OXYGEN DIFFUSION INTO TITANIUM

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Key Words: titanium, oxidation, microhardness, diffusion, solid solution strengthening, activation energy

Prerequisite Knowledge: basic knowledge of diffusion processes and hardness

Objective: to measure D_o and the activation energy for diffusion of oxygen into titanium

Equipment:

1. Ovens capable of reaching 900^{o}C
2. Metallographic specimen preparation equipment
3. Microhardness tester
4. Optical or scanning electron microscope

Introduction:

Titanium is well known for its excellent resistance to corrosion primarily due to a passive oxide layer at the surface. When exposed to air at elevated temperatures, 300^{o}C or more, this oxide layer will grow and simultaneously oxygen will diffuse into the metal. The oxygen atoms that do diffuse into the metal can occupy both interstitial and substitutional sites, making the material harder, and since the concentration of oxygen at the surface would be greater than concentration deeper into the metal it should be harder near the surface and softer in the interior. The correlation between the concentration profiles and hardness profiles suggests that microhardness testing can be an effective tool in studying the oxygen diffusivity in titanium.

The governing differential equation for diffusion, known as Fick's second law, is:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{1}$$

where D is the diffusivity and C is the concentration of the diffusing species [1]. The solution to this differential equation, where surface concentrations are held fixed and the diffusion medium is infinitely long, generates the concentration profile described by the equation

$$\frac{c - c_o}{c_s - c_o} = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right) \tag{2}$$

where c_o is the concentration at infinity, c_s is the concentration at the surface, x is the distance from the surface, and t is the time.

Rosa [2] has proposed using the following dimensionless correlation between hardness and oxygen concentration,

$$\frac{H - H_o}{H_s - H_o} \propto \frac{c - c_o}{c_s - c_o} \tag{3}$$

where H refers to point hardness values, H_o refers to hardness values at infinity, and H_s refers to hardness values at the surface. Substitution into equation 2 gives

$$\frac{H - H_o}{H_s - H_o} \propto 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right). \tag{4}$$

By measuring the hardness values from the surface of the metal inward, a hardness profile that is scaled to the concentration profile can be generated. This means that instead of using complicated and expensive analytical machines to measure the oxygen concentrations directly, a microhardness tester can be used to measure these hardness profiles and ultimately to determine the diffusivity.

This experiment involves determining the activation energy and diffusion rate of oxygen into titanium from a series of microhardness profiles. Several aspects presented in materials science courses are ultimately covered in this experiment, three of which are high-temperature oxidation, diffusion, and solid-solution hardening. The goal of this experiment is to provide upper-division materials science laboratory courses with a relatively inexpensive procedure for measuring the diffusivity coefficients and activation energies while emphasizing fundamental issues of materials science.

Procedure:

Material

Commercially pure, 0.75-inch (19 mm) diameter titanium rods were used in this experiment. Pure titanium was used to avoid issues related to the presence of other alloying elements and, since it is an α alloy, there won't be any α-case to complicate matters.

Heat Treating

The temperature range used in this study range from 700 to 800°C. At roughly 890°C, titanium transforms from a close-packed hexagonal α-phase to a body-centered cubic β-phase, which remains stable to the melting temperature 1670°C. By limiting the temperature of the metal to just a single phase region during annealing, in this case the α-phase, we did not have to take into account the different diffusivities for the α and β phases and the moving α-β phase interface.

The 0.75-inch (19 mm) diameter titanium pieces were cut into 0.75-inch (19 mm) long pieces and degreased with acetone and ethanol rinses. The samples were annealed in air at temperatures and times shown in table 1.

Table 1. Annealing temperatures and times.

Sample #	1	2	3	4	5	6	7
Temperature [C]	700	700	700	700	700	750	800
Time [hr]	20	50	100	200	500	100	100

Metallography

The annealed pieces were sectioned and mounted in Epomet mounting material, which is considerably harder than most mounting materials. This choice provided excellent edge retention, which is vital for accurate hardness data. The mounted specimens were then polished using 240, 320, 420, and 600 grit SiC abrasive papers, followed by intermediate polishing using 6 and then 3-micron diamond paste and finally 0.05 micron alumina on a vibratory polisher.

