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SORPTION OF TRITIUM BY NICKEL DURING PLASTIC DEFORMATION

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ABSTRACT— The effect of plastic deformation on the amount of tritium absorbed, the surface concentration, and the apparent diffusivity was determined by comparing elastically and plastically deformed sections of nickel tensile tubes that were filled with tritium during deformation. Plastic deformation increased the amount of tritium absorbed by the metal and adsorbed on the surface, but decreased the apparent diffusivity. These observed data for nickel can be explained by the trapping theory developed for iron; where the dislocations created during deformation are postulated to trap the tritium, thereby producing higher values for interior and surface tritium concentrations, and lower values for tritium diffusivity.

INTRODUCTION

Movement of hydrogen with dislocations has been postulated as being important in the mechanism of hydrogen embrittlement of metals.¹ Plastic deformation of specimens containing hydrogen causes enhanced release of hydrogen. This release has been interpreted as due to dislocations dragging hydrogen with them.² Similarly, if a specimen is deformed in a hydrogen environment, dislocations nucleated at the surface might also drag hydrogen into the specimen and cause a greater amount of hydrogen to be absorbed. Information about the effect of plastic deformation in a hydrogen atmosphere would help to explain the mechanism of

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environmental hydrogen embrittlement. This study shows that plastic deformation in a tritium atmosphere leads to greater tritium sorption, but a decrease in the apparent diffusivity. These results are explained by trapping theory, with dislocations being the primary traps.

MATERIALS AND PROCEDURES

Test specimens were fabricated from Materials Research Corporation V-P nickel. Tensile tubes were machined as shown in Figure 1. All but one of the tubes were vacuum annealed at 873°K for one hour, and then were filled with a 96 vol % tritium -4 vol % deuterium mixture at 27.6 MPa. Filling required two hours at room temperature (294°K). Immediately after filling, some tubes were stored at 196°K until tested. The others were held at room temperature for various times. All tubes were tested to failure at room temperature at the strain rates given in Table I. Sections were removed from the shoulder and the gauge length of each tube. The tritium concentration as a function of depth into the tube was determined by incremental chemical dissolution followed by liquid scintillation counting. Only the time at room temperature is shown in the table and considered in the calculations.

Annealed pins were inserted into two of the annealed tubes to serve as independent controls for determining the tritium distribution in unstressed nickel.

RESULTS

SORPTION

Plastic deformation affects the total quantity of tritium absorbed into an annealed specimen as shown by the differences in the areas under the two curves in Figure 2. The total quantity of tritium absorbed (per unit surface area) to a depth of 2×10^{-4} m is tabulated in Table I for the various specimens. For the annealed tubes, 7.5 times as much tritium was absorbed in the gauge length (plastically deformed) as was absorbed in the shoulder (elastically deformed). Tritium absorbed in either section of the cold worked specimen (Figure 3) was about the same as the amount absorbed in the annealed pins (Figure 4) and in the shoulder of the annealed specimens (Table I). The shape of the curves in Figure 3 are indications of short circuit diffusion paths, as discussed in another paper.³

The best value for the tritium surface concentration was determined by assuming that the concentration profile would be due to Equation (1) for diffusion into a semi-infinite solid. The relatively short diffusion times justify the use of this equation rather than the more complicated solution for diffusion

into a tube. The solution for these conditions is

$$C/C_0 = \operatorname{erfc} \left(\frac{X}{2\sqrt{Dt}} \right) \quad (1)$$

where:

C = the concentration at X penetrating the tube wall, moles/m³

C_0 = the tritium surface concentration, moles/m³

D = the diffusivity, m²/s

t = the diffusion time, s

The error function complement, erfc , is related to the probability function. If this relationship (Equation 1) is obeyed, a plot of the concentration on a probability scale vs. distance will be linear and will facilitate the estimation of the best values for C_0 and D . Such a plot is shown in Figure 5. C_0 is the value found by extrapolation to $X = 0$.

