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THE SELF-DIFFUSION OF NIOBIUM—I

First Annual Progress Report, January 1, 1956 to June 30, 1957

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February 1, 1958

Research Laboratories
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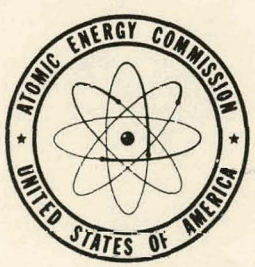
Bayside, New York



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Abstract

The measurement of the self-diffusion coefficient of niobium as a function of temperature has been undertaken. It is planned to prepare the diffusion couples by the deposition of Nb^{95} onto the surfaces of niobium discs from the $Nb^{95}Cl_5$ vapor phase and to anneal the couples in the temperature range 1600° to 2000°K. Details are given of the construction of the vapor deposition apparatus and of the preparation of $Nb^{95}Cl_5$ from the oxalate form in which the isotope is received. Preliminary measurements of the diffusion coefficient in a Nb-8 w/o Ti alloy and in a Nb-1.4 w/o V alloy indicate that the diffusion coefficient in the former is approximately $10^{-9} cm^2/sec$ at 1600°C and is approximately 8×10^{-11} cm^2/sec in the latter at 1400°C.

THE SELF-DIFFUSION OF NIOBIUM

I. Introduction

In view of the rapidly growing interest in the possible use of niobium as a high temperature structural material, there is need for more basic data on its properties. Self-diffusion coefficients are important as they bear on creep, sintering rates, homogenization of alloys, bonding of clads, and similar phenomena. Therefore, measurement of the diffusion constants over a range of temperature and of the activation energy for the process has been undertaken.

II. Method

A. Preliminary Considerations

The standard method for determining self-diffusion coefficients is the tracing of the diffusion of a radioactive isotope into a non-radioactive mass of the same metal. Fortunately, niobium has an isotope, Nb^{95}, which is suitable for this purpose, which has a 37-day half-life, and which emits 0.745 mev gamma rays. This isotope is supplied by the Oak Ridge National Laboratory in the form of an oxalate solution. Initially, consideration was given to the form of the diffusion couple. If a sandwich-type couple were to be prepared by the pressure welding of two niobium discs, one containing Nb^{95}, it would be necessary for one to reduce the radioactive oxalate to metal and to introduce this metal into a melt of normal niobium in order to prepare the radioactive disc. Both reduction of the oxalate to metal and preparation of a melt containing Nb^{95} involve high temperature fusion processes which would have necessitated the procurement of vacuum arc-melting equipment for the radio-chemistry laboratory. The problem of carrying out the fusion steps with radioactive niobium also seemed rather formidable and, therefore, this method was

eliminated. It was decided that the possibility of a thin film of tracer being deposited on a standard niobium disc by a suitable plating operation would be investigated.

The high melting point of niobium indicated that unusually high temperatures would have to be reached for the diffusion runs, and it was anticipated that a special vacuum furnace would be necessary to prevent oxidation of the niobium. Long time runs at low temperatures were considered to be undesirable because of the possibility of appreciable grain boundary diffusion.

In order to gain an approximation of the rates of self-diffusion of niobium, which would be useful in the establishment of the times and temperatures for the diffusion anneals, a number of sample calculations were made. Eager and Langmuir[1] have reported that self-diffusion in tantalum may be described by the relation $D=2 \exp.(-110,000/RT)$. Since tantalum has a melting point of about 3000°C, as compared to 2400°C for niobium, one would expect as a first order approximation that the activation energy for volume diffusion in niobium is of the order of 90,000 cal/mol. If it is assumed that D_o equals 1, calculated values of D range from 9×10^{-15} cm^2 per second at 1400°K to 1×10^{-11} cm^2 per second at 1800°K. On this basis, the time at temperature required for a reasonable diffusion penetration (approximately 0.050 cm.) will be roughly 58 days at 1800°K.

