SURFACE MIGRATION OF OXIDES ON SODIUM CHLORIDE SUBSTRATES

B. K. Annis

THIS DOCUMENT CONFIRMED AS
UNCLASSIFIED
DIVISION OF CLASSIFICATION
BY I. L. Cicchiara/wer
DATE 6/18/73

MASTER

BLANK PAGE

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22151
Price: Printed Copy \$4.00; Microfiche \$0.95

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

ORNL-4854

Contract No. W-7405-eng-26

REACTOR CHEMISTRY DIVISION

SURFACE MIGRATION OF OXIDES ON SODIUM CHLORIDE SUBSTRATES

B. K. Annis

JUNE 1973

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830
operated by
Union Carbide Corporation
for the
U. S. Atomic Energy Commission

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

fy

TABLE OF CONTENTS

	Page
I. Introduction.	1
II. Theoretical Interpretation.	5
III. Experimental.	7
IV. Results	9
A. La_2O_3	9
B. SrO	18
V. Summary	25
VI. ACKNOWLEDGEMENTS	28
REFERENCES	29

BLANK PAGE

LIST OF FIGURES

	Page
1. Schematic Representation of the NaCl Coupons Used in the Surface Diffusion Studies. The arrow indicates the direction of the surface diffusion	8
2. Relative Concentration Profile of La_2O_3 Deposited on an NaCl Surface	10
3. Relative Surface Concentration Profile of La_2O_3 on NaCl After a 352 hour Anneal at 420°C	13
4. Sputtering Curves for La_2O_3 at 250μ ●, 460μ ○, and 770μ ■ from the Edge of the Deposit.	15
5. Sputtering Curve for La_2O_3 at 2000μ	16
6. Surface Concentration of La_2O_3 on NaCl after an 880 hour Anneal at 420°C	17
7. Electron Microprobe Profiles of the Edge of SrO Deposit. . . .	20
8. Sputtering Curves for SrO Sample at 45 and 80μ from Deposit Edge	22
9. Sputtering Curves for SrO Sample at 120 and 2000μ from Deposit.	23
10. Superposition of Ion Probe Data on Theoretical Curves, Annealing Time 920 Hours	24
11. Superposition of Line Scan Data for SrO (920 hour Anneal). . .	26
12. Superposition of Line Scan Data for SrO (444 hour Anneal). . .	27

ABSTRACT

The surface migration of radioactive species is a matter of some concern in connection with the salt mine radioactive waste repository concept. Consequently an experimental study of the behavior of lanthanum and strontium oxides was carried out. The behavior of strontium oxide of course was of intrinsic interest, whereas the lanthanum oxide was employed to simulate plutonium. The investigation indicated that the surface migration of La_2O_3 at 693°K was well characterized by a diffusion coefficient of $3 \times 10^{-10} \text{ cm}^2/\text{sec}$. The behavior of SrO proved somewhat ambiguous, but at 583°K the surface diffusion coefficient appeared to be less than $3 \times 10^{-12} \text{ cm}^2/\text{sec}$.

I. INTRODUCTION

Mass transport along the surface of a solid is one of the least understood of the many forms of diffusion phenomena. Two factors are primarily responsible for the ambiguity. The first involves the concept of a solid surface. For example, processes occurring on the surface of a polycrystalline material may be expected to behave quite differently from those on the surface of a single crystal face. While the latter case would appear to represent the most controllable type of surface, there still exists considerable latitude for uncertainty. The orientation of the crystal face, the possibility of structural defects, such as valleys and terraces, and the presence of contaminants, such as nitrogen, oxygen, and water vapor, can all affect experimental reproducibility and complicate the formulation of realistic mathematical models for surface movement.

The second source of ambiguity arises from the manner in which the diffusing component is distributed upon the surface. This aspect of the problem has two facets. One is concerned with the amount of surface area occupied by a single layer of atoms, while the other involves the vertical distribution, or the possibility of a multilayer deposit of the diffusing species. Barrer,¹ in a review of the early work on surface diffusion, stresses the importance of the first type of concentration dependence and indicates that differences in the diffusion coefficient of one to two orders of magnitude may occur due to the distribution over the surface. Unfortunately, the possibility of a concentration-dependent diffusion coefficient can render intractable the mathematical analysis of a diffusion problem, and consequently it would appear that this aspect has been largely ignored in subsequent investigations.

Somewhat more progress has been made on the question of vertical distributions. Langmuir and Taylor² hypothesized for cesium diffusion on tungsten that the ratio of the heat of adsorption for an atom in a monolayer to the activation energy for migration in the first layer remained constant as additional layers were deposited. The diffusion coefficient characteristic of the second layer was estimated to be approximately six orders of magnitude larger than that for the first layer at room temperature.