Microhardness Testing

A Kentron Micro Hardness Tester, equipped with a Knoop indenter, was used to measure hardness of the prepared specimens. Indentions were made using 100 grams load and a dwell time of 90 seconds, beginning from 30μm from the edge of the sample, approximately the width of one indentation. Additional indentions were made in increments of 25.4 μm toward the center until a depth of roughly 3 mm. A diagonal pattern was used so that many closely spaced readings, relative to the surface, could be made.

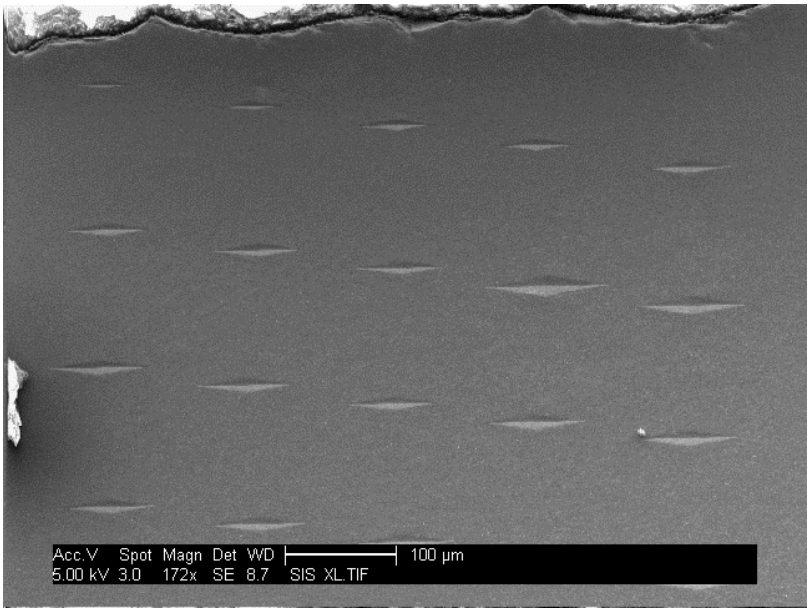

Figure 1 SEM image showing the microhardness indentations of a sample annealed at 800°C for 100 hours. Smaller indentations indicate higher hardness.

Results:
Figure 1 shows typical microhardness indentions. Note that the excellent edge retention made it possible to make measurements very close to the surface. Also note the diagonal pattern used. By distributing these indentations horizontally it was possible to space them close together vertically.

Microhardness Profiles as a Function of Time
The hardness profiles for the samples heat treated at 700°C and for times up to 500 hours are shown in figure 2. H_o was calculated by averaging the flat-line portion of the hardness profiles and was determined to have a value of 47.2 KHN. H_s and the diffusivity coefficient, D, were determined simultaneously by utilizing the "solver" utility in Excel and were determined to be 184.0 KHN and 1.14×10^{-11} cm^2/sec respectively. The constraining factor for the solver application was minimization of the sum of the square of the differences between calculated and experimental hardness values. The resulting fit between the data points and the calculated profile yielded a root mean square error in the range of 3.7 to 6.5 KHN.

