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A SUBMICRON SECTIONING TECHNIQUE FOR ANALYZING DIFFUSION SPECIMENS OF TANTALUM AND NIOBIUM

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ABSTRACT

A microsectioning technique for tantalum and niobium was successfully used which permits uniform sections of metal less than 100 A in thickness to be removed from the surface. The technique, based on the formation and subsequent stripping of an anodic oxide film, is presently being used as a tool to study diffusion phenomena in these metals. The apparent sensitivity is sufficient to permit low-temperature diffusivity measurements to be made in reasonable times. It may also be possible to describe more quantitatively "anomalous" diffusion behavior near the metal surface. The present paper considers the details of the experimental technique and presents some typical diffusivity data for the diffusion of Nb^{95} in tantalum.

INTRODUCTION

Recent diffusion studies involving a wide range of tracer and host metals have indicated that an anomalously low diffusivity may exist near the surface of the specimen.[1–4] Since the explanations proffered by several of the investigators in this field have yet to reach a common plane, it appears that a critical study of such phenomena would contribute to filling an important gap in the phenomenological picture of diffusion from a free surface.

An inherent requirement for such measurements is a highly sensitive sectioning procedure capable of removing layers a fraction of a micron

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[1] V. D. Ignatkov and V. E. Kosendo, Fiz. Tverd. Tela. 4, 1627 (1962).

[2] D. L. Styris and C. T. Tomizuka, J. Appl. Phys. 34, 1001 (1963).

[3] G. P. Williams, Jr., and L. Slifkin, Acta Met. 11, 319 (1963).

[4] T. S. Lundy and J. F. Murdock, J. Appl. Phys. 33, 1671 (1962).

thick from the metal surface. Several methods, both physical and chemical, have been shown to be acceptable for microsectioning certain metals.[1,2] It is a virtual certainty, however, that no single method will have universal, trouble-free application, and it is thus important to be sure that for a given metal the sectioning procedure is not subject to its own form of anomaly when applied to extremely thin layers.

In the present investigation on diffusion in the refractory metals tantalum and niobium, use was made of the fact that very uniform, thin, anodic oxide films may be formed and mechanically stripped from suitably prepared surfaces of these metals. Thus, a microsectioning tool well suited to the tracer method for diffusion measurements was potentially available. In principle, diffusion coefficients as low as 10^{-19}–10^{-20} cm^2/sec could be determined by this technique. This is several orders of magnitude lower than the range currently available using more conventional mechanical sectioning techniques and offers some advantages over chemical sectioning for purposes of studying anomalous diffusion behavior near the surface.

The purpose of this paper is to relate the details of the microsectioning technique and to report preliminary results of some low-temperature diffusion studies of Nb^{95} in single crystals of tantalum.

EXPERIMENTAL PROCEDURE

The tantalum specimens were cut from single crystal rods (Materials Research Corporation) to form cylindrical disks 1/4 in. in diameter. The faces of the disks were carefully mechanically polished and then electropolished for 1 hr in a 90% H_2SO_4–10% HF solution. The surfaces of specimens so prepared appear as bright mirrors to the naked eye and in the light microscope. Previous examinations[5] using electron microscopy indicated that the surface of tantalum prepared in this way has a corrugated texture resembling a bubble raft. At high magnification, this texture was seen to consist of an array of surface depressions approximately 100 A deep with an average separation of some 700 A. Therefore,

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[5]R. E. Pawel, J. V. Cathcart, and J. J. Campbell, J. Electrochem. Soc. 107, 957 (1960).

the tantalum surface, while not precisely planar, would not be expected to cause serious restrictions regarding the particular assumptions or boundary conditions commonly used with the tracer technique for diffusion studies.

The Nb^{95} tracer was applied to one face of the electropolished tantalum specimen as a dilute oxalate solution which was allowed to evaporate to dryness. Upon heating to the diffusion anneal temperature, the oxalate decomposed, presumably forming a $Ta\text{-}Nb^{95}$ suboxide which in turn decomposed, leaving the Nb^{95} as a thin surface layer. Rough calculations indicated that the total amount of the isotope on the surface averaged less than one monolayer.

