MASTER

REPORT NO. SEP-252

TR. 59-1916

SEP-252

THE SELF-DIFFUSION OF NIOBIUM - III

R. RESNICK

L. S. CASTLEMAN

L. SEIGLE

FINAL PROGRESS REPORT
JULY 1, 1958 TO JANUARY 1, 1959

SYLVANIA RESEARCH LABORATORIES
A DIVISION OF SYLVANIA ELECTRIC PRODUCTS INC.
BAYSIDE, NEW YORK

971 001

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.

Report No. SEP-252
Project No. 1916
Metallurgy and Ceramics
(Category UC-25)

THE SELF DIFFUSION OF NIOBIUM - III

R. Resnick

L. S. Castleman

L. Seigle

Final Progress Report

July 1, 1958 to January 1, 1959

Contract AT(30-1) 2102
AEC Division of Research

Issued: March 30, 1959

Sylvania Research Laboratories

A Division Of

SYLVANIA ELECTRIC PRODUCTS INC.

Bayside, New York

*Do not
Photocopy*

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 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 to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

Don't
Chad

Report No. SEP-252

PRELIMINARY DISTRIBUTION

(This report will be given standard distribution on Metallurgy and Ceramics, Category UC-25, by TIS, Oak Ridge.)

Number of Copies

Battelle Memorial Institute	1
Battelle Memorial Institute (Mr. E.M. Sherwood) . . .	1
(Defense Metals Information Center)	
Bettis Plant (WAPD)	1
Knolls Atomic Power Laboratory	1
Raytheon Mfg. Co. (Research Division) (E. H. Weeks). .	1
Sylvania Corning Nuclear Corp.	2
Sylvania Electric Products Inc.	5
University of Illinois (R. W. Balluffi)	1
U.S. AEC, Brookhaven, N.Y. Patent Group	1
(Mr. C. Meyerson)	
U.S. AEC, NYOO (Mr. I. Zazik)	1
U.S. AEC, Washington, Division of Reactor Development	1
U.S. AEC, Washington, Division of Research	3

Handwritten signature and initials, possibly "J. D. 3/24", with a large "X" over it.

TABLE OF CONTENTS

	<u>Page Number</u>
ABSTRACT	5
INTRODUCTION	6
EXPERIMENTAL TECHNIQUES	6
RESULTS	8
DISCUSSION	8
REFERENCES	9
TABLES	10 & 11
LIST OF PREVIOUS REPORTS	12

ABSTRACT

The self-diffusion coefficient of niobium has been measured over the temperature range 1535°C-2120°C, using the radioactive isotope Nb⁹⁵ as the tracer. The data for the temperature dependence of the self-diffusion coefficient are best fitted by the equation

$$D = (12.4 \pm 0.2) \exp \left[\frac{(-105,000 \pm 3000)}{RT} \right] \text{ cm}^2/\text{sec.}$$

Introduction

The increasing need for high temperature structural materials has stimulated considerable interest in the properties of niobium since it is a strong, ductile metal with a high melting point -- in the vicinity of 2450°C .⁽¹⁾ One fundamental property which has not heretofore been measured is the self-diffusion coefficient of niobium, which as is well known, is a measure of the rate with which ions migrate in the niobium lattice. The self-diffusion coefficient plays an important role in theories of oxidation,⁽²⁾ creep,⁽³⁾ sintering,⁽⁴⁾ and other phenomena. Accordingly, the investigation reported in this paper was undertaken to determine the value of the self-diffusion coefficient of niobium and its temperature dependence.

Experimental Techniques

The experimental techniques used in determining the self-diffusion coefficient of niobium were conventional⁽⁵⁾ except for the preparation of the diffusion couples. At the beginning of the program, it was anticipated that difficulties would arise in specimen preparation for the following reasons: (a) the high melting temperature and chemical reactivity of niobium would complicate the preparation of the radioactive isotope in metallic form by pyrometallurgical techniques; and (b) the radioactive isotope cannot be deposited as a metallic layer by being plated onto niobium from an aqueous solution. Consequently, a rather cumbersome but workable procedure was developed for depositing the isotope by means of vapor deposition. This process yielded the thin film type of diffusion couple used by Johnson⁽⁶⁾, Mead and Birchenall⁽⁷⁾, and others.

Niobium may be vapor-plated by hydrogen decomposition of niobium pentachloride vapor at elevated temperatures⁽⁸⁾. Therefore, the first stage of the experimental procedure was developed to convert the isotope from the oxalic acid solution into NbCl_5 , according to the following scheme:

1. Approximately 0.1 millicuries of isotope is diluted with non-radioactive carrier, which must also be in the form of an oxalic acid solution to assure complete chemical mixing. The carrier is necessary since the specific activity of Nb^{95} is very high. It is prepared by dissolving two grams of niobium metal in a mixture of nitric and hydrofluoric acids. After the solution is diluted with water, ammonium hydroxide is slowly added until a flocculent precipitate of niobium hydroxide forms. This is quickly separated from the liquid by centrifuging, and re-dissolved in a warm solution of oxalic acid.

