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THE DIFFUSION OF LITHIUM IN ALUMINUM

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by

L. P. Costas

Pile Materials Division

February 1963

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E. I. du Pont de Nemours & Co.
Savannah River Laboratory
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ABSTRACT

The diffusion of lithium in aluminum was measured at various temperatures with diffusion couples of aluminum-LiAl. The activation energy, E, is 33.3 kcal/mol, and the diffusion factor, D_o, is 4.5 cm^2/sec.

THE DIFFUSION OF LITHIUM IN ALUMINUM

INTRODUCTION

One of the two methods used in the determination of the solubility of lithium in aluminum by Costas and Marshall(1) involved study of the diffusion zone on the aluminum-rich side of the aluminum-LiAl interface. Although that work was specifically designed for solubility relationships and not for diffusion studies, estimates of the diffusion constants of lithium in aluminum were possible. This report describes the determination of the diffusion factor, D_o, and the activation energy, E, used in the Arrhenius equation, $D = D_o\, e^{-E/RT}$.

DISCUSSION

The diffusion work was performed with the same capsules that were used in the previous studies(1).

Metallic lithium (99.8 wt % minimum purity, containing less than 0.02 wt % sodium) was inserted into thick-walled aluminum (99.99 wt %) containers, which were immediately welded shut. The containers were heated in vacuum tube furnaces for various times at selected temperatures. The containers were then removed, quenched in water, sectioned, polished metallographically, and etched in 2% HF to yield suitable surfaces for study. Microhardness profiles were made, and the hardness values were converted to equivalent lithium contents.

The capsule technique has shortcomings as well as advantages. There are two principal faults, so far as obtaining very accurate diffusion data are concerned: (1) since the aluminum-LiAl interface did not exist at the start of the experiment, the method is reliably accurate only if the induction period to form the interface is brief compared to the diffusion time, and (2) relatively large concentration differences (up to 13 atom % of lithium in aluminum) did not allow the diffusivity to be determined as a function of concentration. These two points are discussed in more detail below.

The reactions occurring in the capsules on heating to the selected temperatures can be summarized as follows:

$$\mathrm{Li}_{\mathrm{(solid)}} \rightarrow \mathrm{Li}_{\mathrm{(liquid)}} \tag{1}$$

$$\mathrm{Li}_{\mathrm{(liquid)}} + \mathrm{Al} \rightarrow \mathrm{LiAl}\ (\text{or } \mathrm{Li_2Al}\text{, which decomposes to } \mathrm{LiAl}) \tag{2}$$

$$\mathrm{LiAl} + \mathrm{Al} \rightarrow \alpha\ (\text{a solid solution of lithium in aluminum}) \tag{3}$$

$$\alpha_{\mathrm{(interface)}} \rightarrow \alpha \text{ throughout the aluminum by diffusion} \tag{4}$$

It is our experience that reactions (1), (2), and (3) are rapid in comparison to (4), the diffusion of lithium in aluminum. After reactions (1) and (2) are completed, LiAl gradually decomposes and forms a solid solution of lithium in aluminum in which the limiting kinetic factor is the diffusion of lithium in aluminum. Furthermore, since diffusion is the controlling factor, the concentration of lithium in α at the interface will be maintained at the solubility limit, a known value for any specific temperature. The system, therefore, can be considered as a simple case of diffusion into pure metal by an environment of constant composition. The exposure time of these experiments was such that only a short time, certainly no more than 5%, was involved in completing reactions (1) and (2), and the remainder was allotted to (3) and (4); therefore, the time to form the initial aluminum-LiAl interface did not introduce serious error.