The shoulder sections of all annealed tubes had lower tritium surface concentrations than the gauge length sections. The average value was 0.9 moles/m³. The two unstressed, annealed pins had an average surface concentration of 1.1 moles/m³. Thus, the values for tritium surface concentration of the undeformed material are about the same. A value of about 1.0 moles/m³ is considered to be the equilibrium surface concentration for 294°K and 27.6 MPa tritium gas, in good agreement with other data.^{3,4}

In the annealed specimens, the tritium surface concentrations in the gauge length sections (heavily deformed) were at least ten times higher than the equivalent concentrations in the shoulder sections (Table I). The average value of $15.0 \text{ moles T}_2/\text{m}^3$ was 15 times as great as the average surface concentration in the undeformed region. The gauge length of the cold worked specimen had a tritium surface concentration about twice that of the shoulder section.

DIFFUSIVITY

The marked effect of plastic deformation on diffusivity can be seen from the shape of the concentration profiles in Figure 2 versus those in Figure 4. The effective diffusivity caused by plastic deformation was determined by solving Equation (1) for diffusion into a semi-infinite solid. The time for diffusion was taken as the total time at room temperature for the unstrained sections of the tubes, and the time during deformation for the strained region.

The influence of deformation on the concentration profile was determined by subtracting the profile in the shoulder from that in the gauge length. The change in shape increased the calculated diffusivity by less than 10% and was therefore ignored.

Procedures similar to those for obtaining the surface concentration were used to determine the best value of diffusivity (D). C/C_0 vs. X was plotted on probability paper, and D calculated from the slope. Concentration profiles plotted in this fashion are shown in Figure 6 and values of D are listed in Table I.

For the annealed tubes, the undeformed sections and pins had an average diffusivity of $5.6 \times 10^{-13} \text{ m}^2/\text{s}$. The effective diffusivity in the deformed regions had an average value of $8 \times 10^{-14} \text{ m}^2/\text{s}$, about 10% that of the undeformed sections of the tubes and the pins. Diffusivities in both sections of the cold worked tubes were about the same and similar to those in the gauge length of the other specimens.

The diffusivity obtained from outgassing experiments of annealed nickel at 294°K was $(5 \text{ to } 7) \times 10^{-13} \text{ m}^2/\text{s}$, in excellent agreement with the values from the concentration profiles of the undeformed, annealed sections.

DISCUSSION

The experimental results clearly show that plastic deformation during hydrogen exposure of annealed nickel enhances the uptake of hydrogen and affects its distribution, but that deformation of cold worked material in a hydrogen atmosphere has little influence on the quantity or distribution of absorbed hydrogen. The results can be explained by the theory of trapping developed primarily to

explain the anomalous behavior of hydrogen in iron,⁵ where low temperature solubility and diffusivity differ from values obtained by extrapolations of high temperature data. The traps are defects in the metal lattice that contain higher concentrations of hydrogen than the lattice. In general, trapping increases the apparent solubility and decreases the apparent diffusivity of hydrogen in iron. Plastic deformation of nickel in a tritium atmosphere produces the same effects.

Oriani⁵ derived a theoretical equation to relate the apparent diffusivity influenced by traps (D_x) to the true lattice diffusivity (D_L) when trapping occurs with local equilibrium:

$$D_x = D_L \left[\frac{C_L}{C_L + C_x(1-\theta_x)} \right] \quad (2)$$

where:

C_L = the normal lattice solubility

C_x = the trapped hydrogen

θ_x = the fraction of trapped sites occupied

when $\theta_x \ll 1$, the equation can be reduced to:

$$D_x = D_L \left[\frac{C_L}{C_L + C_x} \right] \quad (3)$$

The primary effect of plastic deformation on trapping sites should be the increase in the density of dislocations. The average dislocation density of a heavily cold-worked metal would be $\sim 10^{16}$ trapping sites per cubic meter. At this dislocation density, and considering only the dislocation core, 10^{28} trapping sites per cubic meter would be present in the deformed section. The total concentration, $C_L + C_X$, in the gauge length section is 15 moles T_2/m^3 or 9×10^{26} atoms of tritium per cubic meter of nickel. The normal lattice solubility is 1.0 moles T_2/m^3 or 6.0×10^{25} atoms of tritium per cubic meter of nickel. These values can be used to calculate Θ_X , which equals $(C_T - C_L)/N_X = 8.4 \times 10^{26}/10^{28}$, where N_X is equal to the theoretical number of trapping sites in the dislocation core. Therefore, Equation 3 should be a valid description of the data. This is particularly warranted as this calculation underestimates N_X , because other trapping sites than simply the dislocation core are in the stress field around the dislocation.