After the diffusion anneal, a thin layer of metal was filed from the periphery and the specimen was then sectioned by successively removing layers of anodically formed oxide. The details of the anodization process for tantalum and niobium are well known.[6] The important aspects as far as its application to microsectioning are concerned are: (1) on well-prepared surfaces, oxide films of very uniform thickness can be formed with a high degree of reproducibility and (2) these films may be mechanically stripped from the metal surface if a very small amount of HF is present in the anodizing solution.

In the present investigation, the tantalum specimens were anodized in a 0.5% solution of Na_2SO_4 to which about 2 drops of 48% HF/100 cc had been added. The thickness-voltage relationship agreed well with those reported previously.[6] Using weight gain measurements on a specimen with large surface area (approximately 300 cm^2), a straight line of slope 15.0 A of pentoxide per volt (corresponding to about 6.5 A of metal per volt) satisfactorily described the data from 10 v to at least 200 v. After anodizing, the diffusion specimen was washed in distilled water and dried in an oxygen blast.

Stripping the anodic film from the surface is, of course, a critical part of the procedure and requires care and patience. If the specimen is completely free of scratches and other imperfections, stripping with

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[6]See, for example, L. Young, Anodic Oxide Films, Academic Press, New York, 1961, and appropriate references contained therein.

plastic tape gives good results. However, if fine scratches or pits having a wide size spectrum exist on the surface, it may not be possible to obtain a perfect strip with the tape method. In this case, small segments of the anodic film may remain on the surface, resulting in an undesirable contribution to some subsequent section. It appears, however, that the deleterious effects of incomplete stripping are minimized, or at least postponed, if the series of anodizations is made at the same voltage. Apparently, if this procedure is followed, the small proportion of film which does not strip after the first treatment clings tenaciously to the surface during subsequent stripping. It is important only that each successively stripped film comes as nearly as possible from the same area as its predecessor. The extent to which this is achieved will be reflected – usually with considerable amplification – in the data. For the three experiments reported in this paper, the films were stripped with tape. However, some experiments were performed that indicated stripping improvement occurred if the anodic films were coated with a backing material such as parlodion prior to applying the tape.

After each film was stripped from the specimen, the tape was folded back upon itself, assuring that no part of the film would be lost during handling. Each film, corresponding to a section of specimen, was then transferred to a gamma-counting facility in order to establish the distribution of the Nb^{95} in the specimen. The counting was performed with a single-channel analyzer using a 3 × 3 in. NaI(Tl) scintillation crystal in a lead container.

RESULTS

For the case of unidirectional diffusion of a radioactive species from a plane source into an infinitely long homogeneous medium, the following equation is applicable:[7]

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[7]J. Crank, The Mathematics of Diffusion, 1st ed., Oxford University Press, 1956.

$$A(x,t) = \frac{M}{\sqrt{\pi\ Dt}} \exp\left(-\frac{x^2}{4\ Dt}\right) \tag{1}$$

where

$A(x,t)$ = the activity at a distance x into the specimen at time t

M = the total activity at $x = 0$, $t = 0$

D = the diffusion coefficient

t = the annealing time.

If a single mechanism for diffusion is operative and if the diffusivity associated with this mechanism is not affected by concentration or surface effects, a plot of ln A vs x^2 should be linear with a slope of $-\frac{1}{4\ Dt}$. It is conventional to report data obtained by the isotope technique in this fashion. In the event that the profile does not describe a straight line throughout and anomalous behavior is observed for small penetration distances, it is expedient, if not precise, to consider the "apparent diffusivity" to be related directly to the slope of the curve at the point in question.