B. Deposition of Nb^{95} on Non-Radioactive Niobium

Since Nb^{95} will be obtained in the form of a niobium complex in oxalic acid, it was considered advisable to look into the possibility of electroplating the isotope out of an aqueous solution. A survey of the literature on the electroplating process indicated that considerable disagreement existed about the feasibility of electroplating niobium from aqueous solutions.[2] Several Russian investigators report

the deposition of niobium from solutions of Nb_2O_5 in KOH containing organic acids. Also, some Japanese patents claim deposition from unspecified complex salts. Unfortunately, attempts to verify such claims have failed. Further, experience at this laboratory in attempts to electroplate uranium, a similarly reactive metal, indicated that the probability of electroplating niobium as a uniform, thin plate is not very high. In spite of this, a few exploratory tests were made because of the great advantages that electroplating holds over other deposition techniques in simplicity of equipment and procedures for the handling of radioactive isotopes. A number of solutions were prepared by the dissolution of Nb_2O_5 in hydrofluoric acid, in sulfuric acid, and in hydrochloric acid. Niobium anodes and cathodes were inserted, and sufficient voltage was applied to produce a direct current density of 50 to 180 amperes per sq. ft. In the case of the sulfuric and the hydrochloric acid solution, a gray film (presumably oxide) formed on the anode, and the current dropped to zero. With the hydrofluoric acid solution, both anode and cathode were etched by the electrolyte, but no plating was observed. A few other solutions were tried (KOH in oxalic acid and NH_4F in methyl alcohol) with similar lack of success.

In view of the negative results, other possible methods of sample preparation were investigated. It has been reported [3] that niobium will produce an adherent deposit on the heated surfaces of various metallic and non-metallic shapes by the hydrogen decomposition of niobium pentachloride vapor. The apparatus required for this technique and shown diagrammatically in Fig. 1 is somewhat complex, but equipment which could be converted for this purpose was available in the laboratory, and therefore, it was decided to adopt this method. A description of the method follows:

1. The reaction chamber is completely evacuated so that all traces of oxygen are removed.

2. The flask containing the niobium pentachloride is cracked open at the top by a magnetic hammer and heated to about 150°C.

3. The vaporized pentachloride is carried in dry hydrogen gas and condenses in glass coils which are immersed in a thermostatically controlled oil bath at 100°C. The partial pressure of niobium pentachloride entering the reaction chamber is controlled by the temperature of the oil bath.

4. The specimen is heated inductively to 900°C.

5. As the niobium pentachloride-hydrogen mixture passes over the hot specimen, the pentachloride is decomposed to metallic niobium in the form of an adherent layer on the specimen.

6. Excess pentachloride condenses in the cold traps, and the hydrogen is exhausted through the vacuum pumps into an exhaust hood.

Since the pentachloride vapor is radioactive, and since considerable quantities of hydrogen pass through the system, it was deemed necessary to enclose the entire apparatus in a large hood. The equipment is illustrated in Fig. 2.

Much time has been spent in the setting up of the plating system and in the establishing of the correct conditions for plating. For example, the specimen temperature and the partial pressure of $NbCl_5$ as it passes over the specimen are fairly critical for uniform plating. As the specimen is heated inductively, there is a tendency for the gases in the reaction chamber to ionize so that an accurate temperature reading cannot be obtained with an optical pyrometer. Therefore, the specimen has been heated under high vacuum, and a calibration of temperature as a function of power input to the induction coils obtained. Since it is not expected that the same power setting will achieve the same

temperature with a gas flow through the system as with vacuum, the best setting for plating must be obtained by trial and error. Up to this time, no completely successful runs have been made. The chief difficulty is the prevention of oxidation of the specimen during the plating. A few modifications are being made in the system in an attempt to eliminate all sources of oxygen. These modifications consist mainly of the removal of several stopcocks which were close to the reaction chamber and had to be heated by heating tapes; the vacuum grease decomposed under heat and permitted air leakage into the system.