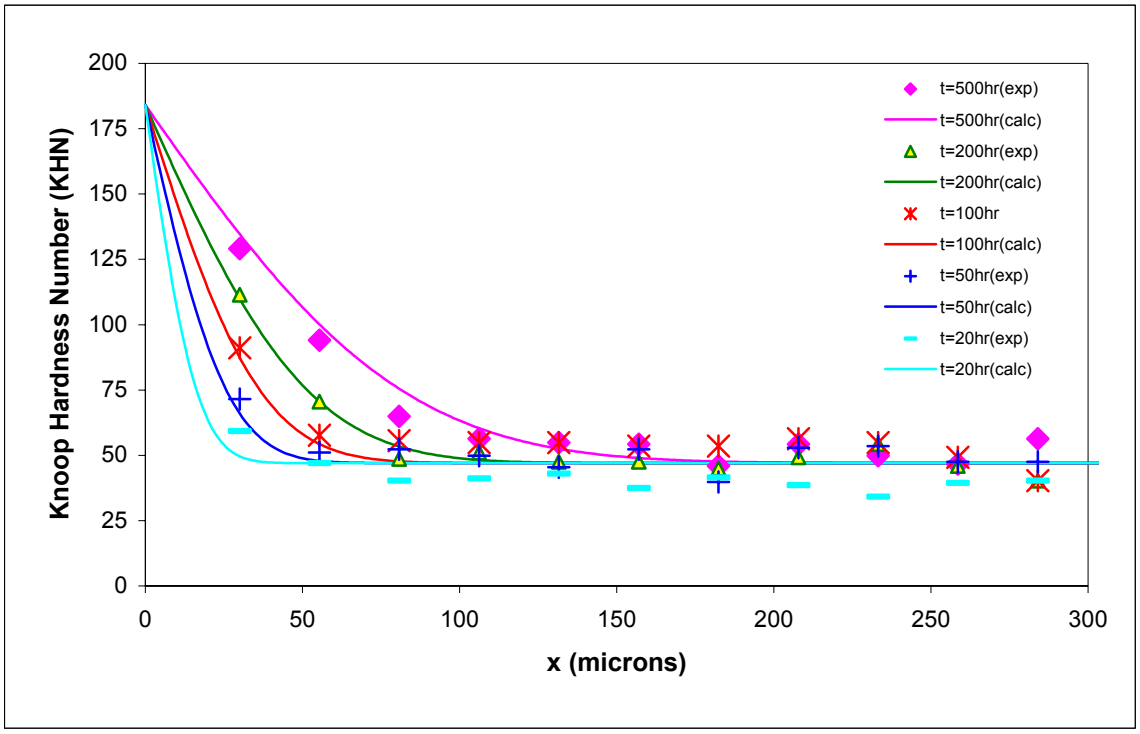

Figure 2 Microhardness profiles for samples annealed at 700°C

Microhardness Profiles as a Function of Temperature
In order to determine the activation energy of the system, annealing was done at three different temperatures, 700, 750 and 800°C and the annealing times were 100 hours each. The hardness profiles for two of these three samples are shown in figure 3.

Unfortunately, at the beginning of this series of microhardness tests the indenter was damaged. A new indenter was borrowed from another laboratory, but when it was used

to test a calibration standard the lengths of the indentations were half of what they should have been. Therefore, a correction factor of 2 was used in these measurements. A new indenter will be purchased and these measurements will be repeated.

Values for H_o and H_s found from the 700°C profiles were carried over to the 750 and 800°C profiles. Again, the "solver" component in Excel was used to determine values of D for these profiles. The resulting fit between the data points and the calculated profile was excellent, with a root mean square error of 4.5 to 5.5 KHN. The diffusivity coefficients, D, for the 750 and 800°C profiles, were 3.44×10^{-11} and 9.76×10^{-11} cm^2/second respectively.

