24
746
9/16

440

AI-AEC-12726
COPY

SELF-DIFFUSION OF URANIUM AND CARBON
IN URANIUM MONOCARBIDE

AEC Research and Development Report

ATOMICS INTERNATIONAL

A DIVISION OF NORTH AMERICAN ROCKWELL CORPORATION

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of 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. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Printed in the United States of America
Available from

Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U.S. Department of Commerce
Springfield, Virginia 22151

Price: Printed Copy \$3.00; Microfiche \$0.65

SELF-DIFFUSION OF URANIUM AND CARBON
IN URANIUM MONOCARBIDE

By

G. G. BENTLE
G. ERVIN, JR.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

ATOMICS INTERNATIONAL

A DIVISION OF NORTH AMERICAN ROCKWELL CORPORATION

CONTRACT: AT(04-3)-701
ISSUED: AUGUST 30, 1968

DISTRIBUTION

This report has been distributed according to the category "Metals, Ceramics, and Materials" as given in the Standard Distribution for Unclassified Scientific and Technical Reports, TID-4500.

CONTENTS

	Page
Abstract	4
I. Introduction	5
II. Material	6
III. Procedures and Results	7
A. Carbon Diffusion	7
B. Uranium Diffusion	9
C. Discussion	15
IV. Conclusions	20
References	21

TABLES

1. Summary of Diffusion Data for Carbon in UC	11
2. Summary of Diffusion Data for Uranium in UC.	15
3. Comparison of Various Results Reported in the Literature.	17

FIGURES

1. Apparatus for Thin Sectioning	8
2. Activity-Penetration of Carbon Diffusion in UC 4.9 wt % C	10
3. Self-Diffusion of Carbon in UC	10
4. Unbonded Pair of Specimens.	12
5. Specimen Surface Before and After Treatment.	13
6. Concentration-Penetration of Uranium in UC 4.9 wt % C	14
7. Concentration-Penetration of Uranium in UC 4.6 wt % C	14
8. Arrhenius Plot of Uranium Diffusion in UC.	16

ABSTRACT

Diffusion coefficients of carbon and uranium in uranium carbide 4.4 to 4.9 wt % C were measured by tracer and sectioning techniques on specimens annealed at 1100 to 2000°C. Carbon diffusion was faster than uranium diffusion by two or three orders of magnitude. There was a small dependence on composition; higher carbon caused some increase in carbon diffusion and a decrease in uranium diffusion. The specimens varied in grain size but no significant differences were found between the coarse-grained and fine-grained specimens. Breaks occurred in the Arrhenius curves at about 1500°C; the lower activation energies below 1500°C were attributed to short-circuiting by grain boundary or sub-grain boundary transport in the low-temperature region. Five studies of self-diffusion in UC are reviewed and compared with the present results.

I. INTRODUCTION

The use of uranium carbide (UC) as a nuclear fuel has stimulated interest in its atomic transport properties. Several studies of self-diffusion in UC have been made. Measurements of self-diffusion using radio-tracer techniques have been reported by Chubb et al.,¹ Lee and Barrett,² Lindner et al.³ and by Villaine and Marin.⁴ None of these studies has been a complete study of both uranium and carbon diffusion over a range of C/U ratios. A survey of the results reveals areas of qualitative agreement and of disagreement in the experimental data and in the interpretation of the data. The present study deals with both carbon and uranium self-diffusion in high-purity specimens. The material was of varying stoichiometry and grain size, and a wide range of temperature was covered.

The study used radio-tracers, applied as a thin film, followed by vacuum annealing and sectioning to depths of a few mils. Both carbon and uranium diffusion specimens of one composition came from a common rod. This work represents a comprehensive study of self-diffusion in UC, and suggestions are offered to resolve some of the experimental disagreements.

II. MATERIAL

Material for testing was either arc-melted and cast UC or was prepared from UC by induction-zone melting. The cast material contained 500 to 700 ppm non-metallic impurities (oxygen, nitrogen, and hydrogen) and about 1000 ppm total metallic impurities while the zone melted material contained 200 to 300 ppm non-metallic and 500 to 800 ppm metallic impurities. Rods of the zone-melted material were either 3/8 or 1/2 in. in diameter and were 4 to 6 in. in length. Across most of the diameter, the rods contained one or two "single crystals," with a periphery of fine-grained material. The grains, although termed "single crystals," contained subboundaries; non-stoichiometric material also contained a second phase of either uranium metal or UC_2 depending on the composition. The approximate carbon content of the cast rod was retained in the induction-zone melted material. The composition was determined by chemical and metallographic analysis.