The activity profiles for three tantalum specimens annealed at 1250, 1170, and 1050°C are shown in Figs. 1, 2, and 3. The nonideal penetration behavior in the vicinity of the surface is obvious in all three figures, but is most dominant in Fig. 3 where the sectioning thickness chosen was sufficiently sensitive to define the curve near the surface with the highest degree of precision. In this figure, the ln A vs x^2 plot appears to be curved throughout, although presumably if the sectioning were continued, a constant slope would finally be approached, as indicated in Figs. 1 and 2. The curvature of these plots near the surface makes the maximum apparent diffusivity difficult to calculate accurately. Conservative estimates, shown in the figures, indicate that a smooth decrease of perhaps two orders of magnitude from the bulk diffusivity value is not unrealistic.

Also obvious from the three figures is the high degree of self-consistency of the data. Each of the three experiments utilized different sectioning thicknesses, and thus each plot represents a different sensitivity of measurement. For example, the data of Fig. 2 were taken from sectioned layers of 650 A thickness. For the given time

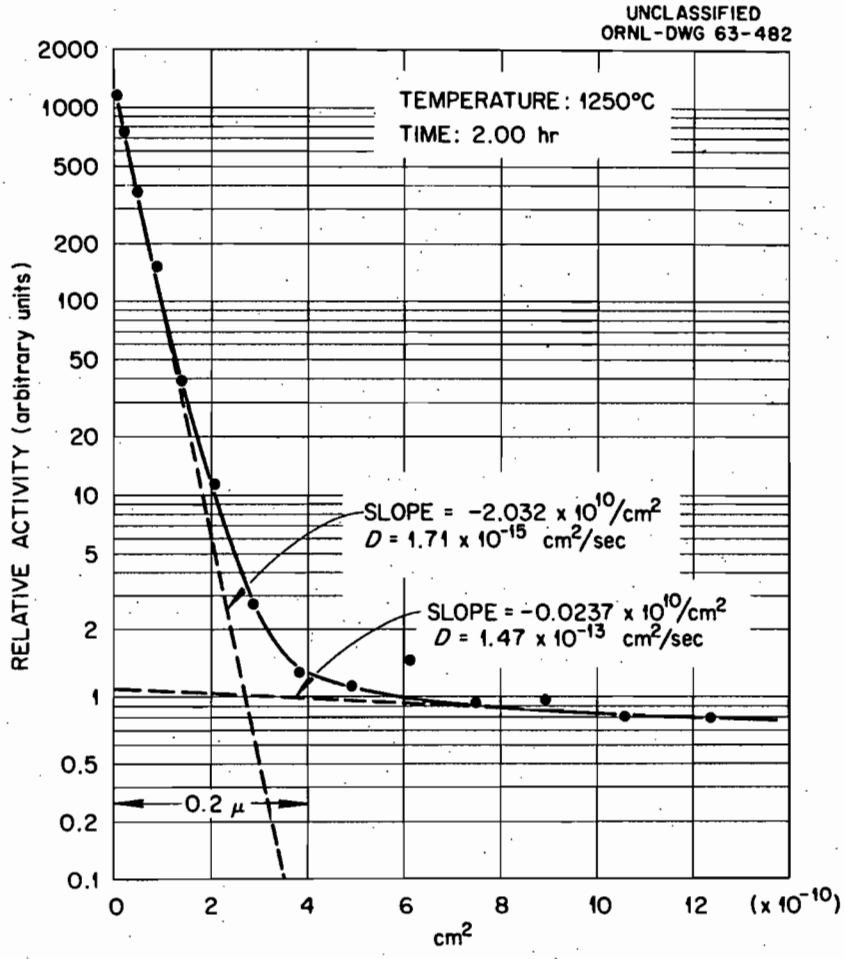

Fig. 1. Activity Profile for Diffusion of Nb^{95} into Tantalum Single Crystal after 2.00 hr at 1250°C. Each stripped anodic layer removed 260 A of metal from the surface.