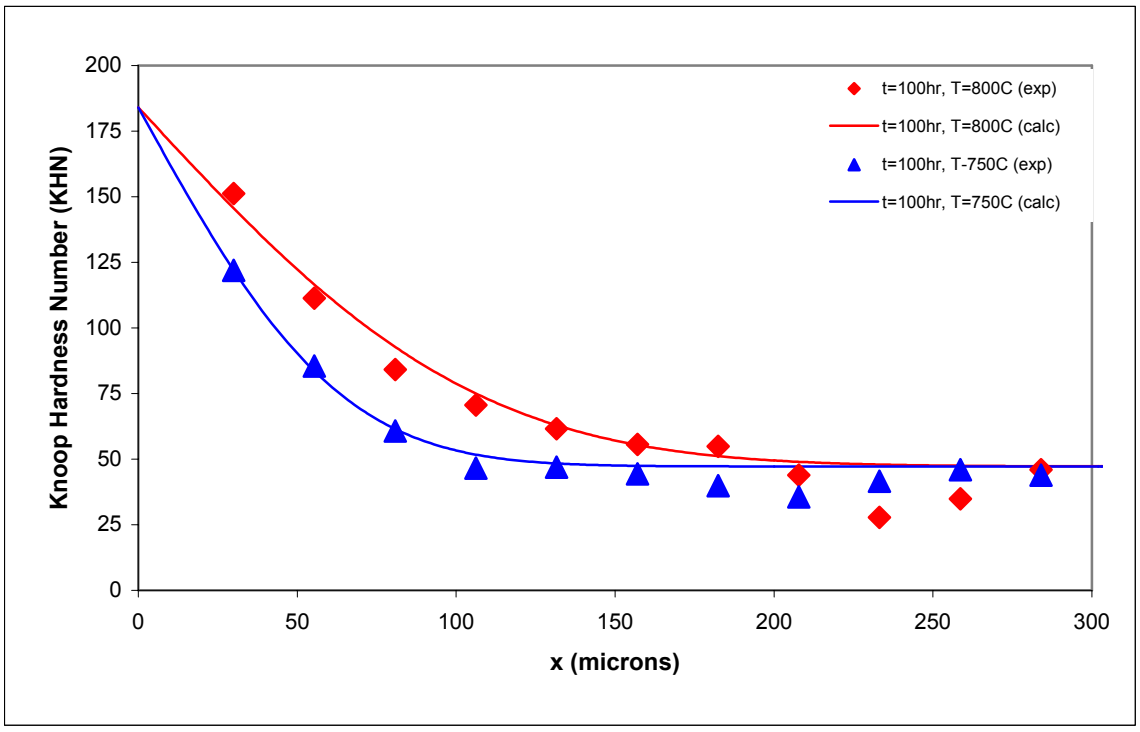

Figure 3 Microhardness profiles for samples annealed at 750 and 800°C for 100 hours.

Analysis of the Activation Energy

The experimentally determined activation energy for oxygen diffusion in α-titanium was found to be 186 kJ/mol. The slope of lnD vs. 1/T was used to determine this value, and the linear equation that fits the three data points is shown in figure 4. The activation energy is in the range reported in the literature.

Discussion:

Microhardness Profiles

The hardness profiles generated by this experiment look just like concentration profiles. In fact, the correlations suggested by equations 3 and 4 are indeed reinforced by the plots shown in figures 3 and 4. Variables such as activation energies and diffusion coefficients found through hardness testing can be used to predict the hardness values and therefore the relative concentration of oxygen at other temperatures, times, and depths.

The Stability of the Value of H_o

H_o is the initial hardness of the material, before any oxygen diffusion has taken place. H_o, however, can change due to other factors, such as recrystallization and grain growth. In this work annealed titanium was used to avoid this problem. Our results showed that for heat treatments done at 700°C and higher, and 20 hours and longer, the value of H_o did not change. It is possible that if this experiment is extended to lower temperatures and shorter times that it could change.