BLANK PAGE

Experimental evidence for such an effect may be found in the measurements of Arnikar and Mehta³ who investigated the self diffusion of I^- on copper for monolayers and for films of approximately one hundred layers. The multilayer diffusion coefficient was larger by a factor ranging from three to ten.

Similar evidence comes from an investigation of the migration of H_2 , CO , and O_2 over tungsten by Gomer.⁴ He observed that deposits of approximately a monolayer or less were essentially immobile; however, when the coverage was in excess of a monolayer, spreading occurred with a sharp boundary. This was interpreted as the result of second or higher layer atoms skating with relative ease over the primary layer, falling off the edge, and becoming chemisorbed on the substrate.

Discussion of a somewhat similar problem may be found⁵⁻⁹ in which the existence of a layer extending into the substrate and characterized by higher diffusivity than the bulk material has been postulated. Such a concept necessitates the introduction of an additional parameter, corresponding to the layer thickness, into an analysis of the concentration distribution of the diffusing component. At the present time estimates of this layer thickness range from one atomic layer (10^{-8} cm) to 10^{-6} cm.

In view of the numerous experimental and conceptual difficulties, it is not surprising that numerical values for surface diffusion coefficients, particularly those related to NaCl, are sparse. Only two direct measurements appear to have been made. Nikitine and Goltzene¹⁰ reported a tentative value of 2×10^{-8} cm²/sec at 423°K for the diffusion of Cu^+ over RbBr. The Cu^+ originated in a layer of CuCl deposited on the crystal surface. No diffusion of CuCl was observed.

More recently Tan et al.¹¹ have observed the diffusion of ^{110}Ag on thin layers of silver bromide for the temperature range 368-433°K. By varying the thickness of the AgBr layer that formed the substrate, it was possible to see the effect of migration into the bulk of the AgBr upon the surface transport. The results presented in Table I were obtained by extrapolating to a zero thickness layer of AgBr, and consequently the diffusion coefficients should be representative of the surface region. At 368°K the apparent surface diffusion coefficient for a thick layer was found to be approximately an order of magnitude smaller. The measurements at 433°K were terminated before a minimum value of the

apparent surface diffusion coefficient was obtained; however, the data do indicate a reduction by at least a factor of 4.

The remaining studies were primarily directed toward an investigation of the nucleation of adsorbed molecules being deposited on a surface. Such studies provide a value for the activation energy of migrating molecules, from which the diffusion coefficient can be inferred through the use of the relation¹²

$$D = a^2 \nu \exp (-Q_D/RT), \quad (1)$$

where a is the distance between absorption sites, ν is the atomic vibration frequency, and Q_D is the activation energy. Reference 12 suggests values of $4\text{\AA}$ and $7 \times 10^{12} \text{sec}^{-1}$ for a and ν , respectively, and these were used to compute the diffusion coefficients in Table I. In the case of In-NaCl¹³, values for the mean diffusion length λ_s and the lifetime on the substrate λ , were reported; the diffusion coefficient can then be estimated from the equation

$$\lambda_s^2 = D\tau. \quad (2)$$

Unfortunately, it does not appear to be possible to make a comparison of the computed values with a direct measurement. However, it is worth noting that in the case of Ag on mica, a direct measurement¹⁷ of D , using ^{110}Ag as a tracer, yielded an activation energy approximately an order of magnitude larger than that obtained by studying the nucleation process.¹⁸

Another factor influencing the reliability of the values in Table I is the necessity of using a theoretical model to explain the nucleation process. In the case of Pt-NaCl, two different analyses of the data have been made, with quite different results.

A final study that indicates the possibility of rather divergent evaluations of a surface diffusion coefficient is found in the work of Geguzin et al.^{18,19} The authors present a theoretical and an experimental analysis of the coalescence of islands of gold deposited on a NaCl crystal and obtain a value of $10^{-16} \text{cm}^2/\text{sec}$ at 573°K . It is admitted that this is an anomalous result, and that the discrepancy may be due to the existence of electrical charges on the gold.