Taking D_L to be that calculated from the data in the unstrained region of the tubes and pins, and the lattice solubility to be surface concentration from these same regions, then the apparent diffusivity would be:

$$D_X = 4 \times 10^{-14} \text{ m}^2/\text{s} \quad (4)$$

The average measured value for diffusivity in the gauge length was $8 \times 10^{-14} \text{ m}^2/\text{s}$, which is in good agreement with the value calculated above according to the trapping model. This also agrees with the diffusivity calculated in the cold-worked specimens, $5 \times 10^{-14} \text{ m}^2/\text{s}$, where the same type of dislocation traps should be operative.

The effect of strain rate on the sorption of tritium is not clear from the results. For example, the specimen tested at the highest strain rate ($4.2 \times 10^{-4} \text{ m}^2/\text{s}$) has a higher apparent D in the gauge than in the shoulder indicating the effect of plastic deformation on the sorption of tritium may be decreasing at higher strain rates. However, data are insufficient to establish the relationship between strain rate and the sorption processes during deformation in a hydrogen atmosphere.

CONCLUSION

The data clearly show that plastic deformation of annealed nickel in a tritium environment influences the absorption and the apparent diffusivity of tritium. The results can be explained by the trapping model, with the dislocations generated during deformation being the primary traps. These results are different from those obtained by Fricke, Stüwe, and Vibrans⁶ on the effect

of plastic deformation of iron in a hydrogen environment. They concluded that plastic deformation creates fresh surfaces where the hydrogen is able to enter the metal more easily. This effect may be operative in these experiments, but the effect of plastic deformation on the apparent diffusivity and the higher surface concentrations in cold worked specimens suggest that this is not the only effect. The present work supports the hypothesis that dislocations are traps for hydrogen in nickel and their movement influences the kinetics of the absorption process.

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TABLE I. Sorption of Tritium by Nickel During Plastic Deformation

Time Filled with T ₂ , 10 ³ sec	Time During Deformation, 10 ³ sec	Strain Rate, 10 ⁻⁴ /sec	T ₂ Absorbed, 10 ⁻⁴ moles/m ²		Surface Concentration, moles/m ³		Diffusivity, 10 ⁻¹³ m ² /sec	
			gauge	shoulder	gauge	shoulder	gauge	shoulder
<u>Annealed</u>								
25.	4.8	0.8	21	0.9	15	0.25	0.1	12
7.2 ^a	6.3	0.8	10	1.8	18	1.2	0.2	3.4
72.	2.2	1.7	10	1.6	10	0.6	0.7	2.5
7.2 ^a	2.8	1.7	14	1.8	20.0	1.5	0.4	8.8
25.	0.9	4.2	11	2.5	13.	1.6	3	1.5
7.2 ^a (pin 1)				1.3		1.4		5.4
7.2 ^a (pin 2)				1.3		0.9		5.4
7.2 ^a Cold Worked	0.4	0.8	2.5	1.3	6	3.0	0.5	0.6

a. Time at 196°K not included.