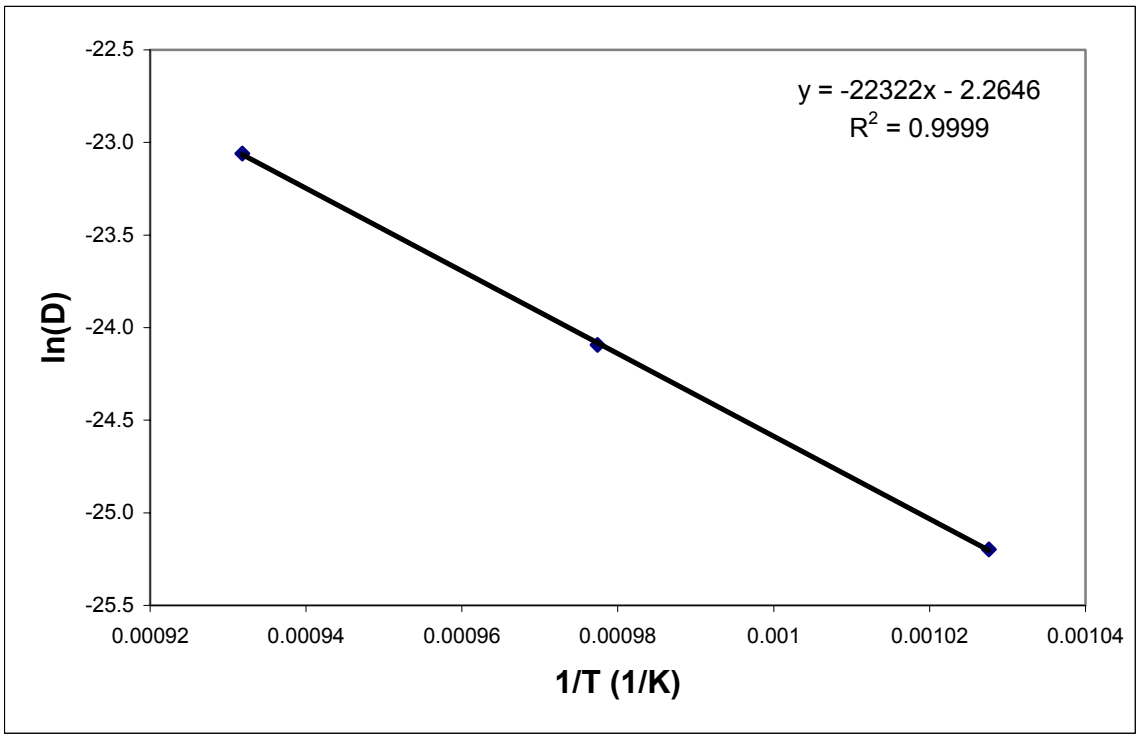

Figure 4 Arrhenius plot of the diffusivity

Using Solver to Find H_s and D

Using the solver capability of spreadsheets helped us to determine the hardness value at the surface, H_s, and the diffusion coefficients, D. These values, along with the value of H_o, were used in equation 4 to calculate the profiles. Using this numerical approach was necessary. It was not possible to measure H_s for the reasons mentioned below. We were concerned about the possibility that this approach could lead to multiple solutions. However, we had only two unknowns in a single equation, and we had 7 sets of data and a total of over 140 data points. The results turned out to be very reasonable and the RMS error for all 7 data sets was around 5 KHN, which is about the same as the scatter in the data.

The hardness value at the surface would have been impossible to obtain since it would need an indentation right at the surface. The diamond-shaped indentions were roughly 25

μm wide, and our best attempt to place the indenter close to the edge would generate fractures that would reach the edge. The best way to solve this problem was to allow approximately 30 μm of relief from the edge. The surface hardness determines where the profiles begin, but the diffusivity coefficient greatly influences the shape of the curve. The values for D and H_s were automatically adjusted so that the calculated profiles fit as close as possible with the experimental data points. Minimizing the sum of the difference between the calculated hardness (equation 4) and the experimental hardness for the profile(s) in each temperature group at fixed distances led to values for H_s and D. For the cases of the 750 and 800°C, the value for H_s found with the 700°C profiles was used since it already provided the best fit for five profiles. The value of D was determined numerically for each temperature.

Activation Energies

The activation energy found in this experiment is within the range of other values cited in the literature [2,4-7] and is very close to the value of Ti tracer diffusivity [8]. This suggests that the diffusion of oxygen in α-Ti occurs by a substitutional vacancy mechanism.

The table below lists the activation energies reported for earlier microhardness-based diffusivity studies as well as for other methods, including the tracer diffusivities for pure titanium.

Table 2. Activation energies for the diffusivity of oxygen in titanium.