Table I. Surface Diffusion Coefficients on NaCl and Related Substrates

System	T, °K	Q_D (kcal/mole)	D (cm ² /sec)	$(2Dt)^{1/2a}$ (meters)	References
Cu ⁺ -RbBr	423		2×10^{-8}	1.2×10^1	10
Ag ⁺ -AgBr	433	7.7	2.3×10^{-8}	1.2×10^1	11
	693		7×10^{-7}	6.6×10^1	
Au-KCl	473	2.8	6×10^{-4}	2×10^3	14
	673		1.4×10^{-3}	3×10^3	
In-NaCl	293		2×10^{-2}	1×10^4	13
Ag-NaCl	473	4.6	8×10^{-5}	7×10^2	15
	673		3.6×10^{-4}	1.5×10^3	
Pt-NaCl	473	4.15	1.3×10^{-4}	9×10^2	12
	673		5×10^{-4}	1.8×10^3	
Pt-NaCl	473	10.4 ± 1.1^b	1.8×10^{-7}	3.4×10^1	16
	673		4.7×10^{-6}	1.7×10^2	

a. Root mean-square displacement after 10^6 yrs as ascertained from a one dimensional random walk model.

b. Reinterpretation of data in Ref. 12 by Lewis.¹⁶

Hopefully, the data on the diffusion of atoms and atomic ions collected in Table I represent an upper limit on the possible values for molecular surface diffusion. Some idea of the lower limits may be obtained from data on the surface self diffusion of aluminum oxide (Al_2O_3) and magnesium oxide (MgO). The value for the diffusion coefficient of Al_2O_3 at a temperature of 693°K , which corresponds to the temperature of the La_2O_3 measurements to be discussed later, is in the range 10^{-23} - 10^{-34} cm^2/sec . Similarly, the diffusion coefficient for MgO at 583°K , which corresponds to the temperature of the SrO measurements, is about 10^{-24} cm^2/sec . These values were computed by using parameters²¹ which were determined from studies made over the temperature range 1373 - 1973°K and consequently may be off by several orders of magnitude.

II. THEORETICAL INTERPRETATION

As pointed out in the introduction, the interpretation of surface migration phenomena contains many ambiguities, and in essence only the simplest type of analysis will be made here. The first assumption is that the diffusion coefficient is independent of concentration. This is a common assumption, and, certainly in the case of the most quantitative data, that obtained by the ion probe for La_2O_3 , appears justified. The next problem is concerned with whether or not the migration is confined to the surface or requires consideration of diffusion into the substrate.

Even within the first possibility, that the diffusion is restricted solely to the surface, a diversity of opinion as to the appropriate mathematical solution may be found in the literature. The three solutions generally used are:

$$C = \text{const.} (2\pi Dt)^{-1/2} e^{-x^2/4Dt}, \quad (3)$$

$$C = C_0 \operatorname{erfc} \frac{x}{2(Dt)^{1/2}}, \quad (4)$$

and

$$C = (C_0/2) \operatorname{erfc} \frac{x}{2(Dt)^{1/2}}, \quad (5)$$

where t is the time for the duration of the diffusion, x is the distance along the direction of diffusion, and D is the surface diffusion coefficient. The first solution applies to a situation such that the material initially at $x = 0$ decreases with time. This condition ought to be best realized by a line deposit only a monolayer thick.

Equation (4) corresponds to the case in which the concentration at $x = 0$ remains constant for all time and consequently requires, in principle, an infinite amount of material as well as a mechanism for replenishing the concentration at the origin. Equation (5) refers to a similar situation but differs in requiring that the concentration at $x = 0$ be one-half the initial value for all diffusion times greater than zero. Either of the last two solutions seem better suited to the experimental situation of interest here, in which the initial deposit is a few hundred monolayers thick. The method chosen to evaluate the diffusion coefficient turns out to be independent of the coefficient of the complementary error function of Eqs. (4) and (5), and indeed even when the data are analyzed in terms of Eq. (3) the resulting diffusion coefficient values, for the purposes of the current investigation, are not significantly different.

The diffusion coefficients were obtained from the experimental profiles by computing the logarithm of C/C_0 for a number of values for the diffusion coefficient and plotting $\ln (C/C_0)$ as a function of distance. Similar plots were made of the logarithm of the experimentally determined concentrations, and by superposing the two plots a diffusion coefficient characterizing the curve which best agreed with the data could be obtained. With this method there is no need for the actual value of C_0 .