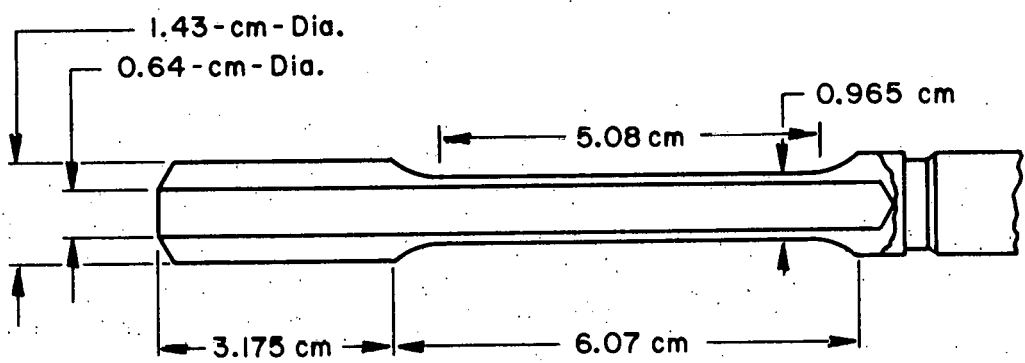


Figure 1. V-P Nickel Tensile Tube

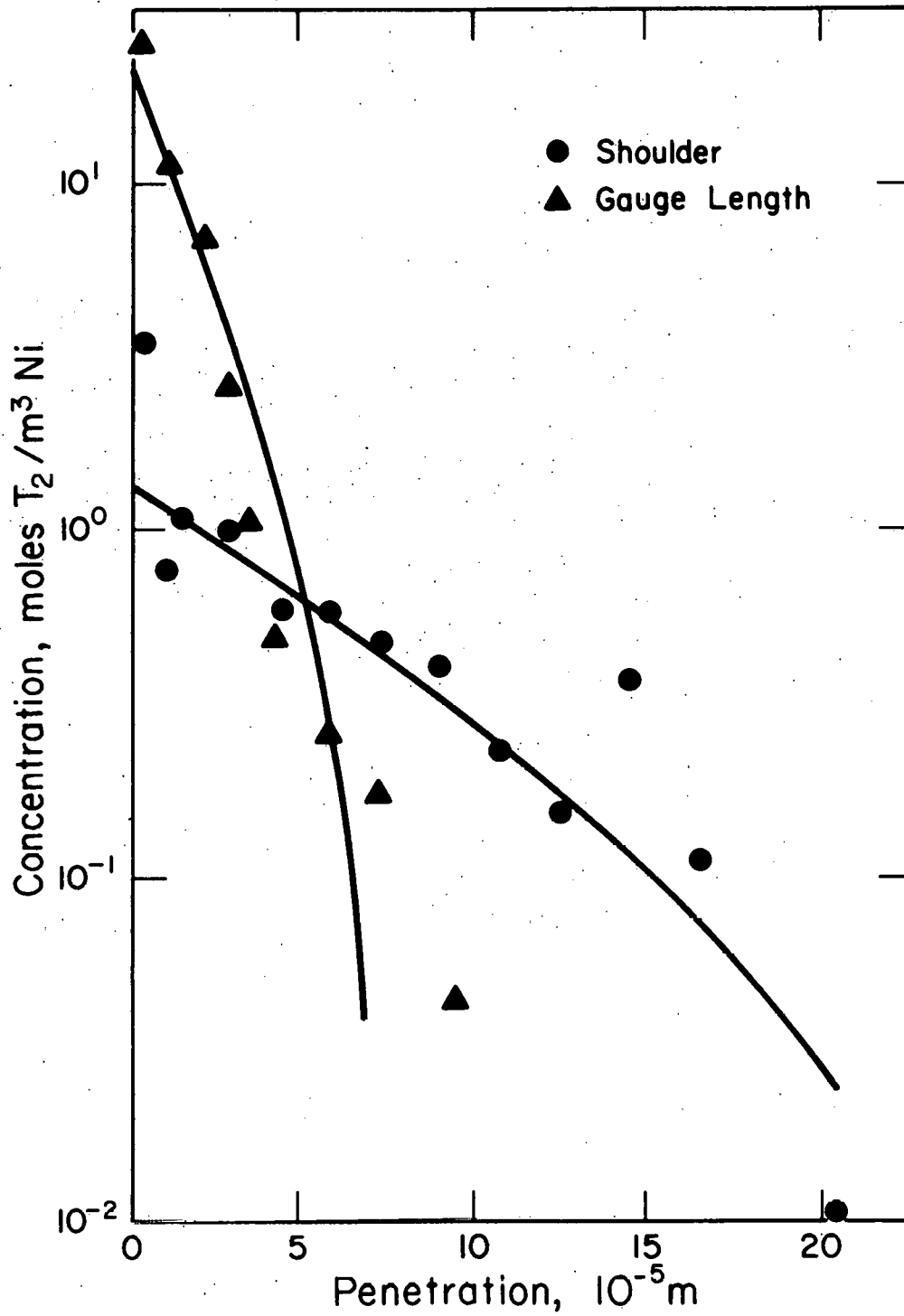


Figure 2. Tritium Penetration in Annealed Nickel Tensile Tubes after 7.2×10^3 s at 294°K