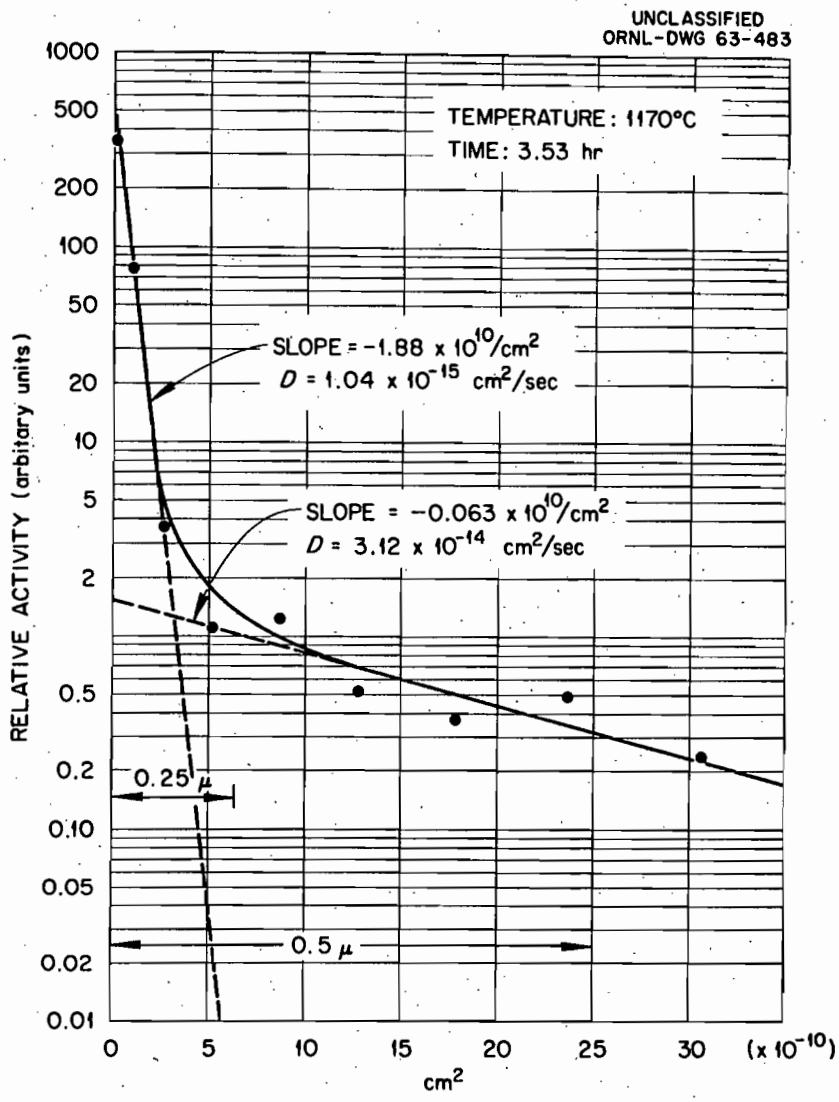

Fig. 2. Activity Profile for Diffusion of Nb^{95} into Tantalum Single Crystal after 3.53 hr at 1170°C. Each stripped anodic layer removed 650 A of metal from the surface.