III. PROCEDURES AND RESULTS

Rods of depleted uranium carbide (0.22% enriched) 3/8 to 1/2 in. diameter and several inches long were cut into 0.040 in. thick specimen discs by electrical discharge machining. Metallographic examination was made of specimens taken every 1/2 in. along the rod. Uniform composition which corresponded to the chemical analysis was usually found. The specimen discs were mounted on the grinding device with thermally sensitive cement, Figure 1, and ground parallel. They were then demounted for annealing.

A. CARBON DIFFUSION

A slurry of ^{14}C powder (specific activity 4 mc/gm) in butyl-alcohol was painted on one face of the specimen. The ^{14}C particles adhered to the specimen surface, permitting handling of the specimen. The uniformity of the coating was investigated with a microscope. Uniform activity was observed on small surface areas checked after annealing. The anneals were performed in molybdenum containers on pairs of specimens with the active faces together. The diffusion anneals were in the temperature range 1100 to 2000°C for time intervals of 2 min to 2 weeks. A diffusion pumped environment (10^{-5} to 10^{-6} mm Hg) was used for annealing above 1500°C. Below 1500°C, ion pumped environments (10^{-8} to 10^{-9} mm Hg) were used, with controlled electron beam heating. Because of the much longer exposure time at low temperatures, the better vacuum is necessary for the lower temperature anneals in order to avoid oxygen contamination. All temperatures were measured with thermocouples in near contact (1/8 in.) from the specimens. About 0.020 in. was removed from the periphery of each specimen disc before it was sectioned.

Ten to 15 sections 0.0005 in. thick were removed from the active surface of each specimen for analysis. A gas flow proportional counter was used; this counter enables separate determination of alpha and beta activity in the same specimen. The alpha and beta activity of the material removed with each section was determined. The alpha activity, which was uniform throughout the specimen, was assumed to be proportional to the amount of material removed; this was verified by determining the activity of various weighed amounts of UC. The self-shielding which could occur from relatively thick sections of UC, did

4-20-67

7707-2518A

Figure 1. Apparatus for Thin Sectioning

AI-AEC-12726

not occur for sections 0.0005 in. thick when they were evenly spread over the 1 in. diameter grinding pad shown in Figure 1. After the alpha activity was determined, the ^{14}C beta activity was measured. The alpha activity was then used to normalize the ^{14}C activity and to obtain the specific beta activity of each section.

The data were analyzed by the thin film solution which is derived from Fick's second law for diffusion. The solution is ⁽⁵⁾:

$$D = \frac{-0.1086 (6.45) (x_2^2 - x_1^2)}{(\log A_2 - \log A_1) t}$$

where

D = diffusion coefficient (cm^2/sec)

x_2, x_1 = penetration depth (in.)

A_2, A_1 = activity at depths x_1 and x_2 , respectively (cpm)

t = time for diffusion (sec)

From the equation, plots of log activity vs depth squared should give straight lines with slopes inversely proportional to the product Dt .

Typical activity-penetration curves are shown in Figure 2 for UC 4.9 wt % C. The Arrhenius plot for all the carbon data is shown in Figure 3. Least squares fitting of the data was used. A summary of the carbon results is given in Table 1. The data for 4.9 wt % C material agree with data by Chubb et al⁽¹⁾ for 5.0 wt % C material. For the other compositions, the diffusion coefficients are lower — below 1900°C — and there is a change in slope at about 1500°C.

B. URANIUM DIFFUSION

The specimens of the same composition for C and U diffusion came from a common rod. U^{235} tracer was vapor-deposited from a tungsten basket containing metallic U^{235} ($\text{U}^{235} > 97\%$) on specimen discs of depleted UC. The diffusion anneals were in the temperature range 1250 to 2050°C for time intervals of 4 minutes to 3 weeks. Annealing environments and sectioning procedures similar to those for carbon diffusion were used. However, the analytical method used for measuring the activity of the sections in the case of uranium diffusion

7-7707-121-4

Figure 2. Activity-Penetration of Carbon Diffusion in UC 4.9 wt % C

Figure 3. Self-Diffusion of Carbon in UC

7-7707-121-3A

TABLE 1
SUMMARY OF DIFFUSION DATA FOR CARBON IN UC

Composi- tion (wt % C)	Type *	Temperature† Range (°C)	Range of D Values (cm ² /sec)	Activation Energy (kcal/mole)
4.6	ZM	1500 - 1900	2×10^{-9} to 2×10^{-7}	94 ± 6
4.7	ZM	1600 - 1900	3×10^{-9} to 2×10^{-7}	92 ± 6
4.8	ZM	1500 - 1900	2×10^{-9} to 2×10^{-7}	84 ± 6
4.6	ZM	1150 - 1500	3×10^{-11} to 2×10^{-9}	53 ± 6
4.7	ZM	1150 - 1600	2×10^{-11} to 3×10^{-9}	54 ± 4
4.8	ZM	1150 - 1500	5×10^{-11} to 2×10^{-9}	51 ± 4
4.9	ZM	1100 - 1900	5×10^{-11} to 5×10^{-7}	60 ± 5

*ZM indicates zone-melted and very coarse-grained material.