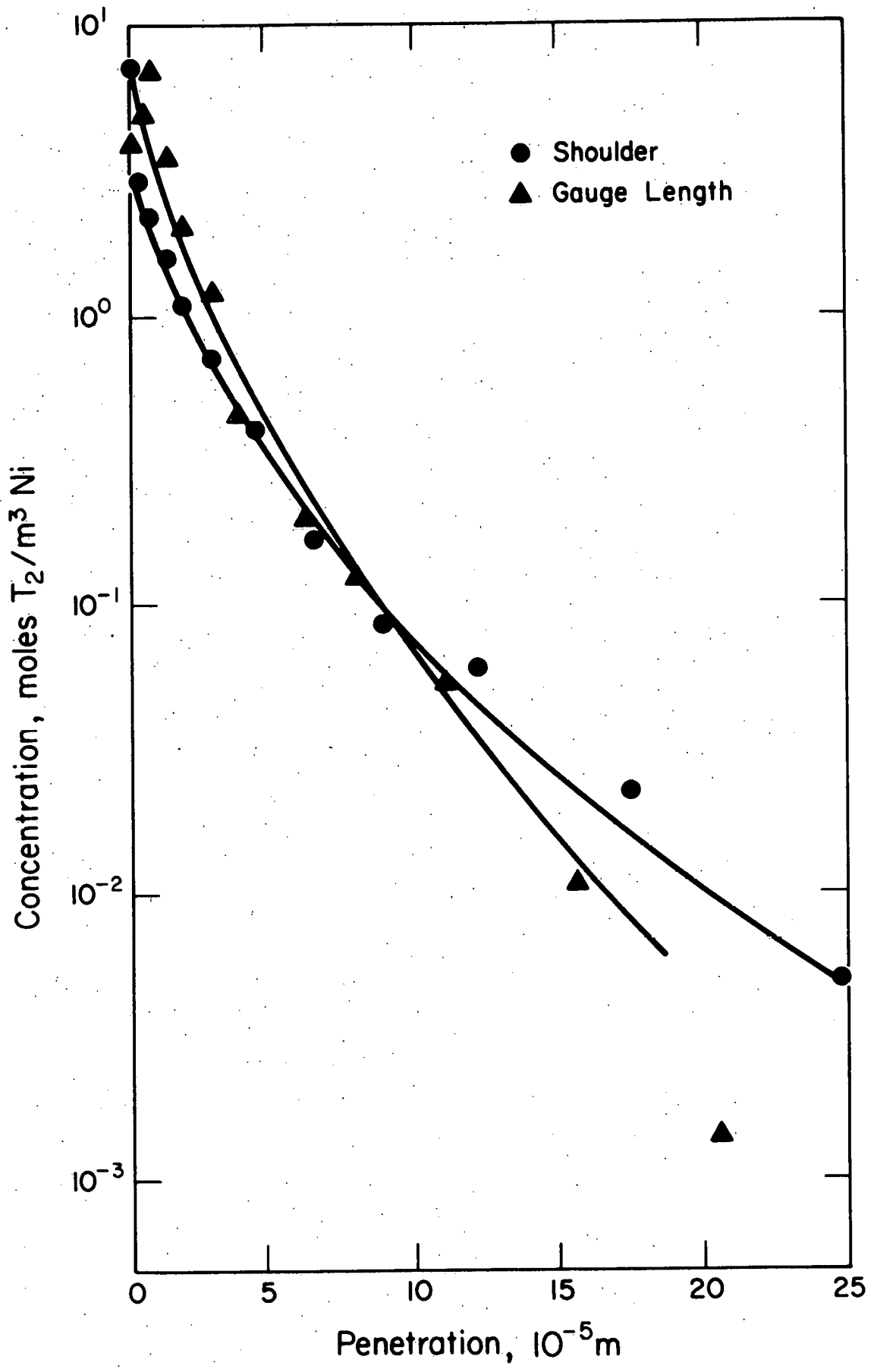


Figure 3. Tritium Penetration in Cold-worked Nickel Tensile Tubes after 7.2×10^3 s at 294°K .