The situation becomes considerably more involved if it is necessary to also consider diffusion of the surface material into the bulk of the substrate. Suzuoka¹⁷ has made a rigorous mathematical analysis of this subject, and finds that a complete description requires both the bulk and surface diffusion coefficients and an additional parameter that specifies the depth of a "surface layer" in which the migration parallel to the surface is characterized by the "surface" diffusion coefficient. In a similar analysis Borisov and Gal'²² demonstrate that the concentration profiles may be quite accurately approximated by the general form:

$$C = (C_0/2) \operatorname{erfc} [K(m_0 t^{-1/4}, n_0 t^{-1/2})x], \quad (6)$$

where $K(m_0 t^{-1/4}, n_0 t^{-1/2})$ is a general scale function which must be determined empirically,

$$m_o = \frac{D_B^{1/4}}{2^{3/2} (aD)^{1/2}}, \quad (7)$$

and

$$n_o = \frac{1}{2D_B^{1/2}}, \quad (8)$$

where D_B is the bulk diffusion coefficient, and a is the effective depth of the surface layer in which the diffusion parallel to the surface is characterized by D . Equation (6) is identical with Eq. (5) if the scale function is given by $[2(Dt)^{1/2}]^{-1}$. Consequently, for any technique based on Eq. (5) and used to determine D , it could be argued that in reality only a value of the scale function of Eq. (6) was obtained. Borisov and Gal'²² claim that if the bulk diffusion coefficient is known, an experimental study of the variation of the scale function with time could be used to determine the effective depth, a , and the surface diffusion coefficient D . However, the method for doing this requires a more elaborate experimental program than could be attempted here. In addition, the lack of data for bulk diffusion coefficients has necessitated the use of the simple analysis of Eq. (5).

III. EXPERIMENTAL

The sodium chloride substrates which are depicted in Fig. 1 were obtained from the Harshaw Company and are approximately 17 mm by 8 mm by 1.5 mm thick. The surfaces were highly polished; under a standard laboratory microscope, no appreciable surface irregularities were detected. Presumably defects on the order of a tenth of a micron would have been visible. On approximately one-half of the crystal a film of either La_2O_3 or SrO was laid down by an electron beam deposition technique. The La_2O_3 purity was specified to be 99.999% while that of the SrO was 99.5%.

The thickness of the La_2O_3 deposit for the results reported here was 633 Å, corresponding to about 40 $\mu\text{g}/\text{cm}^2$. The SrO deposit thickness was about 707 Å, or 33 $\mu\text{g}/\text{cm}^2$. These numbers were not preselected as being particularly relevant to the experiment but instead represent the minimum amounts that could be reliably provided by the deposition technique. In an attempt to reduce the effects of water vapor on the surfaces, the crystals were stored in a vacuum desiccator except during the annealing periods.

Fig. 1. Schematic Representation of the NaCl Coupons Used in the Surface Diffusion Studies. The arrow indicates the direction of the surface diffusion.

The samples were annealed at temperatures ranging from about 473 to 693°K for periods of time varying from about two to 39 days. The annealing was done in air with no effort to control the atmosphere beyond the usual laboratory regulation of the relative humidity in the range 35-60%. After the annealing periods the concentration profiles in the direction of the arrow in Fig. 1 were determined. The profiles were examined through the use of an electron microprobe, ion-induced X-ray fluorescence, spark source mass spectroscopy, and an ion probe.

IV. RESULTS

A. La₂O₃

In view of the lack of information on surface diffusion, the experimental program was begun rather arbitrarily by using an electron microprobe to examine a NaCl coupon supporting a deposit of approximately 100 layers of La₂O₃. The sample had been annealed for approximately 48 hours at 473°K. The data are shown in Fig. 2 along with some theoretical diffusion profiles. At this point in the investigation, the possibility of a multilayer migration process was of some concern, and the theoretical curves correspond to the situation in which the material of the entire deposit could participate in the motion. Equation (5) was thought to provide the most reasonable description.

The results seemed to indicate that the microprobe could be a useful tool and that rather large amounts of material had spread over the crystal in a manner that could not be described by the diffusion model. The most obvious hypothesis was that the stainless steel masks employed during deposition were inadequate. Subsequent depositions were carried out using transparent tape applied directly to the crystal as a mask. The tape was then peeled off the crystal and under a magnification of 100 no evidence of any residue could be found. Microprobe examinations then indicated that the peculiar behavior of the initial sample had indeed been due to the mask. As the work progressed it became clear that the best of the two microprobes used in the analyses had a detection limit of about 0.1-0.2 $\mu\text{g}/\text{cm}^2$. This is estimated as equivalent to approximately 1/2 to 1 monolayer. The results showed that the earlier fears of a multilayer diffusion process were groundless but provided only a rather qualitative idea about the migration that might have occurred on a submonolayer basis.

ORNL-DWG 71-7687

Fig. 2. Relative Concentration Profile of La_2O_3 Deposited on an NaCl Surface.