†Based on least squares fitting of the data.

differed from that used for carbon diffusion. The method used for uranium diffusion was based on the alpha activity of the specimen surface and was measured in the gas flow proportional counter.

The problem of uranium loss from the specimen surface was considered since long annealing times were necessary and penetration depths were very small. A cross section of an unbonded pair of specimens, Figure 4, shows that the uranium-rich specimen 4.7 wt % C, suffers uranium depletion to about 0.001 in. but that the carbon-rich 4.9 wt % C specimen shows no significant uranium loss for a typical annealing treatment (12 hr at 1600°C). UC 4.8 wt % C also showed no apparent loss of uranium from the surface under similar treatment. A specimen at 4.6 wt % C was placed in a UC container of the same composition, and heated 12 hours at 1600°C. After treatment, the surface still showed uranium loss (Figure 5). Pressure bonding was tried; it eliminated composition variation near the surface, but it introduced cracks into the thin specimens. For the actual diffusion anneals the UC 4.8 and 4.9 wt % C were heated in molybdenum containers with the active faces together. The annealing procedure used for the 4.4 and 4.6 wt % C specimens was to place the coated surfaces of specimens of similar composition tightly together in a closed container of UC

7-7707-121-6A

Figure 4. Unbonded Pair of Specimens

containing a slight excess of uranium metal. Some loss of uranium still occurred from specimen surfaces; however, the compositions remained close to the analyzed values.

Typical concentration-penetration curves for uranium in UC 4.9 wt % C and UC 4.6 wt % C are shown in Figures 6 and 7, respectively. A total penetration of only 0.001 to 0.002 in. was used for most of the concentration-penetration curves. Prohibitively long annealing times would be required to obtain penetration of the order obtained for carbon diffusion. Each of the ten to fifteen sections removed was measured to extremely close tolerance with the sectioning apparatus. The device could be read to 0.0001 in. and estimated to 0.00002 inch. The difference between the actual reading and machining results was minimized by using a thin layer of Moly Coat, rather than oil, between the mating parts of the apparatus. The grinding apparatus was handled with gloves to minimize transfer of body heat and thermal expansion.

The very low range of alpha activity in UC makes it possible to measure the activity directly from the specimen surface. The diffusion coefficients were calculated by means of the equation given earlier (p. 9) for carbon. Arrhenius plots

7-7707-121-7A

a. Before Treatment

b. After Heating 12 hr in
Protective Environment

c. After Removing 0.001-in.
from Treated Surface

Figure 5. Specimen Surface Before and After Treatment

Figure 6. Concentration-Penetration of Uranium in UC 4.9 wt % C

Figure 7. Concentration-Penetration of Uranium in UC 4.6 wt % C

for all the uranium data are shown in Figure 8. The curves show a break at about 1700°C for all compositions except UC 4.9 wt % C. There is little difference between the diffusion coefficients for the cast material (grain size about 50 microns) and the induction zone refined material (grain size about 200 to 500 microns). The UC 4.4 and 4.6 wt % C show the highest diffusion coefficients. The data are summarized in Table 2.

TABLE 2
SUMMARY OF DIFFUSION DATA FOR URANIUM IN UC

Composition (wt % C)	Type *	Temperature [†] Range (°C)	Range of D Values [†] (cm ² /sec)	Activation Energy (kcal/mole)
4.4	ZM	1700 - 2050	1×10^{-10} to 1×10^{-8}	125 ± 15
4.6	ZM	1700 - 2050	1×10^{-10} to 1×10^{-8}	125 ± 15
4.8	ZM	1750 - 2050	2×10^{-11} to 1×10^{-9}	125 ± 15
4.4	ZM	1350 - 1700	2×10^{-11} to 1×10^{-10}	32 ± 2
4.6	ZM	1150 - 1750	2×10^{-11} to 1×10^{-10}	32 ± 2
4.8	[ZM Cast	1150 - 1750	1×10^{-12} to 2×10^{-11}	32 ± 2
4.9	[ZM Cast	1400 - 2050	1×10^{-12} to 1×10^{-9}	70 ± 5

*ZM indicates zone-melted, very coarse-grained material. Cast is arc cast, fine-grained material.