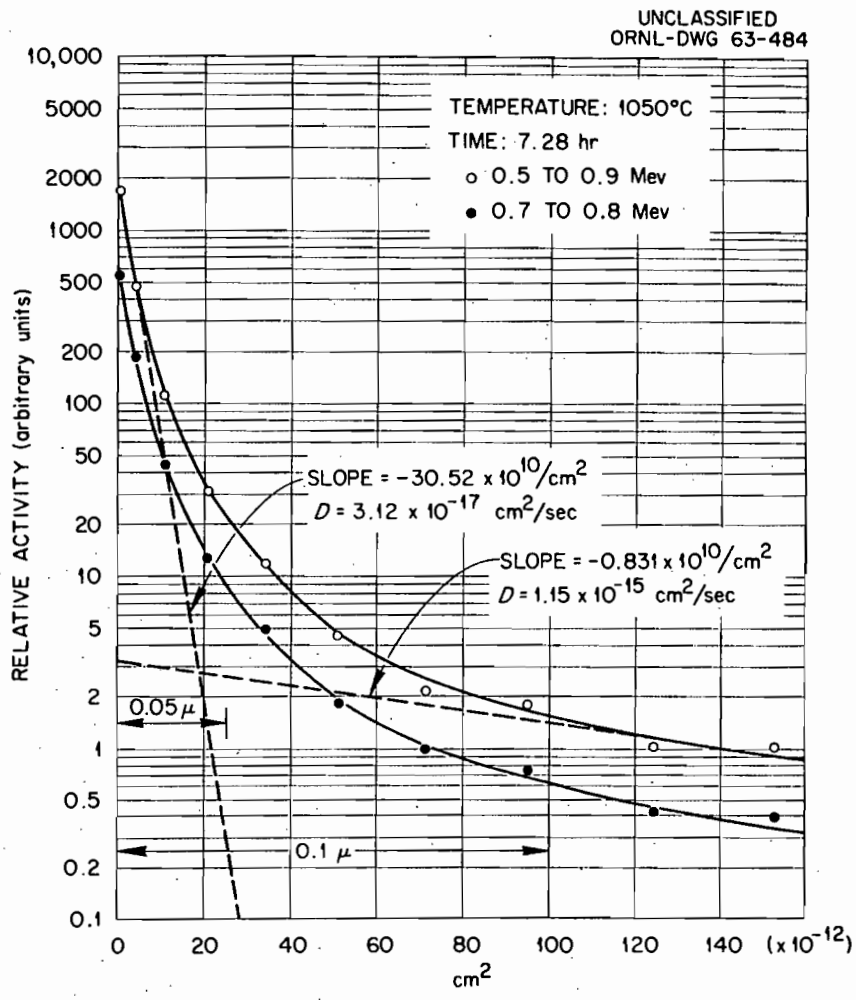

Fig. 3. Activity Profiles for Diffusion of Nb^{95} into Tantalum Single Crystal after 7.28 hr at 1050°C. Each stripped anodic layer removed 130 A of metal from the surface. (The two curves represent counting data taken from slightly different total energy ranges and superimpose within experimental error.)

and temperature, this section thickness is too large to define the region of anomalous diffusivity accurately and the slope depicted on the figure is undoubtedly conservative. Also in this case, the activities of the layers approached the background level after only a very few sections leading to the large scatter in the data.

The data of Fig. 3 were obtained on sections corresponding to only 130 A of metal, and the region of anomalous diffusivity was emphasized to the extent that the data from this experiment never quite reached the region of bulk diffusivity deeper in the specimen. However, in Fig. 1, the layer thickness of 260 A was sufficient to illustrate both important parts of the penetration curve with reasonable accuracy, although here again some difficulty was encountered with low counting rates. Larger specimens treated with a more generous dose of isotope can make this less of a problem without adding measurably to the experimental difficulties.

The results are summarized and compared with those of other investigators[8,9] in Fig. 4. The range of D values encompassed by the two data points at each temperature represents the range of apparent diffusivities indicated by the slope of the penetration curve (ln A vs x^2) as a function of distance into the specimen. Certainly a significant change occurs in the first fraction of a micron, and at this depth essentially bulk values of diffusivity are observed. The fact that the bulk values obtained agree reasonably well with the extrapolated values from other investigations lends credibility to the observed characteristics for the surface behavior. The limits extending from the data points in Fig. 4 indicate the approximate error in the diffusivity which could occur in estimating the slope of the penetration plots as x approaches zero. This possible error is large for the data point at 1170°C because of the large sectioning thicknesses of 650 A of metal.

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[8]P. L. Gruzin and V. I. Meshkov, Vestn. Akad. Nauk. Kaz. SSR 11(4), 85 (1955).

[9]N. L. Peterson, Diffusion in Refractory Metals, WADD-60-793, p 33 (March 1961).

