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SOLUBILITY OF LITHIUM IN SILICON

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Abstract—The solubility of lithium in silicon has been measured as a function of temperature between 592°C and 1382°C. It reaches a maximum impurity atom fraction of $1{\cdot}3\times10^{-3}\pm8$ per cent at about 1200°C, and the distribution coefficient at the melting point is $1{\cdot}0\times10^{-2}$. Li content was measured by flame analysis; comparison of flame analysis results and electrical measurements indicates that serious precipitation occurs during quenching for diffusion temperatures above 650°C. Distribution coefficients are in accord with thermodynamic principles when calculated as the ratio of the above solubility data and a liquidus curve calculated from the eutectic point.

Additional information regarding the Li–Si phase diagram was obtained which indicates a melting point of 720±20°C for $Li_{4n}Si_n$, 750±10°C for $Li_{2n}Si_n$, and a eutectic point at 58±5 atom per cent Li and a temperature of 590±10°C. The melting point of Si is 1408±2°C, based on a literature survey and our own measurements. The melting point of Li_2CO_3, a product of the reaction of $Li_{4n}Si_n$ with room air, was found to be 715±10°C, instead of the 618°C usually quoted.

INTRODUCTION

THE general shape and behavior of a solid solubility curve is prescribed by thermodynamic principles. In particular, the log of the distribution coefficient vs. $1/T$ should fall along a straight line which, extrapolated to $1/T = 0$, should not be far from unity in value.(1, 2) There may be exceptions to this general principle, but data which appear to violate it must be rigorously checked. We have remeasured the solubility of lithium in silicon(3) to see if it constitutes such an exception, and we have found that previous discrepancies can be explained by precipitation during quenching. We have not been able to prevent such precipitation (in fact, our Hall effect measurements, which are not sensitive to precipitated Li, reproduce the earlier measurements very closely), but by using flame analysis to measure the Li content we have been able to include this precipitated Li in our measurements.

PROCEDURE

1. *Lithium solubility* (*solidus*)

Li was prealloyed to Si at about 600°C in a hydrogen bottle. This temperature is sufficient to cause the voluminous and powdery $Li_{4n}Si_n$ which forms at about 200°C to remelt and alloy with the Si. The Si used was in the form of roughly a ⅛ in. cube, and the Li amounted to about 20 atom per cent of this, except at the highest diffusion temperatures, where the prealloyed Li had to be reduced to as little as 5 atom per cent to prevent complete melting of the sample. Lithium hydride formation during prealloying was insignificant; use of helium instead of hydrogen did not affect our results.

The prealloyed sample was placed in a ½ in. diameter ×1 in. molybdenum crucible, spacing the Si from the crucible walls with crystals of silicon carbide. Argon was flowed in to replace the air, and a closely fitting molybdenum cover was added. Crucible and cover were inserted into the cool end of a quartz tube furnace heated by a graphite heater in its own separate concentric quartz compartment. (Fig. 1) After flushing the furnace with argon, the sample was moved into the hot zone for the Li diffusion. In one run, the argon atmosphere was replaced with helium, using an inverted crucible to prevent trapping of air; the results were identical to those with argon.

The closed crucible technique was chosen to prevent Li loss by evaporation. Known data on Li evaporation rates in vacuum suggest that it could easily be troublesome even under an atmosphere and at our lower diffusion temperatures. On the other hand, an experimental check of Li evaporation from a prealloyed sample in our furnace indicates that it is not serious until about 1100°C, and that the evaporation rate is about 10^{-5} of the rate in vacuum; such a low rate is surprising and may be caused by the inhibiting effect of an oxide layer. In an earlier set of experiments using the sandwich diffusion technique,(3) appreciable erosion of the quartz furnace walls by Li vapor was observed after many runs at 1000°C.

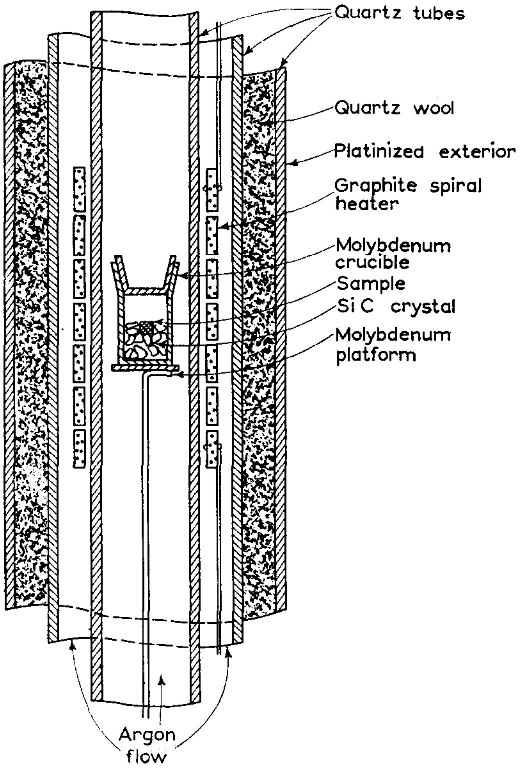

FIG. 1. Schematic cross-section of diffusion furnace with sample.

