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THE SELF-DIFFUSION OF NIOBIUM—II

Second Annual Progress Report, July 1, 1957 to June 30, 1958

By
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L. S. Castleman
L. Seigle

June 30, 1958

Metallurgical Research Laboratory
Sylvania Electric Products Inc.
Bayside, New York

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ABSTRACT

The self-diffusion coefficient of niobium is being measured as a function of temperature. Procedures have been developed for the preparation of $NbCl_5$ from a solution of radioactive Nb^{95} in oxalic acid, and the subsequent vapor plating of a radioactive metallic layer from this volatile compound. Initial measurements made at 2000°C and 1800°C yield values for the self-diffusion coefficient of 3.2×10^{-9} cm^2/sec and 1.7×10^{-10} cm^2/sec respectively.

I. INTRODUCTION

The rate of self-diffusion of a metal influences many of its important properties, such as creep and sintering rates, ease of homogenization of alloys, and the bondability of clads. In order to provide this much-needed information, the self-diffusion rate of niobium is being measured as a function of temperature. The preliminary considerations and experimentation required to establish the most suitable technique for making these measurements were treated in detail in the first annual report(1). The technique adopted is a standard one wherein a layer of radioactive isotope, in this case Nb^{95}, is deposited onto the surface of a disc of non-radioactive metal and diffused inwards by a high temperature annealing treatment. After diffusion, layers are machined perpendicular to the diffusion direction, and analyzed for the concentration of isotope by means of a gamma scintillation counter. The diffusion coefficient can be calculated from this information in a manner to be described later.

II. METHOD

There are essentially four stages to the experimental procedure:

A. Preparation of niobium pentachloride from a Nb^{95} complex starting material;

B. Vapor plating of the isotope onto the diffusion specimen from gaseous niobium pentachloride;

C. Annealing of the diffusion couple; and

D. Analysis for the diffusion coefficient.

These will be discussed under separate headings.

A. Preparation of $Nb^{95}Cl_5$

A procedure for preparing $Nb^{95}Cl_5$ was described in the first annual report. However, several important changes in the process have since been made in order to increase its efficiency and reproducibility. A detailed description follows:

1. The solution of radioactive oxalate containing 0.1 millicuries of isotope is diluted with non-radioactive carrier. The carrier must also be in the form of an oxalate solution to assure complete chemical mixing. This is prepared by dissolving two grams of niobium metal in a mixture of nitric and hydrofluoric acids. After dilution with water, ammonium hydroxide is slowly added until a flocculent precipitate of niobium hydroxide forms. This is rapidly separated from the mother liquor by centrifuging, and re-dissolved in a warm solution of oxalic acid.

2. The solution is evaporated to dryness and ignited in order to convert to Nb_2O_5.

3. The oxide is reduced to metal by calcium reduction at 930°C in a vitrified clay crucible.

4. Since iron contamination is picked up from the crucible, it is necessary to separate the niobium metal from the other reduction product. This is accomplished by immersing the reduction cake in a dilute solution of hydrochloric acid. The undissolved residue is primarily niobium metal and unreduced niobium oxide.

5. The niobium metal is chlorinated by heating to 200°C under a chlorine atmosphere. The $Nb^{95}Cl_5$ which forms is volatile and therefore distills into a collecting flask sealed to the cool end of the reaction chamber. Yields of approximately 90% have been obtained by this method.