C. Preparation of $NbCl_5$

Since it is planned to deposit the niobium isotope by decomposition of the pentachloride, it was necessary to develop a chemical process for the conversion of niobium oxalate to niobium pentachloride. It was initially intended that the radioactive pentachloride would be prepared by a commercial supplier who had expressed an interest in doing so; however, after considering the problem carefully, the supplier felt that he was not sufficiently well equipped to handle this type of material. It thus became necessary to develop a method of preparing $NbCl_5$ from the oxalate solution at our own laboratory. The chief difficulty which had to be overcome was the elimination of all sources of oxygen during the process, since $NbCl_5$ readily converts to $NbOCl_3$. The following procedure was finally adopted after a number of developmental trial runs had been made with non-radioactive niobium:

1. The dilute solution of radioactive oxalate is diluted with non-radioactive oxalate carrier and evaporated to dryness.

2. The residue is ignited in a platinum crucible and converted to Nb_2O_5.

3. The Nb_2O_5 is reduced by calcium. A reduction cake consisting of calcium metal, niobium metal, calcium oxide, calcium chloride, flux and other impurities results.

4. The reduction cake is chlorinated, and $NbCl_5$ and $NbOCl_3$ sublime. A rather complete separation of the two takes place by their condensing in different zones of the reaction tube.

The radioactive $NbCl_5$ will be diluted with non-radioactive chloride before being placed in the vapor plating system.

III. The Diffusion of Titanium and Vanadium in Niobium

In view of the difficulty experienced in the preparation of a self-diffusion couple of niobium, it seemed worthwhile to obtain an approximation of the self-diffusion rate by measurement of the diffusion of solute elements in a dilute solution of niobium. Several sandwich-type diffusion couples were prepared by the pressure welding of discs of niobium to discs of a niobium-8 w/o Ti alloy and a niobium-1.4 w/o V alloy. Vanadium, being in the same group of the periodic table as niobium, its rate of diffusion in niobium should more closely approximate self-diffusion in niobium than the rate of diffusion of titanium in niobium. However, a supply of the niobium-titanium alloy was on hand, and the first couple was prepared from it.

The only furnace available in the laboratory which was capable of reaching 1600°C under vacuum was a carbon resistance furnace. The niobium-titanium couple was annealed for ten hours at 1600°C, and it was found that the furnace was incapable of maintaining the temperature constant to better than ± 50°C. Since it is possible to make an approximate correction for the temperature fluctuations, one-mil sections were machined parallel to the diffusion direction, and chemically analysed for the percent titanium present. D was calculated from the relation given by da Silva and Mehl[4]

$$D_2\ (T) = \exp.\left[\frac{Qav}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] D_1\ (T)$$

to be of the order of $10^{-9} cm^2/sec$.

Only one niobium-titanium couple was run, since a supply of vanadium was subsequently acquired and sandwich diffusion couples containing vanadium could be made. The first of these couples was heated at 1400°C for eight days in a globar-heated vacuum furnace in which the temperature was constant within 5°C. Fig. 3 is a plot of the diffusion curve obtained for this specimen. Analysis for the diffusion coefficient yielded a value of $8 \times 10^{-11} cm^2/sec$. It is apparent from the scatter of the experimental points, that this value is only an approximation.

As a further aid in the establishment of the proper diffusion periods for given temperatures, the two diffusion coefficients were used to compute an activation energy which was about 80,000 cal/mol. This value is, of course, only a rough approximation, but it is useful as a guide. If the activation energy for self-diffusion in niobium is about 80,000 cal/mol, and D_o is assumed to be equal to 1, as before, D should vary from 2.5×10^{-12} cm^2/sec at 1400°K to 4.5×10^{-9} cm^2/sec at 1800°K. The time required to obtain a 0.050 cm penetration at 1800°K will be reduced to about 20 minutes. If these estimates are reasonably accurate, a more precise measurement of the self-diffusion of niobium can be made than had hitherto been considered feasible.

IV. Future Work

As soon as the vapor plating apparatus is functioning properly, that is when a uniform, adherent, metallic deposit can be made, an order will be placed with Oak Ridge for a supply of Nb^{95}, and self-diffusion couples will be prepared. Once this is done, the diffusion coefficients should be obtained within a few months.

Also, several more niobium-vanadium diffusion couples will be annealed at a series of temperatures ranging from 1400°C to about 1800°C in vacuum in order to establish the approximate self-diffusion rates of niobium as a function of temperature promptly.