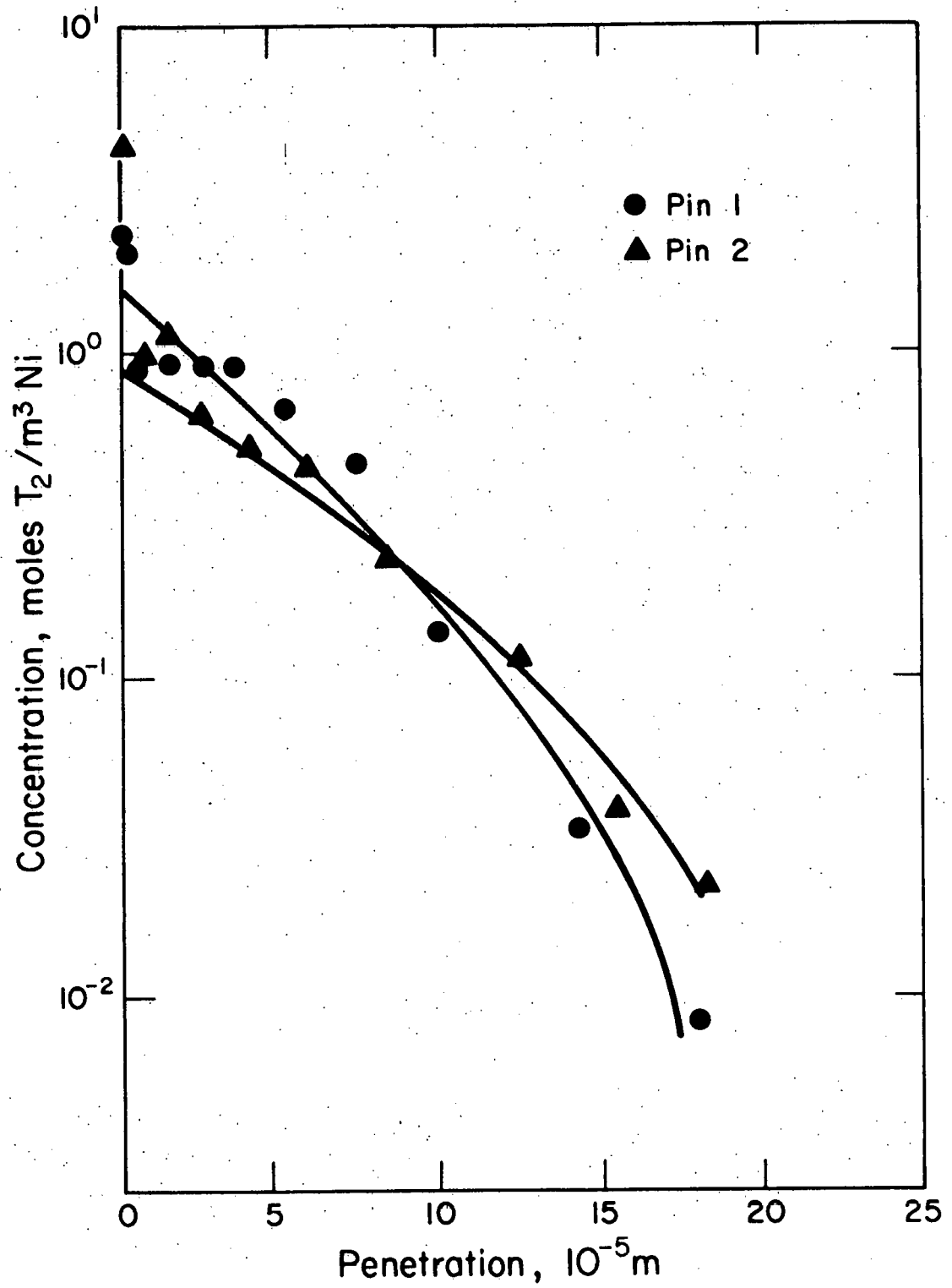


Figure 4. Tritium Penetration into Unstressed Nickel Pins after 7.2×10^3 s at 294°K