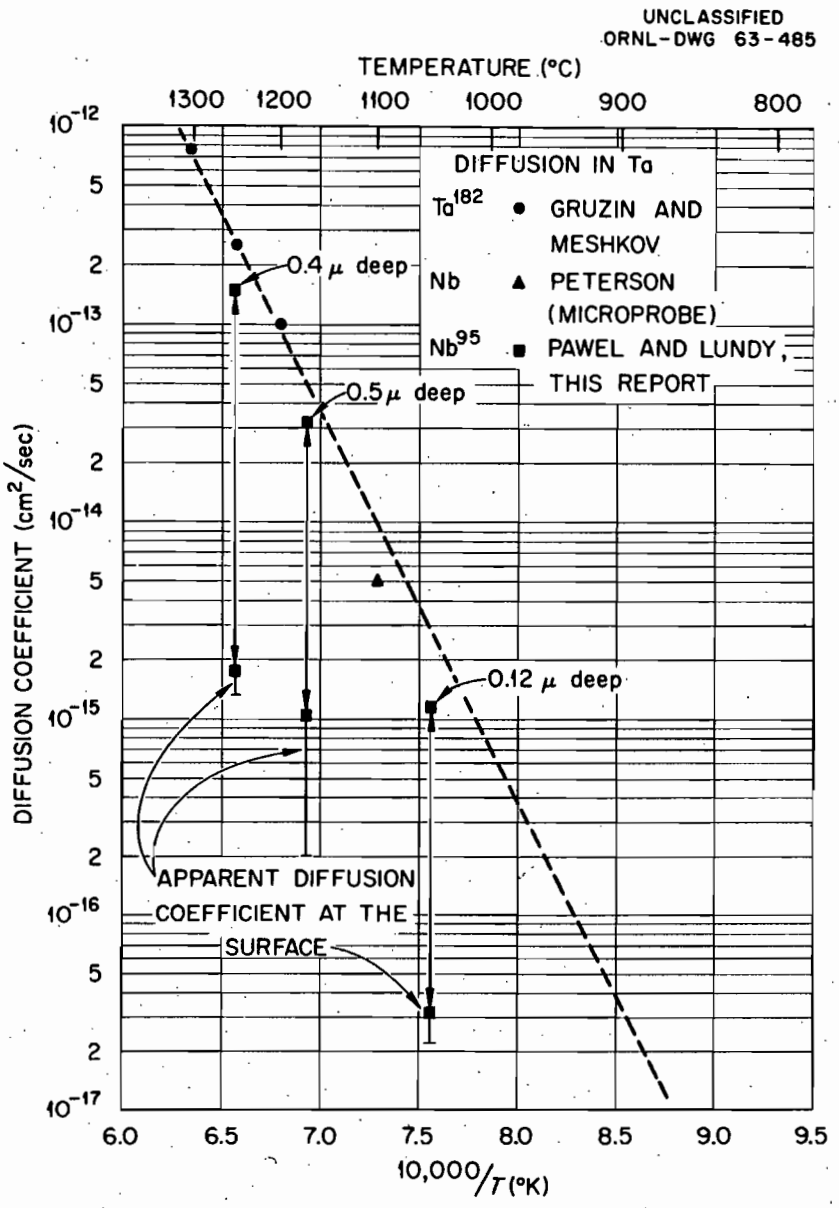

Fig. 4. Diffusion in Tantalum. Comparison of diffusion coefficients with those from other investigations. The extremes shown are the range of the apparent diffusion coefficient at the surface and that approximately 0.5 μ beneath the surface.

CONCLUSIONS

A microsectioning technique which permits taking sections of metal in the submicron range was used to study the diffusion of Nb^{95} in tantalum single crystals. The data obtained were self-consistent and serve to point out the applicability of the method as a powerful tool for the study of diffusion near the surface.

It is beyond the scope of the present paper to argue cause or mechanism for the observed anomalous penetration effects observed in these experiments. This research is being extended in an effort to characterize further the phenomenon. Presently the data seem contradictory to several existing arguments or explanations which have been made for other systems, for in this study anomalous penetration plots were observed in single-crystal specimens where the solubility of the diffusing species was very large and where the probability of a surface oxide phase existing was small.

ACKNOWLEDGMENT

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