slow" heating, designated as S. In this procedure, the sealed sample was placed in the cold furnace, then the power was applied at a setting predetermined to hold 400°C . However, the temperature overshoots to about 550°C before controlling at 400°C .

3. Constant heating rate to 450°C . The DTA apparatus¹ was used to heat a small crystal at rates of $5^{\circ}\text{C}/\text{min}$, $20^{\circ}\text{C}/\text{min}$, $50^{\circ}\text{C}/\text{min}$, or $100^{\circ}\text{C}/\text{min}$. Power was turned off at $\sim 500^{\circ}\text{C}$, and the system was cooled to near room temperature, usually in 20 min. The DTA system heated at a constant rate only after a relatively slow initial climb

to about 50°C. The time vs temperature curves for the various annealing conditions are shown in Fig. 1.

The results from the annealing experiments are listed in Table 1. Bubble sizes were determined by replication electron

Table 1. A summary of annealing data.

Sample	T_{IRR} (°C)	Dose (Grad)	Annealing procedure	$\bar{r}_{IRR}$ (Å)	$\bar{r}_{ANN}$ (Å)	$\left(\frac{\Delta V}{V_0}\right)_{IRR}$	$\left(\frac{\Delta V}{V_0}\right)_{ANN}$
B7-1	90	0.9	F, S, and 50°C/min	—	—	0.015	0
B7-3	120	1.20	F	80	355	.046	0.024
			100°C/min	80	1820	.046	—
			50°C/min	80	1030	.046	—
B7-2	171	1.30	100°C/min	250	1880	.064	.060
			50°C/min	250	1900	.064	.057
			20°C/min	250	2040	.064	.062
			5°C/min	250	2420	.064	.043
			S	250	3230	.064	.074
B7-4	190	1.31	F	395	660	.065	.078
			100°C/min	395	1630	.065	.056
			50°C/min	395	1720	.065	.073
			20°C/min	395	2010	.065	.068
			5°C/min	395	2750	.035	.065
B7-5	220	1.33	S	570	2760	.072	.085
B12-1	76	5.5	S	—	2120	.080	.037
B12-3	130	6.6	S	205	2800	.097	.096
B12-2	140	7.0	S	245	3850	.114	.101
B12-4	203	7.2	F	485	890	.154	.162
B12-5	207	7.2	F	500	970	.160	.162
B3-3	265	25.8	F	1450	1340	.062	.043
B5-3	215	3.2	S	640	4830	.116	.127
B5-2	220	3.5	S	690	3850	.129	—
B5-4	267	3.6	S	1485	2570	.104	.111
B8-5	215	0.5	S	340	3550	.018	.025
B3-2	200	22.1	F	725	—	.249	.188
B5-5	265	3.6	F	1430	—	.112	.104
B1-1	42	36.1	F	—	—	.166	.122
B1-3	85	45.4	F	—	—	.166	.122

Table 1 (continued).

Sample	T _{IRR} (°C)	Dose (Grad)	Annealing procedure	$\bar{r}_{IRR}(\text{\AA})$	$\bar{r}_{ANN}(\text{\AA})$	$\left(\frac{\Delta V}{V_0}\right)_{IRR}$	$\left(\frac{\Delta V}{V_0}\right)_{ANN}$
B2-1	50	11.1	F	—	—	.091	.051
B2-3	100	13.9	F	—	—	.127	.094
B2-4	160	14.4	F	—	—	.216	.200
B2-5	195	13.2	F	—	—	0.223	0.205
B5-1	120	2.7	F	—	—	0.070	0.041
B8-1	87	0.4	F	—	—	.008	0
B8-3	116	0.5	F	—	—	.011	0
B8-2	161	0.5	F	—	—	0.015	0.011

microscopy,^{4,5} and density was measured by flotation³ or with a gas comparison pycnometer⁶ when big enough samples were available. It was not always possible to measure bubble size because of the poor physical condition of some irradiated samples. A cleavable crystal chip is needed to prepare a replica and often the irradiated LiH was shattered into very small fragments.

Figure 2 is a photograph of a replica of one sample (B7-5) annealed by Procedure S, that is representative of the pictures used to measure bubble size. The range of bubble sizes here is 1000-10,000 Å. The relationship between swelling recovery after annealing and irradiation temperature is shown in Fig. 3. In general, it is found that samples irradiated below 170°C always recover some of the volume increase caused by irradiation. Three points are seen where all of the swelling disappeared. In these cases, the irradiation temperature was fairly low and the irradiation dose was less than 1 Grad. No correlation was seen with the irradiation

dose, the amount of swelling from irradiation, or the annealing procedure.

Examination of Table 1 shows that large increases in bubble size results for materials annealed at constant heating rate or S, whereas relatively small changes are found for Condition F. Since the original procedure used was F, the interpretation of the back-reaction process excluded the possibility of bubble coalescence,² as mentioned above. Possibly the determining factor in whether large changes in bubble size occur or not is the time in a small (but undefined) temperature interval. Examination of Fig. 1 suggests that either this temperature interval is $\lesssim 200^\circ\text{C}$ or that the differences may be due to the fact that temperature never exceeded 400°C for F. If the latter is the case, then for some samples, bubble growth occurs after the back-reaction is complete, and the proposed mechanism² is not invalidated. Lack of samples and time have prevented a systematic investigation.