Consequently, additional analytical methods were sought. A batch of samples with $160 \text{ \AA}$ ($10 \text{ \mu g/cm}^2$) films of La_2O_3 were annealed for approximately 336 hours, and the concentration profiles were examined using spark source mass spectrometry and an ion-induced fluorescence technique. Spark source mass spectrometry proved to be capable of placing an upper limit of $0.01\text{--}0.04 \text{ \mu g/cm}^2$ on the samples examined. This was a considerable improvement over the electron microprobe; unfortunately the method required cleaving the salt coupons into thin strips with the small dimension parallel to the diffusion direction. In practice, the minimum thickness that could be obtained was approximately 1 mm. In addition, adjacent 1 mm strips could not be cleaved with any consistency, so the method provided only a rather coarse measure of the profiles.

The ion-induced fluorescence method was developed by Saltmarsh, van der Woude, and Ludemann.²³ This method involved bombarding the samples with 20 MeV oxygen ions and detecting X-rays produced in collisions with the surface and near surface atoms. The ion beam impinged on a rectangular area with dimensions of about 250 by 450 μ . The preliminary results indicated that La in amounts of 0.03 to $0.06 \text{ \mu g/cm}^2$ could be detected.

The combination of the three methods, electron microprobe, spark source mass spectrometry, and ion-induced fluorescence was felt to have the potential to provide sufficiently quantitative information to accurately assess the surface diffusion problem, and a final batch of samples was prepared. The La_2O_3 films were $633 \text{ \AA}$ ($40 \text{ \mu g/cm}^2$) and the samples were divided into three groups. The first group was not annealed, whereas the remaining two were annealed at 693°K for periods of 352 and 880 hours, respectively. The concentration distributions of the three types of samples were examined by the three methods.

The results of the concentration analyses were mixed. Unfortunately, for unknown reasons, the statistical error of the ion fluorescence method increased by a factor of 5-10 so that the minimum detectable amount of La became about $0.2 \text{ \mu g/cm}^2$. On the other hand, the microprobe data had a similar statistical uncertainty of about $0.1 \text{ \mu g/cm}^2$. Thus, although the data precluded any multilayer diffusion, the results were not unequivocal for diffusion involving submonolayer quantities of La.

The results obtained with the electron microprobe and mass spectrometric techniques from samples annealed for 352 hours are shown in Fig. 3. In the analysis displayed in the figure it was assumed that transport occurred only at sub-monolayer coverage, and it was necessary to assume a value of the effective initial source concentration, C_0 . This was done by estimating the area of an La_2O_3 molecule and the number required for monolayer coverage. The result corresponded to a coverage of $0.22 \mu\text{g}/\text{cm}^2$. When the mass-spectrometric data, which are designated by horizontal bars in the figure, were considered independently, it was possible to estimate both the diffusion coefficient, D , and C_0 . The latter result was in reasonable accord with the estimated value. The points correspond to data obtained with the electron microprobe; the error bars indicate twice the standard deviation, i.e., the so-called 95% confidence level.

The upper curve in the figure corresponds to a hypothetical concentration profile (based on Eq. 4) which would result from a surface diffusion process whose characteristic surface diffusion coefficient is $10^{-8} \text{ cm}^2/\text{sec}$; the lower curve is representative of $10^{-10} \text{ cm}^2/\text{sec}$. The mass spectrometric data, which actually yield only an upper limit of the magnitude of the diffusion process, appear to correspond with the upper curve, whereas the electron microprobe data seem to favor the lower curve. Similar results were obtained for samples that had been annealed for 880 hours.

At this point in the investigation the availability of an ion probe became known. In this device, material sputtered off the surface by an ion beam of variable size, is collected and analyzed in a mass spectrometer. The ion beam can be scanned over the surface much like the electron microprobe.

One of the samples annealed for 880 hours was examined using the ion probe and the results were quite rewarding. The ion beam had an intensity of 4.4 nanoamp and consisted of 20 Kev O^+ particles. The sputtered area was approximately $60\mu \times 78\mu$, with the shorter edge parallel to the diffusion direction. An electronic aperture was used to minimize counts from the edge of the sputtered area. By taking the ratio of a signal far from the edge of the deposit to the signal from a spot in the deposit, the minimum

Fig. 3. Relative Surface Concentration Profile of La_2O_3 on NaCl after a 352 hour Anneal at 420°C . The data points and associated vertical error bars correspond to electron microprobe measurements, whereas the horizontal error bars denote the results of spark-source mass spectrometric determinations. The two solid curves are theoretical profiles corresponding to the diffusion coefficient values indicated.

detectability was estimated at less than $4 \times 10^{-4} \mu\text{g}/\text{cm}^2$. Figure 4 shows the form of the data taken at 250, 460, and 770 μ , and Fig. 5 the data at 2000 μ . The vertical axis corresponds to the number of counts obtained in a 10 second counting interval, while the horizontal axis corresponds to the number of such intervals. The general shape of the curve is determined by the following considerations. The surfaces of the specimens must be electrically conducting and are coated with a thin carbon deposit. Initially the ion beam etches away this carbon film and essentially no lanthanum is detected, but as the actual surface of the salt coupon is reached the lanthanum signal increases and passes through a maximum as the surface layer is sputtered away.