B. Vapor Plating

This procedure was also described in some detail in the initial report(1). Briefly, the $Nb^{95}Cl_5$ is volatilized and the vapor carried in hydrogen over discs of non-radioactive niobium, which are inductively heated to approximately 900°C. The pentachloride decomposes to form a radioactive metallic coating. As of the last report, the major fault yet to be eliminated was the tendency for air leaks to develop in the system. The problem was solved by removing several stopcocks which were inconveniently positioned too near the reaction chamber, and consequently overheated during operation. The only other major change has been to re-design the flask which contains the $Nb^{95}Cl_5$. Originally, the flask was cracked open with a magnetic hammer and heated to 150°C. The pentachloride distilled into glass coils immersed in an oil bath maintained at 100°C. The purpose of the coils was to maintain a constant partial pressure of $Nb^{95}Cl_5$ in the system throughout the run. Subsequently, this was found to be unnecessary, and the coils (which were difficult to decontaminate after each run) were eliminated. In the current set-up, $Nb^{95}Cl_5$ is vaporized directly from the containing flask into the reaction vessel where it is decomposed by reaction with hydrogen to form the thin coating of radioactive metal on the hot specimen surface. Fig. 1 is a schematic representation of the apparatus.

The following operating conditions have been established for efficient plating:

1. Hydrogen pressure equals 18 mm Hg.
2. Flow rate equals 2 cc/sec.
3. Temperature of specimens being plated is approximately 900°C.
4. Temperature of $Nb^{95}Cl_5$ equals 160°C.

The average plate thickness obtained in this manner is 0.0005", but may vary considerably among specimens. Since the only requirement for this program is that the plated layer be completely adherent, and less than 0.002", no serious attempt has been made to refine the procedure to the extent that reproducible plate thicknesses could be obtained. The plate obtained on any one specimen is uniformly thick, with the exception of slight irregularities which are visible in the microstructure at the surface of longitudinal sections. The effect of these irregularities on the course of diffusion should be negligible.

C. Annealing of the Diffusion Couples

Experience with diffusion studies on other metals indicates that the refractory nature of niobium metal results in low diffusion rates at temperatures normally attainable in ordinary laboratory furnaces. Therefore, the use of an R. D. Brew Co. Model No. 420 high vacuum furnace capable of attaining 2000°C at a vacuum of 1×10^{-5} mm Hg was obtained for these experiments. At such high temperatures, measurements must be made with an optical pyrometer, which limits the accuracy to ± 25°C. The range of temperature to be covered is 1400°C to 2000°C; the annealing times have to be increased considerably at the lower temperatures to permit a measurable penetration of isotope.

D. Analysis of the Diffusion Couples

After the diffusion anneal is completed, 0.001" layers are machined from the specimen surface perpendicular to the diffusion direction. Each layer is separately collected and analyzed for the isotopic content by means of a gamma scintillation counter. The machine turnings are weighed and spread on a metal tray which is inserted in the detecting unit. In this way, constant geometry is obtained for each sample and the activity per unit weight may be measured. Since the solution to the diffusion equations for the initial and boundary conditions which apply to these specimens is

$$A = \frac{Q}{\sqrt{\pi D t}} \exp\left(-x^2/4Dt\right) \quad \text{or} \quad \ln A = \ln \frac{Q}{\sqrt{\pi D t}} - \frac{x^2}{4Dt}$$

where: A = The radioactivity which is directly proportional to the concentration of Nb^{95}

Q = Product of the initial concentration of Nb^{95} and the thickness of the deposited layer

t = diffusion time

X = penetration

D = Self-diffusion coefficient

The diffusion coefficient is calculated from a plot of ln A vs. X^2 which yields a straight line whose slope is $-\frac{1}{4Dt}$.

III. MEASUREMENT OF SELF-DIFFUSION COEFFICIENT AT 2000°C

A pair of specimens was prepared in the above manner and annealed at 2000°C for one hour. A specimen holder illustrated in Fig. 2 was constructed so that the plated faces of the specimens would oppose each other during annealing without touching. The purpose of this arrangement is to hinder the evaporation of isotope from the surface of the specimens. Fig. 3 is a plot of ln A vs. X^2 for both specimens. The lower surface activity of specimen #2 is due to the fact that less isotope was deposited on this specimen than on specimen #1.

The average self-diffusion coefficient was calculated from the two curves to be 3.2×10^{-9} cm^2/sec. A second specimen annealed at 1800°C for 7-1/2 hours yielded a diffusion coefficient of 1.7×10^{-10} cm^2/sec.