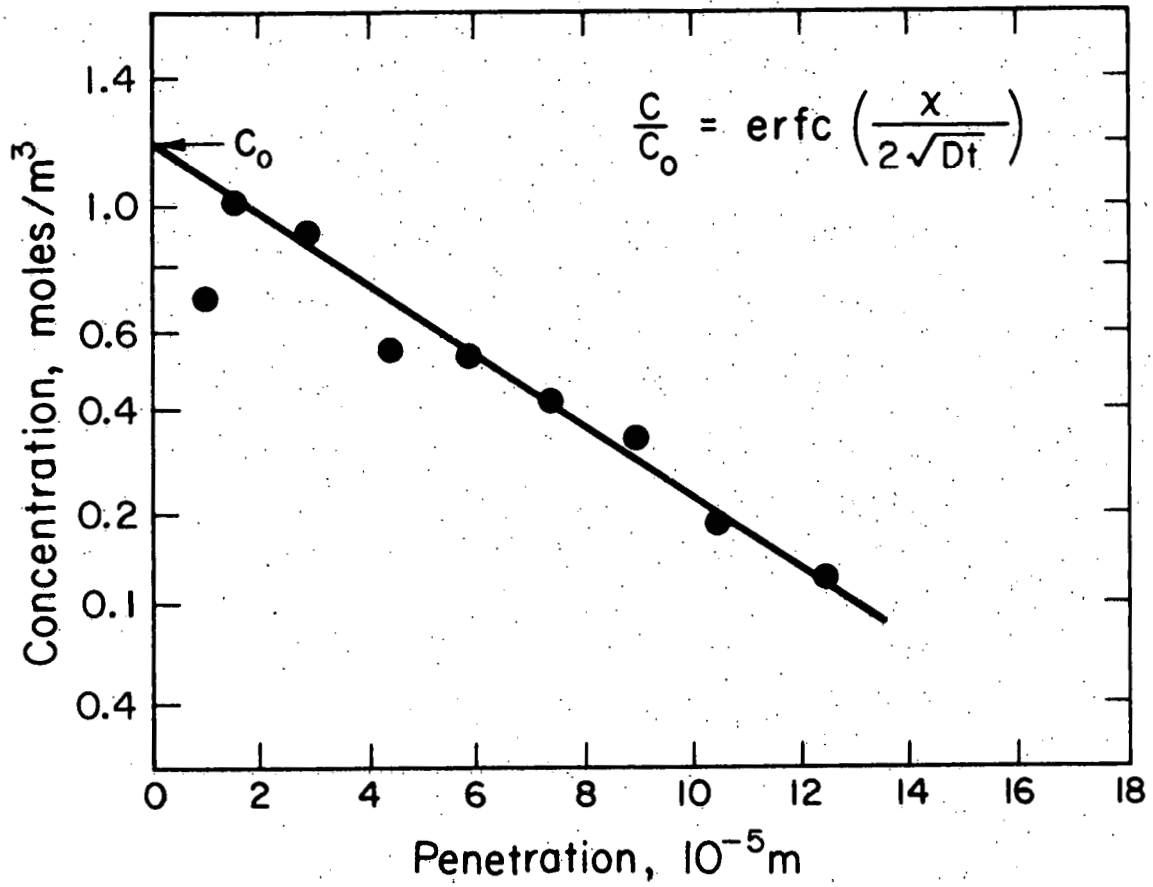


Figure 5. Probability Plot of Tritium Distribution to Estimate Surface Concentration