In principle the amount of La_2O_3 at each point is proportional to the summation of the counts in all the intervals necessary to reduce the signal to the original background level or, in other words, the area under the curve. However, due to the scatter in the data to the right of the maximum, and the length of time necessary to reach the background level again, it was assumed that the total area was proportional to the sum of the counts in intervals 10 through 26, and the comparison with theory was made on this basis.

The final results are shown in Fig. 6, which is actually a superposition of two plots. One plot corresponds to the logarithm of the experimental concentrations as a function of distance, while the other is composed of curves for the logarithm of the theoretical concentrations corresponding to various values of the diffusion coefficient. The data may be seen to fit the curve corresponding to a value of D of $3 \times 10^{-10} \text{ cm}^2/\text{sec}$. The precision is estimated at 30 to 50%. A few data points, corresponding to distances closer than 250 μ , were purposefully omitted. They appeared to lie on a curve characteristic of a diffusion coefficient of about $10^{-11} \text{ cm}^2/\text{sec}$. While this initial behavior may have been an artifact of the deposition technique, which was below the level of detection of the electron microprobe examinations of the unannealed samples, it is interesting to note that a similar behavior has been observed in studies of the surface diffusion of sodium on mica.¹⁷

ORNL-DWG 73-1358

Fig. 4. Sputtering Curves for La₂O₃ at 250μ●, 460μ○, and 770μ■ from the Edge of the Deposit.

Fig. 5. Sputtering Curve for La_2O_3 at 2000 μ .

ORNL-DWG 72-7819

Fig. 6. Surface Concentration of La_2O_3 on NaCl After an 880 Hour Anneal at 420°C . The data points represent results obtained utilizing an ion probe technique, whereas the solid lines are theoretical results corresponding to the surface diffusion coefficients indicated.

B. SrO

Although the studies of surface migration of La_2O_3 indicated that isotope transport by this mechanism would be insignificant, in order to present a more forceful argument the investigations were extended to include strontium oxide. This molecule, besides providing a system of direct relevance to the salt mine program, is also attractive from the standpoint of molecular size. In addition to being smaller and lighter than La_2O_3 , SrO has the same crystal structure as does NaCl, and the unit cell dimensions agree to within 10%. Consequently, the interactions with the substrate might be rather different from that of La_2O_3 .

The disadvantage of the SrO system is that the usual laboratory relative humidity range (35-60%) could provide sufficient water vapor for the reaction

to occur at the annealing temperature. Since the ion probe does not readily provide information on the chemical environment of the strontium, no estimate of the extent of the reaction can be made, and two possible alternatives arise. One is to heat the sample to a temperature high enough to reduce the probability of $\text{Sr}(\text{OH})_2$ formation. This situation would not conform to the conditions present in the salt mine, and is further complicated by reports of two different values, 648°K and 808°K, for the melting point of the hydroxide. On the other hand, a temperature below the minimum reported melting point seemed to be a more appropriate approximation to conditions of the storage area, and a temperature of 583°K was used.

It was felt that the experience with La_2O_3 provided some idea as to appropriate annealing periods and distances which could be analyzed effectively. Accordingly, a group of SrO-NaCl couples were annealed for periods of 36, 444, and 920 hours, and it was hoped that by varying the diffusion time by over an order of magnitude some insight into the nature of the scaling function of Eq. (6) might be obtained. Unfortunately, data from the two samples with the longer annealing periods indicated that quantitative information ought to be very difficult to obtain from the sample with the 36 hour anneal, and it was not examined. Further, the available data proved to give only a marginal fit to the complementary

error function curves of either the simple surface diffusion model of Eq. (5) or the more complex situation described by Eq. (6), and within the context of the simple diffusion model, both samples gave essentially the same surface diffusion coefficient. Consequently, further investigation of the alternative description of the combined surface and bulk migration by means of the available data seemed unwarranted.