2.

2. The solution is evaporated to dryness, and the residue ignited for conversion to Nb_2O_5 .

3. The Nb_2O_5 is reduced to metal by calcium reduction at 930°C in a vitrified clay crucible under an inert gas atmosphere.

4. Since iron contamination is picked up from the crucible, it is now necessary to separate the niobium metal from the other reduction products. This is accomplished by immersion of the reduction cake in dilute hydrochloric acid. The undissolved residue is primarily niobium metal and unreduced Nb_2O_5 .

5. The niobium metal is chlorinated by heating to 200°C under a chlorine gas atmosphere. The NbCl_5 which forms is volatile at this temperature, and therefore distills into a collecting flask sealed to the cool end of the reaction chamber. Yields of up to 90% have been obtained by this method.

6. The radioactive chloride is next sealed into the vapor-plating apparatus which is schematically illustrated in Figure 1. The NbCl_5 is volatilized by being heated to approximately 120°C , and the vapor carried by a flow of hydrogen over the discs of non-radioactive metal which are inductively heated to about 900°C . The flow rate of hydrogen is approximately 2cc/sec, and the pressure between 18 and 30mm. hg. On contacting the hot metal surface, the chloride decomposes, and an adherent metallic layer is formed. On the average, these layers were found to be about 0.0005 inch thick.

The diffusion couples were annealed in pairs with the radioactive faces in apposition, and separated by short lengths of 0.010 inch tungsten wire. This arrangement decreased the possibility of introducing error by the loss of radioactive material through evaporation. All the diffusion anneals were conducted in a high temperature, high vacuum furnace built by the R.D.Brew Company. The heating elements of the furnace consisted of two tantalum sheets bent and welded to form a 3 x 5 inch hot region, which, with a power consumption of 20 KVA, reached a maximum temperature of 2120°C . A vacuum of approximately 1×10^{-5} mm. Hg was maintained throughout the runs, since niobium is a highly reactive metal. Temperatures were measured with an optical pyrometer, and are believed to be accurate to $\pm 10^\circ\text{C}$. Readings were taken with several instruments for comparison purposes and were corrected for intensity losses occurring in the sight glass.

After the annealing treatment, 7 to 10 slices roughly 0.001 inch thick were machined from the surface of each diffusion couple. The machined turnings were weighed, and their radioactivity measured by means of a gamma scintillation counter.

Results

The diffusion coefficients were computed from a standard, linear plot of $\ln A$ vs. x^2 where A is the activity per unit weight of material, and x is the penetration. Fig. 2 shows such a plot for a typical specimen annealed for 93 hours at 1775°C. The computed values of D are given in Table I.

The temperature dependence of D was found to be best fitted by the usual relation: $D = D_0 \exp (-Q/RT)$ where the D_0 is equal to $12.4 \pm 0.2 \text{ cm}^2/\text{sec}$, and Q is equal to $105,000 \pm 3000 \text{ cal/mol}$. R is the gas constant, and T is the diffusion temperature in °K. The constants were computed from a least squares analysis which assumes an error in measurement of both the diffusion constant and the temperature;⁽⁹⁾ and the error given for the activation energy and D_0 represents a two sigma variation which was obtained by approximating the actual estimation technique with a maximum likelihood estimator⁽¹⁰⁾. Figure 3 is a semi-logarithmic plot of D vs. $1/T$; the solid line represents the least squares fit.

Discussion

It is interesting to compare these data to what might have been expected on the basis of various theories of diffusion. Nachtrieb and Handler⁽¹¹⁾ developed a linear relationship between activation energy and heat of fusion, $Q = 16.5 \Delta H_f$, which seems to apply to many face-centered and body-centered cubic metals. If we use the estimated value of 6,400 cal/mol for the heat of fusion of Nb⁽¹²⁾, the activation energy for diffusion, Q , is calculated to be 105,600 cal/mol which agrees with the present data.

Other commonly employed approximations relate the activation energy to either the melting point in degrees Kelvin, or to the heat of sublimation. These relations, proposed by Johnson⁽⁶⁾, and compared against additional data by LeClaire⁽¹³⁾ give the following average values: $Q/T_m = 38$, and $Q/\Delta H_s = 0.64$.

Table II compares the experimental values of the activation energy against the values calculated from the approximations. The experimentally determined activation energies for self-diffusion in tantalum⁽¹⁴⁾ and tungsten⁽¹⁵⁾ are included in the table, since both tantalum and tungsten, like niobium, are refractory metals.

The observed values of the activation energies for all three fall generally lower than the calculated values; however, the values calculated on the basis of melting temperature and heat of fusion are within the range of experimental error for niobium and tungsten. It therefore appears that the above approximations which were derived for relatively low melting metals also apply to the refractory metals.