An interesting trend is shown in Fig. 4 where the bubble concentration is plotted

Fig. 2. Electron microscope photograph of a carbon replica of sample B7-5, annealed.

Fig. 3. Relative recovery of swelling of thermally annealed LiH as a function of irradiation temperature. ΔV_{IRR} is the increase in volume/cm³ after irradiation. ΔV_{ANN} is the remaining volume increase/cm³ after annealing.

against irradiation temperature for both as-irradiated and annealed samples. The bubble concentration, ρ , is defined as²

$$\rho = \frac{\Delta V}{(1 + \Delta V)(\bar{r})^3},$$

where

ΔV = swelling volume, and

$\bar{r}$ = average bubble size.

It appears that, except for F, all annealed samples have approximately the same bubble concentration independent of irradiation conditions or the as-irradiated properties. Since these materials have a considerable range of swelling volume and bubble size, obviously some other property is determining this behavior. If energy minimization is involved, then we

Fig. 4. Bubble concentration as a function of irradiation temperature for as-irradiated and annealed LiH.

Fig. 5. Internal surface area per cm^3 associated with bubbles shown as a function of irradiation temperature for as-irradiated and annealed samples.

should consider the internal surface area of the bubbles because of their associated surface energy. If this area is defined as

$$A = 6(\bar{r})^2 \rho = \frac{6\Delta V}{(1 + \Delta V)\bar{r}}$$

we find that this, too, is constant for annealed materials (except those annealed F). This is shown in Fig. 5 where it can be seen that the annealed materials have a specific internal surface area of $1 - 2 \times 10^4 \text{ cm}^2/\text{cm}^3$. The significance of this is not clear since the minimum energy condition is for zero internal area. In the annealed state, the bubbles are actually voids since the hydrogen has all

back-reacted and there is no balance between internal pressure and surface energy to determine bubble size. It happens that the surface energy calculated from the bubble size and gas pressure is not a constant, as noted earlier.⁵ Apparently equilibrium between surface energy and internal pressure is not achieved, according to the expression

$$P = 4\gamma/r$$

where P is pressure, r is bubble size, and γ is surface energy. We have plotted P versus $\bar{r}$ in Fig. 6 together with the expected relationship for two values of γ and the lack of agreement is obvious. The

Fig. 6. A comparison of the observed pressure-bubble size relationship with that expected for equilibrium, with surface energy.

$$P = \frac{4\gamma}{r}$$

Fig. 7. Distribution of bubbles as a function of size in the as-irradiated B7 series. The fraction of the total is plotted as a function of size.

Fig. 8. Bubble size distribution of annealed B7-2 for four constant heating rates.

value of γ for LiH is expected to be in the range of 250-500 $\text{ergs/cm}^{2.5}$.

The distribution of bubble sizes in as-irradiated and in annealed samples was also examined. The B-7 series of samples was studied most extensively because the quality of replicas was generally good for these materials and because more material was available than for other samples. Figure 7 shows the bubble size distribution found in the as-irradiated B-7 samples, and the distributions for sample B-7-2 annealed at four constant heating rates are plotted in Fig. 8. A distinct difference is found in the type of size distribution between as-irradiated and annealed materials when the cumulative fraction of bubbles sizes is plotted versus

normalized size, Fig. 9. The as-irradiated distributions are shown as the open circles and the distributions for annealed samples are shown as full circles. Materials annealed under all conditions are included. It is clear that after annealing, the bubble size distribution is truncated at smaller sizes compared to the as-irradiated condition. For completeness, the individual bubble size populations for all as-irradiated and annealed materials not already shown are included in Figs. 10-16. The irradiation conditions and annealing procedures for these are listed in Table 1. The resolution in size distribution was determined by the number and quality of the available electron micrographs.

Fig. 9. Cumulative fraction of bubble sizes plotted against bubble size normalized to the average size. Open circles are for as-irradiated samples; filled circles are for annealed samples.

Fig. 10. Bubble distribution for as-irradiated and annealed samples. Fractional population is plotted versus size.

Fig. 11. Bubble distribution for as-irradiated and annealed samples. Fractional population is plotted versus size.

Fig. 12. Bubble distribution for as-irradiated and annealed samples. Fractional population is plotted versus size.

Fig. 13. Bubble distribution for as-irradiated and annealed samples. Fractional population is plotted versus size.

Fig. 14. Bubble distribution for as-irradiated and annealed samples. Fractional population is plotted versus size.

Fig. 15. Bubble distribution for as-irradiated and annealed samples. Fractional population is plotted versus size.

Fig. 16. Bubble distribution for as-irradiated and annealed samples. Fractional population is plotted versus size.

Acknowledgments

We owe particular thanks to Sam DiGiallonardo for help with the replication procedure and for providing us with many superior electron micrographs. We also wish to thank P. C. Souers, T. S. Blake, and T. Imai, who all participated in the early stages of these experiments.

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