Since we wished to go up to 1400°C, use of a closed crucible seemed imperative. No attempt was made to seal the crucible; slow leakage was relied upon to reduce Li loss sufficiently. Since quartz erosion was not noticeable, it is felt that Li loss was negligible.

The crucible material, molybdenum, was chosen because of its inertness to Li. There was no macroscopic evidence of Li attack even near 1400°C, though frequent cracking of crucibles at this temperature may have been caused by some more subtle reactions between Li and Mo. Since Mo alloys with Si, it was necessary to prevent the Si from touching the crucible. This was accomplished with silicon carbide crystals, which showed no macroscopic reaction with either Li or Si.

Diffusion times were chosen with the aid of known diffusion data(4) so as to achieve Li concentrations roughly 90 per cent of equilibrium, and the resulting Li analyses were raised 10 per cent in compensation. The possibility of being far short of equilibrium was checked by doubling the diffusion time for one run at 1000°C; there was no change in Li concentration within the probable error of a single determination (±13 per cent).

The oven temperature was monitored before each run with a Pt–Pt 10 per cent Rh thermocouple which was calibrated against the melting points of gold (1063°C) and nickel (1455±1°C on 1927 International Temperature Scale,(5) or 1453±1°C on 1948 International Temperature Scale).* These temperature readings and the power input to the heater were subsequently calibrated against thermocouple measurements of the crucible temperature itself (it was not convenient to measure the crucible temperature directly during the diffusion runs because of the desirability of moving the crucible into and out of the hot zone while the oven remained sealed against the entry of room air). The difference between the thermocouple oven-temperature measurement and the actual crucible temperature was as much as 18°C at 1400°C and is attributable to the temperature gradient in this furnace. It is believed that the calibrated temperatures are accurate to ±4°C, based on experimental attempts to reproduce a desired temperature.

During the diffusion period, Li diffused from a region of molten Li-Si alloy into the solid Si until the solubility limit was reached. The crucible and sample were then removed to the cool part of the furnace and allowed to cool by radiation, conduction, and convection. This cooling period was amply short to prevent Li loss from the sample by diffusion, the excess Li either remaining in solution or forming precipitates. The sample was then differentially etched in $HF–HNO_3$ (1 : 3) etch to remove the previously molten alloy region. (The alloy region etched much more rapidly, and at the sacrifice of but a small fraction of the Si, this proved to be an easy and reliable method for removing the alloy.)

The remaining Si, with its dissolved and precipitated Li, was then analysed by an outside laboratory,† using flame analysis. The quoted limit-of-error for 95 per cent confidence, for our size samples, was ±20 p.p.m. This estimate of error was checked statistically with ten samples diffused at 1000°C. The statistical study indicated a mean probable error in each determination of ±13 per cent, which is about three times the probable error estimated by the analysts for this Li content. The difference is attributable to unknown errors in our diffusion techniques and/or errors in the analysts' estimates of error.

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* We used the procedure wherein a small piece of pure nickel is used to bridge the ends of the thermocouples, with the nickel physically isolated from the Pt by short pieces of tungsten to prevent alloying, the melting point being indicated by a sudden open circuit. With nickel, a slightly-reducing atmosphere should be used—even as little as 0·24 per cent oxygen in the nickel will depress the melting point 20°C. On the other hand, if the atmosphere is too reducing, it will embrittle the Pt. We found 1 per cent H_2 in A to be satisfactory.

† Large Steam Turbine Generator Materials and Processes Laboratory, General Electric, Schenectady.

2. *Lithium-silicon liquidus*

To determine the distribution coefficient, one must also know the liquidus. One can obtain good values for the distribution coefficient by using the liquidus for a perfect solution, as long as one remains in the region of dilute solution. An approximate knowledge of the eutectic point (or any other point on the liquidus), plus accurate knowledge of the melting point, permits one to obtain somewhat better values for the distribution coefficient. We therefore desired to know the melting point and the eutectic point.

Melting point of silicon. This was found by raising the temperature in small steps until the Si sample collapsed. The molybdenum crucible used in the previous experiments was replaced with a tantalum crucible to prevent possible contamination of the Si with evaporated molybdenum oxide. This crucible contained a quartz cup for the Si and was supplied with an attached thermocouple calibrated against the melting points of gold and nickel. We found the melting point to be 1409±2°C. This was not a refined technique, but the results compare favorably with more careful determinations which give 1408±2°C,† 1409±2°C,* 1410°C,† and 1408±5°C.‡ We consider 1408±2°C to be the best present value for the melting point.