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3. C. F. Powell, I. E. Campbell, and B. W. Gonser, Vapor Plating, John Wiley and Sons, Inc., 1955.

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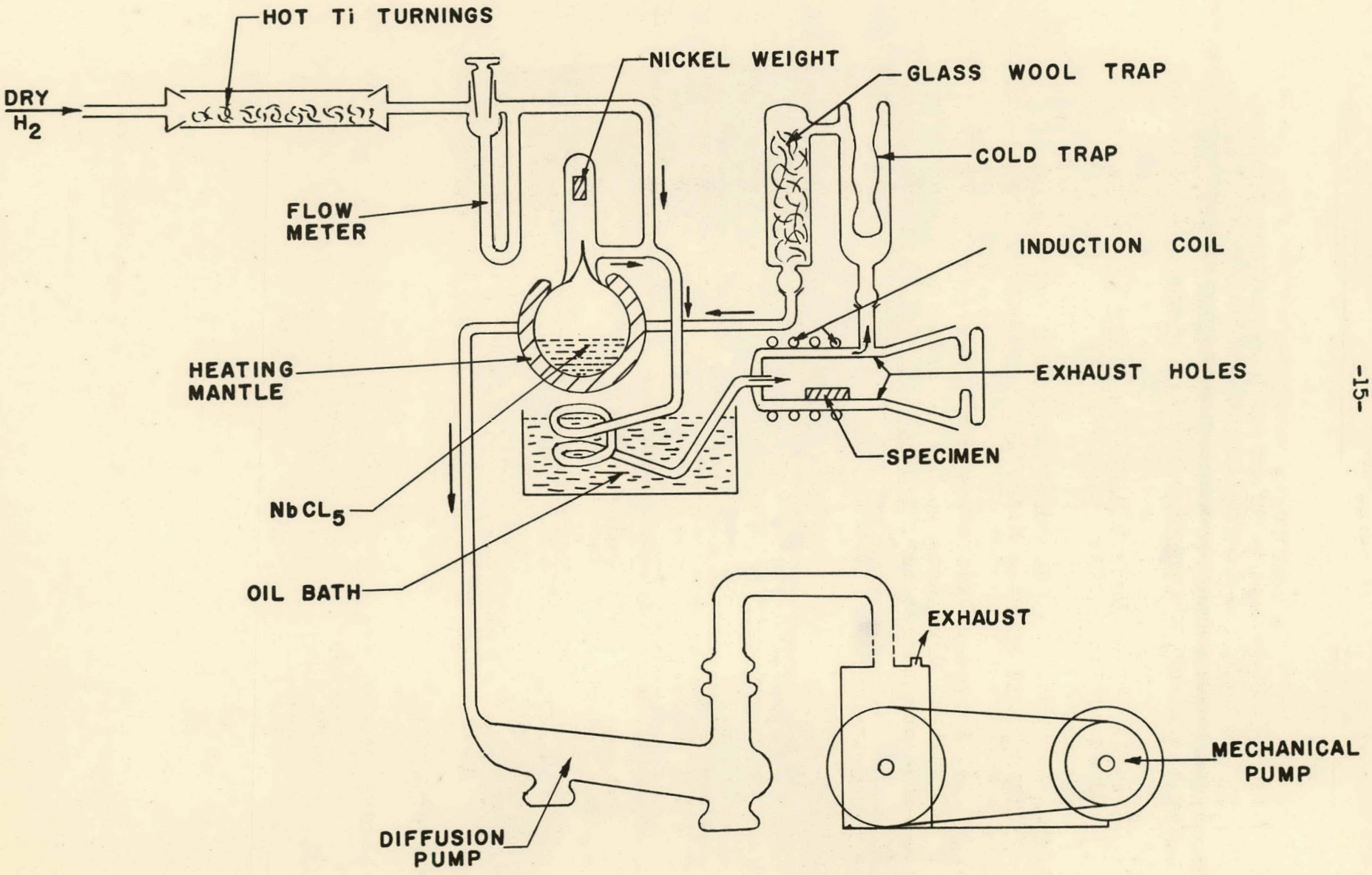

Fig. 1. Schematic representation of vapor plating process.