The microprobe examination of the SrO samples proved to provide even less sensitivity than was the case in the La_2O_3 analysis. It is estimated that an amount of SrO equivalent to $3-4 \times 10^{-3}$ of the original deposit should have been detectable. This amount of material corresponds to a layer $2.1 \rightarrow 2.8 \text{ \AA}$ thick, or $0.1-0.13 \text{ \mu g/cm}^2$, which is estimated to be slightly greater than a monolayer. One striking feature that the microprobe analysis did reveal was a rounding off of the corner of the deposit extending down to about 60-70% of the maximum value and occurring over a distance of about 100μ . No such effect occurred with the La_2O_3 samples. Figure 7 shows the profiles for two locations on a sample annealed for 920 hours and two locations on an unannealed control sample. It is not clear that there is any significant difference in the curvatures over the range 0.6-1.0 for the two types of samples. However, in the region below 0.2 there is some indication of a less drastic concentration reduction for the annealed sample. If this is indeed the case a small migration of several monolayers of SrO must have occurred.

The determination of concentration profiles with the ion probe was begun by using the conditions that had yielded good results in the La_2O_3 samples. The sputtering ion was O^- , and a beam intensity of three to four nanoamps was used. The spot size was somewhat reduced to a rectangle of 30 to 40 microns; the shorter dimension was parallel to the diffusion direction. The data indicated that detectable amounts of Sr were present out to 3000 microns from the edge of the deposit and remained at a rather constant level until 120 microns from the edge. Complete data for the instrumental background and the value for the SrO deposit are not available, but it can be estimated that the ratio of the Sr background to the signal obtained from the deposit is in the range 7×10^{-6} to 1.5×10^{-5} . This would correspond to about $(2.3-5.0) \times 10^{-4} \text{ \mu g/cm}^2$. Of the three patches

Fig. 7. Electron Microprobe Profiles of the Edge of SrO Deposit.
 ● denotes annealed samples, ▲ denotes unannealed.

examined within 120 microns, only those centered on 80 and 45 microns gave reasonable results; a third centered at 15 microns from the edge showed a definite indication of including a portion of the deposit. Some of the data are shown in Figs. 8 and 9. The points at 80 and 45 microns are fitted to a simple surface diffusion curve in Fig. 10 and indicate a nominal value for the diffusion coefficient of 3×10^{-12} cm²/sec.

Apart from the small Sr background, the general behavior of the results was reasonable, and it was desirable to obtain more closely spaced data points within the apparent diffusion distance of 100-150 microns. This could have been accomplished by changing the rectangular beam pattern to a narrow line but would have reduced the effective beam intensity. Consequently, a change was made to an N₂⁺ ion beam with an intensity of about 18 nanoamps, and the scanning pattern was reduced to a line about 85 microns long by 10 microns. The shorter dimension was parallel to the diffusion direction.

In this mode the sputtered signal had a quite different form from that shown in Figs. 8 and 9. In essence, the first ten second interval of sputtering accounted for the majority of the detectable Sr for positions off the deposit, while for the O⁻ beam 10 to 20 such intervals had been required. An analysis of the ratio of the Sr background far out on the crystal to the deposit signal resulted in a value of 4.5×10^{-5} , which was about a factor of three larger than the ratio for the unannealed control sample. It was noted that the behavior of the sputtered ion signal from the deposit area was also radically different from that obtained with the O⁻ beam. Instead of taking several minutes to pass through a maximum and begin a slow decline, a peak was obtained in ten seconds which was then reduced by about two orders of magnitude during the next 20 to 30 seconds. This sharp cutoff may be due to a phenomenon called "charging" and arises from an accumulation of charge on the surface of an insulating material such as NaCl. The charge accumulation creates stray electric fields that can inhibit passage of the sputtered ions to the detection system. If "charging" was occurring, the signals may have attained only a fraction of the possible value, and it is problematical as to whether or not the same fraction applied to both the thickly deposited area and the portions of the crystal

Fig. 8. Sputtering Curves for SrO Sample at 45 and 80μ from Deposit Edge.

Fig. 9. Sputtering Curves for SrO Sample at 120 and 2000 μ from Deposit.

ORNL-DWG 73-1361

Fig. 10. Superposition of Ion Probe Data on Theoretical Curves, Annealing Time 920 Hours. Horizontal bars show extent of sputtered area.

containing only trace amounts. When the line scanning technique with the N_2^+ beam was used on the unannealed control sample, the background to deposit signal ratio was about 1.6×10^{-5} , or about a factor of three smaller than on the annealed specimen. It was also found that the signal obtained from the deposit area was about 60% greater than that for the annealed sample.

No reason is known for the high Sr background; it can only be conjectured that the observation may be associated with the formation of $Sr(OH)_2$ and subsequent evaporation.