Eutectic point. This was determined only roughly, by two experiments. In the first, the solidification temperature was measured for a series of alloys varying between 50 and 67 atomic per cent of Li. This was done in a bell jar under He by probing the sample while going both up and down through the melting point. The solidification temperature will lie close to either the solidus or a eutectic temperature. From this experiment we were able to conclude that the eutectic temperature was 590±10°C and that the eutectic mixture was 58 per cent Li or less. The second experiment consisted in alloying a known amount of Li to a known amount of Si at a series of temperatures above 600°C and then differentially etching off the alloy to find how much Si had been alloyed. This method worked best at lower temperatures where the differential etching effect was greatest, and comparison of the results with a theoretical liquidus indicated that the eutectic mixture was 58 atom per cent Li or more. Considering both experiments, we conclude that the eutectic point lies at 590±10°C, 58±5 atom per cent of Li.

RESULTS

The present data are tabulated in Table 1, and in Fig. 2 we have plotted the solubility of Li in Si as determined by the present experiment and also as measured in earlier experiments. Below 650°C, our data and earlier data are in good agreement, but above this temperature the present data indicate smoothly increasing (retrograde) solubility, reaching a maximum of $1{\cdot}3\times10^{-3}$ at about 1200°C. We have also included electrical measurements of Li content, using the Hall effect, in our relatively slowly quenched samples; and it is seen that the results lie parallel to the earlier solubility data based on electrical resistivity measurements of more rapidly quenched samples. One datum point from a special experiment (in which we used a sandwich technique for the diffusion and a special furnace to permit rapid quenching by dropping the sample into ethylene glycol) is also exhibited, and it is seen that this Hall measurement of Li content is in excellent agreement with the earlier data. This dependence of dissolved Li content (using the Hall effect) upon quench rate, in conjunction with the much higher total Li content as measured chemically, is almost incontrovertible evidence of precipitation during quenching. It may be of interest to note that our rapidly quenched samples were extremely brittle, all but the one crumbling during the measurements; slowly quenched samples were mechanically durable, but the high-diffusion-temperature samples with high Li content (mostly precipitated) etched more rapidly than the original

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[*] F. Hoffman and A. Schulze(6) obtained 1411±2°C with a calibrated thermocouple and 1409±2°C with a pyrometer. These values are to be reduced 2°C because of the change in the International Temperature Scale in 1948.

[†] H. Stöhr and W. Klemm(7) found 1412° for the melting point, which is to be reduced 2°C because of the change in the temperature scale.

[‡] M. Hansen, H. D. Kessler, and D. J. McPherson,(8) obtained 1410±5°C by an incipient melting technique, which is to be decreased 2°C because of the change in the temperature scale (private communication from McPherson states that the melting points of nickel and platinum based on the 1927 scale were used in their calibrations).

Table 1. *Tabulation of experimental data*

T(°C)	$10^4/T$(°K)	Calculated liquidus (atom fraction)	Solidus (atom fraction)	Distribution coefficient
1382±4	6·04	0·046±·006	$5{\cdot}6\times10^{-4}\pm8\%$	$1{\cdot}22\times10^{-2}$
1333±4	6·23	0·108±·005	$8{\cdot}6\times10^{-4}\pm13\%$	$8{\cdot}0\times10^{-3}$
1283±4	6·43	0·158±·004	$1{\cdot}05\times10^{-3}\pm8\%$	$6{\cdot}7\times10^{-3}$
1185±4	6·86	0·241±·003	$1{\cdot}3\times10^{-3}\pm8\%$	$5{\cdot}4\times10^{-3}$
987±4	7·94	0·371±·003	$1{\cdot}0\times10^{-3}\pm4\%$	$2{\cdot}7\times10^{-3}$
790±4	9·40	0·478±·002	$4{\cdot}5\times10^{-4}\pm10\%$	$9{\cdot}4\times10^{-4}$
592±4	11.57	0·578±·002	$9{\cdot}0\times10^{-5}\pm30\%$	$1{\cdot}56\times10^{-4}$

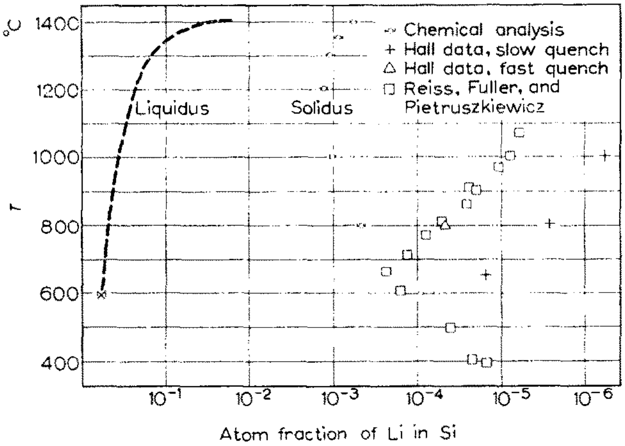

FIG. 2. Solubility of Li in Si.