[†]Based on least squares fitting of Arrhenius plots of the data.

C. DISCUSSION

Although several studies have been made on diffusion in UC, the mechanisms of diffusion are not yet properly understood. Table 3 compares most of the experimental findings reported in the literature with the present results. There are some significant points of agreement among the various studies. The first is that carbon diffusion is much more rapid than uranium diffusion. Processes which depend on the transport of the faster moving species (the growth of a carbide layer⁽⁶⁾ and the oxidation of UC⁽⁷⁾) have, in fact, been shown to depend on the rate of diffusion of carbon. Also, the values given by Chubb⁽¹⁾ for carbon diffusion in a 5.0 wt % C composition and by Lee for a 5.0 and 5.1 wt % C

7-17-68 UNCL

7707-4704

Figure 8. Arrhenius Plot of Uranium Diffusion in UC

AI-AEC-12726

TABLE 3
COMPARISON OF VARIOUS RESULTS REPORTED IN THE LITERATURE

	Chubb ⁽¹⁾	Lee ⁽²⁾	Lindner ⁽³⁾	Villaine ⁽⁴⁾	This Work
<u>CARBON</u>					
D (cm ² /sec) 4.8 to 5.1% C, 1600°C	3 x 10 ⁻⁸	1 to x 10 ⁻⁸	-	-	1 to 3 x 10 ⁻⁸
Activation Energy (kcal/mole)	50	63	-	-	51 to 94
Grain Boundary Effect	No	Yes?	-	-	No
Variation of D With % C	-	Increases sharply	-	-	Increases irregularly
<u>URANIUM</u>					
D (cm ² /sec) 4.8 to 5.0% C, 1600°C	5 x 10 ⁻¹¹	10 ⁻¹¹	10 ⁻¹⁴	3 x 10 ⁻¹⁴	1 to 5 x 10 ⁻¹¹
Activation Energy Above 1500°C	65	104	70 to 90	80	70 to 90
Activation Energy Below 1500°C (kcal/mole)	-	-	28 to 33	-	32
Grain Boundary Effect	-	No?	Yes	Pronounced	?
Method	Sectioning	Sectioning	α -energy degradation	α -energy degradation	Sectioning
Depth Observed (μ)	100	10 to 80	0 to 5	1 to 10	2 to 30
Variation of D With % C	-	-	Decreases	Decreases	Decreases

agree well at all temperatures with the present data for 4.9 wt % C. Lee's data agree with ours for the 4.8 wt % C composition, but for the 4.7 wt % C composition, Lee's data are lower than ours by about an order of magnitude. Thus Lee's data show a consistent increase in both activation energy and diffusion coefficient as the carbon content is decreased, which our data do not show.

The data of various investigators for uranium diffusion show the same trend for activation energy; above about 1500°C there is an increase in the slope of the Arrhenius curve with activation energies ranging from about 65 to 105 kcal/mole. The investigations that have included lower temperatures show that there is a break in the curve and that much lower activation energies, about 30 kcal/mole, are found below 1500°C. Lindner⁽³⁾ attributes the break in the curve to grain boundary or sub-grain boundary diffusion at lower temperatures. At lower temperatures the material which moves rapidly along these channels is a significant fraction of the total amount of diffusing material; at higher temperatures volume diffusion predominates. The change in slope of the Arrhenius curves results in the carbon and uranium diffusion rates moving closer together at low temperatures. Direct experimental evidence for preferred diffusion along grain boundaries is furnished by the autoradiographic results of Villaine et al and of Lindner et al.

Among the studies tabulated in Table 3, serious disagreement is evident for the uranium diffusion coefficient. Two studies used an alpha-energy degradation method while the others, including the present study, used sectioning to determine concentration-penetration curves. The first method has given diffusion coefficients which are three orders of magnitude lower than those given by the sectioning method. The main difference between the methods is the depth of penetration. The alpha-energy degradation method used typical depths of about 5 microns, whereas the sectioning method used depths of 30 to 40 microns. There may be a different diffusion coefficient in the near surface layer, as indicated qualitatively by the concentration-penetration curve for 1800°C (Figure 7); the slope of the part of the curve for the first five microns is steeper than the slope of that portion based on activity deeper in the specimen. The steeper slope would result in a much lower diffusion coefficient than the one calculated from the curve for the activity deeper in the specimen.