The line scanning technique did provide more data on the concentration profile but, unfortunately, the additional information only tended to make the interpretation ambiguous. The data from a typical scan on the sample annealed for 920 hours is superposed on theoretical curves in Fig. 11. Although the resulting diffusion coefficient appears to lie in the range $1-3 \times 10^{-12} \text{ cm}^2/\text{sec}$, and is reasonably consistent with the result discussed previously, it appears that the shape of the profile differs from that of the theoretical model.

The data from the sample annealed for 444 hours are shown in Fig. 12 and show a similar behavior. Once again, assuming the model to be correct, a diffusion coefficient of about $3 \times 10^{-12} \text{ cm}^2/\text{sec}$ is obtained.

V. SUMMARY

Quantitative information on the surface migration at temperatures relevant to a salt mine waste repository for the oxides La_2O_3 and SrO has been obtained. To the extent that the laboratory experiments successfully mimic the actual conditions in the repository, it would appear that surface transport of radioactive isotopes is of little consequence.

The surface diffusion of La_2O_3 at $693^\circ K$ is well characterized by a diffusion coefficient of $3 \times 10^{-10} \text{ cm}^2/\text{sec}$. The data for SrO at $583^\circ K$ indicate a somewhat more ambiguous situation. The exact chemical nature of the migrating Sr is open to question, and the presence of a low but constant Sr background on the diffusion samples may indicate some vapor phase transport. Nevertheless, apart from this background, the concentration profiles roughly correspond to a diffusion coefficient of $3 \times 10^{-12} \text{ cm}^2/\text{sec}$ or less.

Fig. 11. Superposition of Line Scan Data for SrO (920 hour anneal).

Fig. 12. Superposition of Line Scan Data for SrO (444 hour anneal).

VI. ACKNOWLEDGEMENT

A large number of people were involved in experimental aspects of this work and the author would like to acknowledge H. Adair and H. Harmon for the film deposition activities; H. Henson for electron microprobe examination; J. Carter for spark source mass spectrometry; and M. Saltmarsh, A. Van der Woude and C. Ludemann for the analyses with the ion fluorescence technique. Finally, the ion probe results, which provided the bulk of the quantitative information, were provided through the efforts of S. Cristy.

REFERENCES

1. R. M. Barrer, Diffusion In and Through Solids, Cambridge University Press, New York (1941).
2. J. B. Taylor and I. Langmuir, Phys. Rev. 44, 423 (1933).
3. H. J. Arnikaar and O. P. Mehta, J. Phys. Chem. Solids 24, 1633 (1963).
4. The Solid-Gas Interface, p. 597, E. A. Flood, Ed., Marcel Dekker, New York (1967).
5. Ya. Ye. Geguzin, G.N. Kovalev, and O. M. Ratner, Phys. Met. Metallog. 10 (1), 45 (1960).
7. P. G. Shewmon, J. Appl. Phys. 34, 755 (1963).
8. V. A. Panteleyev and V. S. Metrikin, Phys. Met. Metallog. 23 (6), 96 (1967).
9. B. Ya. Pines, I. P. Grebennik, and I. V. Gektina, Sov. Phys. Crystallog. 12, 556 (1968).
10. S. Nikitine and A. Goltzene, Phys. Letters 13, 290 (1964).
11. Y. T. Tan, W. Perkett, and R. Powell, J. Appl. Phys. 42, 4752 (1971).
12. G. Sumner, Phil. Mag. 12, 767 (1965).
13. V. M. Kosevich and S. N. Grigorov, Sov. Phys. Solid State 10, 1998 (1969).
14. V. I. Trofimov, A. E. Chalykh, and V. M. Lukyanovich, Sov. Phys. Solid State 11, 698 (1969).
15. D. Walton, T. N. Rhodin, and R. W. Rollins, J. Chem. Phys. 38, 2698 (1963).
16. B. Lewis, Surface Science 21, 289 (1970).
17. V. I. Solunskii and A. A. Dobrikov, Sov. Phys. Dokl. 14, 497 (1969).
18. V. S. Postnikov, V. M. Ievlev, I. V. Zolotukhin, Sov. Phys. Solid State 10, 2531 (1969).
19. Ya. E. Geguzin, Yu. S. Kaganovskii, and V. V. Kalinin, Sov. Phys. Solid State 11, 203 (1969).
20. Ya. E. Geguzin, Yu. S. Kaganovskii, and V. V. Slyozov, J. Phys. Chem. Solids 30, 1173 (1969).
21. W. M. Robertson, J. Nucl. Materials 30, 36 (1969).
22. V. T. Borisov and V. V. Gal', Phys. Met. Metallog. 26(2), 132 (1968).
23. M. J. Saltmarsh, A. Van der Woude, and C. Ludemann, Appl. Phys. Letters 21, 64 (1972).