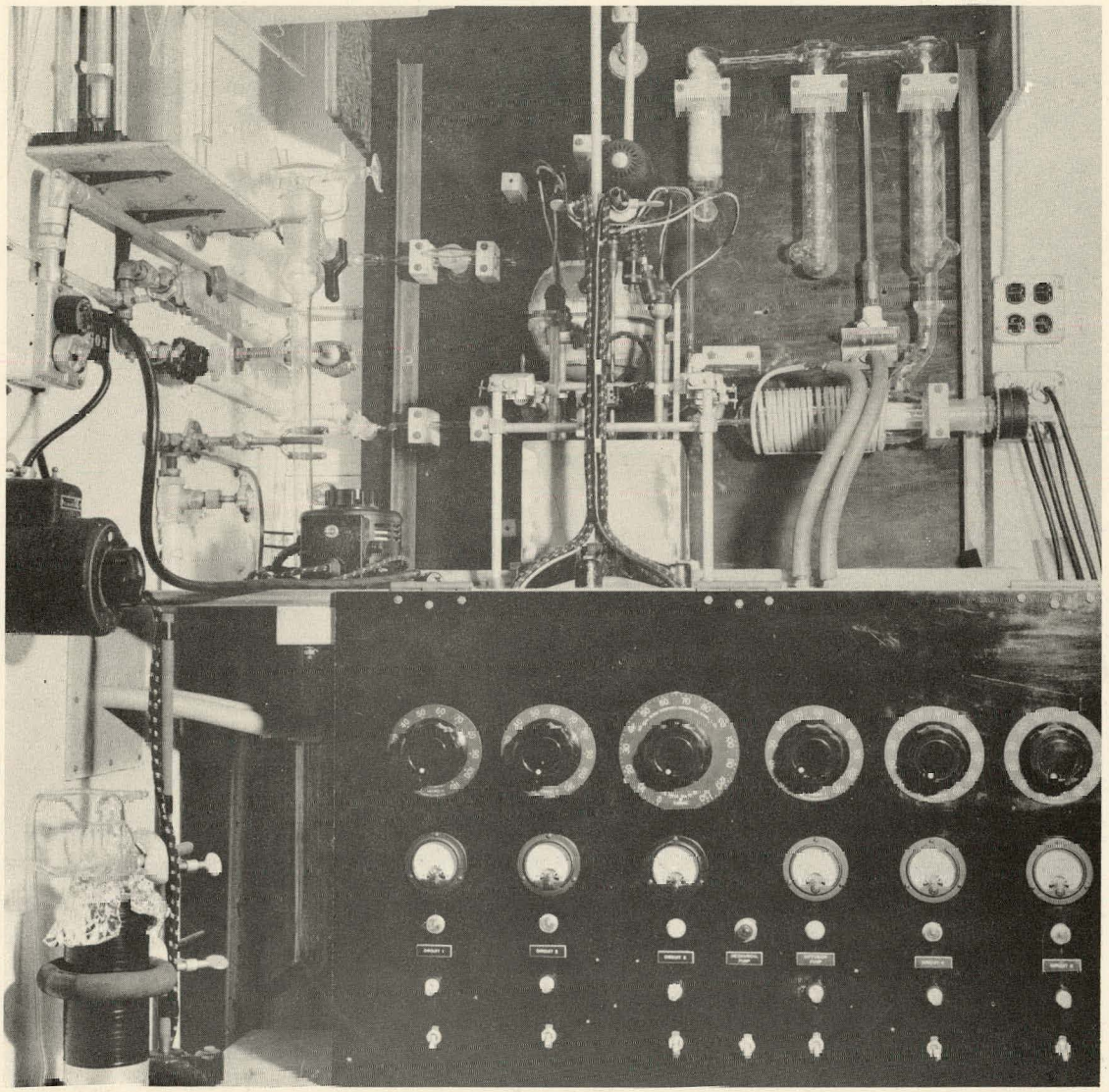

Plate No. 4000

Fig. 2. Photograph of the niobium pentachloride vapor deposition equipment.