IV. FUTURE WORK

Pairs of diffusion couples will be annealed at the following temperatures for suitable times: 1400°, 1600°, 1800° and 2000°C. Once the diffusion coefficient is known as a function of temperature, the activation energy for the process will be computed.

REFERENCES

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.

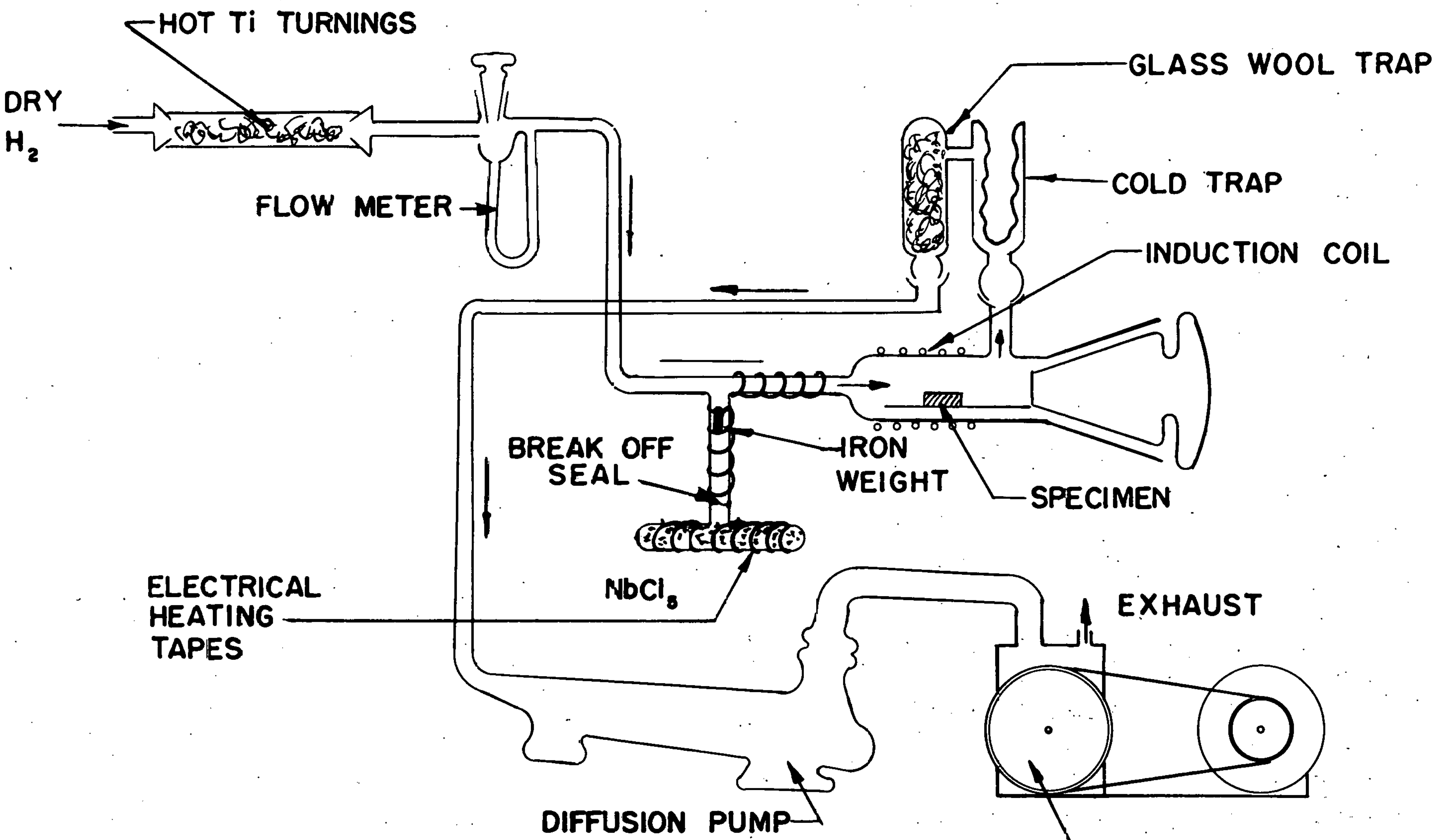

HOT Ti TURNINGS
DRY
H_2
FLOW METER
GLASS WOOL TRAP
COLD TRAP
INDUCTION COIL
BREAK OFF SEAL
IRON WEIGHT
SPECIMEN
ELECTRICAL HEATING TAPES
$NbCl_5$
EXHAUST
DIFFUSION PUMP
MECHANICAL PUMP