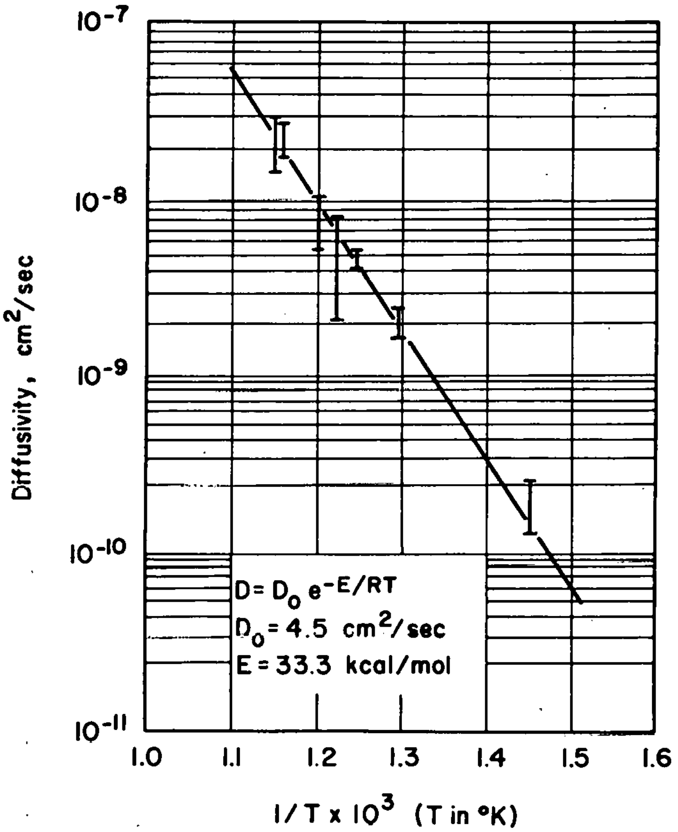
The other factor that limits the accuracy of the diffusion data is the large concentration differences within the α phase during diffusion. In other binary systems in which aluminum is the solvent, diffusion rates vary as much as tenfold, depending on the solute concentration, so it must be recognized that the diffusion values obtained in this work are average values. For the majority of cases, however, average values are sufficiently accurate.

The principal advantage of the technique is that the LiAl-α interfaces were formed originally in an inert atmosphere, and they remained free of contamination throughout the runs because of the encapsulation. Furthermore, the interface between the aluminum and LiAl was attained by chemical reaction, not by the mechanical means that are often used to butt the interfaces together and which may or may not break up oxide films that are unavoidably present on such reactive metals as aluminum and lithium. The presence of any foreign film between the diffusion metals could seriously impair the mobility of the atoms and result in erroneously low diffusivity values.

Diffusivity, D, was calculated from standard tables[2] that relate the ratio $(C-C_o)/(C_s-C_o)$ to $X/\sqrt{DT}$, where C is the concentration of lithium at X distance from the interface, C_s is the interface concentration, C_o is the initial lithium content of the aluminum, and T is the diffusion time. Since in this experiment C_o was zero, the ratio reduces to C/C_s. The distance, X, was 0.5 mm for all runs; C_s was the solubility limit at each temperature.

The table lists the time, temperature, and resulting diffusivities. The data are plotted in the figure as log D versus the reciprocal of the absolute temperature. They show that the Arrhenius relationship is followed, indicating that only one diffusion mechanism is operating.

Temperature, °C	Duration of Run, hr	Diffusivity, cm²/sec
597	232	$1.5 - 2.8 \times 10^{-8}$
589	408	$1.7 - 2.8 \times 10^{-8}$
559	261	$5.5 - 10.0 \times 10^{-9}$
538	450	$2.2 - 8.6 \times 10^{-9}$
529	450	$4.2 - 5.2 \times 10^{-9}$
500	502	$2.0 - 2.8 \times 10^{-9}$
417	1020	$1.2 - 1.7 \times 10^{-10}$
310	2064	Not measurable



At temperatures above 400°C very smooth interfaces were formed, but on a run that was attempted at 310°C there was some evidence of diffusion along grain boundaries. This low temperature run failed because diffusion was so slow that the 2064-hour period was not sufficient to produce a measurable diffusion zone. The fact that rapid diffusion is noticeable along grain boundaries has been noted in many other systems.

The activation energy, E, and the diffusion factor D_0, are 33.3 kcal/mol and 4.5 cm^2/sec, respectively. The value for activation energy agrees with those listed in Smithells(3) for Ag, Cu, Na, Mg, Si, and Zn in aluminum.

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