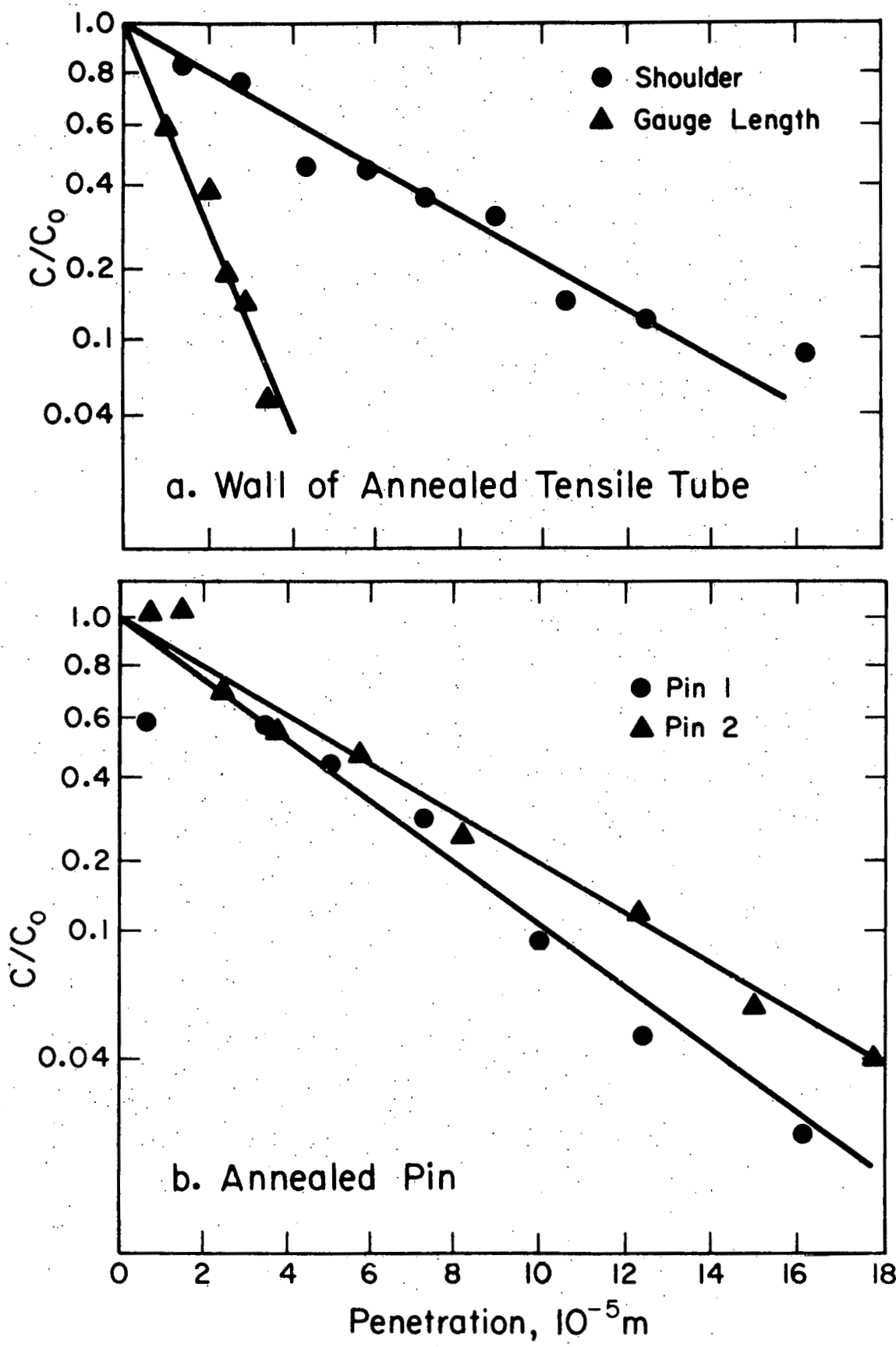


Figure 6. Probability Plot of Tritium Penetration