Fig. 1

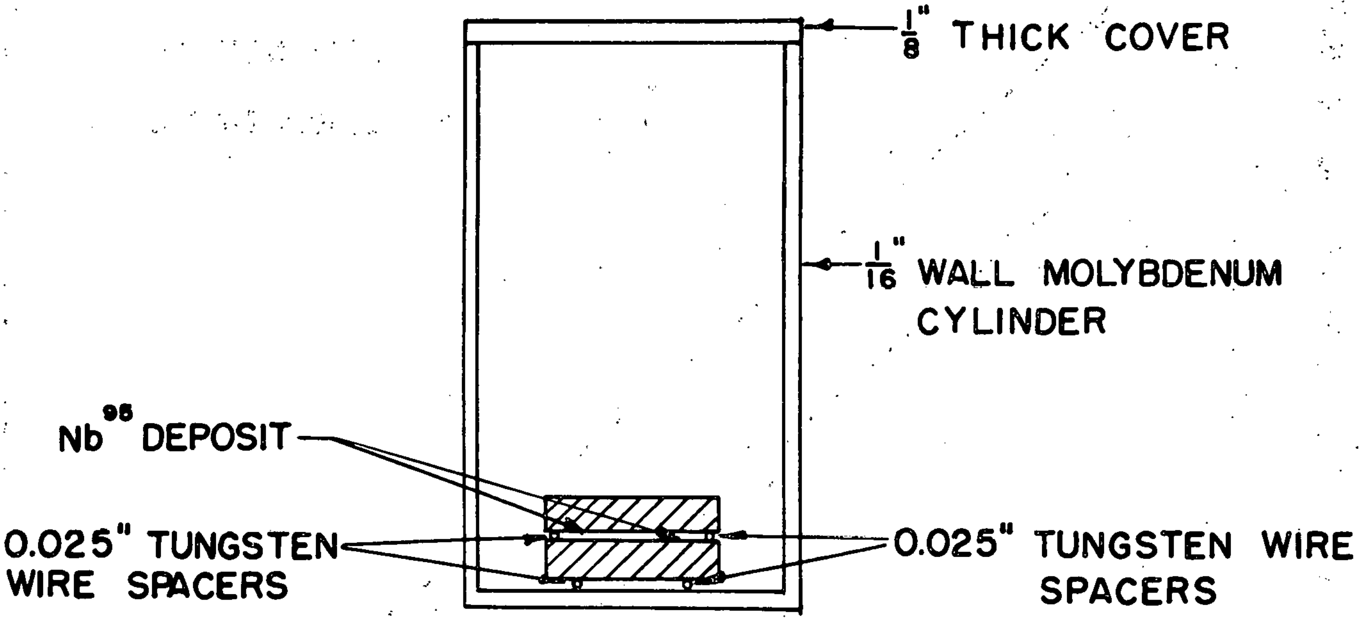
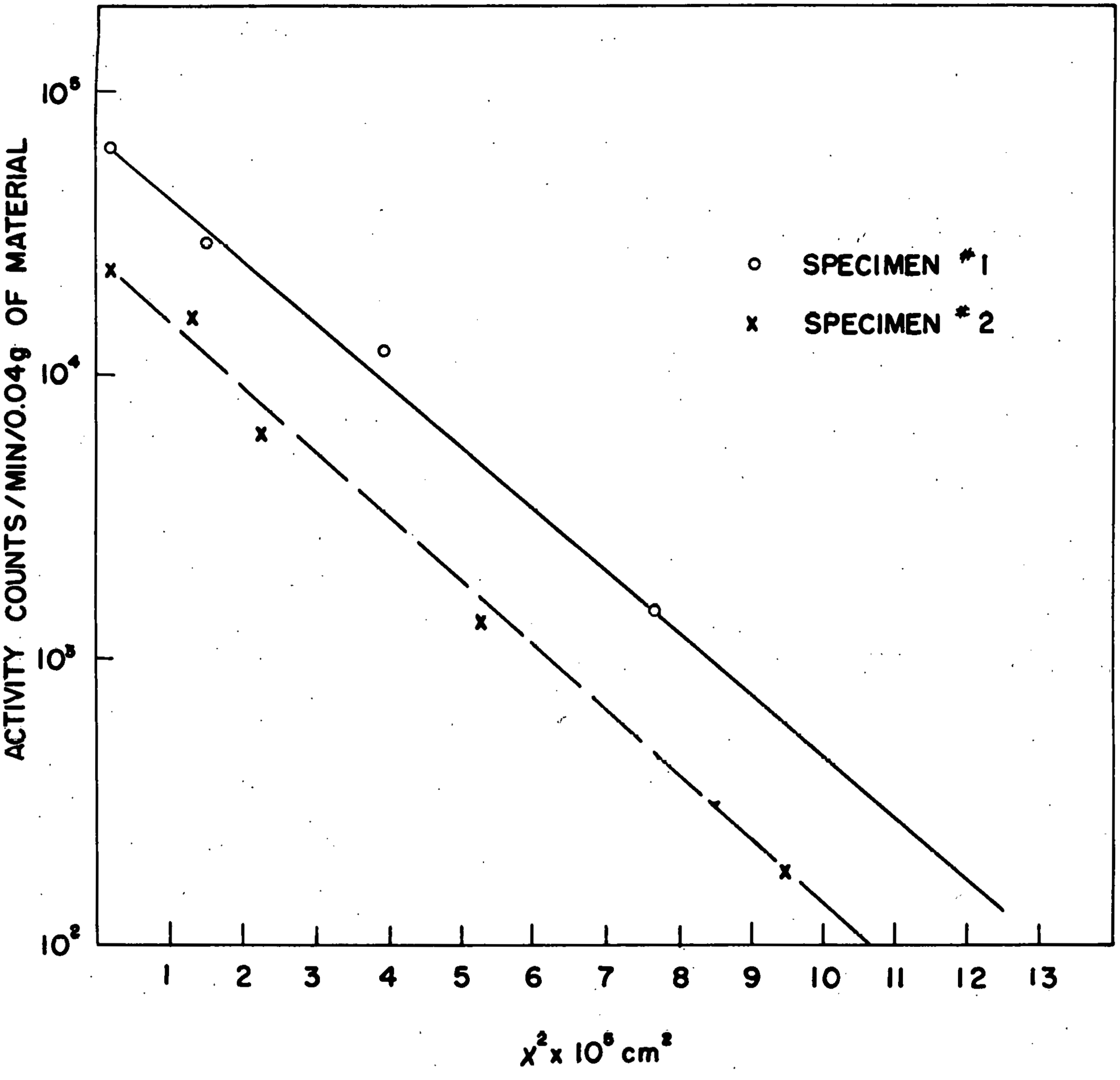

1/8" THICK COVER
1/16" WALL MOLYBDENUM CYLINDER
Nb95 DEPOSIT
0.025" TUNGSTEN WIRE SPACERS
0.025" TUNGSTEN WIRE SPACERS

Fig. 2



ACTIVITY COUNTS/MIN/0.04g OF MATERIAL
10^5
10^4
10^3
10^2
1
2
3
4
5
6
7
8
9
10
11
12
13
$x^2 \times 10^5$ cm^2
○ SPECIMEN #1
x SPECIMEN #2

Fig. 3