Si and to a matte surface instead of the usual shiny surface.

Using the values for melting point and eutectic point discussed earlier, the remainder of the liquidus curve was determined by assuming the solution to be "regular",* and this liquidus was used in calculating the distribution coefficient. It is known from thermodynamic principles that the distribution coefficient, k, should follow, approximately, the relation $\ln k = (T_m/T) \ln k_m$, where T_m is the melting point in °K and k_m is the distribution coefficient at the melting point.(2) We have accordingly plotted $\ln k$ vs. $1/T$ (Fig. 3), and the results are seen to be in good agreement with the theory.

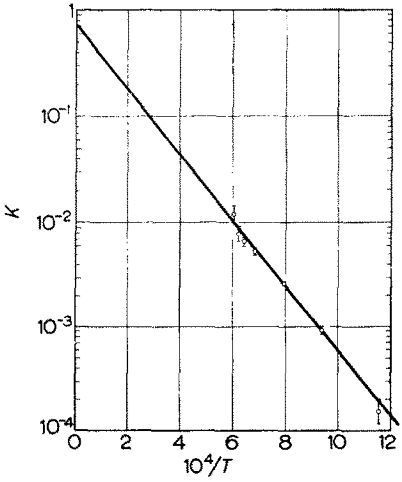

FIG. 3. Distribution coefficient for Li in Si.

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* For an example of such a calculation, see C. D. THURMOND *J. Phys. Chem.* **57**, 827 (1953).

Miscellaneous new information on Li–Si chemistry and phase diagram

In performing the above experiment, we obtained some data pertaining to Li–Si chemistry which does not appear to have been published previously. This is collected in the Appendix.

CONCLUSIONS

(1) The solubility of Li in Si is greater than previously realized, reaching a maximum atom fraction of $1{\cdot}3\times10^{-3}\pm8$ per cent at about 1200°C.

(2) The behavior of the distribution coefficient vs. $1/T$ is in accord with thermodynamic principles. At the melting point, it has a value of $1{\cdot}0\times10^{-2}$.

(3) The melting point of Si is 1408±2°C on the 1948 International Temperature Scale.

(4) There is a Li–Si eutectic point at 58±5 atom per cent of Li and 590±10°C.

(5) Using typical fast quench techniques, Li is unavoidably precipitated from solution when the sample is quenched from temperatures above about 650°C.

(6) $Li_{4n}Si_n$ has a melting point of 720±20°C and it reacts with room air to form Li_2CO_3 plus a Si compound; Li_2CO_3 has a melting point of 715±10°C; $Li_{2n}Si_n$ has a melting point of 750±10°C.

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APPENDIX

(1) With clean surfaces, Li reacts with Si at 185–200°C (probably near the Li melting point of 186°C) to produce a crystalline powder, with a large increase in total volume and no apparent liquid intermediate phase. Weight analysis indicates that this compound is of the composition $Li_{4n}Si_n$, and X-ray powder patterns identify it with a compound of similar composition found by earlier investigators.(9) This compound reacts slowly with room air to produce Li_2CO_3 (50 per cent conversion in 8 hr in room air at 20 per cent R.H.). The product was identified as predominantly the carbonate by weight analysis, X-ray powder pattern, and melting point. (Using C.P. Li_2CO_3, we have found the melting point to be 715±10°C inctead of the 618°C quoted in many handbooks.) The compound $Li_{4n}Si_n$ has a melting point of 720±20°C, measured in He, on sapphire or SiC. It ignites spontaneously in air at temperatures above roughly 100°C, and it reacts violently with water.

(2) A mixture of composition $Li_{2n}Si_n$ (which has been identified as a compound by earlier workers(9)) has a melting point of 750±10°C, as measured on sapphire in He.

(3) The molten alloy on the Si side of the 58 per cent Li eutectic point appears to dissolve large amounts of H_2. When cooled, the H_2 "boils" out near the eutectic temperature; however, the melting points discussed above, and the general behavior of the Li–Si compounds, are not significantly affected by the presence of H_2. This phenomenon does not occur with He.

(4) For alloys richer in Li than $Li_{2n}Si_n$, the only crucible material which we have found to be satisfactory is SiC. On the Si side of this compound, sapphire seems to be satisfactory. Pure alumina reacts with the Li even with 50 atom per cent mixtures.

(5) Any alloy richer in Li than roughly 50 atom per cent can be etched with water; if not too much richer in Si, dilute $HF–HNO_3$ etches are satisfactory.

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