Investigator	**Alloy**	**Method**	**Activation Energy kJ/mol**	**Year and Reference**
Present work	CP – Ti	Microhardness	186	2002
Gupta and Weinig	Ti-0.2[a]% O-based alloy	Internal friction	188	1962 [3]
Pratt et al	Ti-3.5[a]%O	Internal Friction	201	1954 [4]
Roe et al	Ti75A	Microhardness	140	1960 [5]
Rosa	CP – Ti	Microhardness	203	1970 [2]
Revyakin			150	1954 [6]
Tracer Diffusivity				
Dyment et al	α - Ti[44]	Tracer	173	1968, [7]

The experimental methods used in several of the investigations listed in table 1 were quite complex, requiring very expensive analytical machines. Our experiment shows how hardness testing can be used as an inexpensive method of determining the activation energies.

Other Factors

All of the heat treatments were done in air, and while this might better represent typical service conditions, air contains four times as much nitrogen as oxygen. Nitrogen diffusion has been addressed in other studies [8]. The activation energy of nitrogen

diffusion is similar to that for oxygen but its diffusion rate in the present temperature range is a factor of 4 lower than for oxygen. In general nitrogen does not seem to concern people as much as oxygen, perhaps because a thick layer of TiO_2, not TiN, forms on the surface, and because of the lower diffusion rate. The matter was also not addressed here so that we could concentrate on a phenomenon that could be presented in a classroom setting.

One other factor that influences the results of these types of studies is the effect the oxide itself has on the diffusivity. Once the oxide forms the value of c_s changes from that of air to that of the oxide. Since the oxide forms immediately, c_s probably never was equal to the oxygen concentration of air. This means that c_s was probably constant and therefore H_s was probably constant.

Conclusions:

The results obtained here are similar to those reported in the literature. This experiment also incorporates a number of fundamental concepts, such as diffusion, solid solution strengthening, phase diagrams and practical skills such as heat treating, metallography, microhardness testing and data reduction. It is also a relatively inexpensive experiment that can be done as a group experiment. All of these factors make it very attractive as an experiment for the teaching laboratory.

It should be noted that the linear correlation may not be the best approximation. Data showing hardness as functions of oxygen concentration in pure titanium shows a slight nonlinear (concave down) relationship [9]. The nonlinear might not be enough to change the results significantly but a new analysis should be attempted. It would be interesting to split the students into two groups, ask each to use one of these approaches, and then compare the results and debate the merits of each.

This experiment required us to find new ways to analyze the data. The "solver" capabilities of the Excel spreadsheet allowed us to solve for multiple unknowns using regression, which is not common in undergraduate education.

An interesting side-benefit of this experiment is that all of the specimens one would need to conduct an experiment on the kinetics of grain growth of titanium are already prepared. All that has to be done is to etch the samples and measure the grain sizes.

Finally, similar experiments could be developed for other systems. We have shown here is that in certain cases microhardness testing can be used to investigate the diffusivity of materials.

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Biographical Information:

Aaron Broumas is in his senior year at the University of California, Davis and is double-majoring in chemical engineering and materials science. He is working as an intern in Materials Science Central Facilities and is proficient in metallography, specimen preparation techniques, scanning electron microscopy and EDS and is learning x-ray diffraction and other materials characterization techniques. Aaron is also helping users of the facility and is a principal operator of our two scanning electron microscopes. He is also engaged in the analysis of dust samples collected over Puerto Rico and in the northern deserts of China.

Nick Degnan is a junior at the University of California, Davis double-majoring in mechanical engineering and materials science. He is working as an intern in Materials Science Central Facilities learning metallography, specimen preparation techniques, optical microscopy, scanning electron microscopy and EDS. He is also engaged designing and building a laser diffraction demonstrator for use in class, rebuilding laboratory equipment and assisting users of the facility.

Michael L. Meier received his B.S. in Materials Engineering from North Carolina State University in 1979 and his M.S. (1986) and Ph.D. (1991) in Materials Science and Engineering from the University of California, Davis. After a two-year post-doctoral research at the Universität Erlangen-Nürnberg in Erlangen, Germany he returned to UC Davis where he is now the director of Materials Science Central Facilities, a materials characterization facility, and is very active in developing the laboratory teaching program.