It has been established for some metals^(8, 9, 10, 11) that there is a difference in transport behavior in a thin surface layer as compared with the bulk. The difference in diffusion coefficients with depth in metals is similar in magnitude to that found for uranium carbide. For metals, it has been attributed to differences in lattice perfection with depth and to inaccurate analysis of diffusion data, but a truly satisfactory explanation has not been found.⁽¹¹⁾

Storms⁽¹²⁾ has shown sharp increases in carbon activity and decreases in uranium activity as carbon/metal ratios increased through 1.0. While there is a tendency for carbon diffusion to increase and for uranium diffusion to decrease with increase in carbon content, the data are incomplete and inconsistent. The data of Lee and Barrett for carbon show a smooth increase paralleling the activity change calculated by Storms, but the present work shows only a slight change at the higher temperatures considered by Storms (above 1800°C). From the viewpoint of solid state defects, an increase in carbon diffusion rate with increase in carbon content would suggest that carbon transport occurs by the movement of interstitial carbon as opposed to movement of carbon vacancies. This seems to be a reasonable mechanism. On the other hand, similar reasoning applied to the uranium diffusion data suggests transport by uranium interstitials and this is not a reasonable mechanism in view of the larger size of the uranium atom.

IV. CONCLUSIONS

Conclusions from the study are listed below.

- 1) Self-diffusion of carbon in UC is about a thousand times greater than that of uranium as measured by tracer methods.
- 2) There are breaks in the Arrhenius curves such that activation energies for diffusion of carbon are 90 kcal/mole above 1500°C and 50 kcal/mole below 1500°C while, for uranium diffusion, the break comes at about 1700°C with 125 kcal/mole for the high-temperature branch and 32 kcal/mole for the low-temperature branch. However, these breaks were found only for the stoichiometric and hypostoichiometric samples and the hypostoichiometric samples showed a single intermediate activation energy.
- 3) Only a slight dependence on carbon stoichiometry was found, consisting of an increase for the carbon diffusion and a decrease for the uranium diffusion, with increase in carbon content.
- 4) No differences were found between the diffusion rates in zone-refined material, with predominately low-angle sub-grain boundaries, and the rates in fine-grained samples. Breaks in the Arrhenius curves were attributed to rapid channel diffusion along grain boundaries and to sub-grain boundaries in the low-temperature region.
- 5) Comparison of results of studies in different laboratories shows agreement on some items but large differences in the uranium diffusion data. It is suggested that the very low values found by techniques which examine a very thin surface layer may be explained by a real difference in diffusion in a surface layer as compared with the bulk.

REFERENCES

1. W. Chubb, C. W. Townley, and R. W. Getz, "Diffusion in Uranium Monocarbide," *J. Nuclear Materials* 13, 63 (1964)
2. H. M. Lee and L. R. Barrett, "Measurements of Self-Diffusion in Uranium Carbide and Their Application to Related Activated Processes," *Proc. Brit. Ceram. Soc.* 7, 159 (1967)
3. R. Lindner, G. Riemer and H. L. Scherff, "Self-Diffusion of Uranium in UC," *J. Nucl. Mat.* 23, 222 (1967)
4. P. Villaine and J. F. Marin, "Autoradiographic Evidence for Intergranular Diffusion of U in UC," *Compt. rend.* 262C, 1660 (1966), P. Villaine and J. F. Marin, "Self-Diffusion Coefficient of Uranium in Uranium Monocarbide," *Compt. rend.* 264C, 2015 (1967)
5. P. G. Shewmon, *Diffusion In Solids*, McGraw Hill Co., New York 1963
6. S. Takeuchi, T. Honma, and T. Satow, "Studies on the Reaction of Uranium with Graphite at High Temperatures," *Trans. Japan Inst. Metals* 5, 111-15 (1964)
7. G. Ervin, Jr., "Oxidation of Uranium Monocarbide at High Temperatures and Low Pressures," Third International Symposium on High Temperature Technology at Asilomar, September 1967
8. C. P. Williams, Jr. and L. Slifkin, "Tracer Insolubility and the Anomalous Diffusion of Rare Earths in Silver and Lead," *Acta Met.* 11, 319 (1963)
9. R. E. Paul and T. S. Lundy, "A Submicron Sectioning Technique for Analyzing Diffusion Specimens of Tantalum and Niobium," *J. Appl. Phys.* 35, 435 (1964)
10. K. Hirano, M. Cohen and B. L. Averbach, "Diffusion of Iron, Cobalt and Nickel in Silver," *Acta Met.* 11, 463 (1963)
11. W. Bierman, F. R. Winslow, and T. S. Lundy, "Comment on Diffusion of Iron, Cobalt and Nickel in Silver," *Acta Met.* 12, 328 (1964)
12. E. K. Storms, *The Refractory Carbides*, Academic Press, New York 1967.