REFERENCES

1. T. H. Schofield, J. Inst. Metals, 85, Part 8, 372, (1956-57)
2. C. Wagner, Atom Movements, A.S.M., (1950)
3. C. Herring, J. Applied Physics, 21, May, 1950, p.437
4. G. C. Kuczinski, Trans. A.I.M.E., 185, 169, (1949)
5. R. E. Hoffman, Atom Movements, A.S.M., (1950)
6. W. A. Johnson, Trans. A.I.M.E., 143, 107, (1941)
7. H. W. Mead and C. E. Birchenall, Trans. A.I.M.E., 9, No.7, 874, (1957)
8. C. F. Powell, I. E. Campbell, and B. W. Gonser, Vapor-Plating: The Formation of Coatings by Vapor Deposition Techniques, Wiley, (1955)
9. J. F. Kenney, Mathematics of Statistics, Part I - D. Van Nostrand Co. (1947)
10. J. F. Kenney, and E. S. Keeping, Mathematics of Statistics, Part II - D. Van Nostrand Co. (1951)
11. N. H. Nachtrieb and G. S. Handler, Acta Met; 2, 6, 797, (1954)
12. Thermodynamic Properties of the Elements, Published by the American Chemical Society, 1155-16th Street, N.W., Washington 6, D.C., (1956)
13. A. D. McClaire, Progress in Metal Physics I, edited by B. Chalmers, Interscience Publishers Inc., New York, N.Y. (1949)
14. R. L. Eager and D. B. Langmuir, Phys. Rev., 89, 911, (1953)
15. V. P. Vasil'ev and S. G. Chernomorchenko, Zavodskaya Lab., 22, 688, (1956) C. A. 50, 16249c.

TABLE I

Diffusion Coefficients for Self-Diffusion in Nb

<u>Diffusion Temp.</u> <u>°C</u>	<u>Diffusion Time</u> <u>Hours</u>	<u>D. cm²/sec.</u>
1585	135.5	7.55×10^{-12}
1585	135.5	7.05×10^{-12}
1640	144	8.70×10^{-12}
1640	144	1.26×10^{-11}
1660	170	1.10×10^{-11}
1660	170	1.10×10^{-11}
1700	309.3	2.16×10^{-11}
1700	309.3	1.43×10^{-11}
1775	92.8	8.73×10^{-11}
1775	92.8	1.11×10^{-10}
1800	7.5	1.90×10^{-10}
1800	8.0	1.16×10^{-10}
1800	8.0	1.28×10^{-10}
1910	28.0	2.80×10^{-10}
1910	28.0	4.76×10^{-10}
1925	17.8	2.03×10^{-10}
1925	17.8	2.37×10^{-10}
1980	1.9	1.14×10^{-9}
1980	1.9	8.96×10^{-10}
2000	1.0	1.30×10^{-9}
2000	1.0	1.30×10^{-9}
2070	2.0	9.79×10^{-10}
2070	2.0	1.10×10^{-9}
2100	2.1	1.29×10^{-9}
2100	2.1	1.66×10^{-9}
2120	1.0	2.76×10^{-9}
2120	1.0	2.76×10^{-9}

TABLE II

<u>Metal</u>	Q obs.	T _m °K	ΔH fusion cal/mol	ΔH sublimation cal/mol	Q = 16.5ΔH _f cal/mol	Q = 38 T _m cal/mol	Q = 0.64ΔH _s cal/mol
Niobium	105,000±3000	2740(1)	6,400 ⁽¹²⁾	177,500 ⁽¹²⁾	105,600	104,120	113,600
Tantalum	110,000 ⁽¹⁴⁾	3270 ⁽¹²⁾	7,500 ⁽¹²⁾	186,800 ⁽¹²⁾	123,750	124,260	119,500
Tungsten	135,800 ⁽¹⁵⁾	3650 ⁽¹²⁾	8,420 ⁽¹²⁾	200,000 ⁽¹²⁾	138,930	138,700	128,000

LIST OF PREVIOUS REPORTS

1. The Self-Diffusion of Niobium - I, R. Resnick, L. S. Castleman and L. Seigle, First Annual Progress Report, January 1, 1956 to June 30, 1957, SEP-244.
2. The Self-Diffusion of Niobium - II, R. Resnick, L. S. Castleman and L. Seigle, Second Annual Progress Report, July 1, 1957 to June 30, 1957, SEP-248.

FIG.1 SCHEMATIC DIAGRAM OF VAPOR PLATING APPARATUS.

FIG. 2 DIFFUSION CURVE FOR SPECIMEN ANNEALED
AT 1775°C FOR 93 HOURS.

FIG.3 $\ln D$ VS. $\frac{1}{K}$ FOR SELF-DIFFUSION OF Nb.