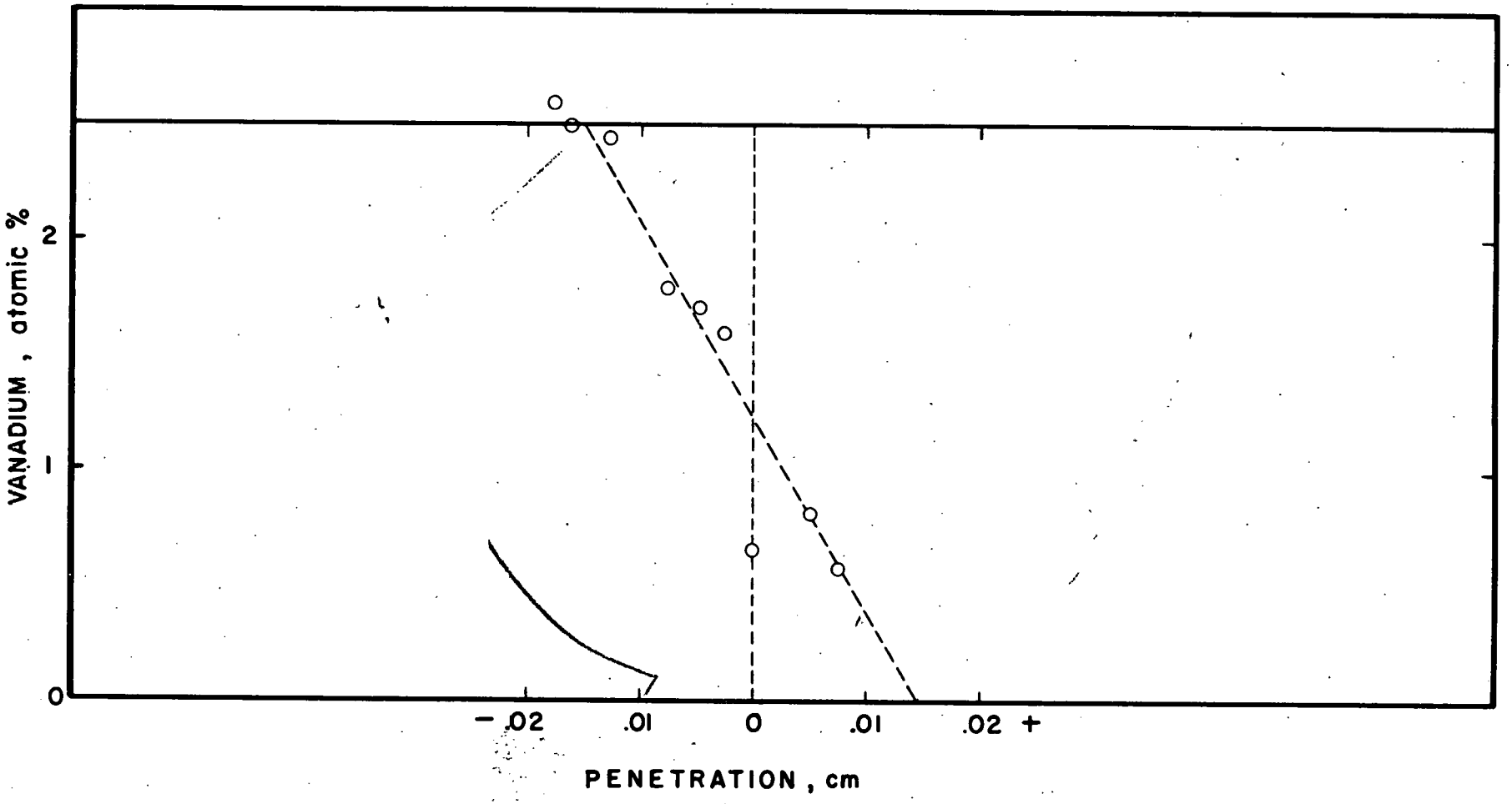

Fig. 3. Diffusion curve for niobium-vanadium couple annealed for 8 days at 1400°C in vacuum.